Ψ_k Newsletter

AB INITIO (FROM ELECTRONIC STRUCTURE) CALCULATION OF COMPLEX PROCESSES IN MATERIALS

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Contents

1 Editorial

As you are most likely aware, this is the 50th issue of the Psi-k Newsletter. It is in a way a jubilee issue marking over 8 years of Psi-k activities which started in September 1993 with the inauguration of the EU Human Capital and Mobility (HCM) Network. The first Psi-k Newsletter appear at the beginning of 1994 essentially in the same format and structure as now. Throughout the years, however, it has grown, mostly in size, but has also become the main vehicle and umbrella for many different networks and activities that have grown out of the original HCM Network. Therefore more and different activities have been reported upon in the consecutive issues, as new events kept on happening.

Many people have contributed to establishing a vibrant and cooperating Psi-k community, and together with it also the Psi-k Newsletter and its identity. Many people should be acknowledged and thanked for making the newsletter possible, providing more and more contributions to preserve its existence and enhance its interest throughout the years. However, Professor Volker Heine has always been the most distinguished driving force behind it all. He has worked tirelessly, dedicating his time end energy to the cause, and we are very grateful to him for all he has done for the various networks, the ESF programme, and the newsletter, of course. As a special treat for this jubilee issue, in the section **Volker Heine's Article**, he shares with us his personal views on **"European Collaboration in Ab-Initio Computer Simulation"**. The article reads as a wonderful story on solid state physics both in England and elsewhere, giving also details on how the European collaboration came into being a number of years ago. In this article Volker mentions the second and fourth biggest mistakes of his professional life, and we hope that in future he will want to tell us also about the first and third mistakes. Other contributions from Volker can be found in the following and the **News from the ESF Programme** sections where, as the chairman of the ESF Programme, he writes about the old and new ESF Psi-k Programmes, telling us how all of us can help in getting the new programme funded. So, please do try to help following Volker's directions. The full proposal for the new ESF Psi-k Programme is placed in the subsection following Volker's write-up.

Similarly to previous newsletters, in this newsletter we also have reports on workshops, and two of them can be found in the section **News from the RTN**, and one in the **News from the ESF** section. All of them contain abstracts of presented papers. Towards the end of the **ESF Programme** section we publish an extended scientific report by Sam Shallcross (*University of Bristol* and *IRC, Liverpool*), containing five tables and four figures of results, on his four months' collaborative visit to Uppsala University. The two subsequent sections contain a number of workshop and available position announcements, while abstracts of newly submitted papers can be found in the **Abstracts** section.

Of special interest to all readers may be a contribution by the Jülich group of Professor Peter H. Dederichs on comparison of PC's to workstations, by the title **"Pc's vs. Workstations: faster and cheaper"**. The latter can be found just before the **Scientific Highlight of the**

Month section. The highlight is on **"Linear-response theory for the calculation of the electron-phonon coupling within the LAPW method"** by C. Ambrosch-Draxl, R. Kouba (*University of Graz, Austria*), A. Taga, L. Nordström, and B. Johansson (*University of Uppsala, Sweden*). Please check the table of contents for further details.

The *Networks* have a home page on World Wide Web (WWW). Its *Uniform Resource Locator* (URL) is:

http://psi-k.dl.ac.uk/

The above contains information on the Psi-k 2002 workshops and hands-on courses. In these pages you can also find information on how to apply for funding to make collaborative visits.

Please submit all material for the next newsletters to the email address below.

The following email addresses, which remain in operation, are repeated for your convenience, and are the easiest way to contact us.

	function
psik-coord@daresbury.ac.uk	**messages to the coordinators, editor & newsletter**
psik-management@daresbury.ac.uk	**messages to the NMB of all Networks**
psik-network@daresbury.ac.uk	**messages to the whole Ψ_k community**

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2 Celebrations and Congratulations

This is the 50th issue of the Psi-k Newsletter which has appeared regularly every two months since 1994 edited by Dzidka Szotek, so punctually that you could set your calendar by it. It is a wonderful achievement. CONGRATULATIONS DZIDKA! MANY THANKS for all your hard work. Thanks also to all the contributors over the years whose articles, reports and the rest have made the Newsletter the success that it is.

Our email address list is also maintained by Dzidka and now numbers over 900 e-dresses. The email list and Newsletter together have become the main medium for job advertisements and conference etc. announcements in our field, not just in Europe but worldwide. Actually the Newsletter is an unusual mixture: as well as giving scientific information, it is the official record of all activities in our ESF Psi-k Programme (and similarly some EU Networks), which explains all those reports.

Successes do not just spring out of nothing. Before the Psi-k Newsletter there was the purely British CCP9 Newsletter, where CCP9 stands for Collaborative Computational Project number 9 on Electronic Structure of Solids. There were 15 occasional CCP9 Newsletters between 1982 and 1992, edited by Walter Temmerman. So rather belatedly, WALTER, MANY THANKS FOR LEADING THE WAY SO ABLY! These CCP's were formed after the purchase in the late 1970's of the first Cray supercomputer by the Research Council in Britain.

Right from the start, CCP9 had a very European outlook with as many invited guests as possible. Quite apart from the Newsletters, Walter and Dzidka have been the core team that has nurtured the growing collaboration across Europe through CCP9, the EU HCM Network in 1994-97, and the ESF Psi-k Programme 1998-2002, as well as playing an active part in other EU Networks. So ADDITIONAL THANKS to them both for all that from our whole community in Europe.

Volker Heine, Chairman
European Science Foundation 'Psi-k' Programme

3 Volker Heine's Article

European Collaboration in Ab-Initio Computer Simulation

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Foreword

I want to talk about the process of doing science. The field of ab initio computer simulations has developed greatly in Europe over the last 20 years, as it has elsewhere, where by 'ab initio' I mean solving the quantum mechanics for the whole system of electrons to describe accurately the chemical bonding between the atoms. This is not a proper history of who did what when, but just my personal view and development, so please excuse omissions and minor inaccuracies.

A river has many tributaries, and I shall just write about one branch that I am particularly familiar with, calculations for solids. There are three themes interwoven: **1.** the evolution of the main scientific ideas, **2.** the development of an unusually high degree of networking and collaboration across Europe, and **3.** my vision of the future of our scientific community.

1 Evolution of the scientific ideas

When I arrived from New Zealand in 1954 to do my PhD in Cambridge, my supervisor Professor Mott gave me my project: "I suggest you go down to the low temperature laboratory and see if you can make yourself useful." Such was his concept of the life of a theoretician. I found that the Fermi surface of aluminium was being measured there by the de Haas-van Alphen effect, the first study of a polyvalent metal. I chose to do an electronic band structure calculation of aluminium in order to help interpret the complicated data being obtained.

The band structure of silicon had just been calculated by the orthogonalised plane wave (OPW) method by Frank Herman in USA, the first polyvalent element besides beryllium. That calculation was of enormous importance in explaining the very anisotropic masses of the electrons and the existence of light and heavy holes. Prior to that calculation, one's only ideas about band structures were the very simple pictures in the textbooks from the nearly free electron (NFE) and the tight binding models. On that basis I chose the OPW method: the group of Harry Jones in London had found that the cellular method based on the pioneering calculation

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[1] Volker Heine was awarded the Max Born medal and prize award for 2001, in recognition of his pioneering theoretical and computational studies of the electronic structure of solids and their application to physical properties.

[2] This article was originally written for the SIMU newsletter (www.simu.ulb.be/newsletters/newsletter.html).

at $k = 0$ by Wigner and Seitz did not seem to extend well to the rest of the Brillouin zone, and the augmented plane wave (APW) method was still beyond the capabilities of the computers for a few more years.

The calculation was done on the EDSAC I computer (and towards the end on the EDSAC II) in Cambridge, the first scientific electronic computer in Europe. All the 'production running' had to be done at night, feeding pieces of paper tape into the reader, and at various times I shared nights with the group of Frank Boys, the originator of Gaussian orbitals for configurational interaction (CI) calculations, the group of David Hartree doing Hartree-Fock calculations on atoms, and Fred Hoyle doing his famous stellar structure calculations. If one was lucky, the machine ran without a breakdown until morning. The computer could only hold 1024 instructions (all written in machine code of course) or half that number of single precision numbers between -1 and +1 with fixed decimal point, so that paper tape formed additional storage. Incidentally for the first twelve years from the beginning in 1954, the solid state theory group in Cambridge consisted almost entirely of foreigners. Aspiring theoretical physicists in Cambridge rather despised solid state physics and rather despised computation: they wanted to do analytical field theory or nuclear physics. So in solid state theory there was John Ziman, Neil Ashcroft (of Ashcroft-Mermin) and myself all from New Zealand, Lu Sham (of Kohn-Sham) from Hong Kong, T M (Maurice) Rice from Dublin, Leo Falicov from Argentina, Federico Garcia Moliner from Madrid, David Pettifor from South Africa and so on. Of course these prejudices can still be encountered sometimes today. A few months ago a young European theorist told me that in his country one could never get a professorship in theoretical physics doing the kind of things that I have done in my academic career, and he is nearly right. For example in France there has been no leading work in this field for nearly 40 years, and in Germany it has developed mostly outside the universities in the Max Planck and other Institutes. But the path for me in Cambridge was already smoothed by Hartree who held a special professorship outside the usual appointment channels and had written what I believe was the first textbook on computational mathematics, as well as being one of the instigators of the building of the EDSAC I computer at the end of World War 2. Also Professor Mott as head of the Cavendish Lab (the physics department in

Figure 1: Operator R. Hall at the control console (EDSAC I) and input paper tape reader, with the racks of electronics in the backround ©University of Cambridge Computer Laboratory, 1999. All rights reserved.

Cambridge) firmly believed in theory close to experiment which clearly could involve computing.

I learnt one important lesson from my band structure calculation on aluminium: solid state physics is a lot easier than chemistry! Consider that the band structure of silicon had already been published when one of my friends, a research student in Boys' group, was calculating the electronic structure of water, the first polyatomic molecule, and that all he got out was the bond length and bond angle: compare that with all the information about electron and hole excitations and optical spectra obtained for silicon. Diamond consisting of wall-to-wall tetrahedral carbon bonds is a simpler material than the methane molecule where there are C-H hetero bonds and the edge of the molecule has a rather diffuse electron density. As became obvious from my band structure calculations, the electrons in a solid cannot 'run away' like at the edge of a molecule: the mean electron density in the solid is rigorously fixed by the lattice constant. Thus self-consistency is much easier to achieve in the bulk solid, though calculations on surfaces are much more troublesome to converge.

Similarly the exchange and correlation effects in the solid, at least for an sp-electron bonded solid such as aluminium, are easier than in a molecule because they are similar to the free electron gas which has been studied in detail. Thus in my calculation I could even do one round of self-consistency, and use the Bohm-Pines theory of the electron gas for the exchange and correlation effects among the conduction electrons. Of course all that would not apply to transition metals for whom reliable band structures only came about a decade later. Incidentally I could also treat exactly the exchange between the conduction electrons and the core using Slater's idea of expressing the exchange term in the Hartree Fock equation as an 'exchange potential', and borrowing the exchange functions from one of Hartree's students who happened to be doing the Hartree Fock calculation on the neutral aluminium atom.

Of course at the beginning of the 1960s the big event was the Kohn Hohenberg Sham reformulation of quantum mechanics in terms of density functional theory (DFT). Well, we recognise it now as a big event, but it did not seem so at the time. That was the second big mistake of my life, not to see its importance, but then neither I think did the authors judging from the talks they gave, nor anyone else. Did you ever wonder why they never did any calculations with it? In fact it seemed to me a step backwards. On the one hand I had included in my band structure of aluminium the exact exchange with the core electrons and the screened Coulomb interaction from the Bohm-Pines theory for the exchange and correlation in the electron gas extended to a non-uniform density, whereas the local density approximation (LDA) for all that in DFT seemed rather cruder. In fact I had also included core-core correlation because I knew how much the core shrank due to correlation from Boys' CI calculations on neon, and I did a LDA for the small conduction-core correlation using the high density theory of the electron gas. Of course we now think of DFT much more broadly, but in the 1960s it was always coupled with the LDA for all exchange and correlation.

But perhaps even more important in my attitude to DFT was a second consideration. The doctrine at that time was that the interesting measurable properties of a solid derive from its thermal, electrical, magnetic, optical etc., excitations, and one had the Landau theory of quasi-particles for the electron excitations. But quasi-particle excitations was just what the DFT said it could not give: well, one could get them in principle but Kohn and Sham gave the impression that one would never in practice want to attempt it. So one was left with the total energy of a lump of aluminium at zero Kelvin, not a very interesting quantity, or so my thinking went. How wrong one can be! The Kohn-Sham (KS) theory did clear up one important point left open by Slater in his X-alpha fudge: in the one-electron-like KS equation, should one use the average value of the exchange potential through the filled band or the value at the Fermi level? So in practice for the next 20 years people just calculated with the KS equation and interpreted the eigenvalues as if they were quasi-particle energies. In fact that turned out rather well because the effective mass corrections are less than 10 % over most of the range of electron density of interest.

The real breakthrough came from the development of pseudo-potentials starting with Phillips and Kleinman in 1959. Eliminating the oscillations of the wave function inside the core of an atom meant that the valence/conduction electrons could be described by pseudo wave functions in the nearly-free-electron model. The applications were very successful for phonons, electrical resistivity, BCS superconducting transition temperature, electrical resistivity of the molten metal and other properties of $sp-$electron metals and for the optical properties and surface states of semiconductors. That was really the first time that quantum mechanical calculations could deliver quantitative results for such varied properties of solids. Moreover the calculations did not just give numbers, but a physical picture. After a talk I gave at Bell Labs, Conyers Herring remarked "Never have I learnt so much physics in one hour." It was a breakthrough indeed, contrary to an oft quoted review just a few years previously by Wigner and Seitz which doubted that such a thing would ever be possible.

With second order perturbation theory these calculations also gave a good account of the crystal structures of the $sp-$bonded (non-transition) metals, at least if one compared different structures at the same observed atomic volume. However if one did a global minimisation of the total energy including relaxing the atomic volume, one sometimes got good results but unfortunately at other times the calculation just ran off the rails.

In the light of later developments, it seems worth asking why those calculations of total energy were not always successful. The pseudo-potentials in the 1960s were not norm-conserving (a concept that only came later) but were designed to have the most rapid cut-off possible in q-space (i.e. in Fourier transform). The reasons for that were the limitations of computers to handle large matrices, the wish to compare with pseudo-potentials fitted to experiment, and the use of second order perturbation theory in the total energy calculations. In some calculations, the charge deficit in the core region (the so-called orthogonality hole) and the energy dependence of the pseudo-potential were corrected for by an extra charge in the Ewald Coulomb energy and an effective mass in the band structure respectively. Indeed if we had pursued that, the global energy minimisation for crystal structures might have become satisfactory, but I did not push it because I was interested in getting a physical understanding of the differences in crystal structures among the elements and I had got that. Also one knew from calculations by Norman March and others that the second order perturbation theory was not adequate for vacancies and presumably other applications where the total electron density is far from uniform, so there did not seem much point.

Thus the big step forward came a decade later with the invention of norm-conserving pseudo-potentials by Hamann, Schlueter and Chiang in 1979. That idea killed with one blow the two problems of energy dependence and electron density deficit in the core region, because of the theorem of Shaw and Harrison connecting the two. That was the fourth big mistake in my life, that I did not myself see the possibility of creating norm-conserving pseudo-potentials. (I will gloss over mistakes one and three!) In the 1970s my work had moved far away from pseudo-potentials and my mind was still conditioned by the original aim of having pseudo-potentials as weak as possible. With those it is simply not possible to have norm conservation. Think of the wave function at $k = 0$, the bottom of the band. Outside the core, it is very nearly a constant as seen in the original calculations of Wigner and Seitz, i.e. very nearly a plane wave with k=0. Inside the core the wave function oscillates rapidly, being orthogonal to the $1s$, $2s$, etc., core orbitals, and its mean square value is roughly half of the constant outside, just like a unit sinusoidal wave has only a mean square amplitude of one-half. Thus the pseudo wave function, in this case a constant, cannot possibly give the right charge density inside the core. The consequence is that the norm-conserving pseudo-potentials have to be much 'harder' (i.e. stronger) in real space and extending to much higher values of q in Fourier space than the smooth pseudo-potentials of the 1960s.

With the norm-conserving pseudo-potentials the total energy calculations of crystal structures gave good results, not now using perturbation theory but summing over all occupied states. This was shown by the group of Marvin Cohen in Berkeley, who investigated all the structures and phase transitions of silicon under pressure.

Those total energy results on the crystal structures were very gratifying, but the event that really sparked off the new era of ab initio computer simulation for me was the calculation by Richard Martin at Xerox of the frequency of the optic phonon mode in silicon. That was not putting some pseudo-potential into some formula for the frequency as heretofore: it was a genuine simulation in which the atoms were pushed out of position and the resulting restoring force was 'measured' in the computer. In the context of electronic structure calculations it was using the computer in a wholly new way: one threw in the atoms and the laws of physics, and saw what happened. This is quite different from having a theory and evaluating a formula at the end. In Martin's simulation the force was obtained for the first time in a solid from the Hellmann-Feynman theorem, and checked by calculating the derivative of the total energy. They agreed! That one could use the Hellmann-Feynman expression came as a surprise to me because I had been indoctrinated by my earlier chemistry friends that one had to have excellent wave functions and charge densities before one could hope to use the Hellmann-Feynman formulation for the force. Actually there is no conflict. As already discussed, the total electron density in a molecule is very sensitive to self-consistency and exchange and correlation effects because the electron density around the edges of the molecule is very deformable. In comparison, the electron density in a periodic bulk crystal is a much more stable quantity with the mean density rigorously fixed by the lattice constant, and this made the Hellmann-Feynman formula useful. Of course nowadays with faster computers and better numerical algorithms calculating the forces is not a problem, but it remains true that calculations at surfaces and defects etc. take longer to converge. Of course using the Hellmann-Feynman force was crucial to simulation. To calculate forces by differencing the total energy requires two energy calculations for one component of one atomic force, whereas one calculation suffices to give all components of all forces with the

Hellmann-Feynman theorem. Without the Hellmann-Feynman theorem, relaxing systems with a hundred or more atoms without symmetry would be totally impossible.

This time I did not make a mistake! I recognised how that simulation of the optic phonon mode opened a new door. It would become possible to do quantitative theory and calculation on all those properties and processes in solids that we had only been able to touch qualitatively previously. Through a lucky coincidence I was able to get a 'new blood' lectureship for Richard Needs in 1983 to learn the new technique from Richard Martin and bring it back to Britain (one of my few ventures into academic politics).

2 Collaboration and organisation in Europe

All this opened a new era in quite another sense, and here really begins the second thread in my story which I mentioned at the beginning. Up until about 1970 I had to operate as an offshoot of the USA because almost all important new developments on electronic structure of solids came from there. I visited USA almost every summer and the Americans were kind enough to keep inviting me and paying for me. I am enormously grateful for their support without which I could have done nothing. All my work depended critically on ideas from across the Atlantic, and it taught me the value of collaboration. But I also learnt that collaboration was not universally embraced. To cite one extreme example from those early days: I visited one research group and was interested to hear what they were thinking about, but the only reply I got was "We don't have any projects here for export"!

Of course there were a few highlights generated within Europe, such as Jacques Friedel's theory of alloys including the Friedel sum rule. There was also Peter Wohlfarth's work on magnetism, and John Pendry's calculation of Low Energy Electron Diffraction at surfaces.

By the 1970's the amount of independent work on this side of the pond had grown. On the Continent an important development was the Linearised Muffin Tin Orbital method by Ole Krogh Andersen, and even more significant was his appointment in 1978 as a Director of a new group in the Max Planck Institute for Solid State Research MPI FKF in Stuttgart. Over the last 23 years that group has provided the most important centre on the Continent for electronic structure theorists from all over Europe and beyond. Other important steps included the development in Bristol, Daresbury and later Germany of the Korringa Kohn Rostocker (KKR) band structure method, particularly with the Coherent Potential Approximation (CPA) for random alloys and ferromagnetic metals at non-zero temperatures. At Daresbury theory and computer codes and a whole support system were produced for Ultraviolet Photo-electron Spectroscopy UPS, XPS, EXAFS, XANES and all the other spectroscopies made possible by the advent of dedicated sources of synchrotron radiation. In Cambridge Haydock and Nex developed the recursion method for electronic structure calculation in terms of the local atomic environment without assuming lattice periodicity. "Throwing out k-space" I called it in a review article. Kuebler in Darmstadt and Karl-Heinz Schwarz started calculations with the Linearised Augmented Plane Wave method.

Let us now return to Richard Needs, coming back from America with what became known as the 'Total Energy and Force' method. How, I asked myself, could one isolated young person in

Britain by himself possibly maintain research at the world forefront? How could he compete successfully by himself against the Americans with their stronger groups and at that time better computing resources? The situation was the same for a few other young researchers in other countries, also returning from USA, namely Matthias Scheffler in Germany, Karel Kunc in France, Sverre Froyen and Ole Nielsen at Nordita, Roberto Car in Italy and Xavier Gonze in Belgium. I therefore called together a day of discussion after our annual British solid state conference, in order to share the latest ideas (which were coming thick and fast) and plan possible cooperation. The baton was picked up by Matthias Scheffler who organised the first real workshop in 1985, and that has continued annually ever since. In alternate years it is a 'mini' workshop like a club meeting of an inner circle plus invited speakers, and in the other years a 'maxi' workshop which is an open conference held in Trieste. There was no difficulty keeping contact also with Americans because they liked to come, particularly Richard Martin and Stephen Louie and later David Vanderbilt, with Kiyo Terakura from Tsukuba.

One cannot overestimate the importance of this regular annual getting together from across the whole of Europe, indeed from the whole world. Graduate students and postdocs were exchanged, but the key element was discussing the latest ideas and freely sharing the latest expertise, and crucially also some computer codes. For example I can remember the occasion after the famous Phys. Rev. Letter by Roberto Car and Michele Parrinello burst upon the world. There were two problems with it. Firstly it didn't seem to work when people coded it up as described. Secondly one brand new idea is often difficult enough to absorb, but this one had four radical new ideas all rolled together, and questions arose whether these could be unrolled and developed further or used separately. It was a unique occasion, having so many leading researchers together for three days, gnawing at the questions like dogs at a bone. People should know better than to present the world with four new ideas in one Letter!

Let me recapitulate how I saw the four new ideas in 'Car-Parrinello' (CP). Firstly one can write down various equations whose solutions, when one arrives at them iteratively, are the same as that of the corresponding Schroedinger equation (or rather the Kohn-Sham equation from DFT, to be precise). In the case of CP it was a time-dependent equation because they were interested in dynamic simulations, but it became apparent that one could use other schemes such as the conjugate gradient method to minimise the total energy for a static problem. Inherent in this was the second idea or viewpoint. One need not think of the Fourier components of one one-electron wave function as simply one whole, i.e. as 'the wave function'. Instead one can consider them as so many separate coordinates of the system, forming a very large vector-space (see below). Thirdly there was the brilliant idea of using both real space and Fourier space for different matrix multiplications, and going between them with a Fast Fourier Transform, thus reducing operations of length N^2 to ones of length $N \log N$ where N is the length of the vector representing a wave function. Nowadays N is usually of order tens of thousands or even more, so that it makes an enormous difference. Without that trick the calculations done today would be quite impossible. Of course like all the best ideas, they seem obvious once they have been pointed out.

Fourthly the whole calculation could be organised much more efficiently. Consider a static calculation for finding the ground state total energy of some solid system with a defect or surface, including relaxation of all the atomic positions to equilibrium, all at zero Kelvin. Previously the calculation had been organised in terms of loops within loops within loops. First (the innermost loop) one solved the Kohn-Sham (KS) equation for the electrons with some assumed potential and some set of atomic positions. The output would be a charge density, and one can then proceed to the next loop to generate a new potential closer to self-consistency, and then re-solve the KS equation. Then when self-consistency has been achieved for the assumed set of atomic positions, one would calculate the Hellmann-Feynman forces on the atoms and move them towards their equilibrium positions. One then starts again on the inner two loops, and so on until the equilibrium atomic positions have been found. This procedure of loops within loops was adopted partly because it was natural and partly because of the belief that one had to have rather a good charge density before one could expect to get sensible Hellmann-Feynman forces. However CP pointed out that it is a waste of time to solve the KS equation accurately for the wrong potential far from self-consistency and for the wrong atomic positions far from equilibrium. The potential is of course determined by the wave functions and so is a complicated function of the Fourier components C(n,k,j) of all the occupied states n at every k-point in the Brillouin zone. Thus one really wants to do a huge global minimisation in the large vector space of all the C's and the atomic coordinates, approaching the correct solution of the KS equations and the achievement of self-consistency and finding the equilibrium atomic positions all together in the most economical way. Some codes still use a self-consistency cycle with a sophisticated mixing scheme of the old and new charge density, while others work directly on the C's taking into account both their role in the KS equation and in the electrostatics which determines the self-consistent potential.

There is absolutely no question but that the regular meeting of the 'Total Energy and Force' mini and maxi workshops enabled the separate researchers in separate countries to form effectively one group, indeed one very strong group. As a result, they were able to remain at the forefront of research, and they have gone from strength to strength, several building leading individual groups of their own, as we know.

At the same time other cooperating circles developed. The group of Ole Andersen in Stuttgart has already been mentioned, with past and present members maintaining contact, to some degree around use of the LMTO code. Similarly other circles developed, around Daresbury with the KKR code, around the 'Wien' LAPW code, and among alumni of a research school such as 'the Italian mafia' revolving around Trieste. These circles frequently intersect, thanks to Ph D students or postdocs from one moving on to become postdocs in another, but not quite as often as would be desirable. I can think of examples of one group not benefiting from the ideas or results elsewhere following the slogan 'NIH' (Not Invented Here).

Mostly these circles developed purely informally without any organisation or official funding. That lack of funding has sometimes been a problem, for example for holding the mini workshops. In Britain the Collaborative Computing Project number 9 (CCP9) was started by the research council as a national scheme to make the best use of the first Cray computer, but under the leadership of Walter Temmerman at Daresbury and Balazs Gyorffy at Bristol we subverted it a little bit into a European organisation by always inviting guests from the Continent.

In the early 1990s came the first European support. One was the start of a series of Euresco (EUropean RESearch COnferences) modeled on the American Gordon conferences. In fact it was the move of the Gordon organisation to start some conferences in Europe that offended some people and pushed the ESF (European Science Foundation) into starting the Euresco scheme, unfortunately without adequate funding. I put my hand up and said there was a need for an annual series of conferences on electronic structure of solids, and organised the first one in 1992, followed by Scheffler in 1993 and Nieminen in 1994 etc.. The series has continued in most years except 1996 and 2000 when there were the big 'Psi-k' conferences for the whole research community. The topics of these Euresco conferences have been much wider than electronic structure calculation, involving also experimentalists and other theoreticians in a particular field which rotated around surfaces, magnetism, excited states etc.. The one in 2002 on 'physics meets biology' will also be the first in a new series under that heading. In this regard our community has been in a sense the vanguard. The conferences have been excellent, but how does one maintain the momentum? The principle of the Euresco conferences is that the participants at one conference vote on the selection of chairman and topic for the conference two years hence, but one needs good suggestions coming forward and the topic should not get 'stuck' in one sub-field such as surfaces or magnetism. It was therefore decided that the chairmen of previous conferences should form an informal group, now under the leadership of Matthias Scheffler, meeting only by email, to stimulate good suggestions. The previous chairmen, having worked hard to make their conferences a success, are motivated to see that the series continues. Unfortunately the funding is somewhat erratic. For example there was a very good proposal for 1997 but it was not funded, and the one for 2003 has similarly just been turned down. The ESF is a club of national research councils and the problem is that they are unwilling to put enough money into the scheme for it to run smoothly. The ESF tries to get money from Brussels for individual conferences, but EU funding is notoriously erratic and irrational, and ESF does not have enough of its own money to plug the gaps and maintain continuity, unlike the American Gordon organisation.

This funding problem is a typical example of the weakness of Europe which one meets all the time on the European scene. It is not only Britain that is lukewarm about European collaboration. The ESF running the Euresco conferences is a club of the national research councils of practically all European countries (not just those in the EU) and its officials and committee members that I have met are dedicated to the cause. But it has become clear to me that the first priority of the national research organisations is the bureaucracy and funding system for research in their own countries. The quality of the research is a consideration but only a secondary one. Think what it would mean if the priorities were reversed, because second class work is almost worthless in basic research, as Professor Mott once commented. Then most research would be organised and funded nationally, except whenever the larger European area needs to collaborate to achieve top class research. In some areas such as high energy particle physics or space science that may mean a large fraction, while in others it would be only a small proportion. In any case since the total amount of money is (here) a conserved quantity, the amount spent in each country on average would be the same as with purely national funding, but through a slightly different circle. I believe in 'small is beautiful'. Thus in our field, most research projects would appropriately be funded on a national basis, but our networking infra-structure and some research projects should be on a European level. Unfortunately no proper commitment or structure for that exists. That shows that the funding problem with the Euresco conferences is not a small glitch such as happens in any activity, but a fundamental flaw of the system. The same applies to the very low success rate with Network and ESF 'Programme' applications, see below: it is difficult to believe that there aren't more good applications than the few that get funded, where European collaboration would significantly enhance the quality of the research, but that is obviously not the consideration that determines the funding priorities.

The second European development was the granting of an EU HCM (Human Capital and Mobility) Network over the period 1993-97. Walter Temmerman was the main driving force, and it turned out to be a major step forward. It brought together all the strands of DFT calculations on solids and surfaces including magnetism, oxides and everything, and the users of all the major techniques i.e. pseudo-potentials with plane waves, LAPW, KKR and LMTO. It established the pattern that has been followed since, with several types of activity:- (i) holding about 5 to 10 workshops per year; (ii) organising some hands-on training in the use of major codes and other advanced courses, needed because of the sophistication of quantum mechanical simulations; (iii) supporting some individuals for research visits that they could not fund otherwise; (iv) publishing the Ψ_k Newsletter every 2 months; (v) keeping an email list for announcements and job advertisements between issues of the Newsletter; and (vi) organising the first big international conference Ψ_k1996 covering the whole field.

The great success of the EU HCM Network can be seen in various ways. One is that the workshops nucleated some more substantial collaborations, a few of which obtained regular EU TMR and EU RTN Networks with postdocs on focused projects such as magnetic multi-layers. Also significant was the high quality of the invited talks at the Ψ_k1996 conference as a result of being in close touch with all the most recent and exciting work across the whole field. The amount of money for individual visits was of course tiny in comparison with all the travel going on, but we were dealing with cases where the visits were crucial for some piece of high quality research and could not be funded otherwise for some reason, often because the researcher was young or from a small group or had to travel across a state boundary. Through our Working Groups and national representatives, we were quickly able to assess the quality of the proposal and reach a decision in two weeks. As an appendix to the newsletter people submit abstracts of their research papers and details of how anyone interested can get in touch. During this period good contact was established with CECAM in the joint organisation of workshops.

The main point about the EU HCM Network is that it brought together for the first time all those in DFT simulation of solids. Experience has shown that there are no clear dividing lines according to area of application or type of code. Also the range of applications was expanding, for example into mineralogy, and so was the number of researchers, some in small or isolated groups.

Thus it was found that there was and remains a need for some organisation to run the broad range of what we may call 'networking' activities as listed above for the benefit of the whole research community. Moreover the activities need to be organised on a European level because one country is too small to contain all the expertise. They serve quite a different purpose from the focused research networks. One computation is normally carried out by one person in one centre on one computer so that in most cases it is sufficient to keep up to date with the latest ideas and developments through such networking.

At the end of the very successful EU HCM Network there was no possibility of another EU Network like that because the EU had changed its mind and only supported the small focused Networks. This was very disconcerting; one got the feeling that Brussels did not care about what the needs of the scientists was, only caring about their own schemes. Fortunately the ESF had a rather new scheme called 'Programmes' to support networking activities. We applied for one, although the statistical chance of getting one seemed to lie between 5 and 10 %, as was the chance with a focused EU network. In view of the small chances, the dying EU HCM Committee decided it was so important for the whole community to carry on the networking activities as best we could that we applied for both an ESF Programme, and for a focused EU TMR Network which we defocused as much as we possibly could to involve 26 groups in 7 teams from 10 countries! To the activities listed above was added (vii) establishing contact with industry because we are keen to see the DFT methodology applied as widely as possible.

We were obviously not very hopeful about success with either application, but as it happened we got both(!), extending over 1997/8 to 2002. However the applications had been an incredible amount of work: my wife was horrified at the amount of work taking over several months, particularly for the EU TMR Network. Luckily I was nearing retirement and able to devote a lot of time to it, as did the other major leaders. Every sentence, every word almost, has to make a sharp point, with clear general aims and focused details: and of course the actual substance of first class research has to be there, and has to be seen to be impressive. One has to articulate the importance of the work, not by boasting but by making explicit what is often so familiar that it is taken for granted. Also it all has to fit on a strictly limited number of pages.

3 The future of our scientific community

I judge the ESF Ψ_k Programme (now in its last year) as highly successful, with excellent activities and organisational advances under all of the categories (i) to (vii) above. We are therefore applying for a new 5-year Programme with new science, pursued through similar networking activities and with a new chairman Peter Dederichs (from his retirement in March 2004). There is no doubt that Europe is now one of the leading areas in the world for our type of research, and our organisation and joint activities are being copied in America, North Africa and Middle East, the Indian Subcontinent, and the Far East. What was said above about collaboration in connection with the young people returning from USA with the 'total energy and force' method in fact applies across the whole subject. What matters is quality of research, and the networking activities spread the expertise and latest developments to everyone interested. The email list now stands at over 900, mostly in Europe, and with the newsletter it has become the prime vehicle for job advertisement in our field. There must be about 2000 researchers in Europe including PhD students.

The major novel aspect is that the new ESF Programme application includes 'computational many-body theory for real materials', using particularly the Quantum Monte Carlo (QMC) method, the GW method and Dynamical Mean Field Theory. These have now reached the stage of useful application to real materials, and are clearly important for greater accuracy and materials with strongly correlated electrons such as in high temperature superconductors and those showing 'colossal' magneto-resistance.

But what of the more distant future? In two sentences: (a) it is clear to me that our field will continue to develop rapidly for at least the next 20 years, with corresponding need for the networking activities; and (b) we therefore need a more stable on-going networking infrastructure, which we must now try to build. I won't say 'permanent' infrastructure because all organisations can ossify, but we want an 'on-going' status reasonably assured of continued funding as long as the organisation is doing a good job as shown by peer review every few years.

Let us take these two points in turn. Certainly computer simulation is not going to go away, and in fact I believe we are only just scratching the surface at present. Industrial applications are still very small, and application to biology/pharmaceuticals had its first ever workshop last summer. There is also the problem of spanning the length and time scales to the meso- and macro-scopic, of interest to both the Ψ_k and *SIMU* Programmes. To get a picture, let us focus on just one little area, namely the QMC method by which I mean Diffusion or Green Function Monte Carlo (not Path Integral Monte Carlo) for getting ground state (and excited state) total energies. This gives 'chemical' accuracy of order 0.01 eV per atom, "which is good enough to tell whether a new drug will kill or cure you, or a new catalyst really work", a remark by Erich Wimmer which I have often quoted. Isn't it obvious that that is going to be important? But the methodology now can be compared roughly with the state that DFT was in about 15 years ago. There are as yet no Hellmann-Feynman forces, and until recently it took several hundred to a thousand times the computer power of DFT calculations. By Moore's law (which may not extend that far into the future) that is about 15 years growth in computer power, but actually new QMC algorithms by Mike Towler are already bringing that down.

I think we can therefore see the continued need for good networking because of the sophistication of the methodology, its rapid advance, the growth in the fields of application, and the training of new entrants wanting to make use of it. Having seen the way the subject has developed over the last 20 years, we can predict a timescale that is at least similar in order to achieve the desired advances.

Clearly there needs to be a more on-going networking organisational infrastructure. There is no future in just applying for five years here and then for five years somewhere else, because we have come to the end of the road as far as schemes that we can to apply to. All funding agencies, love to start novel projects, but few seem to consider continuing those that are successful. (That has always seemed a strange management policy, to start something and then dump it when it succeeds. What, one wonders, was the purpose of starting it?) Until last year, it was not possible to apply for a second time for an ESF Programme, but they changed the rules for us if we could come up with a new application involving new science. We hope that we may be successful, which will then cover the next five years. However I believe the ESF Programme scheme is not intended for providing a longer term infrastructure.

So where do we turn to? Frankly, there is nowhere. Our type of infrastructure needs still to be created on the European scene. It exists of course on the national level, as for example the British CCP9 mentioned above, but not European-wide. Another example of how feeble Europe is. If CCP9 didn't exist in Britain, at least we would have the research council with a clear structure and with the money, and we would know where to go. But even that does not exist on the European level, because the ESF basically has no comparable budget of its own and can only do what the national research councils want it to do. Our only hope is to try to help create this type of networking infrastructure by pressing our case wherever we can in Brussels, Strasbourg (home of the ESF) and the national research councils that direct ESF.

Perhaps not all may be gloom and doom. Infrastructure is a new buzzword in Brussels and presumably elsewhere. From the statements that have appeared, it is clear that they principally have in mind large machines such as synchotrons. The definition has been widened to include databases such as information on protein structures or econometric data, but I doubt that it is elastic enough to include us. The ESF is aware of our situation but I do not know how to engage with Brussels.

If we could design the world to our own choosing, what sort of structure would we want? That is not clear to me, beyond the 'on-going' in the sense defined above with periodic peer review but the prospect of renewal. The Ψ_k community should probably think about this together with the *SIMU* Programme. To have a longer term status, I think we would need to come under the umbrella of a more permanent organisation to administer the funds and act as a secretarial and legal base, much as the Daresbury Lab is the base for CCP9. Frankly I cannot see any funding agency having a longer term relation with something as diffuse as our present Ψ_k organisation.

I wonder whether at some point in the future CECAM (Centre European de Calcul Atomique et Molecular, in Lyon) or the Computational Materials Science Centre in Vienna or Daresbury or some centre like it may have a larger part to play. In Britain it is fashionable for every business and organisation such as a school or research council to have a 'mission statement' of what its purpose is. If we were to write a mission statement for this imagined centre, we could think of a mini mission of running workshops in response to proposals submitted in the field of atomistic and molecular calculations on materials. On the other hand a maxi mission could be to be pro-active in providing all the infrastructure (not just workshops) needed by the European research community in that field, at least those things done best on a European rather than national level. I think such a mission would include all the activities labeled (i) to (vii) above.

Of course staff of the centre would not necessarily have to do all that itself. Indeed I would envisage a Ψ_k committee actually getting on with organising the activities, with the centre acting as the vehicle for the funding and as an aid for securing the funding (from Brussels? or ESF? or national research councils? under some infrastructure scheme?), for arranging the publication of the Newsletter and maintaining the email list and website (once Dzidka Szotek gets tired of doing it), handling the claim forms etc., for all of which there would have to be a modest payment (as there is to ESF and Daresbury now with the present Programme). And I would hope such a centre could do one thing more. Organisations have a life cycle, arising in response to a need and dying when no longer required. But what often happens is that they die because some leader retires or moves on to something else and there is no-one to pick up the pieces. That is especially a danger with scattered organisations such as Ψ_k, communicating only by email except for one meeting per year. If that should happen, I would hope the centre would see it in its own interest to call together the remains of the committee, together with the elders of the tribe, give them a good kick in the pants and tell them to get themselves organised again.

4 News from the Research Training Network (RTN)

COMPUTATIONAL MAGNETOELECTRONICS

4.1 Reports on RTN Workshops

4.1.1 Report on the Workshop on X-Ray Spectroscopies of Magnetic Solids 2001

This workshop was organised by Wolfgang Kuch (Halle, Germany) and Paul Strange (Keele,UK). It took place at the Max-Planck-Institut für Mikrostrukturphysik in Halle, Germany on 8th–9th December 2001. This was the second in a series of meetings that started in Berlin in December 2000. The dates chosen follow directly on from the users meeting for the Bessy synchrotron enabling wider participation than would otherwise be possible.

The objective of this meeting was to bring together theoretical and experimental scientists who work in the field of X-ray spectroscopies applied to research in magnetism with the aim of discussing recent advances in the field. The format of the workshop was a mixture of plenary (45 minutes) and shorter (20 minutes) talks and there was also a poster session. Plenty of time was available for discussion and there was frequent lively debate. The timetable was organised so that speakers interested in particular techniques were grouped in the same session as much as possible. Sessions were held on resonant X-Ray Magnetic Scattering, Absorption and dichroism in absorption, X-ray magneto-optics, photoelectron spectroscopy and theoretical developments. Applications to a wide variety of magnetic materials were also discussed including actinide, rare earth, and transition metal materials in bulk and in two dimensions at surfaces or buried interfaces.

To provide a more detail on the workshop the abstracts of all papers presented are reproduced in this newsletter. Further information, including photographs! are available at the workshop website at

`http://www.mpi-halle.mpg.de/$^{\sim}$xrms2001/`

Future prospects for further experimental developments and higher photon fluxes, together with the number of unresolved issues and the experimental results that lack a theoretical explanation/interpretation convinced all the participants of the value of continuing this series of workshops in future years.

Paul Strange (Keele) and Wolfgang Kuch (Halle)

Abstracts of papers presented at the workshop

Magnetic resonant soft x-ray scattering from thin lanthanide metal films

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With the availability of high-intensity x-rays at third-generation synchrotron radiation sources, magnetic scattering is being developed as a routine method for the study of magnetic structures and correlations in magnetic materials. In this field, resonant scattering in the soft x-ray region is gaining importance due to a huge increase of the magnetic scattering amplitude at the $L_{2,3}$ absorption edges of the $3d$ transition metals and the $M_{4,5}$ edges of the lanthanides. Particularly large effects may be expected in the latter case reported here. Experiments on thin lanthanide-metal films were carried out at the U49/1-SGM beamline at BESSY II using a fully UHV-compatible ($\Theta/2\Theta$) diffractometer that allows growth of monocrystalline films under UHV conditions and *in-situ* studies in a large temperature range down to $\approx$ 30 K. The results obtained at the M_V edges of the lanthanides demonstrate the potential of the method for magnetic-structure studies of ultrathin films and surface magnetism:

(i) The large resonant enhancement of the magnetic scattering amplitude at the M_5 edges allows to extend magnetic-structure studies to ultrathin films with thicknesses of only a few monolayers. This is demonstrated for Ho metal, characterized by a helical antiferromagnetic structure with a period of $\approx$ 10 monolayers, matching the photon wavelength at the M_5 edge. Studies can be carried out on films of hitherto not accessible thicknesses of the magnetic period itself.

(ii) The strongly reduced x-ray penetration depth across the M_5 resonance leads to high a surface sensitivity of the method, allowing a characterization of the magnetic properties of the topmost surface layers. By exploiting the different surface sensitivities of magnetic x-ray scattering at the L_3 and M_5 edges, respectively, the ferromagnetic/antiferromagnetic phase transition of Dy metal was studied in UHV on *in-situ* grown films, revealing a delayed growth of antiferromagnetic domains at the surface.

(iii) Magnetic resonant x-ray diffraction at the M_5 edge of Ho is directly compared to magnetic neutron diffraction. In the case of a 46-Å-thick Ho film, count rates as high as 5×10^7 photons/sec in the magnetic diffraction peak were obtained, compared to $\approx$ 100 neutrons/sec in the latter case. This increased sensitivity allows to perform critical-scattering studies of short-range magnetic correlations above the Néel temperature with unprecedented data quality for these ultrathin films.

This work was supported by the BMBF, project 05 KS1KEE/8.

Soft X-ray Resonant Magnetic Scattering from FePd stripes and Co/Pt nanolines

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Regular magnetic domain patterns are a characteristic feature of many low-dimensional systems with phases stabilized by competing interactions. In ultrathin magnetic films such a domain structure can occur when the spin moments prefer to order perpendicular to the film plane. These systems are of particular interest for magneto-optical storage devices and display the giant magneto-resistance effect utilized in magnetic field sensors. It is the competition between perpendicular magnetocrystalline anisotropy (PMA) and dipolar spin-spin magnetic interaction that leads to the regular domain pattern.

We present the novel method of circular dichroism in soft x-ray resonant magnetic scattering (XRMS) that can be used for depth profiling of these materials. We utilize the strong magneto-optical effect at the $L_{2,3}$ absorption edges of $3d$ transition metals that causes a Faraday rotation of the (linearly) polarized x-rays analogous to, but much stronger than, the Kerr ellipticity in the visible region. The circular polarization allows us to observe correlations between the perpendicular domains and adjacent closure regions. The interference observed between scattering channels is a direct tool to study closure domains and domain walls. Application to single crystalline FePd layers allows to monitor magnetic flux closure domains. It was found that flux closure occurs in samples with low to medium PMA, while a high PMA impedes closure domain formation.

We further used XRMS to study periodic arrays of silicon nanolines covered by a Co/Pt multilayer, with PMA. At the Co L_3 resonance large magnetic signals appear both on top and between the structural diffraction peaks. These superstructure satellites reveal an antiferromagnetic order generated by the interline dipolar coupling. Their intensities are strongly sensitive to the magnetic history and can be enhanced through specific demagnetization processes. By applying an in-situ magnetic field the evolution of the magnetic signal has been monitored through the entire hysteresis loop. The magnetic contribution on the structural superlattice peaks can be quantified by their asymmetry ratio, whose angular variation is partly explained by the angular dependence of the scattering factor. The change of the purely magnetic satellites with the magnetic field is completely reproducible and characterizes the modifications of the magnetic configuration during the reversal process.

Resonant X-ray magnetic scattering from actinides

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Resonant effects, which occur when the photon energy is tuned exactly to a absorption edge of a certain element, have led to the new field of magnetic dichroism, which is based on absorption, as well as new discoveries using scattering techniques. Because Bragg's law can be fulfilled for normal crystals for many edges in the actinides, more work has actually been performed in the actinides than in other parts of the periodic table. Effects have been observed at L_2, L_3, M_2, and M_3 all of which involve promotions of electrons from the $p \rightarrow 6d$ shells, and the M_4 and M_5, which involve $3d \rightarrow 5f$ transitions. The systematics of these results will be discussed showing that, although there is some understanding from atomic physics, many puzzles remain. More recently we have observed large resonant effects at the K edges of anions, such as Ga, As and Se, when incorporated into actinide compounds. This opens up a new form of spectroscopy in the $5f$ materials.

This work has been done in collaboration with N. Bernhoeft, R. Caciuffo, A. Hiess, E. Lidström, D. Mannix, M. Longfield, P. Normile, J. A. Paixão, J. Rebizant, W. G. Stirling, C. Vettier, and F. Wastin, to whom I express my sincere thanks. We also acknowledge the safety teams at Brookhaven, Long Island, NY, and the ESRF in Grenoble for support.

Even and Odd in M: Theory and Experiment of Magneto-X-Ray Spectroscopies

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Magneto-optical effects can be classified in two groups, according to the parity of the effect with respect to the magnetization M, which can either be odd or even. To lowest order in M this distinguishes linear or quadratic in M effects. The latter are much smaller than linear in M effects, and only a few such X-ray measurements have so far been reported. To the X-ray techniques that probe the quadratic in M magneto-optical response belong the XMLD and the X-ray Voigt effect [1], that are both measured with linearly polarized synchrotron radiation. X-ray Voigt spectroscopy is a new tool in the X-ray regime that facilitates the element-selective study of the local magnetization expectation value $\langle M^2 \rangle$. Our *ab initio* calculations provide an excellent description of the X-ray Voigt spectra. Moreover, our calculations demonstrate that the Voigt effect depends crucially on the amount of spin polarization of the $2p$ states. Therefore it provides a unique measure of the spin splitting of the core states. X-ray Faraday spectroscopy which has recently become established in the soft-X-ray regime, is an effect that is odd in M. We discuss our recent experiments and *ab initio* calculations of the X-ray Faraday effect at the $L_{2,3}$-edges of transition metal films. We show that linear in M magneto-optical effects depend only modestly on the spin splitting of the core states.

[1] H.-Ch. Mertins, P. M. Oppeneer, J. Kuneš, A. Gaupp, D. Abramsohn, F. Schäfers, Phys. Rev. Lett. **87**, 047401 (2001).

Soft X-Ray Magneto-Optical Constants at the 2p edges of Fe and Co determined by Bragg scattering and Faraday Effect

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Resonant magnetic scattering data on Fe/C and Co/C multilayers are presented. These data were obtained in Bragg scattering geometry with longitudinal magnetic field using circularly polarized undulator radiation at BESSY. This experiment enabled the direct determination of the refractive and absorptive parts of the optical constants $n_\pm = 1-\delta_\pm+i\beta_\pm$ of ferro-magnetic Fe and Co across their $2p$ edges. An alternative experimental data set was obtained from Faraday experiments [1] on identical but transmission samples. Both results are discussed and compared with recent ab-initio calculations [2].

[1] H.-Ch. Mertins et al., Phys. Rev. B **61**, R874 (2000)

[2] J. Kunes, P.M. Oppeneer et al., Phys. Rev. B (2001) in press

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X-ray magneto-optics in lanthanides: principles and applications

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Conventional magneto-optical methods operating in the visible light regime generally lack element specificity; this has become a severe limitation in research on heteromagnetic exchange coupled systems. – The giant photoabsorption cross section at lanthanide 4d-excitation thresholds in the soft x-ray regime reveals unprecedentedly large magneto-optical signals [1] in reflectivity which, expressed as changes $(\delta^+ - \delta^-)$ and $(\beta^+ - \beta^-)$, amount to 0.05 in size (refractive index $\mathrm{n}^\pm = 1 - \delta^\pm - \mathrm{i}\beta^\pm$ for circular-light propagation parallel + or antiparallel − to the magnetization). Owing to the long wavelength ($\sim 10\,\mathrm{nm}$) these magneto-optical constants give rise to a substantial element-specific magnetic contrast in the reflected light intensity (XMOKE) at experimentally convenient glancing angles of a few 10°.

As one of many examples for potential XMOKE applications we present a temperature dependent study of the *magnetization reversal* process in exchange coupled Gd/Y/Tb trilayer systems. 1..2 nm spacer layers of Yttrium mediate an exchange coupling corresponding to some 100 Oe at 70 K between the ∼ 10 nm thick Gd and Tb layers. The coupling strength drops rapidly with increasing temperature, showing a change from ferro- to antiferromagnetic coupling well below the ordering temperature of the system.

This work is supported by BMBF (05 SC6 KEB-8) and the DFG (Sfb 290).

[1] K. Starke, F. Heigl, A. Vollmer, M. Weiss, G. Reichardt, G. Kaindl, Phys. Rev. Lett. **86**,

3415 (2001).

Probing magnetic susceptibilities using the field-induced magnetic circular dichroism

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The magnetic circular dichroism in X-ray absorption (MCXD) is now a standard tool to probe the spin and orbital moments in magnetic materials by exploiting the so-called sum rules. In these systems the magnetic dichroism may be ascribed to the spontaneous exchange splitting. On the other hand, it its known that the magneto-optical Faraday effect, for example, can be observed for magnetic materials as well as for non-magnetic materials if they are exposed to a magnetic field. Accordingly, magnetic circular dichroism in X-ray absorption should be observable also in non-magnetic materials exposed to a magnetic field. A theoretical description of such an experiment is presented that is based on a combination of a fully relativistic linear response formalism and a corresponding treatment of magnetic circular dichroism. It is demonstrated that application of the magnetic sum rules now gives access to the spin and orbital element projected susceptibility of the system under investigation. In particular one finds that it is only the VanVleck contribution to the orbital susceptibility that is probed. In contrast to spontaneously magnetized systems, however, there are orbital contributions derived from the dichroic signal that stem from the external field and also from the intrinsic spin-orbit coupling. Illustrating examples will be presented for various transition metal systems that will demonstrate the usefulness and applicability of the new approach.

X-ray dichroism and orbital anapoles

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Photo-absorption spectroscopies in noncentrosymmetric systems are discussed, covering both x-ray and optical regions. Integrated dichroic spectra are interpreted using microscopic effective operators, which are obtained by coupling the orbital angular momentum to the orbital anapole. Symmetry arguments afford a classification of valence-electron states in the presence of parity nonconserving hybridisation. Enantiomorphism is identified by a two-particle chiral operator.

Quadrupolar and Dipolar Contributions to Tb XMCD at the $L_{3,2}$-edges: Experiment versus Theory

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The appearance of quadrupolar transitions in the L-edge X-ray Magnetic Circular Dichroism (XMCD) of rare earth compounds has been controversially discussed (see e.g. [1]). Therefore, we investigated the XMCD at the $L_{3,2}$-edges for the first time using a single crystal as a prototype system in order to ascertain the multipolar nature of the features in the dichroic spectra. As known from XMCD experiments for Fe, Co and Ni, spin and orbital moments can be deduced by applying the so-called sum rules. In the case of the 3d metals, at the $L_{3,2}$-edges transitions from the initial $2p_{3/2}$ and $2p_{1/2}$ to the final 3d states can be probed being of dipolar nature only. In contrast, it is discussed that at the L-edges of rare earth metals dipolar (E1: 2p→5d) and quadrupolar transitions (E2: 2p→4f) contribute to the XMCD [2]. Hence, information about the 4f magnetism in addition to the polarized 5d magnetism can be achieved by analyzing the Tb L-edges. We carried out *ab initio* calculations (FEFF code [3]) in order to support our model for the analysis of the experimental data: The line shape of the dominant dipolar contribution in the XMCD can be approximated by calculating the derivative of spin-averaged absorption spectra ($\mu(E)$) [4]. The subtraction of the derivative of $\mu(E)$ from the experimental XMCD data results in the quadrupolar contribution. This deconvolution has to be carried out before applying sum-rules to determine 4f and 5d moments [5]. Here we present high quality temperature-dependent XMCD data for Tb measured at a the ESRF. The high resolution of the data allows for the first time for a clear identification of the E1 and E2 contributions. We observe rather large quadrupolar components at the Tb $L_{3,2}$-edges which result in much more fine structures in the XMCD spectra compared to the ones known for 3d transition metals.

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Combining scattering with resonant magneto-optical effects to gain spatial resolution

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Resonant soft x-ray magneto-optical (MO) effects were initially used to measure element-specific magnetic properties *spatially averaged* over the illuminated area. *Spatial resolution* in magnetic properties can be achieved in many different ways. We are investigating different approaches using soft x-ray resonant scattering to obtain ensemble-averaged spatial resolution of magnetic and chemical properties. One approach uses x-ray standing waves produced by a substrate composed of a multilayer interference structure to *depth-resolve* absorption and MCD spectra at buried interfaces of thin magnetic layers deposited atop the multilayer standing wave generator (SWG). We have used this approach to observe rapid changes in the number of Co d holes and in-plane orbital and effective spin moments of Co with distance across Co/Pd interfaces [1]. In this case the resonant MO effects are confined to the 2 nm thick Co layer atop the SWG, and so are a minimal optical perturbation to the standing wave produced by the multilayer. Another approach uses resonant diffuse small-angle scattering to resolve *in-plane* magnetic and chemical structure in thin films. With these techniques we have resolved magnetic and chemical correlation lengths in Co/Pt films with perpendicular anisotropy [2] and also in magnetic recording media having in-plane and perpendicular anisotropy. The applied field dependence of the scattering, and direct comparison with microscopy results (when available), enable unambiguous resolution of predominantly magnetic and chemical scattering features. We are also learning that analysis of the energy spectra of scattering, using measured resonant charge and magnetic scattering factors, offers another means to resolve and quantify magnetic and charge contributions. Together these scattering techniques provide powerful capabilities to study a range of questions in magnetic materials, especially thin films, in which the spatial variation of magnetization and chemical structure on the nanometer to micron scale is key.

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Probing Buried Magnetic Interfaces with Standing-Wave Excited Photoemission

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In this talk, the role of soft x-ray optical effects in photoemission [1] and soft x-ray emission will first be introduced, including both off-resonance and on-resonance phenomena. The specific application of strong off-resonance standing waves created above a multilayer B_4C mirror to the depth-resolved study of a buried Fe/Cr interface will then be considered. In this case, growing the Fe/Cr bilayer in a wedge configuration permits scanning the standing wave through the interface, and probing composition, local spin moment, and magnetic order via core level photoemission and magnetic circular dichroism. This technique should have various future applications to the study of buried interfaces for both magnetic and non-magnetic systems. The present status of multi-atom resonant photoemission (MARPE) as another effect related to x-ray optics [2] will also be reviewed, including recent data for NiO and other systems.

Work supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences Division, under Contract No. DE-AC03-76SF00098, and the Korea Science and Engineering Foundation
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Investigating magnetic coupling by resonant scattering of polarized soft x-rays

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The use of polarized x-rays of tunable energy has widened the range of application of x-ray scattering techniques. Magneto-optical effects are stronger when one selects photon energies that correspond to the onset of core electron excitations (resonant process), in particular those excitations that directly involve *magnetic* orbitals. Experiments in the soft x-ray region are particularly suited to studying $3p$ or $2p-3d$ resonances in transition metals and $4d$ or $3d-4f$ resonances in rare-earths, as large magnetic signals are thus combined with the element selectivity of core excitations.

Examples will be given of recent applications of resonant scattering of polarized x-rays to the study of the magnetic properties of thin layers, including surfaces and ordered superstructures.

Magnetic Coupling At Antiferromagnetic/Ferromagnetic Interfaces — A Spectromicroscopy Study

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We use dichroism x-ray absorption spectroscopy in a photoemission electron microscope to determine the magnetic coupling between antiferromagnetic NiO(001) and ferromagnetic Co across its interface. We observe large (1–20 μm) antiferromagnetic domains at the surface of NiO(001) single crystals. Thin ferromagnetic layers (1.5 nm) of Co deposited in situ exhibit a strong uniaxial anisotropy. We find that the ferromagnetic anisotropy axes align perfectly parallel domain by domain to the antiferromagnetic axis. Furthermore a weak ferromagnetic moment in NiO parallel to that in Co at the interface could be detected. Upon annealing both, the uniaxial anisotropy and the interface polarization increases. For the first time such an antiferromagnetic-ferromagnetic coupled structure could be completely characterized by means of spectromicroscopy. Possible origins of the interface polarization and its consequences for the magnetic coupling will be discussed in the talk.

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Spin projection of empty partial density of states by resonant X-ray scattering: Applications to antiferromagnetic NiO

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We report the first experimental spin projection of empty partial density of states (PDOS) in antiferromagnetic NiO. Resolving resonantly scattered Ni $K\alpha_{1,2}$ and Ni $K\beta_{1,2}\beta'$ core line spectra into the spin-up and spin-down components the spin character of the dipole-excited Ni p-like and quadrupole-excited Ni d-like conduction band states has been analyzed. The results obtained for NiO and paramagnetic MnO provide the opportunity to proof experimentally the results of spin-dependent (LSDA+U) band structure and cluster calculations. We argue the new spectroscopy complements X-ray magnetic circular dichroism which is silent for antiferro- and paramagnetic materials. So, we get insight into the spin polarization of conduction band states in correlated materials independently on their magnetic ordering.

Layer resolved nanosecond magnetization dynamics in magnetic heterostructures using XMCD

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We have used X-ray Magnetic Circular Dichroism (XMCD) in absorption to investigate the layer resolved magnetization dynamics in magnetic heterostructures. We have studied Co/Cu/FeNi spin valves with different Cu thicknesses, as well as Co/Al_2O_3/FeNi tunnel junctions. The measurements were performed using a pump-probe scheme, where the magnetic pulse (pump) was provided by copper microcoils and the probe by the photon pulses of the ESRF in single bunch mode. The behavior of the different layers was studied using the dichroism at the L_3-edges of Co and Ni.

We have demonstrated that in some cases the coupling between the magnetic layers through the non-magnetic spacer depends on the field sweep rate and can therefore be very different in static and dynamic measurements. The switching coefficients in our measurements, obtained from a linear fit of the reversal time versus the pulse height, are typical for a regime where reversal takes place through the nucleation of reversed domains. In the static regime the reversal takes place mainly through domain wall propagation. This suggest that the difference in coupling is due to the difference in magnetization reversal processes which dominate at low and high sweep rates.

The importance of layer resolution in dynamic magnetization measurements will also be illustrated with results obtained on arrays of 1.3 μm squared tunnel junctions, as well as on Co/NiO/FeNi trilayers showing a 90° coupling.

Characterization of Magnetic Nanostructures using Synchrotron Radiation

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The characterization and modification of the magnetic properties of nanostructures plays an important role in the development of future magnetic storage media, MRAM devices, and sensors. Synchrotron radiation, by means of the polarization, offers the unique possibility to determine the element specific magnetic moments in nanoscale systems. Furthermore, magnetic orientations in ferromagnetic as well as antiferromagnetic systems can be characterized on the nanometer size scale with a resolution far superior to optical methods. Examples to be discussed include the orientation of magnetic moments in fcc Fe grown on Co(0001), monoatomic Co nanowires grown on stepped Pt surfaces, and investigations of the domain structures in ferromagnetic and antiferromagnetic systems using coherent soft X-Ray scattering.

Magnetic Dichroism in Core-Level Photoemission: A Multiple-Scattering Theoretical Approach

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Magnetic dichroism in spin- and angle-resolved core-level photoemission is investigated within the relativistic one-step model of photoemission based on multiple-scattering theory. Photoelectron scattering in emission from $3p$-levels of low-index Fe- and Ni-surfaces is found to affect intensities, dichroism, and photo-electron spin polarizations considerably, in particular in off-normal emission. In general, the calculated spectra agree well with their experimental counterparts in spectral shape, size of the dichroic signal, and spin polarization. Magnetic circular dichroism in a chiral set-up is analysed theoretically using appropriately defined asymmetries. Further, core-level energy positions and photoemission are compared with those obtained within an atomic model.

Angle resolved ultraviolet photoelectron spectroscopy at thin cobalt films on W(110): Experimental results and analysis of the electronic structure

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Spin integrated angle resolved ultraviolet photoelectron spectroscopy at ferromagnetic surfaces and thin films is able to give access to the electronic band structure and, at the same time, on the magnetic properties. Here, experimental results from epitaxially ordered hcp(0001) films on W(110) are presented using tuneable linearly and circularly polarized synchrotron radiation. Photoelectron spectra taken with opposite magnetization directions exhibit intensity differences, i.e., a magnetic linear and circular dichroism in the angular distribution of photoelectrons (MLDAD and MCDAD). Especially these asymmetry effects open the possibility to study magnetic phenomena without additional spin analysis of the emitted photoelectrons. The experimental results from ultrathin cobalt films clearly show large MCDAD and MLDAD asymmetries in the Co 3d band close to the Fermi energy which strongly vary with the photon energy. The data are discussed with respect to fully relativistic band structure and photoemission calculation carried out within the one step theory. Most of the observed MLDAD and MCDAD effects could be related to certain hybridization regions in the initial states of cobalt. A detailed analysis and understanding of these valence band photoelectron spectra is only possible in direct comparison to such calculations. Finally, the data are briefly discussed with respect to an orbital projected band structure.

P1

Electronic and Magnetic Properties of Interfaces Obtained by Dichroic Core-Level Photoemission

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In this contribution we investigate theoretically how the magnetic and electronic structure of interfaces between a ferromagnetic and a nonmagnetic material can be investigated by means of magnetic dichroism in core-level photoemission. The spin-resolved dichroic photocurrent depends strongly on the properties of the two constituents at the interface (e. g., exchange and spin-orbit splitting, hybridization, magnetic ordering, core-level shift) and on the thickness of the covering layer. We choose as prototypical systems ultra-thin films of Fe and Pd because of their large exchange and spin-orbit splittings, respectively. The spin- and angle-resolved dichroic photocurrent was calculated within the relativistic one-step model of photoemission as formulated in multiple-scattering theory. The ground-state properties were obtained by spin-polarised *ab-initio* layer-KKR calculations.

P2

Theoretical description of resonant magneto-optical properties in the X-ray regime

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A version of the Kubo-formula is presented, that allows to calculate the resonant magneto-optical properties in the X-ray regime for arbitrary materials. This is achieved by representing the underlying electronic structure in terms of the Green's function. Calculating the Green's function in the framework of spin-polarised relativistic multiple scattering theory (SPR-KKR) in particular gives access to spin-orbit induced resonant magneto-optical properties. As for the optical regime of light, all magneto-optical properties in the X-ray regime are closely related to the optical conductivity. Our method for calculating of the frequency dependent optical conductivity allows therefore a rather detailed discussion of all experimentally observable magneto-optical phenomena.

Using the Green's function formalism allows in a straightforward way to deal with systems without three-dimensional translational symmetry. Two important examples for these are surfaces and disordered alloys. For the later case we present results of calculations of the Faraday effect for the $L_{2,3}$-edge of Fe and Ni in the disordered alloy $Fe_{0.5}Ni_{0.5}$ making use of the CPA. For the disordered alloy system Co_xPt_{1-x} the same effect has been studied at the L_3-edge of Pt for the whole concentration range. Using these results, in particular the relationship of the complex refractive index with the magnetic of the probed atom, will be discussed in some details. Also the results of calculations for the X-ray resonant scattering – transverse Kerr effect – in the layered systems Fe/Ag and Pt/Co will be presented.

P3

Interfacial magnetism and magnetic moments of Fe/V(001) superlattices studied by XMCD

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Nowadays, x-ray magnetic circular dichroism (XMCD) is a well established technique for investigation of the magnetic properties and magnetic moments in 3d-metals like Fe, Co and Ni. Moreover, it opened new possibilities as an element-specific probe of magnetic multilayers. Recent experimental and theoretical studies [1,2] on Fe/V superlattices have shown that V acquires an induced magnetic moment, which is coupled antiferromagnetically to the one of Fe. However, there exists disagreement between theory and experiments on the magnitude of the magnetic moments at the interface and the layer-dependent moment distribution for both, Fe and V. It is predicted by theory that the induced magnetic moment of V is mainly located at the Fe/V interface and the Fe magnetic moment at the interface is reduced.

We present thickness-dependent XMCD measurements performed at the $L_{2,3}$ edges of ultrathin Fe and V layers in Fe/V(001) superlattices with exceptionally high structural coherence [3]. By combining the XMCD technique with a conventional magnetometry, namely Vibrating Sample Magnetometry (VSM), we deduced magnetic moments for Fe as well as for V in our samples with selected thicknesses between 2-5 atomic layers, where interface effects are easier revealed. We observe a strong dependence of the Fe and V magnetic moments by variation of either the Fe or the V thickness. The outcome is a Fe magnetic moment, which is strongly reduced at the interface *and* a V magnetic moment, which could be as high as $1.1\mu_B$/atom at the interface. Furthermore, by applying the 'sum rules' [4] to the Fe XMCD spectra, an enhanced orbital over spin magnetism is revealed by decreasing the Fe layer thickness. These results are discussed with respect to Ferromagnetic Resonance experiments [3] and *first principle* calculations [5].

This work is supported by BMBF (05 KS1 KEB4), DFG (Sfb 290) and the ESRF.

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P4

Domain imaging of canted magnetization in exchange coupled Co/Cu/Ni trilayers using photoemission microscopy

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Photoelectron emission microscopy (PEEM) in combination with magnetic circular dichroism in soft x-ray absorption (XMCD) allows the element-selective microscopic imaging of magnetic domains. This technique is applied to the study of exchange coupled ultrathin epitaxial Co/Cu/Ni/Cu(001) trilayers. Single element Co and Ni films are known to exhibit opposite magnetic anisotropy when grown epitaxially on Cu(001): Whereas the magnetization in Co/Cu(001) is always in-plane, Ni/Cu(001) shows an out-of-plane magnetization in an extended thickness range. Co and Cu were grown as crossed 200 μm wide micro-wedges with thicknesses of 0–6.5 ML (Cu) and 0–6 ML (Co) on top of 15 ML Ni/Cu(001). The element-selective imaging of the as-grown Co and Ni domain configurations by XMCD-PEEM allows to identify spin-reorientation transitions in each layer separately. Quantitative analysis of domain images for different azimuthal sample orientations can be used for the vectorial determination of the layer-resolved local magnetization directions. For low Cu thicknesses, i.e., strong ferromagnetic coupling between the magnetic Co and Ni layers, both films are magnetically aligned, the local magnetization direction being either fully in-plane or fully out-of-plane. Increasing the Cu thickness in the case of out-of-plane magnetization, a spin-reorientation transition of the Co magnetization from out-of-plane to in-plane takes place. In the case of in-plane magnetization, the Ni magnetization first reorients into a 45° canted state for increasing Cu thickness, followed by a gradual rotation towards a fully out-of-plane configuration at higher Cu thicknesses. A fourth order Ni anisotropy contribution is needed to model this finding in a phenomenological description.

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P5

Interface magnetic coupling in single-crystalline Co-FeMn bilayers

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Despite the recent interest in the coupling between an antiferromagnetic and a ferromagnetic film, fueled by applications in magnetoresistive devices, a full understanding of the observed phenomena is still elusive. This is in part due to the incomplete characterization of the interface in the sputtered bilayers that are typically used for applications. In order to address this issue, we deposited epitaxial fcc Co/FeMn bilayers on a Cu(001) single crystal surface by electron beam assisted thermal evaporation. Oscillations in the diffracted electron intensity during growth of the bilayers as well as scanning tunneling microscopy studies indicate layer-by-layer growth. The magnetic domain configuration was studied by photoelectron emission microscopy (PEEM) in combination with magnetic circular dichroism in soft x-ray absorption (XMCD). Characteristic changes in the Co domain pattern are observed at the transition of the FeMn layer between paramagnetic and antiferromagnetic as a function of FeMn thickness or temperature. These include a drastic reduction in domain size of the as-grown bilayers, and a change in the magnetization direction of the Co domains from $\langle 110\rangle$ to $\langle 100\rangle$ in-plane directions. These results point towards an important role of topological 90° domains in the nominally compensated antiferromagnetic FeMn(001) surface for the coupling between FeMn and a ferromagnetic layer. Ferromagnetic domain images acquired at the Fe and Mn L_3 edges show the same domain patterns as in the Co layer, however with a strongly reduced contrast. Since the Fe and Mn XMCD signal does not change at the transition between antiferromagnetic and paramagnetic, it is concluded that most of these induced moments are not important for the coupling to the Co layer.

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P6

Polarization-dependent soft X-ray resonant magnetic scattering on stripe domains

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Polarization-dependent soft X-ray resonant magnetic scattering (SXRMS) is a new tool for studying magnetic structures in surfaces and thin films on the nanometer length scale [1,2]. A unique feature of SXRMS compared to imaging techniques is that it allows the separation of scattering contributions from bulk domains, domain walls and closure domains. We have extensively explored the possibilities of this technique in a study of 180 nm period dense stripe domains in GdFe5 thin films. Results of magnetic-field dependent measurements in transmission and reflection geometry and with the field applied both parallel and normal to the film plane are presented. Extensive use is made of the possibility to switch the polarization parallel or normal to the stripe direction, as given by the new ID08 undulator at ESRF. The size of the domains, the amplitude of the magnetic modulation, the domain wall-width and the stripe correlation lengths were followed along the magnetization curve up to fields of 0.5 T.

As an example, Fig. 1 compares the intensity of the first diffraction peak and the net in-plane moment as a function of magnetic field applied along the stripes. A magnetic scattering signal was detected close to the critical field for stripe nucleation. At this field we find an undulating stripe structure with only 1% of the original modulation amplitude, which is a convincing illustration of the sensitivity of the method.

P7

X-ray resonant magnetic scattering from Co/Cu multilayers at the Co L_3 edge

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Magnetic and structural properties of magnetron-sputtered Co/Cu multilayers were investigated by complementary methods. Samples with individual layer thickness corresponding to the first and second maximum of the GMR (giant magnetoresistance) were prepared and characterized by transport measurements, MOKE (magneto-optical Kerr effect) and X-ray diffraction. Annealing experiments were performed until the GMR reduced significantly, and alterations of the sample structure leading to a decay of the layer structure were observed. In particular, the unique possibilities of resonant magnetic scattering with polarized soft X-ray radiation were utilized to investigate structural and magnetic properties simultaneously. X-ray reflectometry measurements with polarized radiation tuned to the Co L_3 edge clearly showed the antiferromagnetic (afm) coupling of the Co layers by a half-integer order Bragg peak. This purely magnetic peak is smaller for a sample in the second maximum of the afm coupling compared to the first, and it disappears completely when the radiation energy is far from the L_3 edge. Whereas the second order magnetic peak of the Co/Cu multilayers is overlapped by the structural Bragg peak, we observed for the first time the third order magnetic peak showing still stronger magnetic effects. Hysteresis loops measured at different incident angles in L- and T-MOKE geometry confirm the afm coupling in the as-deposited state. During annealing the magnetic peak reduces, and the hysteresis loops reflect a stronger ferromagnetic coupling contribution, both indicating the decrease of afm coupling of the Co layers. Simultaneously performed in-situ transport measurements correlate the strongly reduced GMR signal to these observations.

4.1.2 Report on RTN Mini-Workshop on "Magnetoelectronics"

Feb. 8, 2002, Orsay, France

The mini-workshop represented a meeting of three working groups of the Research and Training Network (RTN) "Computational Magnetoelectronics", *i.e.* from Daresbury, Jülich and Orsay, with the intention to strengthen the interaction with the experimental group of Albert Fert and coworkers at Orsay. The meeting consisted of 9 talks and was attended by 25 participants. The program, the abstracts of the presentations and the list of participants are listed below.

We thank Albert Fert, Frederic Petroff and Chuck Sommers for the local organisation.

Phivos Mavropoulos & Peter H. Dederichs

Programme

13.30 O. Wunnicke (Jülich)
Ballistic Spin Injection from Fe into ZnSe and GaAs
14.00 A. Fert (Orsay)
Conditions for Efficient Spin Injection from a Ferromagnetic
Fetal into a Semiconductor
14.30 Z. Szotek (Daresbury)
Electronic Structure Calculations of Half-Metallic Transition
Metal Oxides with SIC-LSD
15.00 K. Sato (Jülich)
Ferromagnetism of III-V Dilute Magnetic Semiconductors
15.30 R. Mattana (Orsay)
Diluted Magnetic Semiconductor $Ga_{1-x}Mn_xAs$: from Thin
Films to Magnetic Tunnel Junctions
16.00 Break
16.30 I. Galanakis (Jülich)
Electronic Structure of Half-Metallic Heusler Alloys
17.00 P. M. Levy (New York University)
Spin-Polarized Current-Driven Switching of Magnetic Layers
17.30 R. Tyer (Daresbury)
Electronic Structure Properties of $La_{0.7}Ca_{0.3}MnO_3$
18.00 M. Bowen (Orsay)
Understanding the Bias Dependence of $La_{0.7}Sr_{0.3}MnO_3$-based
Magnetic Tunnel Junctions

Abstracts

Ballistic Spin Injection from Fe into ZnSe and GaAs

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We have performed *ab initio* calculations of the ballistic spin injection from Fe into ZnSe and GaAs by means of the SKKR method. The results show for the Fe(001) orientation a very high spin polarization of up to 99%. This can be explained by the different symmetries of the majority and minority bands in bulk Fe.

Conditions for Efficient Spin Injection from a Ferromagnetic Metal into a Semiconductor

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We adapt the spin accumulation model of the perpendicular transport in metallic magnetic multilayers to the problem of spin injection from a ferromagnetic metal (F) into a semiconductor (SC). We show that the problem of the conductivity mismatch between F and SC can be solved by introducing a spin dependent interface resistance (tunnel junction preferably) at the F/SC interfaces. In the case of a F/SC/F structure, a significant value of the magnetoresistance can be obtained if the junction resistance is chosen between two threshold values depending on the resistivity, spin diffusion length and thickness of SC. These results on F/SC/N structures are at odds with recent theoretical results of Rashba. We will illustrate the results of our model with numerical calculations for Co/GaAs/Co.

Electronic Structure Calculations of Half-Metallic Transition Metal Oxides with SIC-LSD

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In this talk we discuss an application of the self-interaction corrected local spin density approximation (SIC-LSD) to the double perovskites Ba_2FeMoO_6, Ca_2FeMoO_6, Sr_2FeMoO_6, and magnetite (Fe_3O_4). In the double perovskites we concentrate on the electronic and magnetic properties of these compound and in particular the size and relative orientation of the spin moments of Fe and Mo. In all the compounds the calculations find a spin moment of about $0.4\mu_B$ on the Mo sites, with an opposite orientation to the respective spin moments on Fe sites. In addition, we find these double perovskites to be half-metallic, with a well defined gap in the spin-up density of states, and strong hybridization at the Fermi energy between the spin-down Fe $3d$, Mo $4d$, and O $2p$ states. Issues of charge ordering in magnetite are also discussed for both cubic and orthorombic structures, the latter being an approximation to the true, low temperature, monoclinic structure. We find that the charge ordered phase is not the groundstate solution for this compound.

Ferromagnetism of III-V Diluted Magnetic Semiconductors

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The magnetism of GaN-, GaP-, GaAs- and GaSb-based DMS is investigated based on first-principles calculations. Their electronic structures are calculated by the Korringa-Kohn-Rostoker method combined with the coherent potential approximation. Comparing the total energy difference between the ferromagnetic and the spin-glass state, the stability of the ferromagnetism is estimated. It is found that Cr-doped III-V compounds are promising candidates for high-T_C ferromagnetic DMS.

Diluted Magnetic Semiconductor $Ga_{1-x}Mn_xAs$: From Thin Films to Magnetic Tunnel Junctions

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Diluted magnetic semiconductors (DMS) seem to be promising candidates for spin-dependent transport in semiconductor heterostructures. First, we studied $Ga_{1-x}Mn_xAs$ thin films to evaluate the influence of the manganese concentration on magnetic and transport properties. These studies allowed us to use DMS in epitaxial magnetic tunnel junction (GaMnAs/AlAs/GaMnAs). We obtained a large tunnelling magnetoresistance at 4.5K (more than 100%).

Electronic Structure of Half-Metallic Heusler Alloys

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We have studied the magnetic properties of the $C1_b$-type [XMnSb (X=Co,Ni,Pt)] and of the $L2_1$-type [Co_2MnZ (Z=Al,Si,Ga,Ge,)] Heusler alloys. The calculations apply density functional theory in the local density approximation and the screened KKR Green's function method. The $C1_b$ alloys are half-ferromagnets, *i.e.* the spin-down band is semiconducting, while the studied $L2_1$ compounds present a very small spin-down density of states at the Fermi level. We have studied the low-index surfaces of these compounds taking into account different terminations. The surfaces exhibit strong deviations from the bulk electronic structure and the half-ferromagnetic character can be lost.

Spin-Polarized Current-Driven Switching of Magnetic Layers

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The concept of switching the orientation of a magnetic layer of a multilayered structure by the current perpendicular to the layers is investigated. We have developed a model that relates the current-induced torque to the transverse spin accumulation that arises from driving a current across a magnetically inhomogeneous structure. We find that this torque has two components: the first one is similar to the torque predicted by Slonczewski and Berger; the second acts as if a magnetic field is acting on the background. The salient difference between our treatment and previous treatments of spin accumulation, lies in the inclusion of the exchange interaction between the spin accumulation and the magnetic background. Our two terms are derived simultaneously in the same formalism and both depend on the same set of parameters used for understanding the giant magnetoresistance when the current is perpendicular to the plane of the layers (CPP). Furthermore, we have introduced a new length scale for the transverse spin accumulation and clarified the ferromagnetic layer thickness dependence of the switching dynamics. In the simple case where each magnetic layer is described by a magnetic moment of fixed magnitude we find the time dependence of the switching of a magnetic layer due to the torques created by the spin-polarized currents in magnetic mulilayered structures.

Electronic Structure Properties of $LaMnO_3$ and $La_{0.7}Ca_{0.3}MnO_3$

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The application of the self-interaction correction (SIC) to $LaMnO_3$ and doped $La_{0.7}Ca_{0.3}MnO_3$ was described. In the stoichiometric compound, the SIC can reproduce the orbital ordering and the recently observed localisation delocalisation transition associated with the application of high pressure [1], demonstrating that the SIC can adequately describe the subtle correlation effects present in this material [2].

Preliminary results for doped $La_{0.7}Ca_{0.3}MnO_3$ were presented. Calculations were performed using both a rigid band model and using a supercell where an artificial cation order was imposed. The results from these two models were in good agreement, suggesting that the band filling is the dominant effect in determining the manganese valancies [3].

[1] I. Loa *et al*, Phys. Rev. Lett. **87**, 1255 (2001).
[2] R. Tyer, W. M. Temmerman, H. Winter, and G. A. Gehring, to be published.
[3] G. Banach, R. Tyer, H. Winter, and W. M. Temmerman, to be published.

Understanding the Bias Dependence of $La_{0.7}Sr_{0.3}MnO_3$-based Magnetic Tunnel Junctions

M. Bowen, M. Bibes, A. Barthlmy, J. P. Contour, A. Fert, J. L. Maurice, F. Petroff, A. Vaurs, and J. Humbert

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In contrast to the usual bias dependence of tunneling magnetoresistance found in alumina-based magnetic tunnel junctions, the system $La_{0.7}Sr_{0.3}MnO_3/SrTiO_3/Co$ exhibits an asymmetric bias dependence featuring a peak in inverse magnetoresistance thought to be associated with density of states features of the Co/STO interface. On the basis of comparative experimentation, we will propose several explanations to account for this unsual bias dependence: density of states, coherence of the tunneling phenomenon...

Participants

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- New York University:
  P. M. Levy

- Daresbury Laboratory:
  W. M. Temmerman, Z. Szotek, R. Tyer, G. Banach

- IFF, Forschungszentrum Jülich:
  P. H. Dederichs, K. Sato, I. Galanakis, O. Wunnicke, Ph. Mavropoulos

5 News from the ESF Programme

”Electronic Structure Calculations for Elucidating the Complex Atomistic Behaviour of Solids and Surfaces”

5.1 The Old and the New Psi-k Programmes

Where have we got to? In brief, the present European Science Foundation (ESF) ’Programme’ (= mega-network) on ”Electronic Structure Calculations on Solids and Surfaces” is coming to the end of its 5 years in December 2002. We call it the old Psi-k. The full proposal to the ESF for a new Psi-k Programme is printed after this introduction. Our proposal is among the 10 short-listed ones, of which only 4 will get selected in late April for funding.

There are just two aspects of the proposal that I want to refer to. One of the most successsful parts of the EU HCM Network in 1994-97 was having a number of Working Groups to focus networking on a few particularly promising areas of work. We have therefore resurrected that idea and formed 15 Working Groups in the present proposal as you will see on reading it. Anyone can join in with those. But please note that the new Psi-k would support people in ** all ** areas of work, not just those 15.

The ESF Psi-k Programme is the source of money in our community for many of the workshops, hands-on training tutorials, individual visits, the big Psi-k2000 Conference, publication of this newsletter and more. It is therefore VERY IMPORTANT for our whole community that the new Psi-k gets funded. YOU CAN HELP. In fact, you must help, i.e., anyone in Europe. For this you need to understand the set-up. Any money ultimately comes from the individual ** national ** Research Councils, so that they have a strong input into the present stage now of deciding which proposals get selected as the final four, and then later each national Research Council decides after April which of the selected four Programmes it will actually join and put money into.

So there are two sets of people [1] and [2] to contact NOW, and the officials [2] AGAIN in MAY/JUNE if we get through the selection process. They are:-

[1] Your national academic representative on the Physical and Engineering Sciences Committee [PESC] of the ESF which will make the decision, and

[2] the link person in your national research council who is its link to the ESF. Since the national research councils would ultimately put in the money, their views are presumably important. Actually there may be other officials who make the real decisions about money, but the link person should tell you.

(***) I will give you below the directions of how to find the relevant names from the ESF website, as far as this is possible.

Before you contact them, please:-

1. note that the official title of our proposal is "Towards Atomistic Materials Design (acronym 'Psi-k')";

2. have a look at our website

http://psi-k.dl.ac.uk/proposal/

where one can see the full 15-page proposal, the 6-page outline proposal, the list of 156 'participants' listed by country as Annex C, and the detailed research plans of the 15 Working Groups. Of course this list of 156 'participants' is only a very partial list, because we are committed to helping ALL researchers across Europe in ALL aspects of our field.

When talking or writing to the officials, it is particularly important to emphasise that the networking activities (workshops etc.) are important for YOUR work.

You may like to mention the following points.

- Our 'ab initio' computer simulations are a methodology that is important in your work, and important across many areas of science from nano-technology to catalysis, from magnetism to minerals, and now even with applications to biological macromolecules.
- European 'networking' activities of workshops etc. are particularly important in this field because (a) the methodology is extremely complex and sophisticated, with one European country not a large enough unit; and because (b) the methodology is developing rapidly, so that it is important to remain in touch with the latest developments.
- We are not some small club, but scientists from 20 countries have expressed their interest and are represented on the proposed Steering Committee. We aim to serve the networking needs of the whole community across Europe.
- Our active networking over the past ten and more years has made Europe probably the leading area for this type of research, and we want to enhance the quality and quantity of the work even further.
- From our current ESF Programme (coming to an end this year) and an earlier EU HCM Network, we have a good track-record of organising these things, including ... well, all those things listed as 'Networking Activities' in section 5 of the full 15-page proposal.

(***) Would you like to also get others in your country who are interested to contact the same two people mentioned above, whether on our list of participants or not? It would be particularly helpful to share with others in your country the names and emails or phone numbers of the right officials. In Britain there are in fact three key officials, and I have circulated their email addresses to people in Britain. There is the full list of 156 'participants' on the webpage, listed conveniently by country, but of course there are many other researchers in addition.

So good luck to you. The directions to finding the national representatives and the link officials are given below my signature. [Belgians please note that you count as two countries for the ESF, with separate representatives and research councils.]

With warm regards,
yours Volker Heine
Chairman, ESF Psi-k Programme

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1.] **Finding the name of the scientist(s) representing your country on the ESF Physical and Engineering Sciences Committee (PESC).**

(a) Start at the ESF home page http://www.esf.org/

(b) Click on the blue button near the top 'Physical and Engineering Sciences'.

(c) On the left, click on 'Standing Committee'.

(d) Find the paragraph headed 'Membership' and in that paragraph click on the words 'more than 30 leading scientists'. Among those you should find someone as close to your interests as possible, though of course there will be engineers and high energy particle physicists etc.

2.] **Finding the official in your national research council who is the link person to the ESF.**

(a) Start again at the ESF home page as above.

(b) Click on the button 'About the ESF' along the top line.

(c) On the right hand side click on '70 members'

(d) At this stage a map appears which is not much use because it only gives the names of the national research councils. Instead, click on the button above the map labeled 'ESF Directory of Member Organisations', which leads you into a pdf file (easy to read, if you don't know about pdf; even I can cope with it).

(e) This pdf file has about 150 pages, and you first find yourself at the contents page giving the names and pages of the national research councils listed according to country. In case you are not familiar with pdf files, slide the bar on the right side up and down, and click on the arrows along the top to get you to the right page. Use the hand symbol to 'push' the page up to read the lower part.

(f) You should find there the information about your national research council, in most cases with phone number and name of ESF link person, though I notice the information for UK is out of date.

5.2 Proposal for the New ESF Psi-k Programme

TOWARDS ATOMISTIC MATERIALS DESIGN (ACRONYM: PSI-K)

Contact Person: Professor V. Heine, Cavendish Lab.(TCM), Madingley Road, Cambridge CB3 0HE, England. email: vh200@phy.cam.ac.uk

Applicants: In addition to the following three leaders of our research community, the main instigators of this proposal are the Spokespersons of the 15 Working Groups set up for this proposal and the 21 national representatives of researchers in our field as listed further below.

1. Prof. Juergen Hafner
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2. Prof. Matthias Scheffler
Abt. Theorie, Fritz-Haber Institut
Faradayweg 12, D-14195 Berlin, Germany

3. Prof. Börje Johansson (also KTH, Stockholm, see Annex A)
Condensed Matter Theory Group, Physics Department
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Summary: This proposal concerns the very rapidly developing field of computer simulation to understand materials as basic science, but with a strong leaning towards the design of materials for future technology. The simulations are carried out at the atomic level with ab initio quantum mechanical calculations that start only with the atomic numbers of the elements, and represent properly the bonding between atoms. New doors are being opened to novel research on materials across physics, chemistry, materials science, nanotechnology, surface science and even earth sciences and newly biology, with already a small but growing number of applications to industry. The speed of advance is such that many current applications could not have been made three years ago and were hardly dreamt of five years ago. Particularly new aspects include the following. (1) The many-body approaches to electron correlation are included in this proposal because they are reaching the stage of useful application to real materials, where they will greatly improve the accuracy of simulations with 'difficult' atoms or materials. (2) Applications to biology and earth sciences and real catalysts are very new. (3) There is a marked increase in tackling areas of technological relevance such as nanotechnology. The Programme will aim to serve the whole of our research community across Europe. Collaboration will be organised mostly through 15 Working Groups formed for this application. Our community has put Europe

in the world forefront for this type of research. The networking activities (workshops, training and tutorials, newsletter, visits, and one large conference in 5 years) are essential for maintaining the high quality by (a) keeping researchers up to date with a dozen different approaches and a hundred sophisticated special tricks for situations cutting across the different areas of application, and (b) good contact between advances in methodology, areas of application, and experimentalists. These activities produce international collaborations and exchange of young researchers.

Keywords: simulation, modelling, electronic structure, ab initio

TOWARDS ATOMISTIC MATERIALS DESIGN (PSI-K)

1 Scientific context and status of the relevant research

1.1 'Ab initio' atomistic computer simulation and its applications
1.2 Why the methodology makes European networking especially important
1.3 A new dimension: computational many-body theory on real materials with strongly correlated electrons
1.4 What else is new?

2 General objectives

2.1 First class quality in research
2.2 Networking for the whole European research community in our field
2.3 Training of young scientists
2.4 Opening new areas of application
2.5 Research collaboration and exchange of young scientists
2.6 Application to industry

3 The European dimension

3.1 The European research community in our field
3.2 Expected benefit from European collaboration
3.3 'European context': complementing other European activities

4 Research plan: the Working Groups WG1 to WG15 (and 'Other'16)

4.1 The purpose, functioning and list of the Working Groups: Programme collaborators
4.2 Scientific overview of the Working Groups
Greater accuracy; Extending the system size; Exciting new areas of application; Nanostructures for nano-electronics; Other very productive areas of application

5 Networking activities

5.1 Research workshops

1. SCIENTIFIC CONTEXT AND STATUS OF RELEVANT RESEARCH

1.1 'Ab initio' atomistic computer simulation and its applications

The science that our community does rests on three ingredients: (a) computer simulation, (b) properties and processes in materials at the atomic level, (c) using the full quantum mechanical computation of all the electrons in the material.

We first elaborate on these three ingredients. 'Computer experiments' are now widely used to supplement laboratory work in order to see or measure things not amenable to direct laboratory observation, in particular to get a fundamental understanding of a phenomenon in terms of the physics and chemistry of the atoms involved: e.g. corrosion or weathering at a surface, 'hard' and 'soft' magnetic alloys, interaction of a protein with another molecule, semiconductor nano-devices. In other cases the physical conditions drive one to computing, e.g. simultaneous extreme temperature and pressure at the earth's core/mantle boundary. Computer samples typically of tens or hundreds of atoms but repeated periodically make a real extended solid.

In (b) all types of material are included with a very wide trans-disciplinary range of application: metallic, semiconducting, molecular, silicate minerals etc.; and all types of nanostructure: solids, liquids, surfaces, overlayers, biological macromolecules and polymers. One can study dynamical processes as well as structures and structural rearrangements, statically at zero Kelvin or at non-zero temperature. One can stop a dynamic process in midcourse, e.g. to evaluate the height of an activation barrier.

Ingredient (c) rests on the fact that almost all interactions inside and between atoms are due to their outer 'bonding' or 'conduction' electrons, and requires detailed quantum mechanical calculations which include all the electrons of the material. These computations are large, but can be done efficiently at modest cost on a networked cluster of PC's. Such quantum description is an order of magnitude more accurate than classical empirical interatomic force models, especially in the non-standard bonding geometries usually encountered in the midst of processes such as a chemical reaction at a catalytic surface. 'Ab initio' in the present context means that calculations start with just the atomic numbers of the chemical elements involved.

One can distinguish broadly two types of simulation. The first is just to see what happens at the atomic level, such as when a microindentor is pressed into the surface of a material. The second type we would call a 'computer experiment'. It may extend the simulation to cover a range of conditions, or to 'measure' some quantity such as an energy difference. For example in a multilayer structure which could be involved in 'nano' magnetic recording, one can 'measure' the magnetic coupling of two magnetic layers across a non-magnetic region. But a computer is the ultimate control machine for controlling the variables as espoused by 'the scientific method'. Thus one may consider artificial situations in order to 'measure' some quantity required in a theory of some phenomenon.

Computer simulations are also finding a growing use as direct adjuncts to (laboratory) experiments. Some of the modern experimental probes often require a simulation in order to interpret the data uniquely, or to get a quantitative result instead of just a qualitative one. For example Scanning Tunnelling Microscope (STM) images frequently require computer simulation to help identify different atomic species, or to decide whether some feature is a bump or a hollow. Another example is Nuclear Magnetic Resonance (NMR) chemical shift.

Most calculations are static ones at zero Kelvin because thermal agitation is often a small effect, but one can do a dynamic run, solving the complete quantum mechanics at each timestep, though limitation of computing power restrict simulations to picoseconds.

The above examples show how ab initio simulations are contributing at the leading edge of science across a wide range of disciplines. Thus in Cambridge there are 7 separate groups in 5 Departments (Physics 2, Chemistry 2, Materials, Earth Sciences, Electrical Engineering) with two commercial spin-offs. This must be unique, but the same trend is seen elsewhere.

The speed of technological progress is such that it throws up a multitude of basic scientific challenges, and at a few points the gap between basic research in simulation and the daily needs of industry has shrunk to zero. For example a recent talk concerned a problem about corrosion and additives to motorcar oil. See also Sections 2.4, 2.6 and 5.3.

Ab initio computer simulation has developed very rapidly from some breakthroughs around 1980, due partly to the continuous growth in computer power but mainly to improved numerical algorithms. The new ideas discussed in Section 1.3 and Section 4 promise major further developments which we expect to take at least another decade to reach full fruition. The present ESF Programme proposal therefore comes in the middle of a major paradigm addition in the study of all types of material.

1.2 Why the methodology makes European networking especially important in this field

Our type of computer simulation is already highly complex, and the developments in Sections 1.3 and Section 4.2 will make it much more so. It is this complexity with 'horizontal' divisions according to computational technique and 'vertical' divisions according to type of material, with diagonal cross-connections between them according to the process being simulated, that makes European networking so essential in our subject. One country is simply not a large enough unit to have it all. Moreover the tricks and add-on bits of code are developing rapidly. Thus our methodology cannot easily be turned into a universal 'black box'.

We need to explain some fundamentals. To describe the inter- and intra-atomic effects in a system requires a quantum treatment, and nearly 99 percent of current calculations use the Density Functional Theory (DFT) formulation of quantum mechanics. This is particularly suitable for introducing approximations for the troublesome exchange and correlation effect between the electrons when they approach each other closely. There are various versions, all intended for systems where the electrons are not very strongly correlated and not too different from the theoretician's model of a free electron gas, giving accuracies of order 0.1 eV per atom (though much better when comparing very similar situations). Sections 1.3 and 4.2 will discuss the new calculations becoming possible for systems with strongly correlated electrons.

The energy involved in the bonding electrons in a solid is typically of order 200 eV per atom, giving a total of 100 000 eV for a system of 500 atoms. However the energy changes involved in allowing the atoms to move slightly to their equilibrium positions are of order milli electron Volts, so that the computations have to be accurate to a relative accuracy of 1 part in 108.

To achieve these accuracies may need different approaches for chemically different types of material, for different structures e.g. multi-layered ones, and different properties being calculated. Thus there are about five different basic types of computer code, each of which has its own short-cuts, each its own strengths and weaknesses. For example the KKR approach is not the best for most purposes but it allows a rather good simulation of a random alloy or fluctuating magnetism at non-zero temperature.

In addition special problems and special tricks cut across the different basic approaches. Metals have two types of instability due to the high mobility of the electrons and the sharpness of the cut-off at the Fermi level, each with two types of cure. A relativistic treatment is needed for heavy elements and for discussing magnetic anisotropy and properties such as magnetic dichroism. Magnetic polarisation can be treated in either a simple up/down spin approximation, or with arbitrary direction of polarisation (non-collinear magnetism), either as a continuous variable through a solid or approximated as one moment in each atom, features that can be accommodated more easily in one type of code than another. A phase transition induced at high pressure P may need a simulation at constant P instead of constant volume, and with variable cell shape. Different algorithms may be preferred for moving the atoms in achieving an equilibrium structure at zero Kelvin and in simulating the dynamics of thermal agitation. And so on! Clearly these extra features cut across each other and across the matter of basic code. A material containing an element with high atomic number may or may not be magnetic, and may be a metal, half-metal or insulator.

Further to the above complexities come many add-ons to the basic codes, needed to calculate various properties or simulate various situations such as optical properties or NMR line shift which may take a year or two to programme for one particular main code. See also Section 5.7.

1.3 A new dimension: computational many-body theory on real materials with strongly correlated electrons

We introduce here a wholly new dimension which would not have been possible even a few years ago and which will feature importantly in the research plan.

Section 1.2 emphasised that the DFT methodology discussed there makes a crucial assumption of relatively weak correlation among the electrons, which applies to almost all current simulations and the computer codes for them. This is a serious restriction because firstly there are many important situations involving more strongly correlated electrons. These include many compounds of transition elements such as the high temperature superconductors, as well as all materials with rare earth or actinide elements and some more exotic systems such as the electron-hole plasma in a semiconductor laser. Secondly it would be desirable to include a better treatment of correlation than the DFT approach even for systems of relatively weak correlation, in order to achieve higher accuracy. Thirdly there is also a need to overcome another difficulty with the DFT calculations: the methodology is strictly valid only for the ground state, whereas one also wants to treat excited states, e.g. for optical properties and semiconductors.

Various approaches in formal many-body theory have been applied to these three shortcomings in the past, with mixed success. What is new is that some of these approaches have reached the stage of useful calculations on real materials, not just stripped-down mathematical models or very restricted situations. There is a long way to go before 'computational many-body theory' reaches the stage that DFT simulations have achieved. However some of the methods are already delivering some exciting results now on real materials, so that the time is ripe for us to include them in the present ESF Programme proposal. They clearly show great promise for the future. See the Research Plan (Sect. 4.2) for discussion of the GW, QMC, DMFT, TD DFT, SIC, and LDA+U approaches. A related but different development treats also the ions quantum mechanically, e.g. proton tunnelling in hydrogenated clusters.

1.4 What else is new?

All the science described in Section 4 for this ESF Programme proposal is very new. The rate of progress in our field has been such that many current simulations could not have been made three years ago and often were hardly dreamt of five years ago. For example in calculations on heterogenous catalysis, improved 'ultra-soft' pseudopotentials and Projected Augmented Wave potentials plus experience in choosing the most appropriate exchange and correlation functional can now deliver reliable absolute reaction rates.

Four major differences stand out from a review of our field five years ago. Firstly the range of applications has expanded, most notably into Earth Sciences and biological systems with macromolecules, but also new applications have become possible within previous areas. For example in surface science, all the steps and reaction rates have been calculated for the growth of a GaAs crystal from the arsenic and trimethyl gallium vapours, and for the redox reaction of CO and NO on a Pt catalyst, giving a complete picture of very complex processes. Secondly there is now real progress in developing computational schemes where computing time scales linearly with the number of atoms, thus making possible simulations on larger systems. Thirdly it is remarkable how many of the areas picked out are technologically oriented. Fourthly a wholly new dimension is the inclusion of many-body calculations on real materials as discussed in Section 1.3.

As regards organisational arrangements, we have put together for this proposal 15 Working Groups (see Section 4) around the most leading and active areas of research. On the other hand the proposed activities of workshops, training tutorials, newsletter, contact with industry, etc. (Section 5) develop the pattern that has been evolving for a decade.

2. GENERAL OBJECTIVES

2.1 First class quality research

The over-riding purpose of the proposed ESF Programme would be to help European scientists achieve top quality research in the field of ab initio atomistic computer simulation. Networking activities are especially important to keep everyone in touch with the latest and best work in the whole of Europe because this field is advancing so rapidly and is technically so difficult (Sect. 1.2).

2.2 Networking for the whole European research community in our field

The proposed ESF Programme would aim to support the whole community of researchers in our field, estimated as near 2000 scientists including Ph.D. students. Good networking with workshops and training etc. are essential for both (a) leading groups to stay at the world forefront, and (b) new entrants to the field and isolated workers to do relevant, high quality research. The present proposal has the support of scientists in 20 European countries (see Annexes B and C).

2.3 Training of young scientists

One of the keys to excellence in research is good training of the young scientists, especially important with our complex methodology (Sect. 1.2). Training is also required for post-doctoral workers who want to move from classical simulations into the quantum mechanical methods, and for experimentalist to learn what computer simulation can and cannot do so that they can develop integrated research programmes of experiment and simulation.

2.4 Opening new areas of application

We admit to a bit of a missionary zeal to expand the range of applications of our methodology. There are specific examples in each of the Working Groups described in the Research Plan (Sec. 4), but some of those groups represent whole new areas of application. For example the first workshop to apply our methodology to biological systems was held in 2001, brought together by the current ESF Programme 'Struc' and jointly funded with Cecam, out of which the working group WG12 was born. Similarly the work on minerals, group WG13, started just a few years ago with its first two workshops stimulated and supported by the ESF Programme. The two working groups WG8 on molecular electronics and WG15 on design of structural materials also represent very new areas. The recent work on catalysis by people in WG6 has shown that ab initio calculation has begun to make a serious impact on industrial research, with a series of three workshops on 'Catalysis from first principles' including active participation from industry.

2.5 Research collaborations and exchanges of young scientists

Networking often leads to collaboration, especially with our complex methodology where simple exchange of information at a workshop may not be enough to transfer the expertise. The resulting international exchange of young scientists is important for exposing them to more than one branch of our methodology.

2.6 Application to industry

The collaboration on catalysis has already been mentioned in Section 2.4 and other contacts with industry that will be fostered are mentioned in Section 5.3. Commercial application has definitely moved beyond the token stage. For example the VASP code developed in Vienna has been sold to dozens of industrial companies including Ford, Intel, Corning, Norsk Hydro and Electricite de France, though mostly outside Europe. There is a noticeable increase in job advertisements through our email distribution (Sect. 5.4) for postdocs for precompetitive research, e.g. this week one for research in nano-technology and last week on nano-porous carbon for catalysis.

3. THE EUROPEAN DIMENSION

3.1 The European research community in our field

As already discussed in Section 2.2, the leaders of the present proposal are committed to serving the whole community in our field, those in small isolated research groups as well as in large strong centres, and across the whole of Europe. This is necessary to build a strong research effort: many of the present day leaders in our subject have come from unlikely origins.

The proposed Steering Committee (Annex B) includes national representatives from 20 countries, all those who are members of ESF where some significant work in our field is carried out. Actually our field of research is rather underdeveloped even in some large and otherwise strong European countries; for these the European collaboration is particularly valuable.

3.2 Expected benefit from European collaboration

While politicians talk about establishing a European research area, we have been developing it in our field for the past 20 years, because it is clear that one country is too small a unit to achieve the objectives 2.1 to 2.6 for our sophisticated and rapidly developing research. The resulting strong networking over the past 20 years has made Europe probably the leading area in the world for this type of research. A new ESF Programme would help to keep it that way and build further on it (while maintaining contact with developments in America and the Far East).

European collaboration will strengthen science, but conversely building excellence in science together will strengthen Europe. How can Europe overcome the destructive 'tribalism' that has characterised the continent in the past? By working jointly for a common objective we learn that we need each other, and it is this necessity of working together for our own good that can transcend historic divisions. A very few of the leaders of the Psi-k research community are old enough to remember living through World War Two, but this positive orientation to working together is also strongly evident in our younger scientists. Many have experience of one another's countries as graduate students, post-docs or in tenured jobs.

3.3 'European context': complementing other European activities

The current ESF Programme 'Struc' is in its final year, which is prompting the present new Programme proposal.

There are a small number of EU Networks within our area. Those extending beyond early 2003 are: HPRN-CT-2000-00143 ending 30/9/04; HPRN-CT-2000-00144; HPRN-CT-2000-00154 ending 31/8/03; HPRN-CT-2000-00167 ending 31/5/04; two pending, see Annex D. If some more EU Networks develop within the 15 Working Groups set up for the present Proposal then we would consider that a positive achievement from the wider networking. Such EU Networks have just a few groups for some close research collaboration in a small area, so that they do not compete with the proposed ESF Programme. The Networks would hold joint workshops with the ESF Programme to share their results and expertise with all other interested European researchers beyond the EU Networks which the Networks are not allowed to pay for.

We would have some joint workshops with Cecam (Centre Europeen de Calcul Atomique et Moleculaire), with mutual benefits (see Sect. 5.8). See also Sections 5.2 and 5.8 regarding collaboration with summer schools, ESF Euresco conferences and the European Materials Research Society conferences which all complement the proposed Programme.

4. RESEARCH PLAN: THE WORKING GROUPS WG1 TO WG15 (AND 'OTHER'16)

4.1 Purpose, functioning and list of the Working Groups: Programme collaborators

Sections 1.1 to 1.4 have already given an overview of how our field of research touches many disciplines from catalysis to semiconductors, magneto-electronics to biological macromolecules. The proposed ESF Programme would serve the networking needs of the whole research community (see Sect. 2.2 and 3.1), but to give focus to the networking we have picked out the following 15 leading active areas of research and formed Working Groups WG1 to WG15 on those. The names of the spokespersons are given in brackets.

Working Groups on "Ab initio quantum many-body calculations on real materials". [Walter Temmerman (UK) Coordinator and Spokesperson for methods not included below]

WG1 GW method [A. Rubio (Spain)]
WG2 Quantum Monte Carlo method (QMC) [Claudia Filippi (NL)]
WG3 Dynamical Mean Field Theory (DMFT) [A. Georges (France)]

Working Groups on "Tackling larger systems"

WG4 Linear scaling and local orbitals [P. Ordejon (Spain)]
WG5 Hybrid quantum and classical methods [A. De Vita (Switzerland and Italy)]
WG6 Catalysis and surface science [J. Hafner (Austria)]

Working Groups on ”Semiconducting electronics”

WG7 Semiconductors and nanotechnology [R. Nieminen (Finland)]
WG8 Electronics at the molecular level [group just being formed]

Working Groups on ”Magnetism” [P. Dederichs (Germany) Coordinator]

WG9 Magneto-electronics [P. Kelly (Netherlands)]
WG10 f-electron systems [A. Svane (Denmark)]
WG11 Complex magnetism and nanostructures [S. Bluegel (Germany)]
WG12 Ab initio simulations for biology [P. Carloni (Italy)]
WG13 Minerals and related materials [S. Scandolo (Italy)]
WG14 Grain boundaries and interfaces [C. Elsaeser (Germany)]
WG15 Ab initio design of structural materials [I. Abrikosov (Sweden)]

’Other’16 Actively participating scientists in other areas of application

The preliminary list of 156 Programme collaborators is given in Annex C (and under the Working Groups on the website given below), but this list is very incomplete: see comment at the beginning of Annex C. If and when the Programme is funded, a call will go out for people to join the Working Groups.

The prime purpose of the Working Groups would of course be to get on with their research, but they would also reach out to assist new people wanting to enter their area. For example workshops would be advertised and open to all, and special training might be appropriate. The outreach is important for high quality in an expanding subject. Outreach and publicity are also important to reach people who can use achievements in the Working Groups for other areas of research. The modest Programme budget would not allow each Working Group more than about two or three workshops over the five years, but this should be sufficient for people to get into and maintain contact.

We want to emphasise that the Programme would be for the benefit of all areas of research, including those not covered by the Working Groups, e.g. ferroelectricity, high pressure studies, clusters, polymers, liquids and solutions, etc.. Active Programme participants in those areas are listed for convenience as ’Other’16 but do not form a working group.

4.2 Scientific overview of the Working Groups

All Working Groups have produced work plans of a half to two pages, to be found at the website

http://psi-k.dl.ac.uk/proposal/

We here survey the work of all the Groups under 5 headings and how they relate to each other. Broadly the Groups WG1 to WG5 develop the methodology whereas the rest WG6 to WG15 extend the applications.

1. Pushing at the forefront: greater accuracy

Although the DFT methodology is very good in very many areas, there are important situations where one really would like greater absolute accuracy (see Sect. 1.3).

(a) Greater accuracy beyond DFT in ordinary situations. The Quantum Monte Carlo (QMC) group WG2 will develop and test application of the QMC method to situations with normal strength of correlation that are usually treated by DFT. Here QMC can give 'chemical' accuracy of order 0.01 eV per atom, good enough to tell whether a drug will kill or cure you or whether a catalyst will really work. However QMC calculations are computationally nearly 1000 times as expensive as DFT simulations. Thus the GW group WG1 will extend the GW method to calculate ground state energies with intermediate accuracy at only about 10 times the computing cost of DFT calculations. From an important reformulation of the GW theory it will now be possible to calculate the forces on atoms and hence relax their positions to equilibrium. This is at present an unsolved problem in QMC calculations. All these developments will clearly feed into the work of WG6, WG13 and other groups.

(b) More strongly correlated systems. More strongly correlated systems include important nanostructures such as quantum dots on semiconductors and important materials such as conducting polymers and those in Colossal Magneto-Resistance, and the widely used transition metal oxides, as well as all materials with rare earth or actinide elements where the 4f, 5f electron shells tend to be strongly correlated due to their small radius. The QMC and GW groups WG2 and WG1 will apply their techniques to these materials where their efficacy has not yet been completely tested. When successful this work will be applied in WG7, WG13 and other groups. Dynamical Mean Field Theory (WG3) is the latest idea causing excitement among many-body theorists and will be developed to the stage of calculation on real materials, feeding directly into WG10 (see below). Groups WG1 to WG3 will have Prof. Temmerman as an overall coordinator, and to maintain contact with the Self-Interaction Correction SIC, the LDA+U and the Hartree-Fock methods.

(c) Strong electron correlation in f-electron systems. The 4f and 5f electrons in rare earth and actinide elements show an amazing range of behaviour from rather weak to very strong intra-atomic correlation, which controls a whole variety of properties. The Dynamical Mean Field Theory of WG3 promises to give a calculational methodology capable of spanning the range from weak to strong, and WG10 (f-electrons) will join WG3 initially in developing it. Later WG10 will concentrate on the application to the f-electron systems. Interest will focus on crystal structures and magnetic structures where exchange interactions compete with crystal field interactions, spin fluctuations and Kondo screening.

(d) Excited states and optical excitations. As mentioned in Section 1.3, the normal DFT methodology does not pretend to be able to give excitation energies except at a very low level of approximation. Calculating excitation energies is an active area of research since optical properties play an important role in condensed matter science. This will be pursued by the QMC group GW2, and by the GW group GW1 with additional vertex corrections calculated where needed by the Bethe-Salpeter method. The GW group and the coordinator Prof. Temmerman will also keep in touch with research using Time-Dependant DFT. Applications will include technologically relevant semiconductor structures.

2. Pushing at the forefront: extending the system size

The DFT calculations at present are more or less limited to systems of a few hundred atoms, with computation time varying mostly as the cube of the number of atoms which severely restricts application to larger systems. While a few hundred atoms are sufficient to model local chemical situations, larger systems are required wherever strain fields become important.

(a) Methods scaling linearly with system size. The linear Scaling Group WG4 will research different suggestions for algorithms that will give fully ab initio calculation with computation time proportional to the number of atoms. The basis set for the wave function has to consist of local orbitals, with different suggestions having various hoped-for advantages, which will be a focus of research. Another line of work concerns different formulations via the density matrix of the basic quantum mechanics that focuses on the local environment of each atom or bond. A third issue concerns organising all the information in the computer in a way that each search for information by the code is fixed, not proportional to the number of atoms in the system, even when the atoms are moving about. The linear scaling methods will have important future applications in WG5 on hybrid methods, WG12 on biological macromolecules and WG14 on grain boundaries and interfaces.

(b) Hybrid quantum and classical methods. The Hybrid Group WG5 will research various ideas for combining classical and quantum calculations, focusing on a crack propagating under stress through crystalline or amorphous carbon or Si. A classical interatomic force model represents the forces on all the atoms, with the parameters of the model being continuously updated by full quantum calculations. These can be done more often on restricted regions where bond breaking is occurring. This research is in its infancy and ultimately will need some of the techniques of the linear scaling group WG4. It will make a major contribution to work on mechanical properties of materials where long range strain is almost always important.

3. Pushing at the forefront: exciting new areas of applications

(a) Biological macro-molecular systems. Application of ab initio simulation to biological systems is in its infancy but already there are links with the pharmaceutical industry. Two calculations can be cited as demonstrating the sort of projects they will be interested in, one resolving some detail about the prions responsible for the human form of the BSE 'mad cow' disease, and the other the development of a mimetic, i.e. a smaller synthetic potential drug molecule having a similar biochemical effect as a larger natural molecule. Working group WG12 on biological applications will develop this area in close touch with experimentalists in both academia and industry. In fact identifying projects is one of the main problems, i.e. finding a simulation which is feasible with current techniques and computing power, but still addresses a question of genuine importance to biologists.

(b) Materials design. Perhaps the most visionary Working Group, WG15, plans to start turning materials science up-side down. Can one not start with a desired set of properties and design a material to deliver them? The vision of this Group is that enough is now understood about materials to start on such a 'design' approach. A large number of computer simulations would 'test' whether the suggested material works, and would guide the next step in the design process.

(c) Minerals. WG13 will focus on ab initio simulations to understand the behaviour of minerals and related compounds. Five years ago these hardly existed except for a few pioneering calculations, but now they are accepted as state-of-the-art in the mineralogical community. With at least three tenured academic staff recently appointed in European Earth Sciences Institutes using our methodology and a growing number of others in Physics and Materials one can look forward to rapid developments in this field. Work will include the incorporation of water in minerals, of considerable seismological importance, and the defects in the minerals of the earth's mantle involved in its convection. Further ahead lie simulations of the water/silicate interface to understand erosion, weathering and water pollution. Since many minerals contain iron, WG13 looks forward to the results of WG1, WG2 and WG3 on strongly correlated materials.

4. Pushing at the forefront: nano-structures for nano-electronics

Four working groups WG7 (semiconductors), WG8 (molecular electronics), WG9 (magneto-electronics) and WG11 (nano-magnetism) will be concerned with various aspects of nano-technology. The drive towards ever smaller electronic devices is well known, now reaching the nano-scale where novel size effects appear. These include the coupling of electron transport to lasers for opto-electronics and to magnetism for spintronics, and they present a special challenge to ab initio simulation. WG7 including two industrial partners will focus on conventional semiconductor materials, including the growth of thin films and quantum dots of 5000 to 30000 atoms with their linear and non-linear optical response to intense laser pulses. Two groups WG9 and WG11 will be concerned with magnetic structures where electron transport is manipulated not only using the charge on the electron but also its intrinsic spin. WG9 will focus mainly on layer structures, including magnetic tunnel junctions which could form the basis for a new non-volatile magnetic random access memory (MRAM). Collaboration with WG7 will concern the growth of the magnetic layers in contact with the semiconductors and the carrier injection process. One aim is to understand the tunnelling magnetoresistance (TMR) sufficiently well for reliable materials-specific predictions. WG9 will also study half-metallic systems and dilute magnetic semiconductors, which can play an important role in future applications. WG11 will make a basic study of magnetism in all types of nano-structures: ultrathin films, at steps, in chains, wires and adatoms, as well as complex bulk alloys. In these the magnetisation on the various atoms does not all point parallel (or antiparallel) to the same direction. Experimental study of the effect is very difficult, but investigation by ab initio computer simulation has become possible in recent years. All the work on magnetism will be coordinated by Professor Dederichs. The ultimate nano particle is a single molecule, a possibility that has excited academic and industrial research, almost all outside Europe. Nevertheless the subject is sufficiently interesting scientifically and potentially important industrially that research is certain to grow, even in Europe, and an embryonic Working Group WG8 has been formed from senior academics to help stimulate activity. Research is expected to focus on electron transport through the molecule and at the molecule-substrate interface, and the influence on it of temperature, electromagnetic fields and laser beams. Another important topic is the mechanism of self-assembly to make device structures.

5. Pushing at the forefront: other very productive areas

(a) Surfaces. In a way the subtitle of a recent Euresco conference says it all: "From out of the vacuum into the real world". The field of surface science covered by WG6 has been one of the most productive areas for ab initio simulations, with European scientists taking a leading part in catalysis research in collaboration with industry (see Sect.2.4). Whereas earlier calculations were mostly restricted to action at clean perfect surfaces at zero Kelvin, the effects of temperature and high pressure environment will be addressed increasingly in the future. A catalyst in its working environment is often coated with an oxide or suboxide layer or sulphur compounds, whose concentration will vary with T, P and the concentrations of various reactants. These complications can probably be studied better one by one in a controlled way with ab initio computer simulation than in the laboratory. Subsequently the whole catalytic process with many different individual reactions will be modelled using statistical mechanics approaches (kinetic Monte Carlo (MC) or 'smart' MC). Recent experience indicates that it will soon be possible not only to model known experimental facts, but to develop a theory of reaction rates that is predictive and whose parameters are calculated from first principles and carry true microscopic meaning. Zeolites with their pores constituting a large internal surface are a joint interest of the Surfaces (WG6) and the Minerals (WG13) Groups. Ab initio simulation has already changed the way chemists picture the working of a Broensted acid site -Al-0H interacting with methanol in the synthesis of motor car fuel. Catalysis may also occur at included metallic atoms or clusters, while the diffusion channels in the zeolite structure determine the selectivity of the catalytic process.

(b) Grain boundaries. Structural materials are a difficult area at present for ab initio simulations because long range stresses are almost always a crucial factor. This area will therefore benefit greatly from progress by WG4 and WG5 in dealing with larger systems. Simulations with classical interatomic potentials including 'glue' models have been moderately successful for the pure elements, at a lower level of accuracy, but they hardly exist for compounds such as carbides and oxides. For the present the focus of the Working Group WG14 is therefore on grain boundaries and other interfaces. Not only are they important for the mechanical properties of materials, but they are also channels (or blocks) for the transport of heat and electric current in high temperature superconductors for example. One focus of research will be elucidating the detailed atomic structure of grain boundaries and other interfaces, with 'computer experiments' to try to understand the bonding and other principles at work. This will link closely with the second purpose, namely to work in collaboration with experiment (electron microscopy) to help interpret the data and to see how well the observed and calculated structures compare. The third objective will be to test semi-empirical theories of grain boundaries and interfaces and to develop new ones with improved efficiency, accuracy and predictive power.

5. NETWORKING ACTIVITIES

5.1 Research workshops

The main activity would be about 12 workshops per year covering both the 15 Working Groups and other topics. With a budget maximum of 8K euro each, the larger workshops of 30-60 people would have to be co-sponsored with another organisation (Sect. 3.3 and 5.8).

5.2 Various types of training

We would organise and support various types of training. One form gives hands-on experience in the use of an important computer code, together with the background theory. These have been very popular, with one over 100 trainees. Another type is a 'summer school' dealing more with the theory and how to apply computer simulation to solve scientific problems. Sometimes particular training is attached to a research workshop. We would support some conferences specifically to help the attendance of young scientists, e.g. the Euresco series on "Electronic Structure of

Solids and Other Systems" and a symposium organised by us at a European Materials Research Society conference.

5.3 Developing existing and new contacts with industry

As mentioned in Section 2.6 our methodology certainly has some applications in industry. See Section 2.4 for the collaboration on catalysis. Working Groups WG12 (biology) and WG7 (semiconductors) include industrial participants. These contacts will be developed and we see scope for new ones for WG15 (materials) and WG8 (molecular electronics). One of the proposed Steering Committee members, Dr E Wimmer, has wide knowledge of the industrial application of our methodology and has set up his own company.

5.4 The Psi-k Newsletter and email address list

The Psi-k Newsletter and associated email list of over 900 addresses has become the prime medium of communication in our community, particularly for job advertisements and workshop and conference announcements. The Newsletter of over 100 pages appears regularly every 2 months posted on the website, edited by Dr Z Szotek. It will contain reports on all activities of the Programme and 'highlight' articles on scientific advances in our field: also everyone can publicise the abstracts of their research papers. We know of people in isolated situations for whom this has been invaluable. The email list is used for job etc. announcements between appearances of the Newsletter.

5.5 Short individual visits for research consultation or specific training

Almost everyone needing to travel within Europe can get their own funds, but the Programme would support a few cases where this proves difficult, usually a young researcher travelling across his national boundary for short informal consultation.

5.6 One large conference within the five years of the Programme

There are so many cross-connections in our field (see Sect. 1.2) that one large conference Psi-k2005 would stimulate cross-fertilisation in the whole community, as shown by similar conferences in 1996 and 2000.

5.7 'Add-ons' to standard codes for practical applications

Basic DFT codes only give a static structure or dynamic process, and one usually wants various 'add-on' pieces of code to calculate some practical properties. These may be quite difficult to develop and may exist elsewhere. The Programme would try to address the problem of how to produce cleaned up, tested and documented versions for different basic codes, suitable for dissemination.

5.8 Collaboration with other European organisations

See Section 3.3 for a discussion of complementing other European organisations, particularly EU Networks, and Section 5.2 about training. Two to four workshops annually would continue to be considered for joint funding with Cecam, which enables them to be larger than with single funding (Sect. 5.1). An advantage is that Cecam's publicity reaches chemistry circles more than our Newsletter does. An excellent series of annual summer schools in our field is held in Sardinia which we would support. We would try to propose and organise one symposium annually at the European Materials Research Society conference.

5.9 Meetings of the Steering Committee

There would be one meeting per year of the whole Steering Committee listed in Annex B, in order to oversee the progress of all the Working Groups and to discuss and disseminate their most significant scientific advances. These often feed into the work of other researchers.

6. MANAGEMENT AND STEERING COMMITTEE

Prof. Peter Dederichs (FZ Juelich, Germany) will take over the chairmanship on his retirement in March 2004. Until then, Prof. Volker Heine (Cambridge) will be chairman. Prof. Walter Temmerman will be vice-chairman and secretary. For other people with special functions, see Annex B.

The proposed Steering Committee is given in Annex B and there would be a Core Group of about 12 for making decisions. Actually the main management problem would be keeping all parts of the Programme active, as well as communicating within a rather large and diffuse research community. That is why the Steering Committee includes someone from every participating country and the spokesperson of every Working Group (using the same people as much as possible) plus a few others for their special contribution such as contact with industry. There would be one meeting of the full Steering Committee per year for the purposes given in Section 5.9. In between, decisions could be taken by email.

7. PROPOSED PROGRAMME DURATION

We propose a Programme of FIVE years because there is really an ongoing need for this type of infrastructure (Sect. 1.2 and last sentence of Sect. 1.1).

8. ANNUAL BUDGET (IN K EURO)

Core Steering Committee meeting: 7

Review of scientific developments by whole Steering Committee: 10

Publications (Psi-k Newsletter): 16

ESF administrative costs at 5%: 9.3

Visits for reseach and training: 15

One major conference in 5 years (cost spread over 5 years): 15

Nine workshops for the 15 Working Groups (3 each in 5 yrs): 67.5

Six other workshops, tutorials, 'schools' and conferences: 45.2

Total: 185 k euro

ANNEX A.: CONTACT PERSON AND APPLICANTS

Coordinates of contact person

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Curricula vitae of the applicants

1. Professor Juergen Hafner
Born: 24 July 1945, Lunz am See. Nationality: Austrian
1973 Ph. D., Technische Universitaet Wien, (mit Auszeichnung)
1971-75 Assistant, Institut f. Theoretische Physik, TU Wien
1975-79 Research Associate, MPI f. Festkoerperforschung, Stuttgart
1979-82 Assistant Professor, Inst. f. Theoretische Physik, TU Wien
1982-98 Associate Professor, Inst. f. Theoretische Physik, TU Wien
Since 1998 - Full Professor, Inst. f. Materialphysik, Universitaet, Wien
Guido und Karoline Krafft–Medaille d. Technischen Universitaet Wien, 1973
Ludwig - Boltzmann–Preis der Oesterreich. Physik. Gesellschaft, 1979
Kardinal-Innitzer–Foerderungspreis, 1981
Erwin-Schroedinger–Preis d. Oesterreich. Akademie der Wiss., 1995
About 400 research papers in refereed journals and conference proceedings 15 chapters in monographs. Book: "From Hamiltonians to Phase Diagrams".

2. Professor Matthias Robert Scheffler
Born June 25, 1951, Berlin. Nationality: German
1978 Ph.D., Technical University of Berlin, Physics Department
1978-88 Scientist, Physikal.-Techn. Bundesanstalt, Braunschweig
Since 1988 Director and Head of the Theory Department, Fritz-Haber-Institut der MPG, Berlin
Since 1988 Professor of Theor. Physics, Techn. Univ., Berlin

About 330 publications in refereed journals and edited volumes.

3. Professor Börje Johansson Born 12 June, 1942. Nationality: Swedish
1969 Ph.D., Theor. Phys. and Mech., Univ, of Stockholm
1970-76 Lecturer, Inst. Theor. Phys. Univ. of Stockholm
1977-78 Professor in theor. phys., Linkping University
1980-87 Professor in theor. phys., Univ. of Aarhus, Denmark
Since 1985, personal chair in condensed matter theory from Swedish Natural Sciences Research Council
Since 1994 Professor in cond. matter theory, Univ. Uppsala
Since 2000 Visiting Professor, Royal Inst. of Technol. KTH, Stockholm
Since 1995 Full Member, Swedish Nat. Sci. Res. Council
Since 1997 Member ot The Royal Swedish Academy of Sciences
2000 Celsius-medaljen. Highest award, Royal Society of Sciences, Uppsala
More than 450 publications in refereed journals.

Five relevant publications of the applicants in the last 5 years

1. From Prof. J.Hafner

(*) E.G. Moroni, et al.: Supersoft transition metal silicides. Phys. Rev. Lett. 81, 1969-72 (1998)
(*) P. Raybaud, et al.: The adsorption of thiophene on the catalytically active edge-surface of MoS2: An ab-initio local-density-functional study. Phys. Rev. Lett. 80, 1481-4 (1998)
(*) D. Hobbs and J. Hafner: Ab-initio density-functional study of phase stability and non-collinear magnetism in Mn. J. Phys.: Condens. Matt. 13, (Letter)L681-8 (2001)
(*) A. Eichler and J. Hafner: NO reduction over Pt(100): Reaction rates from first principles. Chem. Phys. Lett. 343, 383-9 (2001)
(*) L. Benco, et al.: Ab-initio density functional theory applied to the structure and proton dynamics of clays. Chem. Phys. Letters 333, 479-484 (2001)

2. From Prof. M. Scheffler

(*) X.-G. Wang, et al.: The hematite alpha-Fe2O3 (0001) surface: Evidence for domains of distinct chemistry. Phys. Rev. Lett. 81, 1038-1041 (1998)
(*) C. Stampfl, et al.: First-principles theory of surface thermodynamics and kinetics. Phys. Rev. Lett. 83, 2993-2996 (1999)
(*) X.-G. Wang, A. Chaka, and M. Scheffler: Effect of the environment on alpha Al2O3 (0001) surface structures. Phys. Rev. Lett. 84, 3650-3 (2000)
(*) S.B. Healy, et al.: The role of electronic correlation in the Si(100) reconstruction: a quantum Monte Carlo study. Phys. Rev. Lett. 87, 016105 (2001)
(*) J. Ireta, et al.: Density-functional theory study of the cooperativity of hydrogen bonds in an infinite alpha-helix. Submitted to Phys. Rev. Lett.(Aug. 2001)

3. From Prof. B. Johansson

(*) I.A. Abrikosov, et al.: Order N-Green Function Technique for Local Environment Effects in

Alloys. Phys. Rev. Lett. 76, 4203 (1996).

(*) M.S.S. Brooks, et al.: Density Functional Theory of Crystal Field Quasiparticle Excitations and the Ab Initio Calculation of Spin Hamiltonian Parameters. Phys. Rev. Lett. 79, 2564 (1997).

(*) M. van Schilfgaarde, et al.; Origin of the Invar effect in iron-nickel alloys. Nature 400, 46 (1999).

(*) P. Mohn, et al.: Mystery of the alkali metals: Giant moments of Fe and Co on and in Cs films. Phys. Rev. Lett. 85, 1583 (2000)

(*) H.W. Hugosson, et al.: Restricting Dislocation Motion in Transition Metal Carbides by Phase Stability Tuning. Science 293, 2434-2437 (2001).

ANNEX B.: PROPOSED STEERING COMMITTEE

Chairman (and Coordinator for Magnetism): P. Dederichs [KFZ, Juelich, Germany]

Temporary Chairman until March 2004: V. Heine [Cavendish Lab.,Cambridge, UK]

Vice-chairman and Secretary (and Coordinator for Many-body Groups): W. Temmerman [Daresbury Lab., UK]

National Representatives Austria (and Deputy Chairman and Applicant and Spokesperson for WG6): J. Hafner [U. Vienna]

Belgium (Flanders): S. Cottenier [KU Leuven]

Belgium (Wallonia): X. Gonze [U. Cath. de Louvain]

Czech Republic: I. Turek [Inst. Phys. Materials, Brno]

Denmark (and Spokesperson for WG10): A. Svane [Univ. Aarhus]

Eire: C. Patterson [Trinity Coll., Dublin]

Finland (and spokesperson for WG7): R. Nieminen [Helsinki Univ. of Technol.]

France (and link with EMRS): H. Dreysse [Univ. L. Pasteur, Strasbourg]

Germany (and Spokesperson for WG11): S. Bluegel [Univ. Osnabruek]

Greece: H. Polatoglou [Aristotle Univ., Thessaloniki]

Hungary: J. Kollar [Res. Inst. f. Solid State Phys., Budapest]

Italy: R. Resta [SISSA, Trieste, Italy]

Netherlands (and Spokesperson for WG9): P. Kelly [Univ. Twente]

Poland: A. Kiejna [Univ. Wroclaw]

Portugal: J.L. Martins [INESC, Lisboa]

Slovakia: I. Stich [Technical Univ., Bratislava]

Slovenia: A. Kokalj [Stefan Inst., Ljubljana]

Spain (and Spokesperson for WG4): P. Ordejon [Inst. Materiales, Barcelona]

Sweden: O. Eriksson [Univ. Uppsala]

Switzerland: R. Monnier [ETH-Z Hoenggerberg]

United Kingdom: M. Finnis [Queens Univ., Belfast]

Spokespersons of Working Groups not also national representatives

WG1: A. Rubio [Univ. Pais Vasco, San Sebastion, Spain]
WG2: Claudia Filippi [Univ. Leiden, Netherlands]
WG3: A. Georges [ENS, Paris, France]
WG5: A. De Vita [EPFL,Lausanne, Suisse and Univ. Trieste, Italy]
WG8: not yet known: group just being formed
WG12: P. Carloni [SISSA, Trieste, Italy]
WG13: S. Scandolo [SISSA, Trieste, Italy]
WG14: C. Elsaesser [MPI Metallforsch., Stuttgart, Germany]
WG15: I. Abrikosov [Univ. Uppsala, Sweden]

Advisory members

Psi-k2005 and links: O.K. Andersen [MPI FKF, Stuttgart, Germany]
Many-body theory and links: E.K.U. Gross [Freie Univ. Berlin, Germany]

Applicant: B. Johansson [Univ. Uppsala and KTH Stockholm, Sweden]
Applicant: M. Scheffler [MPI Fritz-Haber Inst., Berlin, Germany]

Link with industry: E. Wimmer [Materials Design sarl, Le Mans, France]

ANNEX C: PARTICIPANTS AND THEIR COUNTRIES AND AFFILIATIONS

Note that the following list of 156 Programme collaborators is very incomplete. For example the Psi-k2005conference is expected to have about 500 participants. Also some of the Working Groups list so far only a small core group who will approach their wider community if and when the Programme is funded. Note: [1],[2],[3], etc., denote the number of the Working Group which the person participates in, and [s1], [s2], etc., the Spokesperson for the Working Group. [n] denotes a national representative on theSteering Committee, [c] denotes other Steering Committee members.

Austria

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K. Schwarz [10,13,11,15; Inst. Material Sci., Techn. Univ., Vienna]
P. Blaha [10,13,11,15; Inst. Material Sci., Techn. Univ., Vienna]

Belgium (Flanders)

S. Cottenier [n,11; Inst. Kern- en Stral.fysica,KU Leuven], F. Peeters [7; Phys. Univ. Antwerpen (UIA)]

Belgium (Wallonia)

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J.-C. Charlier [5; Phys.-Chemie Mater., Univ. Cath. Louvain]

Czech Republic

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M. Sob [15; Inst. Phys. Materials, Acad. of Sci.,Brno], M. Divis [10; Elect. Struc., Charles Univ., Prague], V. Drchal [3,9; Inst. Physics, Acad. of Science, Prague], J. Kudrnovsky [3,9,11,15, Inst. Physics, Acad. Science, Prague]

Denmark

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Eire

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Finland

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Germany

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Poland

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Sweden

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Switzerland

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Gyorffy [3; Physics, Univ. Bristol], D. Bowler [4 Physics, Univ. College, London], S. Kenny [4; Maths, Loughborough Univ.], Carla Molteni [5,12; Theory of Cond. Matter, Univ. Cambridge], O. Dieguez [5; Theory Cond. Matter, Univ. Cambridge], M. Payne [5,6; Cavendish Lab., Cambridge Univ.], D. Bird [6; Physics, Univ. of Bath], C.J. Lambert [9 Physics, Lancaster Univ.], P. Strange [10; Physics, Keele Univ.], Zdzislawa Szotek [11; Daresbury Lab., Warrington], Julie Staunton [11; Physics, Warwick Univ., Coventry], A. Mulholland [12; Chemistry, Bristol Univ.], M. Segall [12; Camitro UK Ltd, Cambridge (industry)], Michele Warren [13; Earth Sciences, Univ. Manchester], J. Harding [14; Materials Res. Centre, Physics, Univ. College, London], P. Bristowe [14; Materials Sci., Cambridge Univ.]

NON-ESF COUNTRIES

Latvia

E. Kotimin [14; Theor. Lab., Inst. Solid State Phys., Riga]

Russia

V. Anisimov [3; Inst. Metal Phys., Acad. Sci., Ekatarinburg] M. Katsnelson [3; Inst. Metal Phys., Acad. Sci., Ekatarinburg]

ANNEX D.: RELATED APPLICATIONS

Previous application to ESF

ESF Programme "Electronic Structure Calculation for Elucidating the Complex Atomistic Behaviour of Solids and Surfaces (STRUC:Psi-k) 1.Jan.1998 to 31.Dec.2002

There have been 7 EURESCO conferences loosely proposed from our research community on varying topics, but organised on a much wider basis jointly with experimentalists. Other current applications to EU etc. Two applications pending for EU RTN Networks, one on f-electrons and one on optical properties.

5.3 Reports on the ESF Workshops

5.3.1 Report on the 3rd Workshop on "Catalysis from first principles"

Universität Wien, February 21-23, 2002

sponsored by

Ψ_k-ESF Network
Research Center and Science College "Computational Materials Science"
Institut für Materialphysik, Univ. Wien
Groupement de Recherche "Ab-initio MD applied to Catalysis"
(CNRS and Institut Français du Pétrole)
Center for Atomic Scale Materials Physics, DTU
Fritz-Haber-Institut der MPG

Scientific committee:
Jürgen Hafner
Jens Nørskov
Matthias Scheffler

Workshop secretariate
Andreas Eichler
Tina Branis

The aim of these meetings is to review the status of ab-initio total-energy calculations as a basis for the modelling and understanding of chemical reactions on solid surfaces at a microscopic level. Particular emphasis is laid on the prospect of ab-initio simulations for finding and designing new catalysts. A further objective of the workshop is to confront theoreticians with the challenges arising from new-experimental results and from practical applications in industry.

The 3rd workshop in this series attracted about 60 researchers from academic and industry who presented 38 oral contributions and 18 poster contributions. In view of the success of these meetings, the scientific committee decided to continue the series in a two-year rhythm, the next workshop will be organized in 2004 by Jens Nørskov - hopefully within the renewed Ψ_k-Research programme.

Automotive Catalysis From First Principles: An Industry Perspective

K. C. Hass, W. F. Schneider, A. Bogicevic

Ford Research Laboratory, SRL MD-3083
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The catalytic control of vehicle emissions is one of those remarkable feats of engineering where the practical technology far exceeds our ability to understand it. The complexity of the materials issues, flow conditions, and durability requirements for practical automotive catalysts is a daunting challenge for any scientific approach, especially one based on first principles computation. This presentation will review our experiences at Ford in integrating a density functional theory (DFT) effort with more traditional industrial catalyst experimentation, characterization, and development. The benefits of a focused multidisciplinary approach with ongoing internal feedback and education will be emphasized. Recent technical progress in the area of lean-NO_x aftertreatment will be highlighted. In this context, DFT calculations have been particularly helpful in clarifying mechanisms of NO_x and SO_x adsorption and transformation reactions on zeolites, metals, and oxides. Our recent discovery of a cooperative enhancement in NO_x chemisorption on oxides may be a key step along the path to improved, rationally-designed NO_x adsorbants.

The restless surface of transition metal catalysts

G.J. Kramer and P. van Beurden

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The classical description of heterogeneous catalysis suggests that the catalyst surface is static. It has been known for a long time, though that metallic catalysts surfaces are modified during catalysis. A well-known example is the roughening of the platinum gauze in ammonia oxidation[1].
Recently it has become clear from a number of experimental investigations that the rate of metal atom displacement is larger than the turn-over-frequency of the reaction that is being catalyzed[2]. This effectively reverses the atom-scale description of catalysis: one should not think in terms of a static active site that awaits reactants, but rather one should think of a surface that constantly reconstructs under the influence of a (changing) adsorbate occupation, occasionally giving rise to reaction.

In this lecture we present the first results of realistic molecular simulations of adsorbate-induced restructuring of catalyst surfaces (seen as the first step towards a full understanding of the dynamic catalyst surface during catalysis). In order to be able to model the large surface systems required, the embedded atom method was used using dedidated parameters[3] and including an extension to surface species[4]. As a first example we discuss the (5×1)-hex reconstruction of the Pt(100) surface under vacuum and its deconstruction under CO adsorption. The study brings a number of interesting novel mechanisms to the fore which are collective in nature. Among other things, the highly non-linear dependence of the rate of deconstruction of the (5×1)-hex surface on CO concentration is reproduced.[5]

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A New Insight into Fischer-Tropsch Synthes

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As the global reserves of oil are being consumed, Fischer-Tropsch (FT) synthesis that converts CO and H2 to high-molecular-weight hydrocarbons becomes a more and more important route for the production of fuels and chemicals. Despite tremendous efforts devoted to this process in the last 70 years, the reaction mechanism of FT synthesis remains uncertain, which hinders its further development. With extensive density functional theory (DFT) studies on FT reactions, we compare, for the first time, all the mechanisms that are likely to be involved. It is found that a new mechanism is favoured over previously proposed ones. We expect that it may be a general mechanism followed by many other catalytic processes involving hydrocarbons.

Applications of Field-Dependent Density Functional Theory to Vibrational Spectroscopic and other Energetic Aspects of Electrode Chemisorption

Michael J. Weaver and Sally A. Wasileski

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Recent years have witnessed important advances in the application of in-situ vibrational spectroscopy for elucidating adsorbate structure, bonding, and reactivity at electrochemical interfaces. Most commonly, infrared reflection-absorption spectroscopy (IRAS) has been utilized. While valuable, especially for single-crystal characterization, IRAS suffers from sensitivity and wavenumber-range limitations. The other major vibrational method, surface-enhanced Raman spectroscopy (SERS), has been used chiefly to characterize coinage-metal substrates. However, by utilizing overlayer- deposition strategies with gold substrates, SERS can be harnessed to acquire rich vibrational spectra on a broad range of electrode materials, including transition metals and other catalytically important surfaces. A crucial attribute of SERS is the ability to detect vibrational modes over wide frequency ranges, including the low-wavenumber region associated with metal-adsorbate modes. Consequently, it is now feasible to obtain rich vibrational spectra for a myriad of adsorbates at metal-solution interfaces over the substantial ranges of external fields that can be generated for electrochemical systems. The recent emergence of Density Functional Theory (DFT) for describing adsorbate energetics at metal surfaces offers a valuable means of forging a detailed quantum-chemical picture of chemisorbate bonding interactions over such variable fields, as well as for the zero-field metal-vacuum interfaces emphasized to date. This talk will illustrate the insight that can be achieved by modeling electrochemical systems by means of interfacial field-dependent DFT calculations, especially with regard to vibrational properties. Illustrative results using both finite-cluster and periodic-slab calculations will be presented. Issues to be discussed include the sensitivity of vibrational frequency-field (i.e., Stark-tuning) behavior to the nature of electrode-chemisorbate coordination. Emphasized will be the central role of bond-polarization, specifically dipole moment- bond length parameters in controlling the nature of such field-dependent behavior.

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Fundamental surface studies of platinum based alloy electro-catalysts for low temperature fuel cells

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The metal vapour deposition (MVD) of ruthenium and tin on Pt(111) and Pt(110) has been investigated using Low Energy Ion Scattering (LEIS), X-ray Photoelectron Spectroscopy (XPS), Low Energy Electron Diffraction (LEED) and Temperature Programmed Desorption (TPD) of carbon monoxide. The electro-oxidation of CO on the ruthenium and tin modified surfaces has also been investigated using cyclic voltammetry following clean transfer from UHV to an electrochemical cell.

Ruthenium lifts the Pt(110)-(1×2) reconstruction by a coverage of 0.5, with evidence of only a small amount of clustering following deposition at 300K. The alloy phases are not ordered, but more stable with respect to oxidative dissolution than the adsorbed phase. LEISS and XPS measurements indicate that ruthenium can be excluded from the top layer by flash annealing, but incorporated into the second and third layers. After annealing to over 1000K, bulk dissolution of ruthenium is observed. The incorporation of ruthenium in the top or second/third layer reduces the adsorption energy of the CO. It is shown, however, that only surfaces in which ruthenium is incorporated in the top surface layer provide a phase which promotes electro-oxidation. The effect of ruthenium is primarily to reduce the over-potential in the activation of water to produce the surface oxidising species in the electro-oxidation process, and that it is water activation that is rate limiting in the overall reaction. Oxidative cycling of surfaces with ruthenium in the second and third layers results in the segregation of ruthenium to the top layer, and re-establishment of the promotional effect of ruthenium.

The results for Pt(110)-(1×2)-Ru are contrasted with Pt(111)-Ru on which the ruthenium has a greater tendency to cluster during deposition. CO electro-oxidation on Pt(111) modified by ruthenium is characterised by two oxidation peaks (ca. 0.6V and 0.7V RHE) in the stripping voltammetry, both at an over-potential significantly lower than that found on Pt(111) under the same conditions. This overall promotion is also associated with the bi-functional mechanism, the reduction in over-potential being primarily associated with the promoted activation of water at the ruthenium atoms in the cluster. The first of the two promoted oxidation peaks (0.6V) is a result of fast Langmuir-Hinshelwood oxidation kinetics associated with platinum sites adjacent to the ruthenium cluster (zone I). The second oxidation peak (0.7V) is associated with oxidation of CO in the remaining sites that lie at least one platinum atom away from the ruthenium sites (zone II). We show that the mobility of CO between these sites is relatively low in the presence of the sulphate anion: The diffusion of CO between sites is not responsible for the second peak in the stripping voltammetry. We suggest that the slower kinetics of the oxidation in the second peak is associated with the rate of spill-over and diffusion of the oxidant produced at the ruthenium sites to zone I sites.

Results are also presented for the electro-oxidation of CO on ordered alloy surface phases Pt(111)- $(\sqrt{3}\times\sqrt{3})$R30-Sn and Pt(111)-p(2×2)-Sn in order to use the well defined ensembles to support the proposition that the promotion of the electro-oxidation of CO on platinum based alloy surfaces takes place through a simple bi-functional mechanism.

A density functional study on the electrocatalysts of low temperature fuel cells

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A kinetic model based on the adsorption energies from density functional calculations is employed to describe the performance of electrocatalysts on both anode and cathode in low temperature fuel cells. The model is as simple as possible with a minimum of parameters, and most are determined directly from density functional calculations of adsorption energies. The results show that both the H_2/CO oxidation process on anode and O_2 reduction on cathode are well described

by the model when compared to experimental results. The model description also indicates that the promotion on both anode and cathode results from the ligand effect by weakening the CO bonding on anode and O bonding on cathode

Computer Modelling of Reaction Mechanisms in Silicate and Oxide Systems

C.R.A. Catlow

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We describe recent applications of DFT methods to key problems in the catalytic chemistry effected by micro- and meso-porous silicates and by oxide systems. Both periodic boundary condition and embedded cluster techniques are employed using both localised and plane wave basis sets. Particular attention is paid to the following systems:

i) methanol synthesis catalysis on Cu/ZnO surfaces, where we describe how the mechanisms of the elementary reactions involved in the conversion of CO/H_2 to CH_3OH may be elucidated;

ii) mechanism of oxygen dissociation on tin oxide surfaces, where our results stress the importance of surface vacancies;

iii) epoxidation catalysis in titanium substituted silicate systems, where cluster calculations are used to identify the structures of key intermediates and the mechanisms of the epoxidation reaction.

Results of the theoretical studies are closely correlated with experimental data.

Alkane Activation and Catalysis at Low Temperatures Alkylation and Isomerization over Zeolites and Mixed Oxides

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The activation and catalytic transformation of light alkanes over acidic catalysts is a demanding and important problem fort he refining and petroleum industry. In many cases, thermodynamic boundary conditions dictate that the reaction temperatures for hydrocarbon transformation reactions are lowered. The benefits include higher potential selectivity and a longer catalyst life time.

Traditionally such low temperature reactions have been carried out by strong liquid acids and there is a strong incentive to replace these by solid acids, which are usually easier to handle. The potential catalysts include zeolites and anion modified oxides. The critical catalytic steps involve hydrogen abstraction from the alkane, the catalytic transformation to the desired compound and the desorption from the catalyst surface. The first and the third of these three steps are rate determining in most cases, while the intrinsic chemical transformation appears to be facile to catalyze. In the lecture the elementary steps of two example reactions the alkylation of iso-butane with n-butene and the isomerization of n-pentane to iso-pentane using zeolites and anion modified zirconia catalysts will be discussed. Similarities and dissimilarities in the presence and absence of alkenes in the reaction mixture are in the focus of the lecture.

Mechanism of the hydrocarbon conversion in zeolites from first principles

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Conversion of hydrocarbons over zeolites is important industrial process used in the production of petrol. Long hydrocarbon molecules split into parts that either liberate as small neutral gas molecules (cracking), or recombine and form large branched compounds (isomerization). The microscopic steps of the conversion, however, are still not fully understood.

In order to examine reaction pathways we have performed static and molecular dynamics DFT calculations on gmelinite zeolite and linear saturated and unsaturated hydrocarbon molecules. Our calculations indicate that the conversion can proceed through the chemisorption of olefins at the inner surface of the zeolite. The desorption of chemisorbed species produces unstable protonated molecules. The protonated hydrocarbons are long-lived being stabilized in the zeolite surroundings. They are considerably deformed and at increased temperatures (~700K) high mobility of the H atoms along the molecular chain is observed[1]. The relocation of the H atom can lead to the formation of structures with maximum stabilization of the positive charge, such as molecules with tertiary C atoms and cyclo-structures of hydrocarbons. The back donation of the proton to the zeolite framework can cause collapse of the linear protonated molecule, as well. Both cracked and isomerized products can be formed upon the back donation. Depending on the O...H-C contact established between the molecule and the framework the H atoms are removed from different C atoms thus starting either cracking or isomerization of the hydrocarbon molecule.

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Alkane cracking in zeolites: an overview of ab initio simulation results

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Catalytic cracking of small saturated hydrocarbons, catalyzed by zeolites, can proceed via two alternative mechanisms, involving carbocations: either by a bimolecular chain reaction proceeding by the formation of carbenium ions or by a unimolecular protolytic mechanism, that involves alkanium ions. These latter species are formed by direct protonation of the alkane by the Brønsted OH groups of the catalyst. Some of the main features of the unimolecular protolytic mechanism, originally proposed by Haag and Dassau, is overviewed in the light of experimental data in the literature and computational results obtained from ab initio VASP calculations.

Transition structures corresponding to various reaction channels were attempted to be localized on a model catalyst corresponding to the chabazite framework and the ethane, propane, n-butane and isobutane substrates. Activation energies are compared with available experimental data and the importance of using reliable adsorption energies is stressed. The properties of transition structures are analyzed in some details in terms of the transition vectors.

Insights into Zeolite Catalysis from First Principles

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One of the prototypical systems in zeolite catalysis is the methanol to gasoline (MTG) conversion process. This has been studied extensively over the last few decades with both experimental methods and by theoretical means. In the last five years it has become feasible to study the initial adsorption of methanol and first stages of the reaction using first principles techniques. The removal of the cluster approximation and the application of ab initio molecular dynamics has led to a number of key new insights into this process which may well have general ramifications.

Prior to recent work, there was much debate concerning whether methanol was physisorbed or chemisorbed. This issue has now largely been resolved since it appears that methanol can reside in either state depending on the particular zeolite and conditions [1]. Beyond the initial adsorption, ab initio molecular dynamics has revealed that the C-O of methanol exhibits significant anharmonic behaviour under conditions close to those used experimentally. Constrained dynamics demonstrate that the zeolite framework largely plays the role of a dielectric screening medium and weak solvent during the formation of dimethyl ether, indicating that surface methyoxy-groups do not lie on this particular reaction pathway [2].

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Skeletal Isomerization of 2-pentene in acidic Zeolites - An ab-initio Investigation

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Within the context of catalysis by acidic zeolites the skeletal isomerization of paraffins and olefins is an important reaction taking place in key processes of the refining industry. Indeed the conversion of light alkanes such as *n*-pentane and *n*-hexane into their branched isomers aims at improving the octane quality of gasoline components. For the conversion of paraffins, it is used the combination of metal and zeolite in one so called "bifunctional" catalyst. The metallic function catalyzes the (de)hydrogenation reactions required for the alkene formation. The alkenes are afterwards protonated into carbenium ions at the acid site of the zeolite.

We have studied the skeletal isomerization of a 2-pentene molecule in ZSM-22 (a one-dimensional medium pore size zeolite) by means of DFT calculations using the VASP code. The most likely mechanism of skeletal isomerization of the intermediate carbenium ion involves the rearrangement of the secondary carbenium ion into a protonated dialkyl-cyclopropane. Starting from a linear alkoxy species a dimethyl-cyclopropane (DMCP) is formed by the back-donation of a proton from the molecule to the zeolite to form a Brønsted acid site. The intermediate configuration shows a physisorbed DMCP at the zeolite acid site. Afterwards the ring is reopened by protonation, a different bond is broken leading thus to a branched secondary pentyl-oxide. Within this mechanism only the more stable secondary transition states and intermediates are involved. The overall reaction starting from a linear alkoxy to a mono-branched one involves in total three transition states and two intermediate configurations. The highest barrier of ~ 98 kJ/mol was found for the proton back-donation. For the ring-opening via the reprotonation of the DMCP molecule an activation energy of 71 kJ/mol was calculated. The barriers for a pathway via a methyl or ethyl shift are much larger compared to the mechanism via the protonated DMCP.

The Identification and Study of Sites of Varying Activity in Zeolites and Transition Metal Catalysts

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We present recent results of the characterization of various sites in the solid acid zeolite, chabazite. In particular, we have computed the proton affinity, structural characteristics, and energies of adsorption of various bases, including acetonitrile, methanol, ammonia, and pyradine. For the sites studied, we have been able to find only very small varitions in these properties. In addition, we have studied the adsorption of sulfur oxides at various sites on Pt(111). We have found significant variations. The most energetically favorable configurations of SO_2 that we find are consistent with experimental results. Finally, we present a likely reaction pathway for the oxidation of SO_2 on Pt(111).

Palladium Model Catalysts probed by Vibrational Sum-Frequency Spectroscopy

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The relevance of surface science studies to catalysis has been under debate for long, in particular because of the different pressure regimes. It has been speculated that weakly bound active species may only appear at high pressure (> 1 mbar) or that "new" adsorbate structures may form. Also, catalysts may restructure at elevated pressure/temperature with impact on the adsorbate structure. The interest to narrow the gap between catalysis and surface science has promoted surface-sensitive techniques that can operate under technically relevant conditions, such as sum frequency generation (SFG) spectroscopy. Infrared-visible SFG specifically probes the interfacial region between two isotropic media and is able to provide vibrational spectra of adsorbates from submonolayer quantities in UHV up to ambient gas pressure.

SFG was employed to examine CO adsorption on a variety of Pd model catalysts, ranging from ideal Pd(111) surfaces over "defect-rich" Pd(111) to well-faceted and rougher Pd nanoparticles supported on a thin Al_2O_3 film [1-2]. A wide range of pressure and temperature (10^-8 to 1000 mbar CO, 100 to 400 K) was examined to identify possible high pressure effects with the experiments carried out in an SFG-compatible UHV/high pressure cell combined with a UHV surface analysis system.

At low pressure (10^-7 mbar) the CO adsorption site occupancy was mainly governed by the surface structure of the different model catalysts. Each surface showed a characteristic spectrum, i.e. with specific resonance frequencies and hollow/bridge/on-top ratios. It turned out that e.g. a Pd(111) surface can hardly model the situation encountered on Pd nanoparticles and vice versa. The evolution of the CO spectra with increasing pressure also depended on the Pd morphology. For instance, on Pd(111) a rearrangement of the CO layer from a bridge/on-top to a hollow/on-top configuration occurred around 1 mbar at 190 K while the curved surface of Pd particles prevented this transition even though a much higher pressure was applied (200 mbar). No evidence for the formation of high-pressure species or major surface rearrangements was found. Special attention will be also paid to experimental artifacts that may occur under elevated pressure and may be misinterpreted as "high pressure effects".

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Nano assembled Pd catalysts on MgO thin films

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Cluster-assembled materials open fascinating new routes for tuning physical and chemical properties by changing cluster size. By depositing gas phase size-selected metal clusters on MgO thin film surfaces in UHV, cluster model catalysts are fabricated which exhibit remarkable catalytic activity. We report experimental and theoretical (first principle DFT) results on the catalytic activity of Pd atoms and clusters deposited on MgO. The reaction considered, the cyclization of acetylene to benzene, 3 $C_2H_2 \rightarrow C_6H_6$, is catalyzed by size-selected Pd clusters and even a single Pd atom deposited on MgO is enough for the reaction to occur. Recent studies have shown the important role of the support. In fact, a free Pd atom is not active in promoting the reaction as it has not enough electron density to bind and activate three acetylene molecules. The reaction, however, occurs when the Pd atom is bound to MgO defect sites, but not to regular terrace sites. Oxygen anions on (001) terraces, in fact, are not basic enough to increase the electron density on the metal. The active MgO sites can be low-coordinated oxygen anions (located at steps and corners), or oxygen vacancies (F centers). These defect centers are very strong "basic" sites: they efficiently transfer electronic charge to any adsorbate, like for instance the inert N_2 molecule. To identify which particular defect site promotes the catalytic activity of the supported species we have computed the reaction paths and the activation barriers for the 3 $C_2H_2 \rightarrow C_6H_6$ reaction and the properties of CO adsorbed on deposited Pd atoms and we have compared the theoretical results with the experimental spectra. The MgO sites involved in nucleation and catalyst activation are the F centers located at the (001) terraces of MgO. This work shows the importance of morphological defects and anion vacancies in particular in catalysis by supported metal nano-particles.

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"New aspects on catalysis by gold supported on TiO2"

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Catalysis by supported gold particles has attracted a great interest in the last years. Gold has been found to be very reactive at room temperature conditions in oxidation processes when it is prepared as small particles deposited on oxides.[1] This is surprising since gold is known to be the most noble of all the metals. [2] In fact, the reasons behind the enhanced gold reactivity when supported on oxides are still far from being understood.

In order to enlight some of the key points on the reactivity of supported particles we have studied the Au/TiO_2(110) interface. For this system a significant amount of experimental data exist. Through Density Functional Theory we have determined the possible role of the support, and also particle size and other morphological effects.

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Alumina as a support for catalysts - DFT studies

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Porosity, thermal stability, availability makes an aluminum oxide (Al_2O_3) an important material in catalysis. Despite the common interest the detailed microscopic bulk structure and the surface properties of alumina polymorphs are still not well known[1]. The (0001) surface and the bulk of the dense α-Al_2O_3 are the best studied among all phases[2].

We present density functional theory (DFT) calculations of the structure and stability of the clean and hydroxylated (0001) α-Al_2O_3 surfaces. The hydroxylated surfaces are the most stable under most of the realistic conditions - water partial pressures $10^{-2} - 10^6$ Pa and temperatures $300 - 600$ K. The hydroxylation significantly lowers the surface energy and affects the surface properties, as an interaction with metals.

As an example we analyse the interaction of palladium with the (0001) surface of α-Al_2O_3 with different stoichiometries. The interaction of Pd with the oxide surface varies from covalent-like for the aluminum rich surface to ionic-like for the oxygen terminated surface. Hydroxylation of the surface does not increase the metal-oxide interaction significantly.

Analysis of the interaction of Pd with clean surface with steps, indicate that strain mediated repulsive interaction between adsorbed atoms is crucial for the nucleation of small islands. We show, that c/6 steps on the α-Al_2O_3 (0001) surface are enriched in oxygen and that they bind Pd atoms and small clusters stronger by more than 1 eV/atom than the terraces.

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CO oxidation catalysis on Ru:
from UHV to high pressure

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CO-oxidation catalysis on Ruthenium is a prime example of the *pressure and materials gap* in the sense, that a very low activity under UHV conditions is contrasted with very high turnover rates at high oxygen pressures. Recent experimental work has connected this change in activity with the formation of oxide patches on the surface [1,2]. Using density functional theory (DFT) calculations for more and more O loaded Ru(0001), the atomistic mechanism behind this surface oxide formation could be explained by a sub-surface O induced decoupling of strongly bound O-Ru-O trilayers, which finally unfold into the rutile structure forming incommensurate $RuO_2(110)$ domains on the surface [3].

An experimental UHV-LEED characterization identified a stoichiometric surface termination of these $RuO_2(110)$ domains, which exposes coordinatively unsaturated (cus) Ru atoms [2]. Combining classical thermodynamics with DFT input, we calculate the surface free energies of all possible $RuO_2(110)$ terminations to predict the lowest-energy structure in equilibrium with a given oxygen environment. We show that the stoichiometric termination, which is traditionally believed to be the most stable for all (110) surfaces of rutile-structured crystals, is in this system only stable under ultra-high vacuum conditions. At higher oxygen partial pressure the cus Ru atoms are completely covered by terminal oxygens (O^{cus}), defining a polar surface termination. While such terminations were hitherto dismissed on electrostatic grounds, we show that the ionic model behind this argument is of little validity at the surface of an oxide, where the additional degrees of structural freedom allow a considerable reduction of the resulting dipole moment [4].

Atmospheric O pressure stabilizes the weakly-bound O^{cus} atoms up to 1000K on the surface, suggesting an active role of the latter in the reported high catalytic activity of the oxide domains. Considering CO as additional gas phase species, we are finally in a position to discuss the real surface structure of these domains under the conditions of a steady-state CO oxidation reaction.

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DFT Studies on the Complex Redox Chemistry of RuO2(110)

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Metallic ruthenium is a poor catalyst for the oxidation of CO at low oxygen coverages, but upon oxidation of the surface the reactivity increases considerably. Joint experimental and theoretical efforts showed that the reactive surface consists of regions of RuO_2 [1]. The $RuO_2(110)$ reveals three different termination upon different preparations. The oxidation of CO has recently been experimentally studied using vibrational spectroscopy and structural analysis [2,3].

We report density functional calculations on the adsorption of CO on the $RuO_2(110)$ surface and reaction energies, pathways and transition states which correspond to different experimentally detected conditions.

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The Role of the O-Ag Interaction in the Function of Silver as an Oxidation Catalyst

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Silver, as a noble metal, is a uniquely effective catalyst for ethylene epoxidation and partial oxidation of methanol to formaldehyde [1,2]. Despite its importance, there are still many open questions and points of controversy: For example, the actual oxygen species that can form and the identification of those which are catalytically active [2,3]. Part of the reason for this lack of understanding is due to the pressure and materials gap separating the real world of catalysis from ideal world of well-characterized, standard Surface Science experiments.

By performing extensive density-functional theory calculations, we examine many possible adsorption structures for the O/Ag(111) system, including on-surface, substitutional, and sub-surface adsorption, as well as oxide-like formation, and ozone-like species. The calculations predict that at low coverage oxygen prefers to be on the surface in the fcc site, but for coverages greater than ~0.25 ML, O enters the sub-surface region. Sub-surface oxygen is found to significantly strengthen the on-surface-oxygen–metal bond. With increasing oxygen content, oxide-like structures are energetically preferred. Recently, experiments (employing polycrystalline substrates and the ozone molecule) have indeed shown the formation of thick silver oxide films [4]. Taking into account the effects of temperature and pressure, however, we find that at atmospheric pressures (of the catalytic reactions), for increasing temperature, the oxide-like structures become increasing less stable, and only thin on-surface plus sub-surface structues are stable around the temperatures of the epoxidation reaction (500-600 K). For higher temperatures e.g. at the very high temperature (∼900 K) of the methanol oxidization reaction, only very low concentrations of chemisorbed oxygen are stable. Considering the possiblitiy of *pre-existing* vacancies, our results suggest that ozone species may be present at the lower temperatures (and coverages $\geq$0.25 ML), and at the high temperatures, oxygen species adsorbed at pre-existing defects are stable.

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Performance of density functionals compared to the Quantum Monte Carlo method: case study of H_2 adsorption on silicon

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Accurate calculations of surface reaction energetics is a key issue in first-principles approaches to heterogeneous catalysis. The reliability of the calculations depends crititically both on the geometrical model used to describe the surface, as well as on the level of theory at which electronic exchange and correlation effects are treated. While density functional theory lends itself to calculations using periodic slab models, some functionals (B3LYP) and most approaches that allow for a systematically improved treatment of electronic correlation effects are feasible only for cluster models. In the present study, we shall employ both cluster and slab models in conjunction with density functional theory (PW91) for calculations of the geometrical properties of reactant, product and transition states of a surface reaction, and for cluster size convergence studies. In addition, we use B3LYP and Quantum Monte Carlo (QMC) calculations performed on the clusters to monitor necessary corrections from an improved treatment of exchange and correlation effects.

As an example for catalytic reactions involving hydrogen transfer, we have studied the dissociative adsorption of H_2 at the Si(100) surface. For this system, a huge amount of experimental data is available, while attempts to describe the reaction pathway theoretically have fueled a still ongoing debate. For the reaction energy in this covalently bonded system, we find that popular semi-local density functionals (PW91, BP, BLYP) lower the Si-H binding energy compared to the local-density approximation (LDA), while QMC calculations predict both reaction energies and barriers significantly higher than LDA. We convinced ourselves of the validity of the QMC method by comparing to the more traditional treatment of correlations within the configuration-interaction method where literature results were available (i.e. for small clusters). For larger clusters, results obtained with the B3LYP hybrid functional are in fair agreement with, though distinctly lower then, the energetics from the QMC calculations. The rather high adsorption barriers found both in QMC and B3LYP are in better agreement than previous DFT results with the observed low sticking coefficient of H_2 on Si(001).

Reactivity of pseudomorfic metal overlayers and alloys

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It has been shown experimentally that the adsorption energy of CO on pseudomorfic metal overlayers depends strongly on the nature of the overlayer[1]. The observed shifts in binding energy can easily be understood in terms of the so-called d-band model where the reactivity is determined basically by the stretching or compression of the metal overlayer as compared to the unperturbed metal overlayer[2]. In a number of experiments we have taken this approach further and also investigated the influence on reactions using both super sonic molecular beams and high-pressure cell experiments. The dissociation of methane, which is of strong relevance for the steam reforming process, has been investigated. The initial sticking of methane was investigated both on Co on Cu(111) and Ni on Ru(0001)[3]. In the Co on Cu(111) case the active metal is deposited on a rather non-reactive metal while in the second case we deposit a reactive metal on an even more reactive metal. The interesting effect, however, is that in both cases we end up with an even more reactive surface than any of the clean metals, which is in complete agreement with the theoretical prediction of the d-band model. Also high-pressure cell experiments have been utilized for studying the reactivity of such metal overlayers. The Ni/Cu(100) and Co/Cu(100) systems were investigated for the methanol synthesis from at gas mixture of CO, CO_2, and H_2 at 2 bars[4]. The Co/Cu(111) clearly illustrates the limitation of pseudomorfic overlayers, while the Ni/Cu(100) nicely illustrates the dynamics of such alloy surfaces as a function of gas composition. It is shown that although CO is not involved in the reaction it promotes the methanol formation from $CO_2$and H_2 by keeping the Ni at the surface. Finally, also overlayers and alloys will be discussed with respect to the ammonia synthesis[5]. The Fe/Ru(0001) system is an example of how modifications by use of pseudomorfic metal overlayers may easily be of minor importance when stronger effects such as defects/steps are involved in the overall reactivity of the surface. Also the Au/Fe(111) system will be discussed.

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Making palladium a better catalyst by alloying : atomic scale approach

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Palladium is expected to be actually the best catalyst for the selective hydrogention of 1,3-butadiene to butenes. Model catalysis on single crystal surfaces have shown that the catalytic activity depends firstly upon the surface orientation, i.e. it depends upon the coordination of surface atoms. For example, the more open Pd(110) (number of nearest neighbours Z=7) is five times more active than the close-packed Pd(111) (Z=9) (see table 1) .

Recent experiments have shown that the catalytic activity of PdNi alloys, having low Pd bulk content, is greatly enhanced compared to that for pure Pd; for example, $Pd_8Ni_{92}(110)$ is about 20 times more active than pure Pd(110). The activity of two-dimensional Pd deposits on Ni(110) is even greater.

In fact, Pd tends to segregate largely at the surface of PdNi alloys, as expected and actually measured by photon, electron and/or ion spectroscopies. Moreover, due to the size mismatch between the parameters of the Ni rich substrate and of the (nearby 10% larger) Pd overlayer, reconstructions occur to accomodate the so induced strains. This generates original structures with very different chemical reactivity. Such structures are clearly identified by the combined use of several surface science techniques, such as LEED, STM, grazing incidence X-ray diffraction, etc .

In conclusion, with a good knowledge of the surface segregation phenomena and related reconstruction processes due to size mismatch effects, bi-metallic catalysts could be tailor made. By exploiting both surface segregation of the most costly and catalytically active element and the induced enhanced turn over frequency, a large atom's economy for a given catalytic reaction could be achieved.

Table 1: Catalytic activity, surface composition and surface structure of Pd based samples for the 1,3- butadiene hydrogenation into butenes (at 293K, 10 torrs H_2, hydrogen/hydrocarbon ratio = 5-10). All these samples show a 100% selectivity into butenes up to the complete conversion of butadiene.

Sample	Pd(111)	Pd(110)	Pd_8Ni_{92}(110)	Pd $_{4ML}$ on Ni(110)
diene→butanes activity ($\times 10^{15}$) ($mol \cdot cm^2 \cdot s^{-1}$)	0.43	2.14	38	74
Pd surface composition	100 %	100%	81 %	100 %
Surface structure	(1x1)	(1x1)	(6x1)	(11x2) nanostructuration

Unsaturated aldehydes on $Pt_{80}Fe_{20}$ (111) alloy surfaces

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Platinum based alloy surfaces, e.g. PtFe and PtSn, have shown to be highly selective for the hydrogenation of α,β-unsaturated aldehydes towards unsaturated alcohols [1], which are important ingredients in many fine chemistry processes. Applying density functional theory we investigated the properties of the $Pt_{80}Fe_{20}$ (111) alloy surface and its behaviour upon adsorption of 2-propenal (Acrolein) and 3-methyl-2-butenal (Prenal) from first principles. The initial surface model consisted of Pt_3Fe (111) slabs covered by a single layer of pure platinum, following experimental results [2] and a prior qualitative investigation using the extended Hückel method [3].

In the first part of the presentation we discuss the geometric and electronic properties of the clean model surface and compare our findings with experimental results. The two inequivalent Pt sites in the surface layer differ largely in their local electronic density of states which influences the local chemical reactivity of the surface.

In the second part we discuss different adsorption modes of the unsaturated aldehydes on the alloy surface. A strong O-Fe interaction can lead to an adsorbate induced segregation profile change as is shown by the use of a simple quasichemical model. We calculated vibrational spectra and the electronic structure of the most stable adsorption modes. The former can help to identify the adsorbate geometry found experimentally, the latter leads to a more comprehensive insight into the adsorbate-alloy interaction and is an important step towards the understanding of the observed selectivity of the alloy surface.

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Theoretical Approach to Sensor Materials Research

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Today‘s air pollution legislation requires the monitoring of a vehicle engine‘s motor control unit to limit emissions. This is fulfilled by measuring the exhaust gas composition i.e. the oxygen content of the motor emissions to adjust deviations from given setpoints. Thus exhaust gas sensors like the Lambda sensor, which are located right in the exhaust system of the car are employed. In the US, Europe and Japan, catalytic after treatment of the exhaust gas using a closed loop three-way catalytic converter has proven to be a highly effective means of meeting the current low emission limits for CO, NO_x and HC. The most effective concept for minimizing pollutants is the so-called "closed-loop control for Lambda = 1", where Lambda is the ratio of the actual air/fuel (A/F) ratio to the stoichiometric A/F ratio. Since the engine must be operated within a very narrow range, where Lambda $= 1 \pm 0.005$, the Lambda probe has to detect elemental deviations. New motor control concepts for spark-ignition engines like lean-burn or the exhaust gas composition monitoring for diesel engines require sensors capable of detecting very low amounts of NO_x, HC or NH_3. As the measuring electrodes of the sensors are constantly at temperatures above 500°C and stressed by varying exhaust gas compositions from oxidizing to reducing, the used materials must be thoroughly selected and tested.

The basic concepts of automotive exhaust gas sensors are based on the normalized A/F ratio Lambda. Lambda can be calculated from the output of the Lambda sensor. For successful motor control, it is essential to measure deviations of Lambda to per mill accuracy for "Lambda = 1"-systems. For lean burn motor control concepts Lambda has to be detected in a broad range from $0.8 <$ Lambda < 2 which means that the sensor is exposed to both reducing and oxidizing atmospheres. The design of modern, planar technology Lambda sensors demands electrode materials to be selective, sensitive, long lasting and unsusceptible to various contaminations originating from the exhaust gas and environmental conditions. One field of basic research is the stability of the applied materials, predominantly noble metal alloys. Selectivity of metal electrodes can be determined by looking at the adsorption strength of the gas species of interest at the respective metal surfaces. Gas reaction at surfaces are also important as Lambda must be measured for the exhaust gas in thermodynamic equilibrium, which means that the sensor electrode has to have catalytic features for some applications. With regard to the selectivity of sensor electrodes it was found that the theoretical prediction from DFT calculations match the experimental results. This was also true for calculations concerning the contamination /

poisoning of electrode metal systems.

Molecular elementary reactions at bimetallic surfaces

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Bimetallic catalysts are widely used for several catalytic processes such as the hydrogenation of unsaturated molecules, or oxidation reactions. These alloy catalysts show an improved selectivity and activity or a higher stability against poisons when compared to the related pure metals. It is hence important to obtain insights in the mechanism of molecular reactions at such bimetallic surfaces, in comparison with pure metals. Several approaches are possible. Surface science is an excellent tool (see the abstract of J.-C. Bertolini). Quantum calculations are very complementary to such experiments, with reasonably accurate structural and energetic informations. Moreover they open the possibility to describe the reaction paths and to determine the transitions states and barriers, and hence to build an understanding of the improved catalytic activity or selectivity of the bimetallic surface. Several elementary reactions will be considered on palladium based bimetallic alloys, in many cases complementary to the presentation of J.C. Bertolini. The first example will be NO dissociation on a PdMn alloy in comparison with Pd. The structure of the NO chemisorption state, precursor to the dissociation, and the stability of the dissociated state are here the most important features. The second example will be the C-Cl bond dissociation for trichloroethene on a PdCu (110) alloy surface. The various intermediates and pathways will be presented in relation with vibrationnal spectroscopy. Simulations of reaction kinetics from the results of the first principle calculations have also been performed. The final case will be the hydrogenation of ethene on a deposit of Pd on Ni(110), a surface which has been shown to be more active than pure Pd for the hydrogenation of butadiene. The reactivity will be related to the specific atomic and electronic structure of the surface.

Carbon monoxide on alloy surfaces: a high-resolution STM view

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It is well-known that the catalytic properties of alloys are often superior to those of pure metals. On the atomic scale, differences between adsorption on pure metals and alloys have been explained by so-called *ensemble effects*, where a certain arrangement of chemical species provides the favored adsorption site, and *ligand effects*, where the properties of an adsorption site are modified by the chemical identity of the atoms ("ligands") surrounding the adsorption site.[1] We have been able to determine adsorption sites of CO by imaging an alloy surface with atomic resolution and chemical contrast and taking images of the adsorbed CO molecules in the same area.[2] Such studies have been performed for PtCo(111), PtCo(110), various PtFe(111) and close-packed CrRu alloy surfaces so far. For both PtCo and PtFe (111) surfaces we find that CO prefers adsorption on-top of Pt atoms. Among the Pt atoms, those with a high number of Co or Fe neighbors in the first layer of the alloy are the preferred adsorption sites, a clear case of a ligand effect. The influence of the neighbors in the second layer is the reverse – Fe or Co neighbors in the second layer weaken CO bonding. The reason for the ligand effects observed can be traced back to a shift of the Pt *d*-band energy by the environment of the Pt atoms in the alloy.

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In situ photoemission spectroscopy investigation of the methanol oxidation over copper

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X-ray photoelectron spectroscopy (XPS) has been a powerful tool in surface science for decades. It has been extensively used for the ex-situ characterization of catalysts' surfaces. Due to the short mean free path of electrons in a gas phase electron spectroscopies generally must operate in high vacuum. Traditional electron spectrometers are therefore not suited for the much needed characterization of catalysts' surfaces under reaction conditions. To overcome these limitations, we have developed a new high-pressure electron spectrometer. Our setup utilizes a differentially pumped electrostatic lens system that refocuses the photoelectrons that are emitted from the sample (which is in a gaseous atmosphere of up to several torr) into the focal plane of a standard electron energy analyzer situated downstream, in the high vacuum region.

Using this instrument we have investigated the methanol oxidation over a polycrystalline copper catalyst, where two main reaction paths are known: the total oxidation of methanol to carbon dioxide and water, and the partial oxidation of methanol to formaldehyde and water. The experiments were performed at a methanol to oxygen flow ratio of 3:1 (total pressure 0.4 torr) in the temperature range from 300 K to 750 K. The correlation of in-situ XPS spectra of the copper surface and the simultaneously obtained mass spectrometer data (which show the catalytic activity) allow us to draw conclusions about the electronic state of the catalyst under reaction conditions. Valence band and Oxygen 1s spectra show that after the onset of the catalytic reaction at T>550 K the copper surface has a metallic character. The Oxygen 1s spectra show that at least three different adsorbates with binding energies of 529.7 eV, 531.4 eV, and 532.7 eV, respectively, are present at the catalytically active Cu surface. The integrated intensity of the O 1s peak at 531.4 eV is proportional to the amount of formaldehyde that is produced in the catalytic reaction.

In-situ STM study of CO-oxidation on Pt(110)

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The activity of a catalyst can depend on the surface structure. In turn, the surface structure can strongly depend on the reaction conditions, e.g. temperature, gas composition and pressure. However, most surface science studies are performed at well-defined, but strongly non-realistic conditions, such as ultrahigh vacuum or very low gas pressures. We have used a scanning tunneling microscope, which is integrated in a small flow reactor, to image a catalytic surface at atmospheric pressures and elevated temperatures and to detect the reaction products simultaneously. This allows us to directly relate changes in surface structure to the catalytic activity.

For CO-oxidation on Pt(110) at P=0.5 bar and T=425K, we find that the CO_2-production rate is bistable. For a high CO/O_2 ratio the CO_2-production is limited by oxygen adsorption, which is CO inhibited. For a low CO/O_2 ratio, the surface can switch from the metallic, CO-covered surface to an oxidized surface. The activity switches correspondingly, where the activity of the oxidic surface is higher by a factor of three. From the observed formation of roughness on this oxidized surface, we conclude that a Mars-Van Krevelen type of reaction mechanism is active, where CO reacts with the oxygen, which is stored in the thin platinum oxide.

Catalytically active sites on MoS_2 nanoclusters

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Earilier work in the IFP directed by Slavik Kasztelan and Hervé Toulhoat suggested that morphology and structure effects determine to a significant extent the properties and active phases of supported hydro-treating catalysts. In the last years our group has proposed a theoretical approach for investigating the morphology of MoS_2 particles under gaseous conditions. Recently STM images revealed the shape and edge structure of single layer MoS_2 nanoclusters synthesized on gold and corroborate the importance of morphology effects.

Extensive DFT studies of large clusters and periodic models have been carried out with VASP to determine surface energies, which determine the interplay between the relevant shapes and types of edges. The step from the vacuum world to realistic hydrotreatment conditions is done by including the dependence on the chemical potential of sulfur, which characterizes the gaseous environment present during typical hydrotreating conditions.

Surface energies of Mo $(10\bar{1}0)$ and S $(\bar{1}010)$ edges with different sulfur coverage have been determined unambiguously with high precision. Interpreting surface energies as a function of chemical potential of sulfur allows us to separate different regimes, which are connected to the real catalytic conditions fixed by temperature and partial pressure of H_2S. At low partial pressures of H_2S the $(\bar{1}010)$ edge is more favored, whereas at high partial pressures the $(10\bar{1}0)$ edge is more stable.

Based on the Gibbs-Curie-Wulff construction the equilibrium morphologies of single layer nanoparticles of MoS_2 are determined. On a finer scale, the sulfur coverage is taken into account and leads to a more detailed stability diagram, especially in the region of interest for catalysis.

A next step towards industrial catalysts is taken by considering the effects of defects, like vacancies, whose presence during experimental conditions is likely. STM images of larger clusters have been simulated within the Tersoff-Hamman approach and they are essential for an analysis of STM images to determine the surface structure during scanning conditions.

A Theoretical Study of the Ziegler-Natta reaction in Heterogeneous catalysis

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The Ziegler-Natta reaction, allowing the polymerisation of α-olefins, is one of the major reactions in catalysis. It is more efficient in heterogeneous conditions. The catalyst is a titanium chloride

($TiCl_4$ or $TiCl_n$ reduced species; momomeric or dimeric species). The catalyst is on a support : $MgCl_2$. The most stable face of the support, the (001) face, is suppose to be the inactive. A cocatalyst is required : AlR_3. Our modelization investigates the stable species at the surface. It discusses the reactivity of the titanium in different oxidation states. It discusses the influence of the support and finally the role of the cocatalyst. We use both cluster and VASP calculations.

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Theoretical Studies on Chemical Nature of Point Defects at $(VO)_2P_2O_7(100)$ Surface

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Chemistry of VPO systems is controlled by the properties of surface defects. Among the various defects, the oxygen vacancies at the surfaces have received particular attention from both experimental and theoretical point of views. Therefore, the effect of isolated vacancies on the reactivity of vanadyl pyrophosphate, the main component of VOP–based catalysts, is studied to obtain better understanding of a real material. DFT calculations are carried out to investigate how the formation of oxygen vacancies modify the catalytic properties of the $(VO)_2P_2O_7(100)$ surface.

The regular $(VO)_2P_2O_7$ surface is modeled by one layer of the bulk structure with the surface perpendicular to the (100) direction, an approximation following from a weak interlayer coupling. To represent the (100) face the $V_{10}P_6O_{50}H_{30}$ cluster is chosen, where $V_{10}P_6O_{50}$ fragment is cut off from the (100) surface and has the geometry taken from the crystallographic data. Hydrogen atoms terminate the valences of the outer O atoms. This cluster is sufficiently large to accommodate all important chemical effects associated with the defect creation. The one–electron Kohn–Sham wave functions are constructed using linear combination of Gaussian type orbitals of double zeta quality (DZVP) augmented by d–symmetry polarization functions on V, P and O ions. The exchange–correlation energy is approximated by Perdew–Wang–91 GGA functional. To describe the problem of electron trapping at the vacancy two different strategies are applied. Assuming that the removal of an O atom leads to the formation of dangling bonds or localized V–V covalent bonds, no basis functions are placed at the position of the missing oxygen (approach often applied to covalent systems). In the second approach, commonly used for ionic compounds, the possibility of electron localization at sites other than nuclei is considered. Therefore, the basis set of the missing atom ("ghost" atom with zero nuclear charge) centered on its location is left to allow the transfer of electron density onto the vacant O site.

Electronic structure and the formation energy for different types of oxygen mono–vacancies (Fso center i.e. vacancy with two trapped electrons) at $(VO)_2P_2O_7(100)$ surface is studied. It is shown that the vacancies significantly modify the physical and chemical properties of the surface, thus influencing its catalytic behavior. A link between the sensitivity of the surface reactivity and the perturbation in the electronic density of the system due to the anionic defect is discussed.

In addition, based on the density of states, the evidence for the presence of color center–induced levels for high–coordinated vacant sites and their lack in the case of low–coordinated vacancies is proven. It is shown that only in the case of high–coordinated oxygen vacancies the band gap is reduced relative to the clean surface. Specific features of the density of states projected onto different cationic and anionic surface sites agree with experimental evidences on their implications in to catalytic performance.

Ultrathin VO_x layers on Pd substrates: a model for an inverse catalyst

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We have fabricated an “inverse catalyst model system”, consisting of a metal single crystal surface decorated with oxide nanoparticles, by depositing vanadium oxides on a Pd(111) surface. The growth and structure of the oxide phase has been characterised by scanning tunneling microscopy (STM), LEED, high-resolution electron energy loss spectroscopy (phonon spectra), and core level photoemission; the oxide structures have been modeled theoretically by density funtional theory (DFT). A sequence of novel oxide phases with layer- dependent structures and oscillating oxidation states has been detected experimentally and understood theoretically. These phases are interface mediated and metastable with respect to further oxide growth.

The changes of the oxide morphology as a result of oxidising and reducing environments have been followed in situ by high-temperature STM, to mimic catalyst pretreatment and activation conditions at the atomic level. We find that the oxide phases are highly mobile during hydrogen and oxygen treatments, at a moderately elevated temperature of 250C, and observe reversible oscillations of the oxide morphology during oxidation-reduction cycles. Under reducing ambient conditions a reduced oxide phase wets the metal thus covering the entire surface area, whereas under oxidising conditions the oxide reversibly dewets and the free metal surface is recovered. The physical origin of this wetting-dewetting behaviour is discussed in relation to the V-oxide/Pd phase diagram as a function of the oxygen chemical potential.

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Combined electronic structure calculations and evolutionary search for catalyst design

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An evolutionary algorithm is developed for use in combination with standart calculational tools of electronic structure theory. The evolutionary algorithm is used to predict materials which have new and interesting properties. Based on an unbiased initial population of materials, interesting materials are quickly identified. The use of the algorithm is demonstrated for the design of stable intermetallics, and its use for catalyst design is discussed.

Bridging the Theory-Practice Gap in Heterogeneous Catalysis: Connecting DFT Calculations with Industrial Reactor Design and Catalyst Selection

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Catalytic ammonia synthesis continues to play a central role in sustaining the growing population of the Earth. Since the pioneering work of Haber, Bosch and Mittasch, nearly a century ago, ammonia synthesis has continuously been the testing ground for new ideas and experimental techniques in heterogeneous catalysis. Consequently, the insight into the ammonia synthesis reaction has for long defined the frontier of our understanding of heterogeneous catalysis. Nevertheless, it has been possible during the last years to significantly extend our understanding of the ammonia synthesis reaction. This progress has only been possible by combining new possibilities in computational catalysis with detailed surface science studies, improved experimental techniques, and microkinetic modelling. From insight into the structure of the active site of ammonia synthesis catalysts, it is possible for all transition metals to calculate binding energies and activation energies along the reaction path by density functional theory calculations. With the use of a recently developed microkinetic model for ammonia synthesis it is thus possible to rationalize the behavior of known ammonia synthesis catalysts. More importantly, it is possible to predict the performance of catalysts under various industrially relevant reaction conditions. Moreover, completely new ammonia synthesis catalyst tailored to exhibit the optimal activity under given reaction conditions can be designed. Finally, we can establish the influence of the reactor lay-out on the choice of the optimal catalyst through the introduction of optimal catalyst curves. In this way, it has been possible for the first time to link DFT calculations with catalyst selection and industrial reactor design.

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Catalysis research with structural databases and combinatorial computations

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Major industrial efforts are currently being devoted to the application of combinatorial methods in the discovery and optimization of catalysts. The major thrust in these efforts is the development of experimental high-throughput equipment together with the associated information technologies. Theoretical and computational approaches, especially electronic structure methods, are not yet really integrated in this process, which presents an interesting challenge and opportunity. In this context, the present contribution describes the combination of experimental structural databases such as CRYSTMET (intermetallics) and ICSD (inorganic crystal structure data) with the combinatorial use of electronic structure calculations based on VASP [1]. This approach enables the discovery of trends and allows the pre-screening of materials to select combinatorial libraries for subsequent experimental testing. This concept will be illustrated for metal oxides, where parameters such as the bonding strength of oxygen atoms as a function of oxidation state and structural coordination play a key role in the catalytic activity of materials. A perspective on future developments will conclude this contribution.

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Using DFT calculations in the search of prospective catalysts

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We have shown previously that ”volcano curves” can be obtained when activity patterns, conveying experimental information on periodic trends in catalysis, are correlated with bond energy ”descriptors” calculated for ideal bulk solids at the DFT/GGA level ([1], [2]). These results can be viewed as illustrating the significance of the Sabatier principle in heterogenous catalysis.

A rather simple kinetic foundation of ”volcano curves” has been proposed a few years ago [3], which can be shown to need only simple bonding parameters to describe the effect of varying the solid catalyst.

I will illustrate the implementation of such a model in the cases of hydrotreating reactions catalysed by transition metal sulfides, and hydrogenation reactions catalysed by transition metals. I will discuss the basic assumptions, the fitting procedures, the physical meaning of the fitted parameters, and the predictions of the models.

I will show in which way DFT ”bond energy descriptors” should prove useful in the ”virtual” pre-screening of putative new catalytic compounds [4].

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Universality in heterogeneous catalysis

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Based on an extensive set of density functional theory calculations it is shown that for a class of catalytic reactions there is a universal, reactant independent relation between the reaction activation energy and the stability of reaction intermediates. This leads directly to a universal relationship between adsorption energies and catalytic activity, which is used to pinpoint what it is that determines the best catalyst for a given reaction. The universality principle rationalizes a number of known facts about catalysts and points to new ways of improving them.

Oxygen and Silver Oxide Adsorption on Ag{111}

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Using density-functional theory (DFT) we have examined the adsorption of oxygen at surface and subsurface sites of Ag{111} within a wide range of coverages (0.04 - 0.25 ML). In addition we have determined with DFT the microscopic structure of Ag oxide epitaxed to Ag{111}. In agreement with recent combined scanning tunneling microscopy (STM) experiment / theory results our calculations indicate that non-stoichiometric ($Ag_{1.8}O$) oxide growth is favoured over the previously assumed stoichiometric (Ag_2O) growth. By calculating the pressure and temperature dependencies on the surface energies of the various chemisorbed O and oxide phases we construct an ab initio derived phase diagram for the O/Ag{111} system. This allows us to draw the important conclusion that under typical catalytic conditions for ethylene epoxidation the active catalyst is a non-stoichiometric $Ag_{1.8}O$ oxide

Strange behaviors of vibrational spectra for small molecules chemisorbed on transition-metal surfaces: A case study of NO/Pt(111) from first principles

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It has long been believed that NO molecules are first adsorbed at bridge sites of the Pt(111) surface, and that they move from bridge sites to atop sites as the coverage of NO is increased. This hypothesis originates in several vibrational spectra (EELS and IR) exhibiting a low-frequency N-O stretch peak at low coverages, which is attenuated with a new high-frequency peak developing as the coverage is increased. Our total-energy calculations from first principles, however, reveal that at the coverage of 0.25 ML, the fcc-hollow site is the most stable, and that at the coverage of 0.50 ML atop species coexist together with fcc-hollow species. We then calculated vibrational spectra in the case of 0.50 ML, and showed that the peak intensity of the fcc-hollow species is the tenth as small as that of the atop species, reproducing the observed vibrational spectra qualitatively. Considering that the fcc-hollow species exist at the surface as much as the atop species, such a phenomenon is quite unexpexted and has been misleading the experimentalists. A well-known intensity transfer effect due to dynamic dipole-dipole coupling is small for two absoprion peaks as much as 200 cm^{-1} apart. We studied the origin of this peculiar transfer effect, and found that the electronic state of the surface and adsorbate plays a pivotal role. Our calculations indicate that such misleading features of vibrational spectra are also seen at other systems such as CO/Rh(111), suggesting that they are quite general phenomena for systems of small molecules chemisorbed at transition-metal surfaces.

Local reactivity of metal adlayers

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An ab-initio study based on density functional theory (DFT) within the generalized gradient approximation (GGA) is presented for the chemisorption of atomic hydrogen on Pd adlayers deposited on Au(100) and Au(111). The hydrogen adsorption energy as a function of the number of Pd overlayers has been calculated at high-symmetry adsorption sites. It turns out that the hydrogen adsorption energy shows a maximum for two Pd layers on Au, both for the (100) and (111) surfaces.

We have carried out a detailed analysis of the electronic structure of the Pd overlayer as a function of layer thickness. In order to understand the trend in the adsorption energies it is not sufficient just to regard the d-band center of the topmost Pd layer, but also the shift of the d-band center of the second layer has to be taken into account.

We have also calculated the hydrogen adsorption energy for two different hydrogen coverages $\theta = 0.25$ and $\theta = 1$ on each Pd overlayer. We find that the adsorbate-adsorbate interaction is strongly related to the adsorption height of the hydrogen atom above the substrate layer.

Electronic Structures of V–O Pyramid Pairs as a Function of their Environment

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Catalysts based upon different V–O–X systems are used in the oxidative dehydrogenation (ODH) reactions, which are of a great importance from a practical point of view due to a fact that alkanes are lower–cost feedstock than their olefin counterparts and become currently utilized. To our studies we have chosen the following compounds: V_2O_5 (V^{5+}, basic system for catalyzing oxidation reactions of hydrocarbons), $(VO)_2P_2O_7$ (V^{4+}, compound industrially used in oxidation of n–butane to maleic anhydride) or $MgVO_3$ (V^{4+}, not applied as catalyst) which form well defined phases with crystallographic structures having V_2O_8 fragment.

The regular and defected (010)V_2O_5, (100)$(VO)_2P_2O_7$, and (010)$MgVO_3$ surfaces are modeled by one layer of the bulk structure by cutting one long V–O bond which is an approximation following from a weak interlayer coupling. A common feature of these three unperturbed surfaces is the pair of edge linked V–O square pyramids differently surrounded: by other V–O square pyramids in vanadium pentoxide, by P–O tetrahedra in vanadyl pyrophoshate, and by Mg–O square pyramids in magnesium vanadate. To represent the respective surfaces the $V_{10}O_{34}H_{18}$, $V_{10}P_6O_{50}H_{30}$ and $V_4Mg_8O_{32}H_{32}$ clusters are used where the $V_{10}O_{34}$, $V_{10}P_6O_{50}$, and $V_4Mg_8O_{32}$ fragments are cut off from the appropriate bulk structures and the dangling bonds are saturated by hydrogen atoms. As defects the point anionic vacancies are considered where the oxygen are removed from different possible sites. The calculations are carried out by DFT method where the one–electron Kohn–Sham wave functions are constructed using linear combination of Gaussian type orbitals of double zeta quality (DZVP) augmented by d–symmetry polarization functions on V, P and O ions. The exchange–correlation energy is approximated by local VWN and gradient corrected RPBE functionals. The electronic structures are discussed using Mulliken charges, Meyer bond orders, total and partial densities of states, electrostatic potentials and analysis of molecular orbitals.

The existence of various V–O, P–O and Mg–O bonds is a source for structurally different oxygen centers, namely singly coordinated V=O, P=O, Mg=O, doubly coordinated V–O–X (X=V, P), triply coordinated 2V–O–X (X=V, P) and 4-fold 2V–O–2Mg, which exhibit different chemical/catalytic properties. The nucleophilicity of oxygen sites scales with coordination number. The most electrophilic is vanadium in pure V–O system. The charges of all atoms are lower than those following from the formal oxidation states, which suggests that all systems exhibit mixed ionic-covalent nature. The difference in catalytic behavior of studied systems follows from their different valence states character.

First steps towards the ab-initio preparation of a Cu/ZnO catalyst for the methanol synthesis

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Zinc oxide with small amounts of Cu at the surface is a widely used catalyst for the synthesis of methanol from H_2 and CO/CO_2. Although pure ZnO is already a good catalyst for hydrogenation and dehydrogenation reactions, only the combination with small Cu particles makes it the highly active and selective catalyst used in technological applications. So far, the structure of the Cu particles at the surfaces and the underlying mechanism for the enhanced catalytic properties are widely unknown.

To study the interesting interplay between the ZnO substrate and the Cu particles, we use density functional based calculations to determine the atomistic and electronic structure of such systems. Our aim is to prepare realistic, fully relaxed Cu/ZnO surface geometries which can be used in dynamic simulations of the synthesis process.

As a first step in this direction we present results on the structure of the different pure ZnO surfaces as well as ZnO surfaces with adsorbed small Cu clusters and CO molecules. CO molecules are often used in experiments to probe changes in the electronic structure.

Electrochemical Vibrational Spectroscopy:

Fundamental Insight from Density Functional Theory

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Vibrational spectroscopy has become an essential tool for determining adsorbate structure, bonding, and reactivity at electrochemical interfaces. Infrared reflection-absorption spectroscopy (IRAS) is commonly utilized for characterizing intramolecular vibrations for molecules bound to single-crystal and polycrystalline electrodes. The other major vibrational method, surface-enhanced Raman spectroscopy (SERS), has the ability to detect vibrational modes over a wide frequency range, including low-wavenumber surface-adsorbate modes. Although SERS is commonly utilized for the characterization of roughened coinage-metal electrodes, overlayer deposition strategies with gold substrates enable a broad range of electrode materials to be investigated, including Pt-group metals of electrocatalytic interest [1,2]. Although vibrational spectroscopy yields significant insight into potential- and electrode surface-dependent adsorbate structure, a fundamental understanding of surface-chemical bonding requires additional information which is usually not experimentally accessible in electrochemical systems.

The emergence of Density Functional Theory (DFT) for describing the energetics and electron distribution of adsorbates bound to metal surfaces enables a detailed quantum-chemical picture of potential-dependent bonding interactions to be developed [3]. In particular, DFT is utilized to investigate the relationships of potential/field-dependent binding energy and vibrational (i.e., Stark-tuning) behavior to the degree and bond length-dependence of metal-adsorbate electron donation/withdrawal [4] for various types adsorbates [5,6] and metal surfaces.

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Why is a noble metal catalytically active? The behavior of the oxygen/silver system as studied by DFT-GGA including effects of the environment

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Silver is an efficient catalyst for certain heterogeneous oxidation reactions, for example for ethylene epoxidation and the partial oxidation of methanol to formaldehyde. Its function however, is still far from understood on a microscopic level. Experiments [1] propose that for the (latter) high temperature reactions (800-900 K), the active oxygen species is "bulk dissolved". This scenario is different to recent findings for other metals which identify *surface oxides* as being the important catalytic material [2]. We have performed systematic density functional theory calculations in order to provide deeper understanding into the O/Ag system, taking into account the effect of temperature and O_2 gas pressure. We find that chemisorbed oxygen starts to incorporate into the sub-surface region after a coverage of a quarter (or less) monolayers, and with higher concentrations, surface-oxide-like structures are energetically favored. We compare these structures with $Ag_2O(111)$ surfaces.

Considering however the effect of the environment, at the elevated temperatures and pressures of catalysis, no oxide-like structures are stable, and also no, or only very low concentrations of chemisorbed oxygen are possible, thus supporting the involvement of bulk disolved oxygen which is strongly held (due to kinetics) but weakly bound.

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The role of sub-surface oxygen in the oxide formation at transition metal surfaces

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We present a density-functional theory trend study addressing the incorporation of oxygen into the basal plane of the late 4*d* transition metals (TM) from Ru to Ag. Occupation of sub-surface sites is always connected with a significant distortion of the host lattice, rendering it initially less favorable than on-surface chemisorption. Penetration only starts after a critical coverage Θ_c, which is lower for the softer metals towards the right of the TM series. The computed Θ_c are found to be very similar to those, above which the bulk oxide phase becomes thermodynamically more stable, thus suggesting that the initial incorporation of oxygen actuates the formation of a surface oxide on transition metals.

Adsorption and reactivity of aromatic molecules on Pt(111) and Pd(111) surfaces: a density functional theory study

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One important step for the catalytic reforming of petroleum compounds is the adsorption of aromatic molecules and their reactivity on different metals and alloys.

Different adsorption modes for a benzene molecule have been studied on (111) surfaces of platinum and palladium with a DFT periodic approach using the VASP software. The influence of numerical approximations and surface model will first be presented, with tests showing the importance of calculation parameters such as the number of k-points and the size of the unit cell used.

The comparison of the adsorption energy for the varius sites on Pt(111) indicates that one bridge site is the most stable (0.25 eV more stable than others), and an optimal geometry is proposed. The same site is favored on Pd(111) but yields a less distorted geometry and a stronger adsorption energy. A similar study was performed for naphtalene on pt(111), and the most stable site can be seen as the combination of two benzene ring bridge site adsorption, hence a similar configuration compared to the case of benzene.

Furthermore, the adsorption energy can be decomposed in a distortion energy for the molecule and for the surface, and an interaction energy between these two parts. This shows that the adsorption is a compromise between a destabilizing distortion of the molecule (0.4 to 0.5 eV for benzene on Pt(111)) and of the surface (0.1 to 0.4 eV) and a stabilizing interaction energy (-1.6 to -2.3 eV). The distortion energy of the molecule is correlated with the distortion geometry, the gap between HOMO and LUMO of the benzene and also with the interaction energy.

A complete determination of vibrational frequencies have been performed for the four most stable adsorption structures, including the degrees of freedom in the two uppermost surface layers. This confirms the site assignment obtained from the total energy, and yields a very good agreement with experimental data.

Moreover, some calculations of the co-adsorption of benzene molecule and hydrogen atom for different adsorption sites, and the adsorption of C6H7 fragments leed to the description of thermodynamic pathways for the first hydrogenation of the benzene.

A Periodic Structure DFT Study of Propylene Chemisorption in Acidic Chabazite: Effect of Zeolite Structure Relaxation

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Density functional theory (DFT) periodic structure calculations have been employed to investigate the interaction of propylene within the acidic chabazite zeolite (Si/Al = 11). In agreement with previous studies, it is found that secondary alkoxy formation is preferred over primary alkoxy formation. Steric constraints appear not to affect the course of the reaction.

Analysis of the radial distribution of the zeolitic atoms with respect to the Brønsted site aluminum atom allows further insight in the reaction. Changes in the zeolite oxygen atom position are more significant than of the zeolite silicon atoms. Relaxation of unit cell size and shape has a dramatic influence on energetic parameters of the reaction path.

Dynamics and mechanism of the CO induced removal of the Pt(100) surface reconstruction

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In studying heterogeneous catalytic reactions, metal surfaces are often considered rigid and invariable under reaction conditions. This rather simplistic view, however, is insufficient to understand, e.g., the oscillatory behavior of CO oxidation on Pt, where surface reconstructions are found to play an important role. Although the CO induced lifting of the Pt(100)-hex reconstruction is experimentally well studied, a detailed atomistic mechanism is still lacking. In order to theoretically model this system, the obvious thing to use is a classical effective potential method, due to the large number of atoms involved ($\sim 10^3$) as well as the relatively large time scale. We choose the Modified Embedded-Atom Method (MEAM), with parameters based on Density-Functional calculations[1]. The results of our simulations of CO on Pt(100)-hex reveal a highly interesting mechanism for the removal of the hex reconstruction: in stead of a local phenomenon, the deconstruction appears to be highly "delocalized" and collective in nature. This results in anisotropically restructured domains, in excellent agreement with STM observations[2]. Also, a highly non-linear CO coverage dependence for the deconstruction rate is found, in agreement with molecular beam experiments[3].

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Structure of Y-doped Zirconia Surfaces
A Density Functional Theory Study

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Zirconia is widely used in catalysis as support, oxygen storage and ionic conductor. Dependent on the temperature there exist monoclinic, cubic and tetragonal modifications. Although at room temperature only the monoclinic phase is stable, also the tetragonal or cubic modifications can be stabilized by doping with yttria or ceria. In particular the tetragonal modification (partially stabilized zirconia -PSZ) is superior for applications, where high mechanical and thermal stability is important.

In this work the structure of the bulk[1] and surface of yttrium-doped zirconia was investigated on the basis od density functional theory calculations. Dependent on the surface orientation yttrium ions prefer positions close to the surface ((111)-surface) or in the bulk of the oxide ((100)-surface).

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Density functional study of the adsorption of CO on Fe (110)

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Density functional studies for the clean Fe(110) surface and for the adsorption of CO on Fe(110) at a half and a quarter monolayer CO coverage are reported. For the clean surface, we find only a modest surface relaxation and a modest increase of the magnetic moment of the first surface layer. At low CO coverage, CO adsorbs on top of Fe. But at half coverage, the density functional calculations predict that an off symmetry position between the hollow and bridge site results in the largest binding energy. Comparison of the vibrational frequencies with experiment however suggest, that the experimentally observed situation corresponds to atop adsorption at both coverage. Possible reasons for the discrepancy are discussed.

Structure and acidic properties of the (001) surface of mordenite. Ab-initio study

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Ab-initio DFT calculations have been employed to explore structural and acidic properties of pure siliceous and Al substituted form of (001) external surface of mordenite. Slab model has been terminated with OH groups to form terminal silanol groups (TSil). Part of TSil groups form a weak hydrogen bonds with O atom belonging to other TSil. The length of hydrogen bond is 2.5 Å. Compared with the bulk, only moderate changes have been found in the slab, no reconstruction of the surface structure has been observed. On average, bonds are elongated by 1 %, maximum change of Si-O-Si intertetrahedral angles is 4 %. The size and the curvature of the largest pore differ negligibly from those in the bulk. The Al substitution causes a local distortion of the structure. Distortion is negligible in third coordination sphere around Al atom. The H-bonds formed by TSil groups depend on the location of substituted Al atom.
The OH stretching frequencies of Brønsted acid sites (BA) located in the center of the slab are similar to those calculated for the bulk structure. On the other hand, frequencies of BA located in the uppermost position are shifted by appr. 25 cm^{-1} compared with bulk. The stretching frequencies of hydrogen bond forming TSil groups are shifted by 100 - 300 cm^{-1} towards lower frequencies. The shift depends on the length of the hydrogen bond.

CO adsorption on close-packed metal surfaces: Where are the trends ?

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The development of modern theoretical surface science provides an opportunity to investigate surface and adsorbate structures on an atomic scale with useful applications in industrial technologies. Much effort has been devoted to CO chemisorption and dissociation on transition metals. There are many papers and reviews which deal with this problem from different points of view.[1−4] One of the central questions is how the strength of the chemisorption of CO and the preference for the specific adsorption site varies across the three transition metal series. One particular case, the CO adsorption on the Pt(111) surface has attracted much attention in the past, since for this system state of the art DFT calculations fail in predicting the correct site preference.[5] The question which arises immediately is, whether this case is the exception or the rule?

To find out trends in CO adsorption on close-packed metal surfaces (111) we have used Co, Ni, Cu from the 3d row, Ru, Rh, Pd, Ag from the 4d row and Ir, Pt, Au from the 5d row of transition metals. In particular, we were concerned with the trends of the adsorption geometry, binding energy and electronic density of states. Here we distinguish trends which appear across the columns and rows in the Mendeleyev Table. Further we selected one of the elements (Pd) and looked at the influence of specific changes in our setup such as the exchange correlation potential (PW91, RPBE, metaGGA), increased cut-off energy, denser k-point mesh, projection to real space and substrate relaxation to improve properties of the adsorption system.

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Oxygen adsorption on Ag(001) :
An ab-initio study

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Despite the progress realized in catalysis during the last decades, there are still unsolved questions for processes as easy as atomic adsorption. One particular example is the adsorption of oxygen on Ag(001) surface. Already an early work-function study [1] indicate a non-trivial adsorption behavior where the work-function change for the (001) surface depends not only on coverage, but also on temperature. Later this 'phase transition' between a high and a low temperature structure could be reproduced characterizing the different phases by high resolution electron energy loss spectroscopy (HREELS) and low-energy electron diffraction (LEED) [2]. A combined LEED, HREELS, x-ray photoemission spectroscopy (XPS) and x-ray photo-electron diffraction (XPD) study confirmed two phases.[3] Finally, in a recent scanning tunnelling microscopy experiment also different species of adsorbed oxygen (T_{ads}=150 K) are reported for low coverages ($\Theta_{\mathrm{O}} \sim 0.1$ ML) and assigned to hollow, bridge and on-top adsorbed atoms.[4]

In this work we address the problem using ab-initio density functional calculation of the O adsorption on the Ag(001). According to our results oxygen occupies on-surface sites for $\Theta \leq 0.5$ML coverage in the 4-fold hollow positions, whereas at higher coverage combinations with sub-surface oxygen are preferred. Further, we investigated the experimentally proposed $p(2\sqrt{2} \times \sqrt{2})R45^o$ missing row reconstruction at the half ML coverage.[3] However, the calculated geometry differs from the experimentaly determined one and there also exist more stable structures for this coverage. For all structures, geometry, workfunctions and vibrational frequencies are presented.

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Ab-initio study of hydrogen adsorption on CeO2$_{2-x}$ (111)

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Ceria is used e.g. in automotive catalysts as a source of oxygen. As a first step towards understanding the physical and chemical properties of ceria surfaces we studied by application of VASP the oxygen terminated (111) surface of CeO_2 including oxygen defects and adsorption of H and H_2. A particular problem for density-functional approaches is the treatment of localized f-states. The role of f-bonding is therefore discussed for the two oxydation steps of Ce according to the bulk compounds CeO_2 and Ce_2O_3. For the clean perfect CeO_2 (111) surface (with Ce in its tetravalent state) the Ce-O f-p hybridization is of importance not only for the energetics but it also shows up in STM images. Adsorption energies of H and H_2 were calculated for different sites and defect concentrations.

Bromine adsorption on the Pt(110) surface: reconstructions and quasi one-dimensional phases

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The interaction of halogens with metal surfaces has attracted a lot of interest for practical reasons concerning electrochemistry, heterogenous catalysis and corrosion, as well as for fundamental aspects like surface self-structuring and halogen-induced reconstruction. Using the Vienna Ab initio Simulation Package (`VASP`) and the Full-potential Linearized Augmented Plane Wave package `FLAIR` we studied the structural and electronic properties of the clean and Br-covered Pt(110) surface. We present a detailed investigation of the quasi one-dimensional c(2×2)-Br/Pt(110) adlayer structure, corresponding to a Br coverage of $\Theta_{Br} = \frac{1}{2}$, supplemented by the analysis of the p(1×2) missing-row (MR) structure of the clean Pt(110) surface. Quantitative low energy electron diffraction (LEED) analyses and first principles calculations (DFT) are in impressive agreement in both cases. For the adsorbate, the analysis retrieves a simple Br-adlayer structure with the Br atoms residing in every second short bridge position on the close-packed Pt rows with the MR reconstruction lifted. The Br-Pt bond length, $L = 2.47$ Å, is almost equal to the sum of the atomic radii. The substrate below the adsorbate exhibits a contraction of the first layer spacing which amounts to half of that calculated for an unreconstructed clean surface. Increasing the coverage a phase transition to a p(3x1) structure occurs, which is best developed for an optimal coverage of $\Theta_{Br} = \frac{2}{3}$. DFT and LEED agree on Br occupying both a short bridge and long bridge site per p(3x1) unit cell. Although Br resides in different sites the Br-Pt bond lengths $L_{sb} = 2.47$ Å and $L_{lb} = 2.52$ Å are very similar which leads to a strong buckling for the Br adlayer and the top two Pt layers. Finally we report on the low coverage adsorption of Br on a clean Pt(110)-p(1x2) MR surface. Scanning Tunneling Microsocopy (STM) experiments show that Br is mobile down to T ≈ 130 K. In order to identify a diffusion mechanism explaining the mobility of bromine as found in the experiment, we have simulated molecular and atomic adsorption and diffusion pathways. We found Br again to adsorb atomically on short bridge sites and to diffuse by normal ad-atom hopping. Under no conditions substitutional or subsurface adsorption is found.

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Report on a Collaborative Visit of Sam Shallcross (Bristol University and IRC for Surface Science in Liverpool) to the Department of Physics, University of Uppsala

2nd Feb – 1st June, 2001

The aim of this visit was to learn how to use a set of first-principals techniques, based on KKR-ASA, with a view to extracting parameters for use in models of alloy vicinal surfaces. Obviously a first stage is to calculate the properties of the relevent principal surfaces, and this was what was accomplished on this visit. The systems considered were the (100) surfaces of CuAu and CuPd. For the former there is a great deal of experimental data avaliable on the surface order-disorder transition of Cu_3Au, making it a good test for investigating how accurately surface properties, in particular surface phase transitions, can be calculated within these methods. This collaboration was with Dr. Igor Abrikosov.

This report will describe the work on Cu_3Au. The layout is as follows. The experimental and theoretical background will be described in the introduction, the computational techniques that have been used will then be described, followed by a report of the results of bulk and surface calculations.

Introduction

Cu_3Au is a well known ordering alloy, which at 663 K undergoes a discontinuous order-disorder transition on a face centered cubic lattice. The low temperature phase is $L1_2$ in which Au atoms will be found preferentially on one of the four cubic sublattices into which the fcc structure may be split.

Over the last two decades it has become clear that at the boundary or defect of a homogeneous system the nature of the order-disorder transition may be changed completely. It is known that for a system like Cu_3Au with a 1^{st} order bulk transition, the transition on the (100) surface may be continuous and above T_0 (Surface Induced Order) or the surface may disorder continuously below T_0 (Surface Induced Disorder) [1]. The question then is whether the transition is a layering transition, with critical exponents belonging to the two dimensional Ising universality class, or whether the surface evokes new critical behaviour. Which one of these senarios will be realised depends on the details of the short range interactions and surface fields.

The (100) surface of Cu_3Au has been extensively studied. Early Low Energy Electron Diffraction (LEED) [2] experiments showed that long range order at this surface vanished continuously as $T \rightarrow T_0$. The exponent β_1 has been measured by SPLEED to be $\beta_1 = 0.77$[3]. Experiments with Low Energy Ion Scattering (LEIS) [4] indicated that the composition of the surface layer was $Cu_{.50}Au_{.50}$, and that this was largely unaffected by either the surface order-disorder transition or the bulk transition, indeed persisting up to some 200K above T_0.

The question of what happens in the sub-surface region has been addressed by X-ray scattering. For T<T_0 then results of evanescent X-ray scattering indicate a wetting transition by the disordered phase consistent with the SID scenario [5]. For temperatures greater than T_0 asymptotic Bragg scattering revealed an exponentially decaying segregation profile governed by the bulk correlation length, which was found to go as $(\frac{T-T^{sp}}{T^{sp}})^{\nu}$ with $\nu = 1/2$ and T^{sp} being the spinodal decomposition temperature.

Computational techniques

During this work a number of different computational techniques have been employed. The total energy calculations for bulk and surface CuAu alloys were carried out in the framework of the density functional theory (DFT) [11] using the KKR-ASA Green's function method [20]. Electronic structure calculations for disordered alloys were done within the coherent potential approximation [13, 14, 15]. The multipole moment correction to the ASA Madelung one-electron potential and total energy (ASA+M) [7, 16] have been used in all our calculations. The effective interactions have been obtained by the screened generalized perturbation method [10] and the Connolly-Williams method in the bulk. The statistical part of the problem has been solved numerically with Monte Carlo simulations.

Density functional theory calculations

The KKR-CPA-ASA+M Green's function method has been applied to the bulk and surface DFT calculations of CuAu alloys. This method is described in detail in Refs. [8, 17, 18]. Surface calculations have been carried out using both a semi-infinite geometry with the surface Green's function technique and a supercell approach. The basis functions have been truncated at $l_{max} = 3$, which allowed us to use the multipole moments up to $2l_{max}$ in the multipole Madelung potential and energy. As has been shown in Ref. [17] this leads in particular to a more accurate description of the inhomogeneous systems. The local Airy gas (LAG) approximation [19] has been used for the exchange-correlation energy.

All the calculations were spin-restricted and we have used the scalar-relativistic approximation throughout our study. The screening contribution to the Madelung potential and energy has been taken into account in the single site approximation as described in Ref. [10]. We have also included the so-called muffin-tin correction to the electrostatic energy which substantially improves the results for the equilibrium lattice spacing.

The energy integration was carried out in the complex plane on a semicircular contour comprising 16 energy points. We have used 101 k-points in the irreducible part of the fcc Brillouin zone for the bulk calculations and 36 $k-$points in the irreducible part of the two-dimensional Brillouin zone for the (100) surface calculations. The thickness of the principal layer is three layers for the surface Green's function calculations.

The effective SGPM interactions

The effective interactions in this work have been obtained by the screened generalized perturbation method (SGPM). In contrast to the generalized perturbation method (GPM) usually applied in first-principles calculations SGPM includes the contribution from the screened Coulomb interactions to the *pair* effective interactions as described in Ref. [10]. Neglecting the renormalization of the one-electron energy term due to screening, such SGPM pair interactions in the bulk may be written as

$$\tilde{V}^{(2,s)}(\sigma) = \tilde{V}^{(2,s)}_{GPM}(\sigma) + \alpha^{(2,s)} \frac{\Delta Q^2}{S}, \tag{1}$$

where $\tilde{V}^{(2,s)}_{GPM}$ is the usual GPM potential and the last term defines the contribution from the screened Coulomb interactions. It depends on the coefficients $\alpha^{(2,s)}$ which can be determined in the supercell calculations, the effective charge transfer $\Delta Q = Q_A - Q_B$, which is the difference between the net charges of the atomic spheres of the A and B components, and the WS sphere radius S. In the case of fcc $\mathrm{Cu}_{75}\mathrm{Au}$ random alloy, for instance, the coefficients $\alpha^{(2,s)}$ (in Ry units and for the spin-variable representation of the total energy) for the first four coordination shells are equal to 0.128, 0.003, -0.009, and -0.007, respectively. In a similar way one can determine contributions to the layer-resolved interactions at the surface $\tilde{V}^{(d,s)}_{\lambda\lambda'\ldots}$ which approach the values of the corresponding bulk interactions $\tilde{V}^{(d,s)}$ within the first few layers.

The one electron contribution to the SGPM interactions, $\tilde{V}^{(2,s)}_{GPM}(\sigma)$, has been calculated in the framework of the KKR-CPA-ASA+M method. In the case of surfaces we have used a supercell geometry: A 14-layer orthorhombic supercell (9 layers of the alloy and 5 layers of vacuum) to simulate the (100) surface. The complete procedure of the determination of the screening contribution to the one-electron potential is described in Ref. [10].

Bulk calculations

Ground state properties

The KKR-(CPA)-ASA+M method with screened Madelung potential and energy deduced from the locally self-consistent Green's function technique [22], as described in Ref. [10], has been used to calculate the equilibrium lattice spacing. The calculated values of the equilibrium lattice spacing for various values of x_{Au} corresponding to the principal ordered structures are shown in Table 1. The overall picture is one of reasonable agreement with room temperature experimental data [23].

Table 1: Ground state lattice parameters for CuAu solid solution

x_{Au}	1.00	0.75	0.5	0.25	0.00
KKR-(CPA)-ASA+M	4.109	4.009	3.888	3.746	3.561
experiment	4.078	3.985	3.876	3.746	3.615

In Table 2 we present the enthalpies of formation of some of the ordered structures of CuAu calculated by different techniques. It is clear that the overall agreement of the KKR-(CPA)-ASA+M results with the results obtained by the more sophisticated full potential techniques is again quite reasonable.

Table 2: The enthalpies of formation (in meV/atom) for various ordered CuAu structures

Method	$L1_0$	$L1_1$	Cu_3Au	Z2	$\beta1$
KKR-ASA+M	-42.0	52.6	-39.5	141.5	64.9
CWM-FP-LMTO [25]	-36.1	60.3	-37.3	136.4	51.0

The SGPM calculations of the effective interactions have been carried out for a lattice parameter of 3.7977 Å, which corresponds to that of the random alloy at a temperature of 810 K estimated in the Debye-Grüneisen model. In order to make a verification of the SGPM calculation we have also obtained the cluster interactions via the Connolly-Williams method. For this we used 9 fcc ordered structures, namely Au_7Cu, $L1_2$, DO_{22}, Z3, Cu_2Au, $\beta1$, $L1_0$, Z2, CH, and $L1_1$, as well as Cu and Au, in the total energy calculations. The total energy calculations for these structures have been performed by the KKR-ASA+M methods. In this case 275 k-points in the irreducible part of the tetragonal Brillouin zone and 16 energy points on a semicircular contour in the complex plane were used for the Brillouin zone and energy integration, respectively. For all structures the lattice parameter has been taken to be equal to the calculated lattice parameter of the disordered $Cu_{.75}Au$ alloy.

In Table 3 we present the first four effective pair interactions, calculated by means of CWM-ASA+M and SGPM. As can be seen, both CW and SRGF methods give very similar values for the pair interactions in the first four shells, and for the corresponding transition temperatures. Note that because of the way the Hamiltonian is written each interaction is proportional to the coordination of that shell.

Table 3: The bulk effective pair interactions (in K) and transition temperatures(also in K)

x_{Au}	Method	$V^{(2,1)}$	$V^{(2,2)}$	$V^{(2,3)}$	$V^{(2,4)}$	T_0^{relax}
0.25	CWM-ASA+M	3812	−46	−261	−163	970
	SGPM	3967	−23	−343	−163	805.5
0.75	CWM-ASA+M	2526	−33	−160	−88	
	SGPM	2736	−37	−195	−95	

In Fig. 1 we show the $L1_2$ ordering energy as a function of the range of SGPM interactions included in the calculation. One finds that the ordering energy is reasonably well converged after four nearest shells of neighbours have been included. For the remainder of the calculation we will limit ourselves to this range of the interactions, as the Monte Carlo part of the calculation is a great deal quicker with a shorter interaction range.

For alloys in which there is a considerable size mismatch between the components, as is the case in the CuAu system, then lattice relaxation effects will be important. These effects can incorporated directly in the Connolly-Williams method but in the case of the SGPM interactions they require a separate treatment. In this work we have employed the effective tetrahedron approximation (ETM) [27], an approach which is very similar to the effective-cluster volume

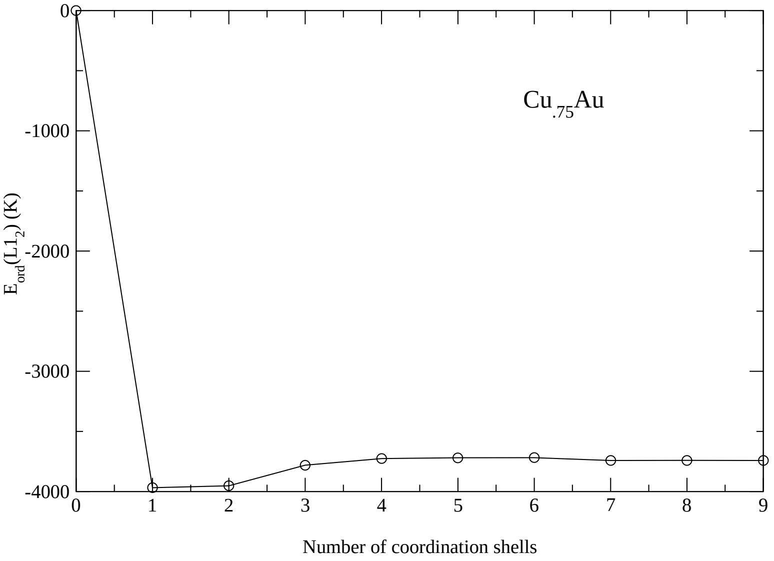

Figure 1: The ordering energy $E^{order}_{L1_2}$ as a function of the number of coordination shells included in the calculation

scheme proposed by Amador *et al.* [26].

This model makes the simplifying assumption that the tetrahedron of the nearest-neighbor atoms is the smallest part of the unit cell which can be used to model the relaxed atomic positions in the lattice. Without lattice relaxation effects the dimensions of this tetrahedron will not depend on which atoms occupy its four sites, and we denote the volume as Ω_0. If we now allow the atoms to relax to their equilibrium positions, they will move in such a way that the distances between the atoms in the three different configurations, A-A, A-B and B-B, will be different from each other and from that of the unrelaxed case. To find these distances we then apply a simple spring model using force constants from first principals calculations of the relevant bulk moduli.

In this way we will find a new tetrahedron volume Ω^{α}_{rel} for each of the five possible configurations of A and B atoms on a tetrahedron. It is instructive to note that for all these tetrahedra there is a simple ordered structure containing *only* tetrahedra of that kind. This suggests that we may suppose the energy assosiated with the relaxation of tetrahedron α to be written as

$$E^{\alpha}_{rel} = E_{tot}(\Omega^{\alpha}_{rel}) - E_{tot}(\Omega_0), \tag{2}$$

where both the total energy calculations are for the structure containing only tetrahedra of sort α, though they are at two different WS sphere radii. In this way we can generate five effective 4-body potentials to describe atomic relaxation.

Finite temperature properties

The statistical mechanics part of the problem requires solving the Hamiltonian

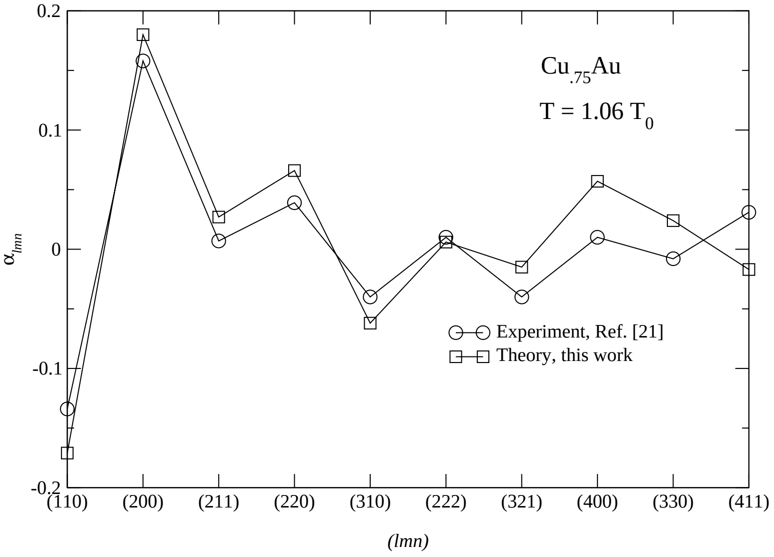

Figure 2: The calculated Warren-Cowley SRO parameters a_{lmn} at the first seven coordination spheres (squares). The experimental SRO (open circles) data are from Ref. [21]

$$E_{tot} = V^{(0)} + V^{(1)} < \sigma > + \sum_s V^{(2,s)} < \sigma_i \sigma_j >^s + \sum_s V^{(3,s)} < \sigma_i \sigma_j \sigma_k >^s + \dots \qquad (3)$$

where i,j and k are lattice sites, $V^{(0)}$ is the reference energy, which, in fact, is the total energy of a random equiatomic alloy and $V^{(d,s)}$ is the effective cluster interaction, which corresponds to the cluster of the order d and type s. For instance, $V^{(2,1)}$, $V^{(2,2)}$, and $V^{(2,3)}$ are the effective pair interactions in the first, second, and third coordination shells, respectively.

A numerical solution of equation 3 is found by canonical Monte Carlo simulation, with the asymmetric Metropolis algorithm used to decide whether atoms should be exchanged or not. Simulation boxes of dimensions 32×32×32 up to 50×50×50 have been used.

In Fig. 2 we show the Warren-Cowley s.r.o parameters for $\mathrm{T} = 1.06\mathrm{T}_0$. The agreement is quite reasonable. In Fig. 3 we show the bulk phase diagram calculated with and without relaxation. One can see that including relaxation improves the order-disorder temperatures quite considerably and enables one to capure roughly the asymmetry of the phase diagram.

However the peak at $\mathrm{x}_{Au} = 0.5$ in the experimental phase diagram is strongly damped in the theoretical result. This is explained by the fact that the $L1_0$ ordered phase has a c/a ~0.94 [23]. This will lower the energy of the $L1_0$ phase, and so raise the transition temperature, however as our calculations have been strictly isotropic this effect is missed althogether. To illustrate this, if within the framework of ETM we make use of a more sophisticated result for the $L1_0$ energy [28], which includes the effect of this anisotropy, then the transition temperature is raised to the point marked by the asterix.

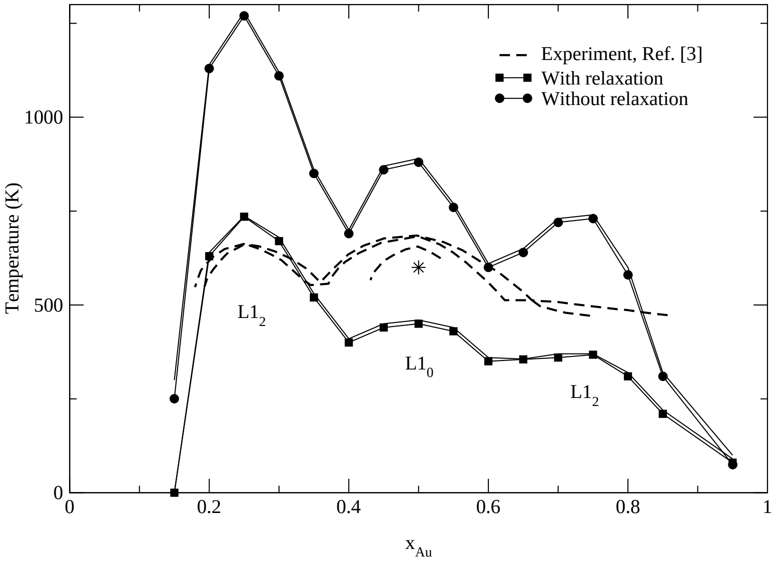

Figure 3: Bulk phase boundary calculated with and without atomic relaxation, experimental data from [23], the double lines indicate uncertaincy as to the temperature at which the phase transition occurs

Surface calculation

In order to describe the physics at the surface of an alloy one needs the modified coupling constants $V^{(d,s)}_{\lambda\lambda'\lambda''...}$ and the surface chemical potential difference $V^{(1)}_{\lambda} - V^{(1)}_{bulk}$. These are the coefficients in the Hamiltonian

$$\begin{aligned} E^{surf}_{tot} &= V^{(0)} + \sum_{\lambda}[V^{(1)}_{\lambda} < \sigma_{\lambda} > + \sum_{\lambda',s} V^{(2,s)}_{\lambda\lambda'} < \sigma_{\lambda;i}\sigma_{\lambda';j} >^{s} + \\ &+ \sum_{\lambda',\lambda'',s} V^{(3,s)}_{\lambda\lambda'\lambda''} < \sigma_{\lambda;i}\sigma_{\lambda';j}\sigma_{\lambda'';k} >^{s} + ...], \end{aligned} \tag{4}$$

which is the inhomogeneous version of eq. 3.

Although the surface effective pair interactions can be calculated with the formalism of GPM, as is well known calculations of partial molar quantities such as the surface chemical potential cannot. This is a consequence of the fact that the renormalization of the effective medium due to the variation of alloy composition is absent. Thus, the surface chemical potentials $V^{(1)}_{\lambda} - V^{(1)}_{bulk}$ must be obtained in direct total energy calculations. In this work we have used the KKR-CPA-ASA+M surface Green's function method [17] to obtain $V^{(1)}_{\lambda} - V^{(1)}_{bulk}$.

Modified coupling constants

We have calculated the surface effective pair interactions using the supercell geometry and SGPM technique described above. Since the number of interactions increases dramatically for even low index surfaces, we have taken into consideration only pair interactions in the first four shells that anyway reproduce the bulk phase transition quite well, as was noted in the previous section. The SGPM potentials are calculated for a supercell ordered perpendicular to the (100) surface, so for odd layers $x_{Au} = 0.25$ and for even layers $x_{Au} = 0.75$. In general, this should be the starting point of an itterative procedure that recalculates a new set of SGPM potentials from the equlibrium alloy profile obtained from solving the statistical mechanical problem with the old SGPM potentials.

However, if the interactions depend strongly on only the lattice parameter then this will be unnecessary. In order to determine the strength of the concentration dependence the ordering energy of L1$_2$ and $L1_0$, *with both structures having the same lattice parameter*, can be calculated via two routes. Firstly, the ordering energy can be calculated directly by KKR-(CPA)-ASA+M. It can then also be calculated from SGPM potentials calculated at one of the stoichiometries. If the concentration dependance is weak then these two methods should produce results which are quite close. In table 4 are shown the ordering energies of L1$_2$ and L1$_0$ at the lattice parameter of Cu$_{.75}$Au and indeed the two methods of calculation produce very similar results. On this basis the SGPM interactions are calculated by stopping at the first itteration, and are shown in are shown in table 5.

Table 4: Ordering energies (in K) for lattice parameter fixed at that of Cu$_{.75}$Au calculated directly and from SGPM potentials

	$E^{order}_{L1_0}$	$E^{order}_{Cu_3Au}$
KKR-(CPA)-ASA+M	-1337	-1007
SGPM at $x_{Au} = 0.25$	-1342	-1061

Table 5: The effective interactions for Cu$_{75}$Au$_{25}$(100) (in K).

	λ			
	1^{st} layer	2^{nd} layer	3^{rd} layer	4^{th} layer
$V^{(1)}_{\lambda} - V^{(1)}_{bulk}$	-2660	273	-157	0
$V^{(2,s)}_{\lambda\lambda+n}$				
	$s = 1$			
$n = 0$	1136	1303	1338	1322
1	2668	2695	2666	2645
	$s = 2$			
0	108	−37	−53	−15
2	−41	−28	−17	−7
	$s = 3$			
1	−149	−175	−202	−228
2	−135	−86	−101	−114
	$s = 4$			
0	−53	−38	−34	−54
2	6	−58	−81	−108

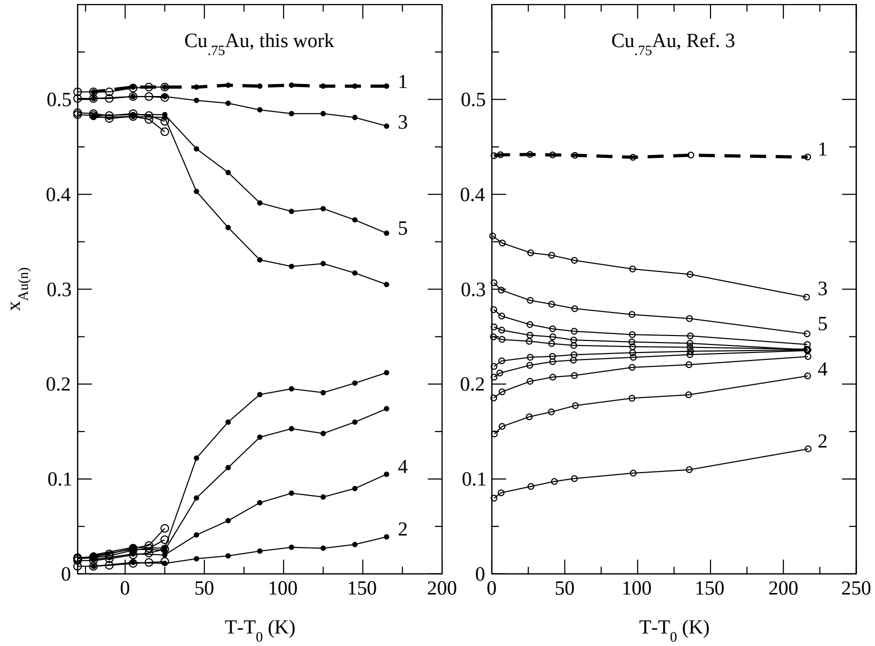

Figure 4: Composition of surface region plotted against temperature, heavy dashed line is surface layer

Surface chemical potentials

From the form of the inhomogeneous version of equation 3 one can see immediately that for equatomic alloy this is the the segregation energy in the λ^{th} layer. However, as we have seen that the interactions depend only weakly on concentration we can calculate $V_{\lambda}^{(1)} - V_{bulk}^{(1)}$ for Cu$_{.75}$Au by performing the same calculation as for the equatomic alloy but with the lattice parameter of Cu$_{.75}$Au. The surface chemical potentials obtained in this way are shown also in table 5.

Finite temperature properties

Monte Carlo simulations for surfaces can be done either in the canonical or grand canonical ensemble. In the canonical ensemble one needs to make L in L×D×D large enough so that the two D×D surfaces are non-interacting. On the other hand, for simulations in the grand canonical ensemble the chemical potential of the system must be pre-calculated for each surface simulation. As this involves numerical derivatives of the results of bulk simulations, which will anyway have some statistical uncertaincy, it is neccessarily takes some work. For the surface simulations in this work a recently proposed novel Monte Carlo method has been used. This works in the grand canonical enesmble but instead of calculating the chemical potential from an *analytic* formula, namely $\frac{\partial F}{\partial c}$, one generates a *numerical* chemical potential in the form of a "bulk reservoir" in a large datafile [29]. As only one bulk calculation needs to be made for every surface simulation this is certainly a more efficient calculation.

In Fig. 4 are presented MC results using the potentials in Table 5 and results from X-ray grazing experiments [5]. Simulation boxes of size 28×28×50 (filled circles) and 50×50×100 (open circles) have been used. It can be seen that although for the segregation in the surface layer theory and experiment are in good agreement, for the composition of the sub-surface region theory and experiment no longer agree. In fact the nature of the surface transition that occurs using the ab-initio potentials is qualitativly wrong. As can be immediately seen from the concentration profile close to the transition temperature in Fig. 4 , the ab-initio potentials lead to Surface Induced Order as opposed to the Surface Induced Disorder seen experimentally.

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5.5 ESF Workshop Announcements

5.5.1 Workshop on Ab initio Theoretical Approaches to the Electronic Structure and Optical Spectra of Materials

CECAM, Lyon, France

23–25 September 2002

This workshop focuses on recent theoretical progress in electronic-structure calculations with a special emphasis on excited-state properties. Its aim is to bring together researchers from solid-state physics, surface physics and materials science with an interest in electronic excitations in order to discuss the present status of the field and perspectives for its further development.

As electronic excitations cannot be accessed within the Kohn-Sham approach, accurate calculations in materials science must either be based on Green-function methods or time-dependent density-functional theory. Although the two schemes are based on different propositions, both are, in principle, exact, and their interplay has proved a particularly fruitful area of research that will be explored at this workshop. Practical implementations now yield accurate quasiparticle energies and optical spectra for many prototype materials, and recent progress in this area will be reviewed. At the same time, applications to more complex systems like nanostructures and surfaces also show the need for conceptual advances beyond the standard approximations, such as the GW or the adiabatic local-density approximation.

The workshop programme features a mixture of invited and contributed talks as well as a poster session for all participants. Ample time is reserved for discussions of current progress in the field and the perspectives for future developments, which are a central aim of this meeting.

Further information about the workshop programme including a list of invited speakers and instructions for applicants are provided at

http://www.fisfun.uned.es/∼athaesos/

Bursaries are available for young researchers, whose participation is especially encouraged.

Organisers:

Pablo García-González (Universidad Autónoma de Madrid)
Maurizia Palummo (Università di Roma “Tor Vergata”)
Olivia Pulci (Università di Roma “Tor Vergata”)
Arno Schindlmayr (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin)
Nathalie Vast (École Polytechnique, Palaiseau)

6 General Workshop/Conference Announcements

6.1 Workshop on ”Electronic Structure of Solids” in Dresden

3-5 July, 2002
First Announcement

This is the first information about the workshop on

”Electronic Structure of Solids”

to be held at IFW Dresden in the first week of July, 2002. The intention is to provide a survey of the field, given by leading experts, and to identify new developments. The workshop will be dedicated to the occasion of Helmut Eschrig's 60th birthday.

Please note the proximity of our workshop to two other events in solid state physics:

The 6th Prague Colloquium on f-electron systems at Charles University, Prague, July 6-9, 2002 (http://195.113.32.128/magevent.htm) and

SCES 2002, Krakow, July 10-13, 2002 (http://www.if.uj.edu.pl/konferencje/sces02).

Please let me know your interest by sending back the following pre-registration form to m.richter@ifw-dresden.de

A second (final) information and registration form will be distributed at the end of March to those who will have pre-registered.

Purpose of Workshop: Survey of the state-of-the art of electronic structure theory.

Organizers:

Joerg Fink (j.fink@ifw-dresden.de)
Ludwig Schultz (l.schultz@ifw-dresden.de)
Klaus Wetzig (k.wetzig@ifw-dresden.de)
Peter Joehnk (p.joehnk@ifw-dresden.de)
Manuel Richter (m.richter@ifw-dresden.de)

Contact: Manuel Richter (m.richter@ifw-dresden.de)

Information: http://www.ifw-dresden.de/events/elstruc.htm

Topics:

density functional theory: methods and applications
correlated electronic states

electronic structure and magnetism
super-conductivity and lattice dynamics
surfaces, interfaces, and small systems
disorder
excitations

Programme: invited talks and contributed posters

Preliminary list of invited lecturers:

Patrick Bruno (Halle)
Peter Dederichs (Juelich)
Gert Eilenberger (Juelich)
Arthur Ernst (Halle)
Matthias Eschrig (Karlsruhe)
Peter Fulde (Dresden)
Yuri Grin (Dresden)
Balazs Gyorffy (Bristol)
Bruce Harmon (Ames)
Barry Klein (Davis)
Klaus Koepernik (Dresden)
Juergen Kuebler (Darmstadt)
Sadamichi Maekawa (Sendai)
Ingrid Mertig (Halle)
Rene Monnier (Zuerich)
Warren Pickett (Davis)
Helge Rosner (Davis)
Matthias Scheffler (Berlin)
Karlheinz Schwarz (Vienna)
Gotthard Seifert (Dresden)
Gerhard Soff (Dresden)
Frank Steglich (Dresden)
Bedrich Velicky (Prague)
Werner Weber (Dortmund)
Peter Weinberger (Vienna)

This list is not yet complete.

6.2 CECAM Workshop

"Computer modelling of atoms, molecules, and materials using approximate functionals of the kinetic energy"

31 July - 2 August 2002, Lyon (France)

organized by T.A. Wesolowski (Geneva) and H. Chermette (Lyon)

Details are available through a link at the CECAM's page:

`http://www.cecam.fr/`

or directly at:

`http://lcta.unige.ch/~tomek/cecam2002/cecam2002.html`

6.3 Symposium and Summer School on Nano & Giga Challenges in Microelectronics Research and Opportunities in Russia

Moscow, September 11-13, 2002

You are heartily invited to take part in the Symposium and Summer School on: Nano and Giga Challenges in Microelectronics Research and Opportunities in Russia, and especially in the section on Atomic Scale Design: Modeling and Simulation.

Details can be found at the web-site

http://www.AtomicScaleDesign.Net/Moscow

where the last updates of the 2nd call and the section program are also available.

Prof. Alexander Bagatur'yants
Photochemistry Center, Russian Academy of Sciences
ul. Novatorov 7a, Moscow, 117421 Russia
Phone: (007-095)-936-2588 Fax: (007-095)-936-1255
E-mail: sasha@photonics.ru
Home page: http://www.photonics.ru/eng/bagat/bagat.htm

The Abdus Salam International Centre for Theoretical Physics (ICTP), Trieste, Italy

6.4 LDA+DMFT Workshop in Trieste

ICTP Internation Workshop on LDA+DMFT in Electronic Structure Calculations

17-21 June 2002

Description

An International Workshop on Correlation Effects in Electronic Structure Calculations will be held at the Abdus Salam International Centre for Theoretical Physics (ICTP), Trieste, from 17 to 21 June 2002. The Workshop will present a pedagogical introduction to the Dynamical Mean Field Method and how it is applied to investigate the properties of correlated materials. There will be lectures in the morning followed by hands-on training sessions in the afternoon. The program will cover orbital based electronic structure methods, calculations of U's, dynamical mean field equations and its solution via perturbative methods and quantum Monte Carlo techniques. It will conclude with a small conference.

DIRECTORS of the Workshop are Vladimir Anisimov (Yekaterinburg, Russia) and Gabriel Kotliar (Rutgers University, USA)

A preliminary list of speakers include V. Anisimov (Ekaterinburg), G. Kotliar (Rutgers), M. Rozenberg (Buenos Aires), A. Lichtenstein (Nijmeigen), S. Savrasov (NJIT).

Details and info for applications at:

http://www.ictp.trieste.it/cgi-bin/ICTPsmr/mkhtml/smr2html.pl?smr1412/Announcement

DEADLINE FOR APPLICATIONS: 31 March, 2002

Contact info:

Name Giuseppe Santoro (local organizer)
e-mail santoro@sissa.it
phone +39-040-3787435
Fax +39-040-3787528
Address: SISSA, Via Beirut 4, 34014 Trieste, Italy

6.5 ES2002 First Announcement

ES2002-Fourteenth Annual Workshop on Recent Developments in Electronic Structure Methods

June 6-8th 2002, UC Berkeley, Berkeley, California

http://www.nersc.gov/conferences/es2002/

The 14th Workshop on Recent Developments in Electronic Structure Methods will be held at the Clark Kerr Conference Center, UC Berkeley Campus. This workshop brings together active participants in electronic structure theory from universities, colleges, government labs, and industrial labs from around the world. The invited presentations and contributed posters will describe new methods for computing previously inaccessible properties, breakthroughs in computational efficiency and accuracy, and novel applications of these approaches to the study of molecules, liquids, and solids. This workshop represents a valuable opportunity for students, postdocs, and senior researchers alike to explain their ideas and learn from each other. A list of invited speakers will be decided at the APS March meeting by the steering committee. A list of the steering committee may be found at

http://www.nersc.gov/conferences/es2002/committee.html

Modest low price accommodation and meals will be provided at the Clark Kerr Campus and can be paid for as part of the registration fee. Accommodation in hotels in Berkeley will also be available to those who do not wish to stay at the Clark Kerr Campus. Registration and hotel information will be posted on the web site at a later date. A welcome reception will be provided on the evening of Wednesday June 5th and a conference banquet will be held on the evening of Thursday June 6th. The conference will end at noon on Saturday June 8th. If you have questions concerning the conference please consult the web site

http://www.nersc.gov/conferences/es2002/

(questions not covered by the web site should be sent to es2002@nersc.gov, do not reply to this email with questions). Please forward this announcement to anyone you know who may be interested in this conference.

This meeting is sponsored by Lawrence Berkeley National Laboratory and Lawrence Livermore National Laboratory both operated by the University of California for the U.S. Department of Energy.

We are looking forward to seeing you in Berkeley for a productive meeting.

The Conference Organizers:

Steven Louie
Michel Van Hove
Lin-Wang Wang
Yeen Mankin
Andrew Canning

7 General Job Announcements

Postdoctoral Position

Chemistry Department, Case Western Reserve University

Cleveland, OH 44106 USA

A position is available in the laboratory of Professor A. B. Anderson for an individual who is experienced with density functional slab band calculations. The initial focus of the research is calculating adsorption bond strengths for water molecules and hydroxyl groups on surfaces of platinum and platinum alloyed with other transition metals. The project is a component of a multidisciplinary effort involving several institutions,academic and industrial, dealing with advancing fuel cell technology, and the position is for up to two years. Please address questions or application to aba@po.cwru.edu. Case Western Reserve University is an Affirmative Action/Equal Opportunity Employer.

Position of Director for a Four Years Term

Centre Européen de Calcul Atomique et Moléculaire
Ecole Normale Supérieure de Lyon, Aile LR5
46 Allée d'Italie, 69364 Lyon Cedex 07, France

CECAM (European Center for Atomic and Molecular Calculations) is searching its future Director for a four years term, starting in October 2002.

CECAM is an organization with more than thirty years of life funded by several scientific institutions from various European Countries (Belgium, France, Germany, Greece, Italy, Netherlands, Switzerland and U.K.). Its aim is to promote the scientific development in the field of large-scale classical and quantum simulations applied to Atomic and Condensed Matter Physics, Chemistry and Biology. The activities of CECAM include the hosting of researchers and the organization of workshops and tutorials. More information on the activities can be found on the web site: http://www.cecam.fr/.

The new Director should be a senior scientist with the level of Laboratory Leader or University Professor, having a large experience in one or more fields such as Condensed Matter, Theoretical Chemistry, Atomic Physics, Statistical Mechanics, Numerical Simulations. The type and the level of the appointment will depend on the qualifications of the candidate.

Applications should be sent to Prof. Carlo M. Bertoni, chairman of the CECAM Council, at the address below, before April 15, 2002. The final selection will take place in Lyon (France) on May 17, 2002, after the interview of the pre-selected candidates conducted by the Council in the same day.

Prof. Carlo M. Bertoni, chairman of the CECAM Council,
Ecole Normale Supérieure de Lyon, Aile LR5
46 Allée d'Italie, 69364 Lyon Cedex 07, France

For further information, if necessary, please contact Prof. Bertoni at the e-mail:bertoni@unimo.it.

Marie-Curie Visiting Doctoral Fellowships at the Research Center and Science College "Computational Materials Science" at Wien, Austria

The Research Center and Science College "Computational Materials Science " (CMS) at the Universität Wien and the Technische Universität Wien (Austria) is seeking highly qualified doctoral candidates for extended visits up to nine months. The candidates will participate in the research program of the CMS, while continuing their studies at their home institutions. The CMS has activities and research interests in a wide area of computational physics, chemistry and materials science, ranging from the development of advanced tools for ab-initio calculations of materials properties and process modelling to application in front-line materials research. The research groups of the CMS have developed the leading plane-wave-based code VASP for ab-initio molecular dynamics simulations, as well as full-potential fully relativistic KKR and Greens-function KKR code and made important contributions to the full-potential linearized augmented-plane-wave code FLAIR. Current research projects include the physics and chemistry of surfaces and interfaces, heterogeneous catalysis on solid surfaces and in the pores of zeolites, the structure-property relationship in inorganic materials (alloys, intermetallic compounds, minerals,....), magnetic materials (permanent magnets, materials with giant or colossal magnetoresistance, ultrathin films and multilayers, nanostructures), fullerenes and nanotubes, melts, colloids and polymers and solid/liquid interfaces. Further details can be found at the home-page of the CMS (http://info.tuwien.ac.at/cms/index.html) and at the home-pages of the particpating institutions (Universität Wien: Institut für Materialphysik and Institut für Physikalische Chemie, Technische Universität: Institut für Theoretische Physik and Institut für Allgemeine Physik).

Interested candidates are invited to send a short description of the proposed research, a curriculum vitae, a list of publications (if applicable) and the names and contact information of at least two referees (one of them must be the doctoral supervisor) to the speaker of the CMS, Prof. Jürgen Hafner. The CMS is an equal opportunity employer. Women are especially encouraged to apply for fellowships. There is no deadline for the applications. EU residency requirements (including associated countries) apply to these Marie-Curie Fellowships. The fellowships consist of a montly subsistance allowance of 1200 EURO, and the cost of return travel between Austria and the country of residence of the fellow.

Contact information:

Prof. Jürgen Hafner
Institute für Materialphysik and Center for Computational Materials Science
Universität Wien, Sensengasse 8/12, A-1090 Wien, Austria
Tel.: +43-1-4277-51400
Fax : +43-1-4277-9514
email: juergen.hafner@univie.ac.at

FELLOWSHIPS FOR STUDIES IN CONSENDED MATTER THEORY

Uppsala University, Sweden

One or two fellowships are open for studies in Condensed Matter Theory at the Department of Physics at Uppsala University, Sweden, in the framework of the European Programme "Improving Human Research Potential and the Socio-Economic Knowlegde Base" (Marie Curie Fellowship). The research programme includes first-principles simulations of electronic and magnetic properties of emergent materials. The fellowship is for short stays (3 months up to one academic year), and is aimed for young researchers pursing doctoral studies in their own institutions who would like to enhance their experties in development and applications of ab initio techniques for the electronic stucture calculations in the framework of the density functional theory. The holder should have a background in fields like condensed matter physics, solid state chemistry, or materials science, and the stay must be directly relevant to the doctoral studies pursued. The stay at the Condensed Matter Theory Group, Uppsala University, must be recognized as an integral part of the doctoral studies by the home university. The fellow must be a national of a EU Member or Associated State, and be a non-Swedish citizen. The fellowship for an amount of 1200 Euro per month is to be used for housing and living expense during the stay. Additional limited support for travel cost will be provided. Further information about the fellowship and the research programme can be obtained from Prof. B. Johansson at the adress: Condensed Matter Theory Group, Physics Department, Uppsala University, Box-530, SE-75121 Uppsala, Sweden, Phone: +46(0)-18-4713623, Fax: +46(0)-18-511784, e-mail: Borje.Johansson@fysik.uu.se

For more information on the fellowships, please, visit

`http://improving.cordis.lu/mc/show-PRJ.cfm?obj_id=MCFellow0000000000003F96`

For more information on the group, please, visit

http://www.fysik4.fysik.uu.se/

POSTDOCTORAL POSITION IN COMPUTATIONAL MATERIALS SCIENCE

LAWRENCE BERKELEY NATIONAL LABORATORY (LBNL)

We have one immediate postdoctoral opening for the modeling of segregation in metallic binary alloy nanoparticles. The object is to understand and predict the segregation of one component to surface sites, including edges and corners, for nanoparticles with about 1000 atoms. The work will involve close collaboration with experiments (group of P.N. Ross at LBNL), such as transmission electron microscopy (TEM) of supported clusters.

The work, performed in LBNL's Materials Sciences Division, will also involve collaboration with the scientific computing group at LBNL's National Energy Research Scientific Computing Center (NERSC): Lin-Wang Wang and Andrew Canning.

A Ph.D. degree in physics or a related field is required and experience in electronic structure calculations and Monte Carlo calculations is preferred. The position is initially for one year with the possibility of renewal for up to three years.

Interested persons should send a curriculum vitae and three recommendation letters to:

Michel A. Van Hove
vanhove@lbl.gov
http://electron.lbl.gov/

TWO POST-DOCTORAL POSITIONS IN COMPUTATIONAL MATERIALS SCIENCE

Large-scale quantum-mechanical simulation of nano-scale materials

National Institute for Materials Science, Tsukuba, Japan

National Institute for Materials Science is starting a major thrust in the area of the research of nano-scale materials. The First-principles Simulation group in the Computational Materials Science Center has post-doctoral openings in (i) large-scale quantum-mechanical simulation of nano-scale materials, including nano-controlled surfaces and interfaces, nano-assembled metal clusters on solid surfaces (model catalysts), molecular electronic devices (quantum transport properties), biomolecules, and so on; (ii) development of simulation algorithms and techniques to analyze the properties of nano-scale materials, especially, order-N algorithms (CONQUEST code) for the large-scale quantum-mechanical simulation. This will be done in collaboration with Prof. M. J. Gillan's group at University College London.

The position will suit post-doctoral candidates who have extensive experience in computational science and a background in surface science and/or nano-science.

Applicants should submit by e-mail a curriculum vitae and a publication list to:

Dr. Takahisa Ohno
Vice-Director
Computational Materials Science Center
National Institute for Materials Science
1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
Telephone: (81) 298-59-2622; Fax: (81) 298-59-2602
E-mail: OHNO.Takahisa@nims.go.jp

A postdoctoral position at University of Tokyo

We have an opening for a postdoctoral fellow preferably with experience in first principle electronic structute theory to be filled immediately. The initial appointment should be for one year from 2002 April 1 but may be extended up to October of 2004 for a successful person. The employment is by the JST as the research fellow and the salary is expected to be about 7,000,000 JYen per year (including social insurance and tax). See the web page of JST: http://www.jst.go.jp/EN

Anyone interested in this position is requested to send a copy of his/her CV, a publication list, and a reference letter to the address given below, either by post, fax or e-mail.

Projects:

New molecular-dynamical method, based on ab initio electronic-structure theory.

Content:

The aim of the present project is to investigate structures and properties of condensed matters using new molecular-dynamical methods, such as order-N method and quantum-classical hybirid method. Our group has developed various codes of electronic-structure calcultions, that is, LMTO code, plane-wave code, and order-N tight-binding code. Some of them are parallelized with MPI commands and are used with some parallel supercomputers. The above codes have been applied to strongly-corelated materials, complex liquids, large-scale systems (more than 1 million atoms), etc.

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URL: http://fujimac.t.u-tokyo.ac.jp/FujiwaraLab/index.html
e-mail : fujiwara@coral.t.u-tokyo.ac.jp

EU funded Post Doctoral Research Associate Davy Farady Research Laboratory, Royal Institution, London, UK

COMPUTATIONAL STUDY OF HYDROGEN DEFECTS IN NOMINALLY ANHYDROUS MINERALS

Nominally anhydrous minerals (NAMs) contain water in the form of structurally bound H defects. These defects can have a major influence on the physical properties of NAMs (eg. melting temperature, electrical conductivity, rheology), even when present at low concentrations. This project will apply state of the art computer modelling techniques to the study of hydrogen defects in NAMs; the mechanisms by which such defects are incorporated into the crystal structures, their vibrational spectra and influence on bulk properties. The work will focus on the pyroxene minerals which are an important constituent of the Earth's Upper Mantle and will assess the impact which these defects have on geophysical models of dynamic processes and water storage in the deep Earth. This project is funded as part of a European Research Training Network involving teams from UK, France, Germany, Sweden and Austria. The PDRA will be based at the Davy Faraday Laboratory of the Royal Institution, which has for may years conducted a successful and wide ranging programme of computational and experimental work in materials chemistry. The laboratory is recognised worldwide as a centre of excellence in the fields of synthesis, characterisation and optimisation of complex materials.

The post is available to start immediately and will continue to Sept. 2004. To qualify, applicants must satisfy the following requirements:

1) Nationality: must be nationals of an EU Member or Associated Member State OR must have resided in an EU member state for at least 5 years prior to their appointment.

2) International mobility: may not be nationals of the UK or have worked or studied in the UK for more than 12 out of the last 24 months.

3) Qualifications: applicants must hold a PhD at the time of appointment in the area of computational materials chemistry, crystallography, solid state chemistry/physics or mineral physics.

4) Age: should be under 35 years of age at the time of appointment. An exemption will be made for those who have been involved in compulsory military service or childcare activities.

Further information can be obtained from Dr. Kate Wright, DFRL, Royal Institution, 21, Albemarle Street, London W1S 4BX, UK (kate@ri.ac.uk).

RESEARCH ASSOCIATE POSITION in Many-Body Quantum Simulations

Theoretical Chemistry
Ruhr-Universitaet Bochum
Germany

Applications are invited for a postdoctoral research associate position (German nomenclature: promovierter wiss. Mitarbeiter, BAT IIa), which includes full health, dental, and social benefits. The appointment will be for two years (with the likely possibility of extending it for two more years if desired). The preferred starting date would be within the year 2002.

Applicants should hold a doctorate in theoretical/computational physics or a related discipline. In addition to excellent programming and computational skills the ideal candidate would have significant experience in path integral techniques and ab initio quantum simulations. She or he would work primarily on the development of novel path integral simulation techniques. In addition, he/she can also be involved in other challenging research projects including both method development and large-scale applications.

The Theoretical Chemistry Group at RUB offers an exciting interdisciplinary environment with excellent working conditions. The general interests of the group are covered in

http://www.theochem.ruhr-uni-bochum.de/go/cprev.html

and additional information can be obtained from the home page.

Candidates should send a detailed resume including an outline of their research achievements and interests as well as the names and email addresses of academic references to

Dominik Marx
Lehrstuhl fuer Theoretische Chemie
Ruhr-Universitaet Bochum
44780 Bochum
Germany

Email: office@theochem.ruhr-uni-bochum.de
Fax : ++49 234 32 14045
Web : http://www.theochem.ruhr-uni-bochum.de/

The University particularly welcomes applications from women.

Ph.D. and Postdoctoral Position

Fritz-Haber-Institut der Max-Planck-Gesellschaft
and
The Pennsylvania State University

A Ph.D. and a postdoc position is available in a joint project of the Fritz-Haber-Institut der Max-Planck-Gesellschaft (Matthias Scheffler, http://www.fhi-berlin.mpg.de/th/th.html) and The Pennsylvania State University (Henry C. Foley, http://fenske.che.psu.edu/Faculty/Foley/index.html, and Kristen Fichthorn, http://fenske.che.psu.edu/Faculty/Fichthorn/index.html).

Theme:

The role of nano-porous carbon in dehydrogenation and oxidation catalysis.

Project summary:

This is a highly interdisciplinary project involving, e.g. extensive density-functional theory calculations and Statistical Mechanics simulations (with DFT derived parameters).

The catalytic production of styrene is one of the most important processes in chemical industry (a key process for making most plastics). Recently it could be shown that the typically employed iron-oxide catalyst is in fact not the active material, but the true catalyst is formed during the induction period: The material that is actually doing the catalysis apparently is "nano porous carbon". This consists of strained and twisted graphite sheets that have a lot of defects (in particular five-fold rings).

`http://www.fhi-berlin.mpg.de/th/Slides/Scheffler_transparencies_pdf/npc-2002.pdf`

summarizes some aspects of our recent work.

The planned research may start with an analysis of the chemical reactivity of nanotubes of different diameter and of the different regions of nano porous carbon. At a later step it is planned to model the dynamics of the flow of steam + ethylbenzene at such carbon structures, and the process of ethylbenzene dehydrogenation.

Where:

The student/postdoc will spend some time in Berlin and some time in the US. Details will be decided along the progress of the work.

We are looking for computational physicists, chemists, or chemical engineers. Good background in electronic structure theory, thermodynamics, and statistical mechanics is important.

Please send your application material to:

Matthias Scheffler
Fritz-Haber-Institut
der Max-Planck-Gesellschaft
Faradayweg 4-6
D-14 195 Berlin-Dahlem
Germany

phone : ++49-30-8413 4711
fax : ++49-30-8413 4701
e-mail: scheffler@fhi-berlin.mpg.de

WWW: http://www.fhi-berlin.mpg.de/th/th.html

PhD or Postdoctoral Position

Theory Department, Max-Planck-Institute of Microstructure Physics,

Halle, Germany

A PhD or Postdoctoral position is available immediately at the Theory Department of the Max-Planck-Institute of Microstructure Physics in Halle, Germany (head of the Department Prof. P. Bruno, home page: http://www.mpi-halle.mpg.de/ theory/).

The project deals with the first-principles study of the physical properties of the multilayer systems containing actinides elements. The work will be performed in close collaboration with a number of European experimental groups. We offer excellent working conditions in an international and interdisciplinary environment. Strong background in solid state theory and programming skills are required for this position. Experience in the density functional theory calculations is advantageous.

Candidates should send the curriculum vitae and names of two referees to:

PD Dr L. Sandratskii
Max-Planck-Institute of Microstructure Physics
Weinberg 2
06120 Halle
Germany
email: lsandr@mpi-halle.de

PhD Studentship

STUDENTSHIPS IN PHYSICS OF CLUSTERS AND CLUSTER ASSEMBLED NANOSTRUCTURES

University of Canterbury, Christchurch, New Zealand

Nanostructure Engineering, Science and Technology (NEST) Group

Field(s): computational physics, condensed matter, low temperature physics, material physics, nanotechnology.

Job Description:

The Nanostructure Engineering, Science and Technology (NEST) group based at the University of Canterbury, in Christchurch, New Zealand, invites applications from well qualified graduates in Physics, Electrical Engineering, or a related subject, to carry out research towards a masters degree or PhD in the physics of atomic clusters and cluster assembled nanostructures.

The NEST group has recently been successful in securing significant research funding as a partner in the MacDiarmid Institute for Advanced Materials and Nanotechnology, and therefore has a number of new scholarships to offer.

Graduate students are urgently needed to work on the following projects:

* Electron Diffraction as a Probe of the Structure of Atomic Clusters
* Novel Electronic Devices Formed by Deposition of Atomic Clusters
* Molecular Dynamics Simulations of Atomic Clusters

Information on these projects can be found at:

`http://www.phys.canterbury.ac.nz/research/solid_state/simonbrown_research.html`

Please note: Unfortunately overseas students must pay fees at the level of around NZ$20 000 per annum UNLESS they are from countries with a fees agreement with New Zealand i.e. Germany, Australia, and France. These fees are NOT covered by any available scholarship.

Information on the NEST group and other Nanotechnology research projects for which studentships are available is at:

http://www.elec.canterbury.ac.nz/research/nest/index.html

Information on research and studentships in other fields within the Department of Physics and Astronomy is at:

http://www.phys.canterbury.ac.nz/

Application Deadline: Apr 30 (Tue), 2002

Contact: Simon Brown
Email: s.brown@phys.canterbury.ac.nz
Phone: +64 3 364 2507; **Fax:** +64 3 364 2469
Address: Department of Physics and Astronomy, University of Canterbury,
Private Bag 4800, Christchurch, New Zealand

PhD Position

Theory Department, Max-Planck-Institute of Microstructure Physics,

Halle, Germany

A PhD position is available immediately at the Theory Department of the Max-Planck-Institute of Microstructure Physics in Halle, Germany (head of the Department Prof. P. Bruno, home page: http://www.mpi-halle.mpg.de/ theory/).

The project deals with the first-principles study and design of the materials for the realization of spin-transport in semiconductor devices. The work will be performed in contact with a number of experimental groups in Germany and industrial companies interested in the results of the project.

We offer excellent working conditions in an international and interdisciplinary environment. Strong background in solid state theory and programming skills are required for this position. Experience in the density functional theory calculations and semiconductor-physics research is advantageous.

Candidates should send the curriculum vitae and names of two referees to:

PD Dr L. Sandratskii
Max-Planck-Institute of Microstructure Physics
Weinberg 2
06120 Halle
Germany
email: lsandr@mpi-halle.de

8 Abstracts

Cu $L_{2,3}$ x-ray absorption and the electronic structure of non-stoichiometric Cu_5FeS_4

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Magnetic Spectroscopy, Daresbury Laboratory, Warrington WA4 4AD, UK
R. A. D. Pattrick
Earth Sciences, University of Manchester, Manchester M13 9PL, UK
J. M. Charnock
Daresbury Laboratory, Warrington WA4 4AD, UK
B. A. Grguric
Earth Sciences, University of Cambridge, Cambridge CB2 3EQ, UK

Abstract

X-ray absorption measurements of the ternary compound Cu_5FeS_4 within a narrow non-stoichiometric range of 2 at% reveal large changes in the relative peak intensities of the Cu $L_{2,3}$ near edge structure. There is a large peak at threshold that can be ascribed to holes in the sulfur ligand band. With increasing amount of excess electrons, as determined by electronprobe microanalysis, the intensity of this ligand-hole peak decreases rapidly and starts to merge with the spectral structure due to the filled *d* band. Simultaneously, an increase of the peak corresponding to the *d*-hole state at ∼4 eV above the threshold peak is observed. This clearly demonstrates the strong sensitivity of the Cu $L_{2,3}$ edge for small changes in the electronic structure. The experimental results are in agreement with a simple cluster model.

(Submitted to Phys. Rev. B)
Manuscripts available from: Gerrit van der Laan (G.VanDerLaan@dl.ac.uk)

Evolution of Co/Cu multilayer conductivity during growth: ab intio study

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Institut für Theoretische Physik, Technische Universität Dresden,
01062 Dresden, Germany
N. Papanikolaou, and I. Mertig[b]
Fachbereich Physik, Martin-Luther-Universität Halle-Wittenberg,
06099 Halle, Germany

Abstract

We present ab-initio calculations for the in plane conductivity of Co/Cu multilayer slabs. The electronic structure of the multilayer slabs is calculated by means of density functional theory within a screened KKR scheme. Transport properties are described using the Boltzmann equation in relaxation time approximation. We study the change of the conductivity during growth of the multilayer, and we can reproduce the anomalous, non Ohmic, behavior observed experimentally in several multilayer systems. Our results show that this behavior can be explained in terms of the electronic structure of the slab only. No extra assumption for the scattering at the interfaces is necessary. The connection of electronic structure and conductivity during layer-by-layer growth is elucidated by analyzing the layer-projected conductivities.

(Accepted for Phys. Rev. B)
Latex-file available from cond-mat/0109293.

Origin and Properties of the Gap in the Half-Ferromagnetic Heusler Alloys

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D-52425 Jülich, Germany
N. Papanikolaou
Fachbereich Physik, Martin-Luther Universität, Halle-Wittenberg,
D-06099 Halle, Germany

Abstract

We study the origin of the gap and the role of chemical composition in the half-ferromagnetic Heusler alloys using the full-potential screened KKR method. In the paramagnetic phase the $C1_b$ compounds, like NiMnSb, present a gap. Systems with 18 valence electrons, Z_t, per unit cell, like CoTiSb, are semiconductors, but when $Z_t > 18$ antibonding states are also populated, thus the paramagnetic phase becomes unstable and the half-ferromagnetic one is stabilized. The minority occupied bands accommodate a total of nine electrons and the total magnetic moment per unit cell in μ_B is just the difference between Z_t and 2×9. While the substitution of the transition metal atoms may preserve the half-ferromagnetic character, substituting the *sp* atom results in a practically rigid shift of the bands and the loss of half-metallicity. Finally we show that expanding or contracting the lattice parameter by 2% preserves the minority-spin gap.

(Submitted to Phys. Rev. B)
Manuscripts available from: I.Galanakis@fz-juelich.de

Novel Properties of CrAs in the Zinc-Blende Structure

I. Galanakis
Institut für Festkörperforschung, Forschungszentrum Jülich,
D-52425 Jülich, Germany

Abstract

The development of new techniques such as the molecular beam epitaxy have enabled the growth of thin films of materials presenting novel properties. Recently it was made possible to grow a CrAs thin-film in the zinc-blende structure. In this contribution, the full-potential screened KKR method is used to study the electronic and magnetic properties of bulk CrAs in this novel phase as well as the Cr and As terminated (001) surfaces. Bulk CrAs is found to be half-ferromagnetic for all three GaAs, AlAs and InAs experimental lattice constants with a total spin magnetic moment of 3 μ_B. The Cr-terminated surface retains the half-ferromagnetic character of the bulk, while in the case of the As-termination the surface states destroy the gap in the minority-spin band.

(Submitted to Phys. Rev. B)

Manuscripts available from: I.Galanakis@fz-juelich.de

Paramagnetic State of Degenerate Double Exchange Model: a Non-Local CPA Approach

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1-1-1 Higashi, Tsukuba, Ibaraki 305-0046, Japan
and
Institute of Metal Physics, Russian Academy of Sciences,
Ekaterinburg GSP-170, Russia

Abstract

The off-diagonal disorder caused by random spin orientations in the paramagnetic (PM) state of the double exchange (DE) model is described by using the coherent-potential-approximation (CPA), which is combined with the variational mean-field approach for the Curie temperature (T_C). Our CPA approach is essentially non-local and based on the perturbation theory expansion for the T-matrix with respect to the fluctuations of hoppings from the "mean values" specified by matrix elements of the self energy, so that in the first order it becomes identical to the DE theory by de Gennes. The second-order effects, considered in the present work, can be viewed as an extension of this theory. They are not negligible, and lead to a substantial reduction of T_C in the one-orbital case. Even more dramatic changes are expected in the case of orbital degeneracy, when each site of the cubic lattice is represented by two e_g orbitals, which also specify the form of interatomic transfer integrals. Particularly, the existence of two Van Hove singularities in the spectrum of degenerate DE model (one of which is expected near the Fermi level in the 30%-doped $LaMnO_3$) may lead to the branching of CPA solutions, when the Green function and the self energy become double-valued functions in certain region of the complex plane. Such a behavior can be interpreted as an intrinsic inhomogeneity of the PM state, which consists of two phases characterized by different electronic densities. The phase separation occurs below certain transition temperature, T_P, and naturally explains the appearance of several magnetic transition points, which are frequently seen in manganites. We discuss possible implications of our theory to the experimental situation in manganites, as well as possible extensions which needs to be done in order to clarify its credibility.

(Submitted to Phys. Rev. B)
Manuscripts available from: igor.solovyev@aist.go.jp

Calculated structural stabilities of U, Np, Pu and Am; new high-pressure phases for Am and Pu

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Commissariat à l'Energie Atomique, DAM-Ile de France,
Département de Physique Théorique et Appliquée, BP 12,
91680 Bruyères-le-Chatel, France

Abstract

The high pressure phase of americium Am IV recently found experimentally, which is a primitive-orthorhombic structure with four atoms in the unit cell, is also found to be stable theoretically at high pressure in Am by a calculation using the full potential linearized augmented plane wave (FPLAPW) method. The possibility of the Am IV structure being a stable high-pressure phase of U, Np or Pu, like in the case of Am, is examined using the FPLAPW method by comparing the total energy as a function of volume with ten other crystal structures. The results indicate that the Am IV structure is not a high pressure phase for U and Np but it is for Pu, for which it is proposed that the sequence under pressure is α-Pu → Am IV → body-centred cubic. Our calculations are reliable because they give theoretically the stability of the crystal α-phases of U, Np, Pu under ambient conditions. The normal pressure phase of Am is modelled by our fully relativistic muffin-tin orbital method with unhybridized 5f electron states.

(Accepted for publication in J. Phys.: Condens. Matter)
Manuscripts available from: michel.penicaud@cea.fr

Ballistic Spin Injection from Fe(001) into ZnSe and GaAs

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Institut für Festkörperforschung, Forschungszentrum Jülich,
D-52425 Jülich, Germany
D. Grundler
Institut für Angewandte Physik und Zentrum für Mikrostrukturforschung,
Universität Hamburg, Jungiusstraße 11, D-20355 Hamburg, Germany

Abstract

We consider the spin injection from Fe into ZnSe and GaAs in the ballistic limit. By means of the *ab initio* SKKR method we calculate the ground state properties of epitaxial Fe|ZnSe(001) and Fe|GaAs(001) heterostructures. Three injection processes are considered: injection of hot electrons and injection of "thermal" electrons with and without an interface barrier. The calculation of the conductance by the Landauer formula shows, that these interfaces act like a nearly ideal spin filter, with spin polarization as high as 99%. This can be traced back to the symmetry of the band structure of Fe for normal incidence.

(Submitted to Phys. Rev. B)
Available at: cond-mat/0201280
Contact person: Olaf Wunnicke (o.wunnicke@fz-juelich.de)

Electronic Structure and Isomer Shifts of Neptunium Compounds

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DK-8000 Aarhus C, Denmark,
W. Temmerman and Z. Szotek
Daresbury Laboratory, Daresbury, Warrington WA4 4AD,
United Kingdom

Abstract

The electronic structures of αNp metal and 28 Np compounds are calculated with the generalized gradient approximation to Density Functional Theory, implemented with the full-potential linear-muffin-tin-orbitals method. The calculations are compared to experimental isomer shifts providing a calibration of the ^{237}Np isomeric transition with a value of $\Delta < r^2 >= (-40.1 \pm 1.3) \cdot 10^{-3}$ fm^2 for the difference in nuclear radius between the excited isomeric level and the ground state. The isomer shift is primarily determined by the chemical environment. Decreasing the volume, either by external or chemical pressure, causes an $f \rightarrow s{+}d$ charge transfer on Np, which leads to a higher electron contact density. The possible f-electron localization in Np compounds is discussed using self-interaction corrections, and it is concluded that f-electron localization has only minor influence on the isomer shift.

(Phys. Rev. B.: submitted)

Manuscripts available from: svane@ifa.au.dk

Cohesive properties of group-III nitrides: A comparative study of all-electron and pseudopotential calculations using the generalized gradient approximation

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Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6,
14195 Berlin-Dahlem, Germany

Abstract

We compare the performance of generalized gradient approximations (GGA's) and the local-density approximation (LDA) in density-functional calculations of the cohesive properties of cubic AlN, GaN, and InN. Employing the widely adopted pseudopotential approach, the calculated data are found to depend significantly on the treatment of the core states of the group-III ions, hampering a conclusive assessment of the GGA and LDA. Here we perform all-electron FP-LAPW calculations which (i) we use to scrutinize the results of pseudopotential calculations, and (ii) provide a proper distinction between the GGA and LDA functionals. We show that the accuracy of pseudopotential calculations is comparable to that of all-electron calculations only if the Ga and In semicore d-states are treated as valence rather than core states. We also show that the use of an f-like local component can further improve the transferability of the Ga and In pseudopotentials. Regarding the PBE-GGA [Phys. Rev. Lett. **77**, 3865 (1996)] we find that the cohesive energies of the group-III nitride crystals (and those of the elemental metals) agree closely with experimental data whereas they are overestimated within the LDA. Lattice parameters are described with similar accuracy within the PBE-GGA and LDA. On the other hand we find that the heats of formation of the group-III nitrides are underestimated by the PBE-GGA and given more accurately by the LDA. For the PBE-GGA, the underestimate is mainly due to the fact that it still overestimates the bond strength of the N_2 molecule. For the LDA, the heat of formation turns out only slightly too large, because of a fortuitous cancellation of the (larger) errors in the N_2 molecule and the bulk crystals. Several other GGA functionals are able to improve over the PBE-GGA for molecules like N_2 due to stronger gradient corrections. Here we find that such more nonlocal GGA's significantly underestimate the cohesive energies of the group-III nitride (and metal) crystals and even further underestimate their heats of formation.

(submitted to: Phys. Rev. B)

Contact person: Martin Fuchs (fuchs@fhi-berlin.mpg.de)

Stability of sub-surface oxygen at Rh(111)

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Abstract

Using density-functional theory (DFT) we investigate the incorporation of oxygen directly below the Rh(111) surface. We show that oxygen incorporation will only commence after *nearly* completion of a dense O adlayer ($\theta_{\rm tot} \approx 1.0$ monolayer) with O in the fcc on-surface sites. The experimentally suggested octahedral sub-surface site occupancy, inducing a site-switch of the on-surface species from fcc to hcp sites, is indeed found to be a rather low energy structure. Our results indicate that at even higher coverages oxygen incorporation is follow by oxygen agglomeration in two-dimensional sub-surface islands directly below the first metal layer. Inside these islands, the metastable hcp/octahedral (on-surface/sub-surface) site combination will undergo a barrierless displacement, introducing a stacking fault of the first metal layer with respect to the underlying substrate and leading to a stable fcc/tetrahedral site occupation. We suggest that these elementary steps, namely, oxygen incorporation, aggregation into sub-surface islands and destabilization of the metal surface may be more general and precede the formation of a surface oxide at close-packed late transition metal surfaces.

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Initial adsorption of Cobalt on Cu(001): A first-principles investigation

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Abstract

We present total-energy calculations for the initial adsorption of Co on Cu(001). By studying different adsorption geometries we find that the substitutional adsorption is strongly favored compared to the on-surface adsorption at a fourfold hollow site. The electronic and structural effects actuating this tendency are analyzed. We investigated the coverage dependence of the adsorption energy and find that it is particularly favorable for low coverages ($\theta < 0.25$ ML) while at higher coverages we predict the formation of compact islands. In addition the paper also explores the influence of magnetism. We find that magnetic Co-adatoms induce a weak spin-polarization in the substrate with an oscillatory character: nearest Cu adatoms couple parallel while next-nearest adatoms couple antiparallel. However, we find that spin-polarization has little influence on the energetic trends. Due to the tendency of deposited Co to adsorb substitutionally it follows that under initial growth conditions two different mobile adatom sorts will be on the surface, on-surface Co (not yet incorporated substitutionally) as well as Cu created by the already substitutionally incorporated Co. The role of the substitutional Co atoms as pinning centers for subsequent island nucleation is investigated quantitatively.

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Adsorption and incorporation of Silicon at (0001) GaN surfaces

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Abstract

Silicon is the most common impurity used as n-type dopant in GaN. While the properties of Si in bulk GaN are well established little is known regarding its effect on surfaces or its incorporation mechanism. Recent growth experiments indicate that Si significantly affects the growth morphology and may even act as an anti-surfactant. We have therefore performed a systematic study of Si adsorption at (0001) GaN surfaces combining first-principles calculations and Scanning Tunneling Microscopy (STM). Calculating the surface energy of a large number of structures with various Si concentrations and various III-V ratios we derive a phase diagram showing the energetically most stable surfaces as a function of the Si and N chemical potentials. Based on these results we identify the equilibrium surfaces and explain the structures seen in the STM study. Analyzing all the structures we identify two competing processes so far not observed for other impurities in GaN. On one side the most favorable structures consist of Si residing in subsurface sites, demonstrating efficient incorporation of Si. On the other hand, all Si-induced surface reconstructions are unstable against Si_3N_4 formation, i.e., formation of Si_3N_4 is a likely cause for the anti-surfactant behavior of Si on GaN.

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9 Presenting Other General Issues

9.1 PC's vs. Workstations: faster and cheaper

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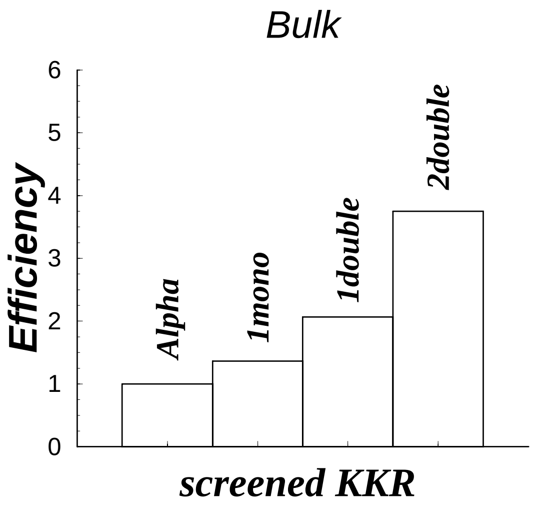
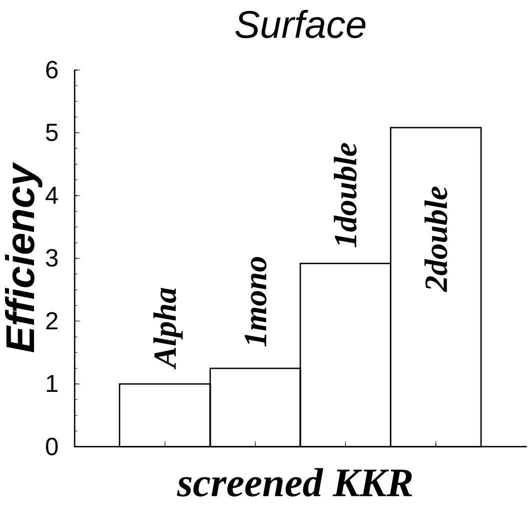
Recently, in our group we decided to change our policy and start purchasing PC's using Linux as operating system instead of the ALPHA workstations that we were traditionally buying the last years. This decision proved to be prodigious as we found out that PC's, which cost only a fraction of a workstation, are actually much faster than the latter ones. We believe that this information is of general interest for our community.

Till now the machines which we were mainly using were the latest Compaq Alpha XP1000 workstations. They have one processor (21264A at 667 MHz) with a total cost of around 8000 EUROs per machine including 1GB of RAM and a hard disc of 10GB. Instead we bought rack PC's, each one having two AMD Athlon XP1800+ processors and 2GBs of RAM with a total price of around 2750 EUROs, which means only one third of the price of one ALPHA workstation. Here we should note that this is the upper limit in prices as rack systems are normally 50% more expensive than normal desktops but have the advantage that they are much easier to stock which is crucial for a large laboratory with a few tenths of these machines. It is interesting to note that in the market of PC's there are new models coming out every sixth months and the top model always has about the same price pushing to lower levels the prices of the previous top models. Also the operating system used in our PC's (Linux) is in principle free, but we preferred to install the latest version of RedHat which costs only around 50 EUROs and contrary to other UNIX operating systems it is not needed to buy the license for a certain number of users; we just had to install the same CD everywhere. An important point is that PC's need very good air-conditioning, especially when a large number of them is bought, but the expenses for air-conditioning are rather small if one room is used to stock all the machines, and in no case balances the lower prices of the PC's compared to the workstations.

The first test presented in this paragraph concerns the screened version of the KKR code used in our group. In the figure we present our results for calculation of a bulk system (4 atoms per unit cell, a tight-binding cluster of 65 atoms and a ℓ_{max} cutoff of 3 for the wavefunctions and 6 for the potential and the charge density) and a surface (42 atoms, a tight-binding cluster of 51 atoms and the same ℓ_{max} cutoffs). We present the efficiency of our machine having arbitrarily assigned an efficiency of 1 to our fastest last generation Alpha Workstation. To compile the program on the PC we used the GNUfortran (g77), which is free of charge, and a level O3 optimization. As a large amount of the time used by our program is consumed in the BLAS (Basic Linear Algebraic Subprograms) library, we have used a very fast version of it named ATLAS (Automatically Tuned Linear Algebra Software). This latter can be tuned on every system and can be downloaded free of charge from the internet (http://www.netlib.org/atlas/). There also exist precompiled versions for different platforms at http://www.netlib.org/atlas/archives/, while information on new developments and known bugs is available at http://math-atlas.sourceforge.net/. Here we have to mention that on AMD processors there are no native libraries and the use of ATLAS proved to speed our program by a factor of 3 compared to the use of the normal BLAS (http://www.netlib.org/blas/), while in Intel Pentium machines the native Intel BLAS library is slightly faster than the ATLAS.





Now we return to our figure. The second values correspond to a monoprocessor job on a PC. The PC was faster by around 40% compared to the Alpha workstation for the bulk calculation and by 25% for the surface calculation. As a next step we made our job to run on two processors. This kind of parallelization is trivial on two processor systems with SMP which is part of the Linux, and there is no need for sophisticated parallelizations using MPI or PVM. It is enough during the compilation to use the g77 flags "-DATL_NCPU=2 -funroll-all-loops". The compiler opens all the loops and distributes the job between the two processors. In reality when the program is executed there is a master processor and a slave one, the latter being used when it is needed. Also using two processors does not mean that the loops are splitted in two parts. If for some loop only 50% of only one of the CPU is actually used, then the compiler decides to split each one of the processors in two and then one sees four parallel virtual processors and the program runs using all of them. This features allows to gain more than double the speed when running one job on two processors compared to the monoprocessor mode, especially for big systems when there is lot of input/output communication between the CPU and the memory (both RAM and cache memories). As a result in the case of a bulk calculation a double processor job has an efficiency of 2.1 compared to an efficiency of 1.4 of the monoprocessor job. But for the surfaces as there is lot of communication, the performance for the double processor job strongly increases and reaches an efficiency of 2.9, more than double the efficiency of the monoprocessor job (1.2) and three times the efficiency of the ALPHA workstation (1.0).

However the real advantage of the double processor machine in terms of the performance/cost ratio shows only up if two double-processor jobs are running at the same time. Each of them chooses a master processor and when needed it uses also the second processor. The operating system itself optimizes the use of each one of the two processors and in this way we manage to use practically 100% of each one of the two CPUs all the time. The management of the system is really excellent as can be seen from the figure. Running two double-processor jobs at the same time results to a slightly smaller speed for each one of them than when each one was running on a different PC. The speed is reduced only by 10% for the bulk case and 14% for the surface case compared to a single double-processor job.

So in order to summarize a double processor PC costs at most one third of the price of one monoprocessor workstation. In the case of small bulk calculations running one monoprocessor job on the PC was 40% faster than the workstation and more important running two double-processor jobs on the same machine was $\sim$ 25 faster than running two monoprocessor jobs on the same PC and 90% faster than running two monoprocessor jobs on the same workstation. The gain in performance is even larger for the surface calculations where the communication between the CPUs and the memory is more important. Running two double processor jobs on a 2-processors PC is 100% faster than running two monoprocessor jobs on the same PC.

At the end of this contribution we have to mention that we also made tests using a KKR-CPA code developed by Prof. Akai (MACHIKANEYAMA2000) which is actually used in our group by Dr. K. Sato. This code uses no external libraries. Compiling this code using the GNUfortran (g77) and an aggressive O5 optimization resulted to 30% gain in speed compared to the ALPHA workstation but using the Intel fortran compiler (ifc) which is FORTRAN95 compatible increased the speed even more and the gain of a monoprocessor job on a PC over the workstations was around 60%.

Already PC's beat workstations in performance costing a fraction of the price of the latter ones. Taking into account the steady increase in performances of the PC's (already there is a new AMD Athlon XP2100+ on the market and Intel has announced that during the next year Pentium 4 will exceed the 4GHz compared to the 2.2GHz of the current model), the overall performance of the PC's will increase at a considerably faster pace than the workstations and the gap between them in favor of the PC's will increase. But already now the PC outperforms the workstation being more than a factor 3 cheaper and by being in addition at least another factor 3 more efficient.

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10 SCIENTIFIC HIGHLIGHT OF THE MONTH

Linear-response theory for the calculation of electron-phonon coupling within the LAPW method

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Abstract

Linear-response (LR) theory in combination with first-principles band structure codes allows to calculate phonons and electron-phonon interaction in an efficient way. We provide a formalism which enables us to apply LR theory within an all-electron framework utilizing the the full-potential linearized augmented plane-wave (LAPW) method. For the electron-phonon coupling matrix elements we have included all correction terms, which are either arising due to the variational solution of the Kohn-Sham equations or due to the LAPW specific basis set. The method is applied to bcc sulfur and hcp beryllium and shows excellent agreement with data obtained by the supercell approach.

INTRODUCTION

The coupling strength of the non-adiabatic interaction between electrons and lattice vibrations is an important quantity for the description of fundamental physical properties of a solid. In conjunction with the features of the phonon spectra it determines the electrical and thermal conductivity and quantifies the pairing mechanism in conventional superconductors. Therefore phonons and their interaction with the electronic subsystem have been the subject of many experimental investigations. Theoretically, the precise calculation of phonon frequencies and electron-phonon coupling constants essentially requires the knowledge of changes in the effective crystal potential upon small displacements of the atoms. This deformation potential can be obtained on an ab-initio basis using first-principles calculations based on density functional theory (DFT) [1, 2]. Within this framework two methodical procedures have been developed: In the first approach, the deformation potential is determined by interpolating potential values for at least two self-consistent calculations: one for the unperturbed system, and a second one for a unit-cell (*supercell*) which is commensurate with the **q**-vector and consists of a frozen-in displacement pattern of the atoms along the eigenvector of the considered phonon. This method is very demanding in terms of computer-time, especially for complex structures (large number of atoms per unit cell) and for phonons with a non-zero, low-symmetry **q**-vector. The bottle-neck lies in the determination of the Kohn-Sham states where the computational effort to solve the corresponding eigenvalue problem scales roughly with the third power of the size of the supercell. An alternative scheme is the self-consistent iterative linear-response (LR) approach, which makes use of the fact that the deformation potential is a first-order quantity in perturbation theory taking the self-consistent crystal potential as a function of the atomic positions. The main advantage of the latter scheme, which will be discussed in more detail below, lies in the fact that the required computational effort is almost independent of the **q**-vector considered.

So far, electron-phonon coupling constants for a few materials have been obtained using either supercell calculations [3, 4, 5, 6, 7, 8, 9, 10] or the iterative LR-approach [11, 12, 13, 14]. Many of these calculations have been carried out within the pseudopotential method, whereas only a few works used all-electron methods, where the charge distribution in the vicinity of the nuclei is fully included in the self-consistency cycle. The crucial advantage of the latter schemes is the treatment of localized and delocalized states on the same footing. We thus have the capacity to reliably describe materials (partially) composed of heavy atoms. Due to this fact the employment of such methods is important for the theoretical study of many materials, which range from simple elemental superconductors, like Hg, Bi, or Pb, to the complex high T_c compounds. The lack of LR investigations within all-electron methods is due to the fact that they require a complex apparatus of formulas which necessitates efficient analytical and numerical tools for their evaluation. In these cases the associated programming work is also quite a tremendous and time-consuming task. The origin for the increased complexity is founded in the site-dependence of the basis sets used in all-electron methods (LMTO, LAPW, etc.). This fact introduces correction terms when a variational solution is constructed for the first-order changes in the electronic eigenstates. Furthermore, similarly to the expression for the atomic forces [15, 16, 17], the traditional electron-phonon matrix element also has to be supplemented by these incomplete-basis-set (IBS) corrections [12].

Although the LR formalism for the calculation of phonon frequencies has been worked out within the linearized augmented plane-wave (LAPW) method [18] and applied to simple materials and the high temperature superconductor La_2CuO_4 [19], it has only been used on the basis of pseudopotentials and for the determination of phonon frequencies and eigenvectors. Concerning electron-phonon matrix elements within LAPW only few data are published [4, 6]. Methodically, the deformation potential was extracted from supercell calculations and the correction terms were not included in the evaluation of the electron-phonon matrix elements [6].

In this work, we present phonon frequencies, and electron-phonon coupling constants obtained from LR theory within the LAPW method. We provide a formalism which allows us to employ LR theory within an all-electron approach.

For the electron-phonon coupling matrix elements we do not only include corrections for the matrix elements following the theoretical framework proposed by Savrasov [12] but also account for the fact that the LAPW basis functions are only continuous up to the first derivative. Our LR results are compared to data obtained by the supercell approach and show excellent agreement.

The paper is organized as follows. In the first part, the theoretical framework is provided. A short review of the variational method to obtain the single particle electronic states is presented in order to introduce the terminology of the LAPW method . In Section we first give an overview of the main ideas and equations governing the iterative linear-response scheme. We generally follow Ref. [18] but focus on the differences to that work which make the calculation easier and allow to perform all-electron calculations. We present a complete set of numerically efficient and analytically simple formulas within the LAPW-method to calculate the first-order change of the electronic states in response to an applied frozen-in phonon displacement. In a next step, we extent the LR formalism to the concept of electron-phonon coupling. In Section we formulate the expressions for the coupling constant within the LAPW basis set including all necessary correction terms to the traditional formulas. In the second part, we present selected results for some test systems. In particular, we applied the LR formalism to the study of the zone-center phonon with the displacement pattern polarized along the z-axis of hcp Be, and of the transversal phonon branch along $\mathbf{q} = [0\ 0\ \xi]$ of bcc sulfur under high pressure. A more elaborate description of the formalism can be found in Ref. [21].

Theory

Basics of the LAPW method

In bandstructure calculations based on density-functional theory [1] the single-particle electronic states $\Psi_{n\mathbf{k}}(\mathbf{r})$ and energies $\varepsilon_{n\mathbf{k}}$ are described by the solutions of the Kohn-Sham (KS) equation [2]

$$\left[-\nabla^2 + V_{eff}(\mathbf{r})\right] \Psi_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_{n\mathbf{k}}\Psi_{n\mathbf{k}}(\mathbf{r}) \tag{5}$$

with the effective potential $V_{eff}(\mathbf{r})$ being the sum of the bare Coulomb potential of the atomic nuclei $V_{nuc}(\mathbf{r})$, the Hartree potential $V_H(\mathbf{r})$ and the exchange correlation potential $V_{xc}(\mathbf{r})$. In practical calculations, Eq. (5) is solved via the Rayleigh-Ritz variational principle. In this procedure the electronic states $\Psi_{n\mathbf{k}}(\mathbf{r})$ (KS-orbitals) are first expanded in terms of a physically appropriate finite set of basis functions $\{\phi_{\mathbf{k}+\mathbf{G}}\}$,

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{n\mathbf{k}}(\mathbf{G})\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) \tag{6}$$

with $\mathbf{G}$ and $C_{n\mathbf{k}}(\mathbf{G})$ denoting a reciprocal space vector and the corresponding variational coefficient, respectively. To determine $C_{n\mathbf{k}}(\mathbf{G})$ the ansatz (6) is inserted into Eq. (5) followed by the minimization of the total crystal energy with respect to the variational coefficients. The eigenvectors and eigenvalues of the resulting matrix equation,

$$\sum_{\mathbf{G}'}(H_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'} - \varepsilon_{n\mathbf{k}} S_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'})C_{n\mathbf{k}}(\mathbf{G}') = 0, \qquad \mathbf{k} \in \mathrm{BZ} \tag{7}$$

with

$$H_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'} \equiv \langle \phi_{\mathbf{k}+\mathbf{G}} | -\nabla^2 + V_{eff} \, | \phi_{\mathbf{k}+\mathbf{G}'} \rangle_\Omega \tag{8}$$

$$S_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'} \equiv \langle \phi_{\mathbf{k}+\mathbf{G}} \, | \phi_{\mathbf{k}+\mathbf{G}'} \rangle_\Omega \tag{9}$$

denoting Hamilton and overlap matrix, respectively, finally provide the numerical values for $C_{n\mathbf{k}}(\mathbf{G})$ and $\varepsilon_{n\mathbf{k}}$. Ω is the volume of the unit cell. In the LAPW-method is partitioned into an interstitial region (Int) and non-overlapping muffin-tin spheres (MT_α) centered on the atomic nuclei. The corresponding basis functions are defined as,

$$\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}}, \ \mathbf{r} \in \text{Interstitial} \tag{10}$$

and

$$\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{S}_\alpha + \mathbf{r}) = \sum_{lm} [A^\alpha_{lm}(\mathbf{k}+\mathbf{G})u^\alpha_l(r) + B^\alpha_{lm}(\mathbf{k}+\mathbf{G})\dot{u}^\alpha_l(r)]Y_{lm}(\hat{\mathbf{r}}), \qquad |\mathbf{r}| \le R_\alpha, \tag{11}$$

where $\mathbf{S}_\alpha$ denotes the position vector of the atomic nucleus α. The radius of the corresponding muffin-tin sphere is R_α. The product of the spherical harmonic $Y_{lm}(\hat{\mathbf{r}})$ and the radial function $u^\alpha_l(r)$ is the solution of the Schrödinger equation for a spherical symmetric potential where the eigenvalue has been replaced by an appropriate energy parameter [20] . The second radial function $\dot{u}^\alpha_l(r)$ is the derivative of the first one with respect to the energy. The coefficients $A^\alpha_{lm}(\mathbf{k}+\mathbf{G})$ and $B^\alpha_{lm}(\mathbf{k}+\mathbf{G})$ are determined for each atom by imposing two requirements. Firstly, the values of the plane-wave (10) and the atomic-orbital like function (11) have to match each other on the surface of the muffin-tin sphere. Secondly, the same has to be true for the values of the first spatial derivatives of the two functions. For later considerations it is important to mention that the second derivative of the LAPW basis functions are discontinuous on the MT-surfaces.

Using the definitions (10) and (11), the overlap and Hamilton matrix within the LAPW formalism will schematically be calculated the following way [22]:

$$S_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'} = \sum_\beta S^{MT_\beta}_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'} + S^{Int}_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'} \tag{12}$$

$$H_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'} = \sum_\beta H^{MT_\beta}_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'} + H^{Int}_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'} \tag{13}$$

with

$$
\begin{aligned}
S^{MT_\beta}_{\mathbf{k+G},\mathbf{k+G'}} &= \langle \phi_{\mathbf{k+G}} \left| \phi_{\mathbf{k+G'}} \right\rangle_{MT_\beta} && (14)\\
S^{Int}_{\mathbf{k+G},\mathbf{k+G'}} &= \delta_{\mathbf{k+G},\mathbf{k+G'}} (1 - \sum_\beta \frac{4\pi}{3\Omega} R_\beta^3) \\
& \quad -(1-\delta_{\mathbf{k+G},\mathbf{k+G'}}) \sum_\beta \langle \tilde{\phi}_{\mathbf{k+G}} \left| \tilde{\phi}_{\mathbf{k+G'}} \right\rangle_{MT_\beta} && (15)
\end{aligned}
$$

$$
\begin{aligned}
H^{MT_\beta}_{\mathbf{k+G},\mathbf{k+G'}} &= \left\langle \phi_{\mathbf{k+G}} \left| -\nabla^2 + V_{eff} \right| \phi_{\mathbf{k+G'}} \right\rangle_{MT_\beta} && (16)\\
H^{Int}_{\mathbf{k+G},\mathbf{k+G'}} &= (\mathbf{k}+\mathbf{G}')^2 S^{Int}_{\mathbf{k+G},\mathbf{k+G'}} + \sum_{\mathbf{K}} V(\mathbf{K}) S^{Int}_{\mathbf{k+K},\mathbf{k+G-G'}}. && (17)
\end{aligned}
$$

For the calculation of the H- and S-matrix in the interstitial region the function $\tilde{\phi}_{\mathbf{k+G}}(\mathbf{r})$ has been introduced. It describes a plane-wave defined in the entire unit cell,

$$
\tilde{\phi}_{\mathbf{k+G}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k+G})\mathbf{r}}, \quad \mathbf{r} \in \Omega. \tag{18}
$$

For the explicit evaluation of (16) and (17) an appropriate dual representation of the effective potential is needed. In the spheres the potential is expanded into spherical harmonics and in the interstitial it is represented by a Fourier series:

$$
\begin{aligned}
V_{eff}(\mathbf{S}_\alpha + \mathbf{r}) &= \sum_{LM} V^\alpha_{LM}(r) Y_{LM}(\hat{\mathbf{r}}), \quad |\mathbf{r}| \le R_\alpha, && (19)\\
V_{eff}(\mathbf{r}) &= \sum_{\mathbf{K}} V(\mathbf{K}) e^{i\mathbf{K}\mathbf{r}}, \qquad \mathbf{r} \in \text{Int}. && (20)
\end{aligned}
$$

A short review about linear-response to phonon displacements

The atomic displacement pattern representing a lattice vibration at wave vector $\mathbf{q}$, i.e.

$$
\begin{aligned}
\delta \mathbf{S}^{\mathbf{T}}_\alpha &= \delta^+ \mathbf{S}_\alpha e^{i\mathbf{q}\mathbf{T}} + \delta^- \mathbf{S}_\alpha e^{-i\mathbf{q}\mathbf{T}} \\
&= \delta^+ \mathbf{S}_\alpha e^{i\mathbf{q}\mathbf{T}} + [\delta^+ \mathbf{S}_\alpha]^* e^{-i\mathbf{q}\mathbf{T}} && (21)
\end{aligned}
$$

can be viewed as a superposition of a forward and backward travelling wave. Real-space lattice vectors are denoted by $\mathbf{T}$, and $\delta^+\mathbf{S}_\alpha$ is a small possibly complex polarization vector. Thus the displaced position vector of an atom α in unit cell $\mathbf{T}$ will be $\mathbf{T}+$ $\mathbf{S}_\alpha+$ $\delta\mathbf{S}^{\mathbf{T}}_\alpha$. Within density-functional perturbation theory (DFPT) [23] this superposition of phonon displacements can be viewed as a static first-order perturbation acting on the electronic system [24, 25]. The knowledge of the corresponding first-order response of the electronic charge distribution $\delta^+\rho(\mathbf{r})$, the effective potential $\delta^+V_{eff}(\mathbf{r})$ and the KS-orbitals $\delta^+\Psi_{n\mathbf{k}}(\mathbf{r})$ is essential for setting up the dynamical matrix at wavevector $\mathbf{q}$ and to determine the coupling strength for the electron-phonon interaction. To calculate these first-order quantities, a linear-response scheme has been developed [26, 27] which relies on the iterative solution of the following three equations:

$$
\delta^+ V_{eff}(\mathbf{r}) = \delta^+ V_{nuc}(\mathbf{r}) + \int \frac{\delta^+\rho(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} d^3r' + \delta^+\rho(\mathbf{r}) \left. \frac{dV_{xc}}{d\rho} \right|_{\rho(\mathbf{r})} \tag{22}
$$

$$(-\nabla^2 + V_{eff}(\mathbf{r}) - \varepsilon_{n\mathbf{k}})\delta^+\Psi_{n\mathbf{k}}(\mathbf{r}) = -\delta^+ V_{eff}(\mathbf{r})\,\Psi_{n\mathbf{k}}(\mathbf{r}) \tag{23}$$

$$\delta^+\rho(\mathbf{r}) = 2\sum_{n\mathbf{k}} w(n,\mathbf{k})\delta^+\Psi_{n\mathbf{k}}(\mathbf{r})\Psi^*_{n\mathbf{k}}(\mathbf{r}). \tag{24}$$

In the current description the local-density approximation is assumed for the exchange-correlation potential. The orbital occupation number is denoted by $w(n,\mathbf{k})$ and the term containing $\delta\varepsilon_{n\mathbf{k}}$ has been dropped in Eq. (23). This is justified by the fact that the change in the eigenvalue is zero for non-zero $\mathbf{q}$-values [18, 28]. It is worth mentioning that in accordance with the applied lattice vibrational pattern (21) the translational behaviour of the first-order effective potential will read

$$\delta^+ V_{eff}(\mathbf{r}+\mathbf{T}) = e^{i\mathbf{q}\mathbf{T}}\delta^+ V_{eff}(\mathbf{r}). \tag{25}$$

It is then straightforward to see from the Sternheimer equation (23) that the first-order KS-orbital will be a Bloch wave of wave vector $\mathbf{k}+\mathbf{q}$.

When we come to the practical realization of this iterative linear-response scheme the main challenge lies in the construction of an efficient variational solution of the Sternheimer equation. The complexity of this task depends on the basis set used in the unperturbed bandstructure calculation. In the case of plane-waves the change in the wave function can entirely be traced back to the change in the variational coefficient [26], and one obtains the corresponding matrix form of the Sternheimer equation:

$$\sum_{\mathbf{G}'}(H_{\mathbf{k}+\mathbf{q}+\mathbf{G},\mathbf{k}+\mathbf{q}+\mathbf{G}'} - \varepsilon_{n\mathbf{k}}\delta_{\mathbf{G},\mathbf{G}'})\delta^+ C_{n\mathbf{k}}(\mathbf{G}') = -\sum_{\mathbf{G}'}\delta H_{\mathbf{k}+\mathbf{q}+\mathbf{G},\mathbf{k}+\mathbf{G}'}C_{n\mathbf{k}}(\mathbf{G}'), \tag{26}$$

with

$$\delta H_{\mathbf{k}+\mathbf{q}+\mathbf{G},\mathbf{k}+\mathbf{G}'} = \left\langle \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \left| \delta^+ V_{eff} \right| \phi_{\mathbf{k}+\mathbf{G}'} \right\rangle. \tag{27}$$

Using position dependent basis sets (LMTO, LAPW, etc.), however, the situation is much more complicated as demonstrated by Savrasov [28] and Yu et al. [18]. To account for the change in the basis functions due to the shift of the atomic nuclei the first-order wave function has to be expanded in the original basis set supplemented by a physically appropriate ansatz for the change in the basis functions. Within this framework it can then be shown that the Sternheimer equation will read:

$$\begin{aligned}
&\sum_{\mathbf{G}'}(H_{\mathbf{k}+\mathbf{q}+\mathbf{G},\mathbf{k}+\mathbf{q}+\mathbf{G}'} - \varepsilon_{n\mathbf{k}}S_{\mathbf{k}+\mathbf{q}+\mathbf{G},\mathbf{k}+\mathbf{q}+\mathbf{G}'})\delta^+ C_{n\mathbf{k}}(\mathbf{G}') \\
= \; & -\sum_{\mathbf{G}'}[\delta H_{\mathbf{k}+\mathbf{q}+\mathbf{G},\mathbf{k}+\mathbf{G}'} - \varepsilon_{n\mathbf{k}}\delta S_{\mathbf{k}+\mathbf{q}+\mathbf{G},\mathbf{k}+\mathbf{G}'}]C_{n\mathbf{k}}(\mathbf{G}'), \qquad \mathbf{k}\in \mathrm{BZ}
\end{aligned} \tag{28}$$

with

$$\begin{aligned}
\delta H_{\mathbf{k}+\mathbf{q}+\mathbf{G},\mathbf{k}+\mathbf{G}'} &= \left\langle \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \left| \delta^+ \hat{H} \right| \phi_{\mathbf{k}+\mathbf{G}'} \right\rangle + \\
&\quad \left\langle \delta^- \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \left| \hat{H} \right| \phi_{\mathbf{k}+\mathbf{G}'} \right\rangle + \left\langle \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \left| \hat{H} \right| \delta^+ \phi_{\mathbf{k}+\mathbf{G}'} \right\rangle \qquad (29) \\
\delta S_{\mathbf{k}+\mathbf{q}+\mathbf{G},\mathbf{k}+\mathbf{G}'} &= \left\langle \delta^- \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \middle| \phi_{\mathbf{k}+\mathbf{G}'} \right\rangle + \left\langle \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \middle| \delta^+ \phi_{\mathbf{k}+\mathbf{G}'} \right\rangle \qquad (30)
\end{aligned}$$

Handling LAPW specific terms

We will now formulate a scheme to explicitly calculate the first-order matrices appearing on the right-hand side of Eq. (28). The scheme is particularly designed to adapt and extend the merits of available practical realizations of the LAPW method in the unperturbed case as given by Eqs. (12) and (13). To start with, we review the ansatz for the change in the basis function due to the shift of the atomic nuclei. The coordinate system refers to the unperturbed situation. As Yu et al.[18] have shown, $\delta^{\pm}\phi_{\mathbf{k}+\mathbf{G}'}(\mathbf{r})$ is only non-vanishing inside the MT-spheres and within the rigid-muffin tin orbital approximation will read:

$$\begin{aligned}\delta^{\pm}\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) \quad \equiv \quad & \frac{\partial\phi_{\mathbf{k}+\mathbf{G}}}{\partial\{\delta\mathbf{S}\}}\delta^{\pm}\mathbf{S} = -\sum_{\alpha}[\nabla\phi^{\alpha}_{\mathbf{k}+\mathbf{G}}(\mathbf{r})]\delta^{\pm}\mathbf{S}_{\alpha} + \\ & \sum_{\alpha} i[(\mathbf{k}+\mathbf{G})\delta^{\pm}\mathbf{S}_{\alpha}]\phi^{\alpha}_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) \qquad (31)\end{aligned}$$

The first term describes a rigid shift of the orbital parts of the LAPW basis function centered on the nuclei and the second term results from the fact that due to the shift of the atomic sphere the matching parameters A_{lm} and B_{lm} change by the phase factor $e^{i(\mathbf{k}+\mathbf{G})\delta^{\pm}\mathbf{S}_{\alpha}}$. In a second step, we provide an appropriate description of the change in the total effective potential again with respect to the unperturbed MT-spheres and interstitial region. Within the atomic spheres $\delta^{\pm}V^{\alpha}_{eff}(\mathbf{r})$ will read:

$$\delta^{\pm}V^{\alpha}_{eff}(\mathbf{r}) = \underbrace{\sum_{LM}\delta^{\pm}\check{V}^{\alpha}_{LM}(r')Y_{LM}(\hat{\mathbf{r}}')}_{\equiv\delta^{\pm}\check{V}^{\alpha}_{eff}(\mathbf{r}')} - \delta^{\pm}\mathbf{S}_{\alpha}\nabla V^{\alpha}_{eff}(\mathbf{r}) \qquad |r'| \leq R_{\alpha}, \qquad (32)$$

where $\mathbf{r} = \mathbf{S}_{\alpha} + \mathbf{r}'$. The first term on the right hand side of Eq. (32) is the 'soft' contribution [6, 17] to the change in the effective potential. It represents the first-order difference between the effective potentials evaluated at point $\mathbf{r} = \mathbf{S}_{\alpha} + \delta^{\pm}\mathbf{S}_{\alpha} + \mathbf{r}'$ with the perturbation being applied and at point $\mathbf{r} = \mathbf{T} + \mathbf{S}_{\alpha} + \mathbf{r}'$ when no perturbation is present. The second term again originates from the fact that the atomic sphere has been rigidly shifted by the position vector $\delta^{\pm}\mathbf{S}_{\alpha}$. In the interstitial region, where plane-waves are the natural choice of basis functions, $\delta^{\pm}V^{int}_{eff}(\mathbf{r})$ is:

$$\delta^{\pm}V^{int}_{eff}(\mathbf{r}) = \sum_{\mathbf{K}}\delta^{\pm}V_{eff}(\mathbf{K}+\mathbf{q})e^{i(\mathbf{K}+\mathbf{q})\mathbf{r}}. \qquad (33)$$

The following should be noted: The dual representation (32) and (33) does not account for the switch of the character of basis functions in those regions of the unit cell where the interstitial region (sphere region) of the unperturbed crystal overlaps with the sphere regions (interstitial region) of the phonon-induced configuration. In fact the same is true for the ansatz (31). Nevertheless, as long as the basis sets are interchangeable in these overlapping regions (implying a small polarization vector) the accuracy of the linear-response calculation is only negligibly influenced by this approximation. When compared to the analytically complete representation [6] the advantage of (32) and (33) mainly lies in its applicability to all-electron bandstructure calculations where the Coulomb-singularity is fully taken into account.

We have now established all necessary representations of wave-functions, potentials and their respective first-order counterparts to evaluate the following matrix elements expressed in terms of the LAPW method [18]:

$$
\begin{aligned}
& \delta H_{\mathbf{k}+\mathbf{q}+\mathbf{G},\mathbf{k}+\mathbf{G}'} - \varepsilon_{n\mathbf{k}} \delta S_{\mathbf{k}+\mathbf{q}+\mathbf{G},\mathbf{k}+\mathbf{G}'} \\
= & \underbrace{\left\langle \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \left| \delta^+ V_{eff}(\mathbf{r}) \right| \phi_{\mathbf{k}+\mathbf{G}'} \right\rangle_{\Omega}}_{R1} \\
& \underbrace{+ \left\langle \frac{\partial \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}}}{\partial \delta \mathbf{S}} (\delta^+ \mathbf{S})^* \left| \hat{H} \right| \phi_{\mathbf{k}+\mathbf{G}'} \right\rangle_{MT}}_{R2} \\
& \underbrace{+ \left\langle \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \left| \hat{H} \right| \frac{\partial \phi_{\mathbf{k}+\mathbf{G}'}}{\partial \delta \mathbf{S}} \delta^+ \mathbf{S} \right\rangle_{MT}}_{R3} \\
& -\varepsilon_{n\mathbf{k}} \underbrace{\left\langle \frac{\partial \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}}}{\partial \delta \mathbf{S}} (\delta^+ \mathbf{S})^* | \phi_{\mathbf{k}+\mathbf{G}'} \right\rangle_{MT}}_{R4} \\
& -\varepsilon_{n\mathbf{k}} \underbrace{\left\langle \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}} | \frac{\partial \phi_{\mathbf{k}+\mathbf{G}'}}{\partial \{\delta \mathbf{S}\}} \delta^+ \mathbf{S} \right\rangle_{MT}}_{R5} \\
& \underbrace{+ \delta^+ \left\langle \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \left| \hat{T} \right| \phi_{\mathbf{k}+\mathbf{G}'} \right\rangle}_{R6} \qquad (34)
\end{aligned}
$$

with

$$
\begin{aligned}
\delta^+ \left\langle \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \left| \hat{T} \right| \phi_{\mathbf{k}+\mathbf{G}'} \right\rangle \equiv & \sum_{\alpha} \delta^+ \mathbf{S}_{\alpha} \oint_{MT_{\alpha}} [\phi^{*\alpha}_{\mathbf{k}+\mathbf{q}+\mathbf{G}}(\mathbf{r}) \nabla^2 \phi^{\alpha}_{\mathbf{k}+\mathbf{G}'}(\mathbf{r})|_{MT_{\alpha}} \\
& -\phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}}(\mathbf{r}) \nabla^2 \phi_{\mathbf{k}+\mathbf{G}'}(\mathbf{r})|_{Int}] d\mathbf{A}_{\alpha}, \qquad (35)
\end{aligned}
$$

representing the contribution stemming from the discontinuous behaviour of the second derivative of the LAPW basis functions on the surface of the atomic sphere [15, 16]. The abbreviations MT_{α} and Int indicate that in the respective surface integral ($\oint_{MT_{\alpha}} d\mathbf{A}_{\alpha}$) over the kinetic energy term the basis functions appropriate for the denoted region have to be used. Inserting (33),(32),(31),(11) and (10) into (34) immediately simplifies many of the matrix elements and in fact expresses them through formulas which are structurally very similar to the expressions describing the unperturbed H- and S-matrix:

$$
\begin{aligned}
& \delta H_{\mathbf{k}+\mathbf{q}+\mathbf{G},\mathbf{k}+\mathbf{G}'} - \varepsilon_{n\mathbf{k}} \delta S_{\mathbf{k}+\mathbf{q}+\mathbf{G},\mathbf{k}+\mathbf{G}'} \\
= & \sum_{\mathbf{K}} \delta^+ V_{eff}(\mathbf{K}+\mathbf{q}) S^{Int}_{\mathbf{k}+\mathbf{K},\mathbf{k}+\mathbf{G}-\mathbf{G}'} + \sum_{\alpha} \left\langle \phi_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \left| \delta^+ \check{V}_{eff} \right| \phi_{\mathbf{k}+\mathbf{G}'} \right\rangle_{MT_{\alpha}} \\
& + \sum_{\alpha} i[(\mathbf{G}' - \mathbf{G} - \mathbf{q}) \delta^+ \mathbf{S}_{\alpha}][H^{MT_{\alpha}}_{\mathbf{k}+\mathbf{q}+\mathbf{G},\mathbf{k}+\mathbf{G}'} - \varepsilon_{n\mathbf{k}} S^{MT_{\alpha}}_{\mathbf{k}+\mathbf{q}+\mathbf{G},\mathbf{k}+\mathbf{G}'}] \\
& - \sum_{\alpha} \delta^+ \mathbf{S}_{\alpha} \oint_{MT_{\alpha}} \phi^*_{\mathbf{k}+\mathbf{q}+\mathbf{G}}(\mathbf{r}) V_{eff}(\mathbf{r}) \phi_{\mathbf{k}+\mathbf{G}'}(\mathbf{r})|_{MT_{\alpha}} d\mathbf{A}_{\alpha} \\
& -\varepsilon_{n\mathbf{k}} \sum_{\alpha} \delta^+ \mathbf{S}_{\alpha} \oint_{MT_{\alpha}} \phi^*_{\mathbf{k}+\mathbf{q}+\mathbf{G}}(\mathbf{r}) \phi_{\mathbf{k}+\mathbf{G}'}(\mathbf{r})|_{MT_{\alpha}} d\mathbf{A}_{\alpha} \\
& - \sum_{\alpha} \delta^+ \mathbf{S}_{\alpha} \oint_{MT_{\alpha}} \phi^*_{\mathbf{k}+\mathbf{q}+\mathbf{G}}(\mathbf{r}) \nabla^2 \phi_{\mathbf{k}+\mathbf{G}'}(\mathbf{r})|_{Int} d\mathbf{A}_{\alpha} \qquad (36)
\end{aligned}
$$

To obtain the fourth and fifth term on the right hand side of Eq. (36) the chain rule of the gradient operator with regard to the product of the wave functions and the effective potential as well as the Gauss theorem to transfer the volume- to a surface integral has been used. Based on a similar procedure the kinetic energy terms of the matrix elements $R2$ and $R3$ involving the gradients of the wave function have been combined with the discontinuity term $R6$ to arrive at the last term of the right hand side of Eq. (36). Utilizing the muffin-tin representations for the wave functions and the potential in term four and five on the right hand side of Eq. (36) would result in rather cumbersome summations over Gaunt-coefficients. To avoid the complexity of the corresponding formulas we exploit the fact that the wave functions and potentials are continuous in value and slope on the sphere surface. In this way we can substitute the muffin-tin representation by the plane-wave representation and then apply the Gauss theorem to back-transfer the surface to a volume integral. Thus, we obtain analytic expressions involving plane-wave integrals over the sphere volumes. These expressions already appeared in the unperturbed overlap-matrix (Eq. (15)) and are easy to program. We explicitly demonstrate the whole idea for the change in the overlap matrix appearing in the fifth term of the right hand side of Eq. (36):

$$\begin{aligned}
&\sum_{\alpha} \delta^{+}\mathbf{S}_{\alpha} \oint_{MT_{\alpha}} \phi^{*}_{\mathbf{k}+\mathbf{q}+\mathbf{G}}(\mathbf{r})\phi_{\mathbf{k}+\mathbf{G}'}(\mathbf{r})|_{MT_{\alpha}}\, d\mathbf{A}_{\alpha} \\
=\;& \sum_{\alpha} \delta^{+}\mathbf{S}_{\alpha} \oint_{MT_{\alpha}} \phi^{*}_{\mathbf{k}+\mathbf{q}+\mathbf{G}}(\mathbf{r})\phi_{\mathbf{k}+\mathbf{G}'}(\mathbf{r})|_{Int}\, d\mathbf{A}_{\alpha} \\
=\;& \sum_{\alpha} \delta^{+}\mathbf{S}_{\alpha} \frac{1}{\Omega} \int_{MT_{\alpha}} \nabla[e^{i(\mathbf{G}'-\mathbf{G}-\mathbf{q})\mathbf{r}}]\, d^{3}\mathbf{r} \\
=\;& \sum_{\alpha} (\mathbf{G}'-\mathbf{G}-\mathbf{q})\delta^{+}\mathbf{S}_{\alpha} \left\langle \tilde{\phi}_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \middle| \tilde{\phi}_{\mathbf{k}+\mathbf{G}'} \right\rangle_{MT_{\alpha}} \equiv \delta S^{Int}_{\mathbf{k}+\mathbf{q}+\mathbf{G},\mathbf{k}+\mathbf{G}'}
\end{aligned} \tag{37}$$

Similarly line (36) and (36) simplify to:

$$\begin{aligned}
&\sum_{\alpha} \delta^{+}\mathbf{S}_{\alpha} \oint_{MT_{\alpha}} \phi^{*}_{\mathbf{k}+\mathbf{q}+\mathbf{G}}(\mathbf{r}) V_{eff}(\mathbf{r}) \phi_{\mathbf{k}+\mathbf{G}'}(\mathbf{r})|_{MT_{\alpha}}\, d\mathbf{A}_{\alpha} \\
=\;& \sum_{\mathbf{K}} V_{eff}(\mathbf{K})\, \delta S^{Int}_{\mathbf{k}+\mathbf{q}+\mathbf{G},\mathbf{k}+(\mathbf{G}'+\mathbf{K})}
\end{aligned} \tag{38}$$

and

$$\begin{aligned}
&\sum_{\alpha} \delta^{+}\mathbf{S}_{\alpha} \oint_{MT_{\alpha}} \phi^{*}_{\mathbf{k}+\mathbf{q}+\mathbf{G}}(\mathbf{r}) \nabla^{2} \phi_{\mathbf{k}+\mathbf{G}'}(\mathbf{r})|_{Int}\, d\mathbf{A}_{\alpha} \\
=\;& |\mathbf{k}+\mathbf{G}'|^{2}\, \delta S^{Int}_{\mathbf{k}+\mathbf{q}+\mathbf{G},\mathbf{k}+\mathbf{G}'}
\end{aligned} \tag{39}$$

To reach a high efficiency in terms of computer time, formula (38) should be evaluated by the use of Fast-Fourier transforms (FFT) routines in a similar way [29] as it is done for the interstitial parts of the unperturbed matrices [22].

Electron-phonon coupling

Conventionally, the scattering process of an electron from state $\Psi_{n\mathbf{k}}$ to $\Psi_{m\mathbf{k}+\mathbf{q}}$ via a phonon of wavevector $\mathbf{q}$, frequency $\omega_{\mathbf{q}j}$ and eigenvector $\mathbf{e}_{\mathbf{q}j}$ is described by the electron-phonon matrix element

$$g^{\mathbf{q}j}_{m\mathbf{k}+\mathbf{q},n\mathbf{k}} = \left\langle \Psi_{m\mathbf{k}+\mathbf{q}} \middle| \sum_{\alpha=1}^{N} \sum_{x=1}^{3} \frac{e_{\mathbf{q}j}(\alpha,x)}{M_{\alpha}\omega_{\mathbf{q}j}} \frac{\delta V_{eff}(\mathbf{r})}{\delta S_{\alpha x}} \middle| \Psi_{n\mathbf{k}} \right\rangle . \tag{40}$$

Here we have assumed that there are N atoms in the unit cell and that the eigenvector component of atom α (atomic mass M_α) in the cartesian direction x is referenced by $e_{\mathbf{q}j}(\alpha, x)$. The essential ingredient to describe the scattering rate between the initial and final electronic state will thus be the expression

$$\left\langle \Psi_{m\mathbf{k}+\mathbf{q}} \left| \frac{\delta V_{eff}(\mathbf{r})}{\delta S_{\alpha x}} \right| \Psi_{n\mathbf{k}} \right\rangle . \tag{41}$$

In DFPT the derivative of the self-consistent effective potential with respect to the atomic displacements caused by a phonon is obtained by numerical differentiation of the finite quantity $\delta V_{eff}(\mathbf{r})$ resulting from the iterative linear-response scheme described in Section . For this reason it suffices to proceed within the terminology and definitions of the previous section and concentrate on the investigation of the matrix element:

$$M^{\alpha}_{m\mathbf{k}+\mathbf{q},n\mathbf{k}} \equiv \langle \Psi_{m\mathbf{k}+\mathbf{q}} \left| \delta V_{eff}(\mathbf{r}) \right| \Psi_{n\mathbf{k}} \rangle \tag{42}$$

which in the framework of a variational solution for the wave functions will read:

$$M^{\alpha}_{m\mathbf{k}+\mathbf{q},n\mathbf{k}} = \sum_{\mathbf{G},\mathbf{G}'} C_{m\mathbf{k}+\mathbf{q}}(\mathbf{G}') \delta H_{\mathbf{k}+\mathbf{q}+\mathbf{G}',\mathbf{k}+\mathbf{G}} C_{n\mathbf{k}}(\mathbf{G}) \tag{43}$$

with the change of the Hamilton matrix being described by (27). It was first shown by Savrasov [12] that the validity of expression (42) to properly describe the scattering rate of the electrons will break down when position-dependent basis sets are used to describe the wave functions. Through the rigorous application of time-dependent quantum mechanical perturbation theory he demonstrated that in such a case (42) should be supplemented by corrective terms which take account of the phonon-induced changes in the basis functions. If we apply this concept to the LAPW basis set and assume degeneracy between the initial and the final state ($\varepsilon_{n\mathbf{k}} = \varepsilon_{m\mathbf{k}+\mathbf{q}}$) we obtain:

$$M^{\alpha}_{m\mathbf{k}+\mathbf{q},n\mathbf{k}} = \sum_{\mathbf{G},\mathbf{G}'} C^{*}_{m\mathbf{k}+\mathbf{q}}(\mathbf{G}) (\delta H_{\mathbf{k}+\mathbf{q}+\mathbf{G},\mathbf{k}+\mathbf{G}'} - \varepsilon_{n\mathbf{k}} \delta S_{\mathbf{k}+\mathbf{q}+\mathbf{G},\mathbf{k}+\mathbf{G}'}) C_{n\mathbf{k}}(\mathbf{G}') \tag{44}$$

with the first-order changes in the H- and S-matrix now being described by Eq. (34). Given the matrix element above, the coupling constant $\lambda_{\mathbf{q}\nu}$ for the phonon branch ν and the wavevector $\mathbf{q}$ is obtained by [6]

$$\lambda_{\mathbf{q}\nu} = \frac{1}{N(0)\omega^2_{\mathbf{q}\nu} \sum_\alpha M_\alpha \langle \delta u^2_\alpha \rangle} \sum_{nm\mathbf{k}} \frac{f(\epsilon_{n\mathbf{k}}) - f(\epsilon_{m\mathbf{k}+\mathbf{q}})}{\epsilon_{m\mathbf{k}+\mathbf{q}} - \epsilon_{n\mathbf{k}}} \left| M^{\mathbf{q}}_{mn} \right|^2 \delta(\epsilon_{m\mathbf{k}+\mathbf{q}} - \epsilon_{n\mathbf{k}} - \omega_{\mathbf{q}\nu}) \tag{45}$$

where $|M^{\mathbf{q}}_{mn}|^2$ stands for

$$|M^{\mathbf{q}}_{mn}|^2 = \frac{1}{2} \left[\left| M^{\alpha}_{m\mathbf{k}+\mathbf{q},n\mathbf{k}} \right|^2 + \left| M^{\alpha}_{m\mathbf{k}-\mathbf{q},n\mathbf{k}} \right|^2 \right] . \tag{46}$$

$N(0)$ is the density of states at the Fermi level per spin, $\langle \delta u^2_\alpha \rangle$ denotes the mean square displacement of all the atoms of one type with mass M_α. In case of a supercell calculation the expression on the right hand side of Eq. (45) has to be divided by the number of single cells contained in the supercell.

Table 1: Atomic displacement δz, the change of the atomic force $\Delta \mathrm{F}_z$ with displacement δz, phonon frequency ω, and electron-phonon coupling constant for the z-axis vibration of hcp Be derived from LR and frozen-phonon calculations, respectively.

	LR			frozen-phonon		
δz [c]	$\Delta \mathrm{F}_z$ [mRy/a.u.]	ω [meV]	λ	$\Delta \mathrm{F}_z$ [mRy/a.u.]	ω [meV]	λ
0.002	-4.27	84.2	0.0	-4.31	84.5	0.0

Table 2: Force contributions and total force acting on the S atom in a bcc sulfur lattice under high pressure. The displacement δz is given in units of the lattice parameter (c=4.2368 a.u.).

	$\mathrm{F}_{\delta z=0}$	$\mathrm{F}_{\delta z=0.005}$	Δ F^{SC}	$\Delta \mathrm{F}^{LR}$
F_{HF}	1.30	8.73	7.43	7.47
F_{IBS}	1.08	0.57	-0.51	-0.52
F_{COR}	-2.88	-7.50	-4.62	-4.63
F_{tot}	-0.50	1.80	2.30	2.32

Results

In the following, results for atomic forces, phonon frequencies, and electron-phonon coupling constants for vibrational modes in different materials are given. All self-consistent calculations have been carried out within the LAPW code WIEN97 [30], which was also used as a basic package for the implementation of the LR scheme worked out within this work. In all cases we used well convered BZ samplings and basis sets, for the wavefuctions as well as the expansions of potential and charge density.

The first example is the z-axes vibration of hcp Be (q=0). We used the lattice parameters of a = 4.21141 a.u. and c = 6.77335 a.u. In Table 1 the atomic force and the corresponding phonon frequency of the LR calculations are compared to the data obtained by a selfconsistent calculation for the displaced atom. The results agree within 1%. Due to the absence of crossing bands at the Fermi level the electron-phonon coupling constant λ is zero.

The following results are obtained for bcc sulfur under high pressure (584 GPa) using the lattice parameter of a = 4.2368 a.u. (2.242 Å). This example has been chosen for comparison with detailed information available in literature [9]. Phonon frequencies and coupling constants have been computed for selected points of the transversal branch along [0 0 ξ] (Fig. 1). All data excellently agree with results obtained by the pseudopotential method (labelled PP) [9]. For the H-point ([001]), it can be seen from Table that all the contributions to the total force, namely the Hellman-Feynman force F_{HF}, the IBS correction F_{IBS}, and the core contribution F_{CORE} are very well reproduced be the LR scheme. For the small **k** point mesh ($10 \times 10 \times 10$ **k**-points) there is a finite remaining force for zero displacement due to the lower point symmetry used

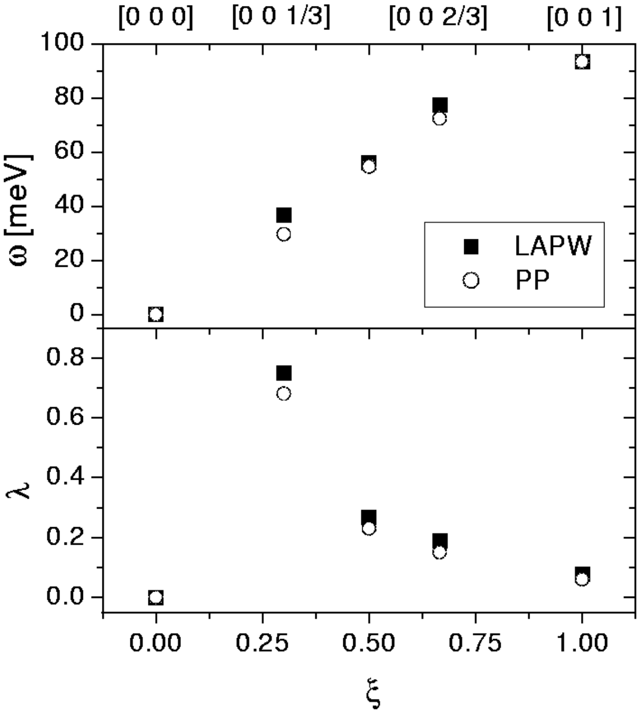

Figure 1: Phonon frequencies ω in eV (upper panel) and electron-phonon coupling constants λ (lower panel) for bcc sulfur for selected points of the transversal branch along $[0\ 0\ \xi]$. The LAPW results (black squares) are compared to data from Ref. [9] (open circles).

in order to directly compare the supercell results with the LR data. These data show that the change of the force is excellently reproduced when the starting point is a configuration with a finite force. Although a rather coarse grid can lead to reasonable phonon frequencies this is not the case for the coupling constants. Since the contributions come from nearly degenerate bands at or close to the Fermi level, a very dense mesh is needed to reliably describe the electron-phonon coupling constants. For well converged values we typically used up to 300 000 points in the whole BZ. In summary, we have worked out the formalism to describe both phonons and electron-phonon coupling within the full-potential LAPW method. Our approach includes the treatment of core-states and all necessary correction terms arising due to the variational solution of the Kohn-Sham equations as well as the LAPW specific correction terms. The results obtained for different materials prove the method to be a reliable and promising tool for more complex materials.

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