Ψ_k Newsletter

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

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Contents

1 Editorial

In this *Newsletter* in the **General News** section readers will find details on the dedicated web-server of both TMR networks and the ESF programme. This server also provides all available information on the Psi-k2000 Conference of next year. Please do keep on checking on the updated information.

In the **ESF** section readers will find a report with the programme and abstracts of the IWOSMA Workshop. In this section we also have call for workshops and collaborative visits. In the **TMR2** network section there is a TMR position announcement. Also, in the general sections advertising positions readers will find a few interesting announcements. As always, we have a number of abstracts in the usual **Abstracts** section. The scientific highlight is by E. Wimmer, J.-R. Hill, P. Gravil and Walter Wolf on **'Industrial Use of Electronic Structure Methods'**. Please check the table of contents for further details.

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 General News

2.1 New WWW Home Page

Please note that the *Psi-k Network* has now its own web-server and our home page is:

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

The above contains pointers to home pages of some of the members of our electronic structure community. If you maintain a home page on your activities we will be happy to include a pointer from the *Network* home page to your home page.

Please note that the home page of the Psi-k Network contains useful information regarding funding of workshops and collaborative visits within the ESF Programme. Its major new feature is a separate highlight section which contains all highlight articles of the Newsletters published so far.

2.2 Psi-k 2000 Conference

Schwäbisch Gmünd, 22-26 August, 2000

"Ab initio Electronic Calculations for Elucidating the Complex Processes in Materials"

Similarly to the Network, the Psi-k2000 Conference has its own web sever:

http://psi-k.dl.ac.uk/psi-k2000

The page contains the latest information on all matters of the Conference and also allows pre-registration to the Conference. There one can also find a suggestion form for the symposia and plenary and symposia speakers. We would appreciate everybody's input on the symposia and speakers. The page is updated on daily basis. Please have a look and help us publicize the Conference. The Conference poster (A3 format) has recently been printed and posted to the key research institutions all over the world. The pdf-file of the poster can also be downloaded from the above site. Please put up the poster in your department and/or distribute it among other, neighbouring research institutions. We can provide additional copies of the poster, so please do contact us if you have not received the printed poster or require more copies.

3 News from the TMR1 Network

"Interface Magnetism"

The "Interface Magnetism" TMR Network has submitted to the EU's FP5 a proposal for a Research Training Network on **Computational Magnetoelectronics**. Its research objectives are to use the power of Density Functional Theory (DFT) to model, understand and predict the transport properties of materials and material systems relevant to magnetoelectronics. This is a very focused effort of leading European computational groups. On the other hand this is also an effort on a very broad front, ranging from the solution of the basic quantum mechanical equations for the ground state of these systems to realistic calculations of the spin-dependent transport properties of industrial prototypes. The basic advantage of our approach is that we can attack all these problems with the same ab-initio methods resulting in a high consistency of the calculated results. Fundamental to this is the use of the Green's function language which allows the formulation, in a transparent way, of spin-dependent transport. Our group has been at the forefront, world-wide, in the development and the application of this methodology. The proposed Network has three inherently connected themes: ground state properties of magnetoelectronic materials, probing the electronic and interface structure of magnetoelectronics materials, spin-dependent transport. These themes are organised into 10 collaborative, scientific tasks of Ferromagnet/Semiconductor Interfaces, Ferromagnet/Oxide Interfaces, Ferromagnet/ Superconductor Interfaces, Magnetic Nanostructures, Magnetooptics, Magnetic X-ray Scattering, Giant Magnetoresistance, Tunneling Magnetoresistance, Spin Mesoscopics, Experimental Data and Assessement of Applicability. Added to this are 3 dissemination tasks of 6 Topical Workshops, 4 Annual Meetings and 24 issues of the Psi-k Newsletter. The Network's composition of ten nodes has as distinguishing features: nodes which comprise all relevant national theoretical activities, the participation of two Central European nodes (HU, CZ), an experimental/industrial (Thomson) node in France, and a US node which substantally adds to the interest of the Community.

Please note that the network also maintains its web-page that is placed on the same server as all information relevant to our Psi-k community accross Europe:

http://psi-k.dl.ac.uk/TMR1

4 News from the TMR2 Network

'Electronic Structure calculations of materials properties and processes for industry and basic science'

4.1 Job Announcements

Postdoctoral Position at the Institute for Physical and Theoretical Chemistry, Vienna University of Technology, Austria

A post-doctoral position funded by the **European Training Mobility and Research Network (Psi-k) "Electronic Structure Calculations of Materials Properties and Processes for Industry and Basic Science "** and the **Forschungszentrum Juelich** is available in the area of electronic structure theory of solids.

The applicant is expected to contribute to the network project on the development of the full-potential LAPW method. The project is a collaboration in an international team, comprising research groups in Juelich, Berlin and Uppsala. Some travel activity between the research centers involved must be foreseen. More detailed information concerning the project can be obtained upon request.

The position is available immediately for a period of one year. The applicant must comply with the TMR rules for network employment of young scientists: The applicant should hold a PhD degree or equivalent in Physics or Chemistry, be younger than 35, and should have some experience in computational Condensed Matter Theory. He/She must be of European Union nationality (or from Norway, Iceland, Israel, or Liechtenstein), however excluding German and Austrian citzens.

She/he should have some experience in computational Condensed Matter Theory and Fortran programming, and is expected to contribute to the development of our full-potential LAPW code "WIEN97".

Cooperations within the TMR network implies that she/he is willing to collaborate with other members of the network (Juelich, Berlin and Uppsala) as well.

Salary depending on qualification is DM 3200 - 4000 / month (taxfree) Further information on our group can be found on:

http://www.tuwien.ac.at/theochem/

Applications with resumes, list of publications, and name (address) of referees should be sent to (preferable by email):

Dr. P.Blaha or Dr. K.Schwarz
Institut für Physikalische und Theoretische Chemie
TU Wien
Getreidemarkt 9/156
A-1060 Vienna, Austria

E-mail: pblaha@email.tuwien.ac.at

5 News from the ESF Programme

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

5.1 Call for Workshop Proposals

Research Workshops and Symposia within the ESF-Psik Research Programme

Applications for research workshops, symposia or smaller conferences to be supported by the ESF-Psik Research Programme on "Electronic Structure Calculations for Elucidating the Complex Atomistic Behaviour of Solids and Surfaces" to be organized in the forthcomming year should be submitted to the Secretary of the Programme (w.m.temmerman@dl.ac.uk) before the end of September. Each application should contain a brief description of the scientific goals of the meeting, information on the expected attendance, if possible a list of invited speakers. The application for financial support should be supported by a budgetary outline. All proposals will be reviewed by the members of the Steering Committee, a final decision whether a proposal will be funded will be taken during the annual meeting of the Core Steering Committee (end October).

5.2 Call for Collaborative Visit Proposals

Cooperative Visits and Secondments within the ESF-Psik Research Programme

The members of the Psik-community are reminded that applications for the support of collaborative visits and secondments are possible at any time. The Core Steering Committee will make a quick decision after consultations by email.

5.3 Reports on Workshops

5.3.1 Report on IWOSMA Workshop

International workshop on **ORBITAL AND SPIN MAGNETISM OF ACTINIDES**
Friday 4 and Saturday 5 June 1999.
Daresbury Laboratory
Warrington WA4 4AD, United Kingdom
http://srs.dl.ac.uk/msg
Sponsors
European Science Foundation (ESF)
http://www.esf.org
Training and Mobility Research (TMR)2 Network Psi-k
http://wserv1.dl.ac.uk/TCSC/HCM/PSIK

A two-day workshop took place in Daresbury Laboratory, bringing together experimentalists and theorists on the theme of orbital and spin polarization in actinides. At this workshop we hoped to emphasise the things that were not understood, rather than those that were understood. An optional tour of the Synchrotron Radiation Source (SRS) and the Ring-O-Bells was included in the program.

Rationale of the workshop

The magnetism of transition metal and lanthanide systems is now fairly well understood, where d and f electrons can be described in a delocalized and localized model, respectively. On the other hand, actinide systems do not fit in such a description. The localization of the 5f is in between that of the 3d and 4f and the strong spin-orbit interaction necessitates a relativistic approach. Furthermore, electron correlation effects play a major role in these compounds. Recently, it has become possible to determine element specific magnetic moments using neutron diffraction and x-ray scattering and absorption. The latter technique makes it even possible to separate the orbital and spin contribution to the total magnetic moment. The results are very interesting but difficult to reproduce with present state-of-art calculations. Not only a very large orbital polarization but also a large magnetic dipole term has been measured in cubic compounds, such as US. This allows for severe testing of the extra terms included in band theory to account for orbital polarization. It is also clear that deeper insight in magnetism can be obtained by studying the unusual behaviour of the actinides. Despite the fact that actinides for health reasons will find less application in technological market products, the understanding of their magnetic and electronic properties will no doubt provide key elements for a general description of electron correlation and relativistic effects.

The organisers
Gerrit van der Laan and Walter Temmerman

Workshop webpage: http://srs.dl.ac.uk/msg/MSG_Events_IWOSMA.html

Summary by G.H. Lander (Karlsruhe)

International Workshop on orbital and spin magnetism of actinides (IWOSMA) held in Daresbury, UK, 4-5 June 1999.

This was the first meeting of its kind - somewhat like a mini-Journee des Actinides - but more concentrated and certainly more theorists. Since its idea originated out of a TMR Network, the latter was perhaps, not surprising. I congratulate the organizers for setting up this format and inviting a number of speakers perhaps peripheral to the main actinide community, but who added considerably to the interesting "mix" that made the meeting a success.

Of course, having a specialised title implying that only experiments relating to the measurement of spin and orbital moments was rather provocative - and no doubt inspired by the new technique of dichroism. However, those discussing magnetic properties in general reminded us of the importance of spin-orbit coupling in defining so many magnetic properties. We heard interesting talks by Havela (Prague) and Kaczorowski (Wroclaw, Poland) on bulk property measurements. There was much discussion of the presence (and importance) of orbital moments in localised and itinerant systems and this came up early on when Lander (Karlsruhe) presented the neutron "view" of orbital and spin moments, and gave some of the new results on UGa_3, in which it is the spin moment that disappears at T_n, and one is left with van-Vleck-like susceptibility in the paramagnetic state.

There was considerable discussion of the paramagnetic state, and it is a complex problem from a theoretical point of view to get the paramagnetic state correct, whereas the ordered state seems to be relatively well understood. Yaounc (CEA, Grenoble) presented dichroism and Compton scattering results on some U compounds, and there are some disagreements with the neutron results. It is perhaps the Compton scattering which needs to be examined more carefully, as a considerable amount of calculation is needed even to interpret the measurements. There is still some differences over the values of the spin and orbital moments in US, but the differences between theory and experiments is still mostly greater than between different experiments.

The question of how to understand what happens as one goes from the ordered to paramagnetic state (or vice versa) came up in connection with the low-T, high-P resistivity measurements presented by Ichas (Karlsruhe). Here magnetic ordering is (probably) seen under pressure, and it has been predicted by LDA-type calculations. The latter are very much dominated by spin-orbit coupling for Pu with 5 5f electrons, so this prediction is a considerable triumph. Oppeneer (Dresden), who was involved in the PuTe theory, presented theory on magneto-optical spectra of U compounds. There seems some dispute over these as the experimental situation is still unclear, and perhaps a new effort should be made.

Sandratskii (Darmstadt) told us about the importance of spin-orbit coupling in defining the symmetry that frequently is at the heart of complex magnetic structures found in the actinides. This use of symmetry combined with LDA methods seems particularly powerful; and has explained many experiments, some of which stretch back over 20 years.

This brought up the second major them of the meeting - HYBRIDIZATION. It is not clear (at least not to this experimentalist!) how the spin-orbit interaction affects the hybridisation, and I would like to see this addressed. On this subject, there were a number of interesting experimental talks. Kaindl (Berlin) told us about XANES experiments on actinides, and how the hybridisation shifts the energy of the edges. This technique is especially interesting when it is performed under pressure. The structures of the elements themselves are, of course, good examples of hybridisation phenomena, and there was a brief reference to some the experiments at 3-rd generation synchrotrons that are re-doing the structures of the elements to higher pressures. Murani (ILL, Grenoble) discussed cerium compounds, and inelastic neutron scattering. This led to a discussion of the difficulty in observing crystal-levels in uranium compounds. Murani suggested the reason for this absence was the strong interaction between the 5f and conduction states. This is indeed generally accepted as such crystal field levels can be seen with neutrons in ionic and certain metallic compounds, UPd_3 is the famous example, but not in most metallic compounds.

C. Vettier (ESRF, Grenoble) told us about resonant magnetic scattering - an effect which is particularly well suited to the actinides, and has given much information, not all of it understood. This led on to a talk by A. Rogalev, also at the ESRF, about the recent observation of a very large resonant signal at the K-edge of S in US. Similarly, Vettier had told us about effects seen in scattering experiments at the K edges of the antiferromagnets UGa_3 and UAs. These observations provoked a considerable amount of discussion. Indeed transferred hyperfine fields have been seen in Moessbaur spectroscopy for many years, and a dichroic signal was after all also seen in EuS, but the surprise is not the presence of an effect, but its size. Vettier made the point that such a size in UAs would correspond to several tenths of a Bohr magneton at the As site, if interpreted as direct 5f-4p mixing, and this is simply impossible. There was much discussion on this, and there remains both more experiments and more thinking to be done on these interesting observations.

Finally Tobin (LLNL, California) talked about recent photoemission experiments on both alpha- and delta-Pu. These are interesting. They show a difference between the two phases. More experiments are needed, but this is a real start on sophisticated experiments on elemental Pu, which up to now has been more talked about than actually done.

Our thanks to Gerrit van der Laan and Walter Temmerman for organizing the meeting so well, and to the Ladies of Daresbury for making it all run smoothly. Jim Tobin has volunteered to have the next meeting in California in 2001 - and there seemed to be little opposition to such a pleasant idea!

Summary by M.S.S. Brooks (Karlsruhe)

The theory contributions to this meeting were based almost entirely upon density functional theory. Johansson covered structure and structural sequences and the influence of spin-orbit interaction through relativistic Stoner theory. The non-collinearity of magnetic order in many uranium compounds was the subject of Sandratski's talk where it was shown that a combination of spin-orbit interaction and hybridization between uranium states and states of other atoms leads naturally to the type of ordering observed. Ground state spin and orbital densities were discussed in some detail and compared with the results of elastic neutron scattering experiments. There was also extensive discussion of spectroscopic properties. Ebert described spin-polarized Dirac theory, it's application to spectroscopy, and showed the results of XMCD calculations for US. He also introduced a new application of linear response theory for the calculation of induced moments for the paramagnetic state with application to the induced form factor of chromium. Van der Laan reviewed the atomic theory of dichroism with application to US and discussed the formalism for jj-coupling. Oppeneer reported on an extensive series of optical and optical Kerr effect calculations for uranium compounds while Brooks showed the results of recent XMCD calculations. Carra demonstrated the meaning of the word flexibility by departing from his abstract to discuss his most recent interest - natural dichroism.

The theme common to all of the theory contributions, with the exception of Carra's, was spin-orbit interaction. This, at least, is a single particle effect. In almost all cases magnetically ordered uranium compounds have orbital moments - induced by spin-orbit interaction - which are anti-parallel to and larger than - the spin component of the moment, in agreement with measurements. It seems to be fairly clear, though, that there remains a problem with the magnitudes of the spin and orbital contributions. There may be additional problems as was made clear by Oppeneer's very detailed description of how he tested the effect of using the LDA+U approximation for magneto-optical effects, and which led to improved agreement with experiment. If the combined experience of theorists working in this area is condensed, it does seem that - in contrast to spin-only magnetism - some modification of the local spin density approximation will be required to describe orbital magnetism correctly. One correction that comes to mind is a correct description of non-collinearity of the orbital and spin magnetization vectors within the atom as well as between atoms.

There was plenty of lively discussion at this meeting with three subjects in particular providing interaction between experimentalists and theorists. The first concerned Yaouanc's reported results on the orbital and spin moments of uranium compounds. In this work Compton scattering is used determine the spin contribution to the moment and XMCD is used to determine the orbital contribution from the sum rules. The problem seems to be that the spin contributions appear to agree neither with those obtained from neutron diffraction nor from theory. Work needs to be done here. The subject was the moment composition obtained from neutron diffraction in the paramagnetic state from the induced form factor. Neutron diffraction for the anti-ferromagnet UGa_3 yield quite different orbital and spin in the paramagnetic and ordered states. The conventional wisdom at the moment is that this is due to the fact that UGa_3 is a weak itinerant anti-ferromagnet with a vanishing moment above the Neel temperature rather disordered local moments. The applied field therefore induces a mostly van Vleck orbital contribution whereas in the ordered state any applied field has little effect, the orbital and spin contributions being determined - in LSDA - by the spin and spin-orbit interaction. The immediate corrolary is that for compounds where a the response in the paramagnetic state is significant on more than one atom a solid state analysis is required to separate the contributions of the atoms at a Bragg point, rather than the purely atomic analysis of the scattering which has been used by tradition. Finally, Rogalev reported a large XMCD signal for the sulphur K-edge which surprised everyone. That there should be a signal is not so surprising since there is hybridization between the 5f-states of uranium and p-states of sulphur and the spin-orbit split components of 5f-states hybridize differently with the p-1/2 and p-3/2 states thus transferring some orbital moment, but this effect is calculated to be small and has not been observed in neutron diffraction. The ensuing discussion of hybridization effects almost became a dialogue of the deaf primarily, in the writer's view, due to the fact that there is more than one way to describe hybridization. If the site-selectivity of XMCD is to be examined critically as a result of such experiments it will be up to band theorists to explain rather carefully how electronic structure can be formulated in terms of both single-centre and multi-centre expansions. A careful examination of the sum rules when the final state lies in the continuum is also required.

A very enjoyable meeting was a credit to the organizers.

The programme and abstracts of the Workshop follow in the next pages.

IWOSMA Timetable

Friday 4th June 1999

09.05 - 10.00	L.Havela	Prague	Electronic structure and magnetism of actinide systems
10.00 - 10.45	M.S.S. Brooks	Karlsruhe	Theory of itinerant magnetism
10.45 - 11.15	Coffee		
11.15 - 11.35	V. Ichas	Karlsruhe	Strong pressure effects on the resistivity of PuTe
11.35 - 12.20	H. Ebert	Munich	X-ray magneto-optical effects
12.25	Posters at the Science Centre + Lunch		
14.00 - 15.00	G.H. Lander	KFA Karlsruhe	Spin and orbital moments as seen by neutrons in actinide systems
15.00 - 15.45	P.M. Oppeneer	Dresden	An understanding of orbital magnetism from magneto-optical spectra
15.45 - 16.15	Coffee		
16.15 - 17.00	G. van der Laan	Daresbury	Are the sum rules letting US down?
17.00 - 17.20	A. Rogalev	ESRF Grenoble	XANES and MXCD study of US : New results
17.20 - 17.40	A. Murani	ILL, Grenoble	Can Ce (sometimes) be considered as an honorary actinide?
17.40 - 18.00	R.J. Cernik	Daresbury	DIAMOND, a source for the new millennium
19.00	Conference Dinner at Lymm Hotel		

Saterday 5th June 1999

09.00 - 10.00	B. Johansson	Uppsala	Electronic structure of actinides
10.00 - 10.45	G. Kaindl	Berlin	X-ray absorption near-edge structure of actinide small compounds
10.45 - 11.15	Coffee		
11.15 - 12.00	P. Carra	ESRF Grenoble	Resonant x-ray scattering in actinides (UO_2, USb, and heavy fermions)
12.00 - 12.30	D. Kaczorowski	Wroclaw	Itinerant 5f electron antiferromagnetism in UGa_3
12.30	Posters at the Science Centre + Lunch		
14.00 - 15.00	Ch. Vettier	ESRF Grenoble	Magnetic resonant effects in U and Np compounds (M and L edges)
15.00 - 15.45	L. Sandratskii	Darmstadt	Non-collinear spin and orbital magnetism in actinide compounds
15.45-16.15	Coffee		
16.15 - 17.00	A. Yaouanc	CEA-Grenoble	X-ray magnetic Compton and magnetic circular dichroism on uranium compounds
17.00 - 17.45	J. G. Tobin	Livermore	Photoemission of actinides
17.45 - 18.15	G. H. Landers and M. S. S. Brooks		Summary of meeting

Electronic structure and magnetism of actinide systems

L. Havela

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Actinides are characterized by the gradual filling of the 5f shell, in analogy to the 4f-shell filling in lanthanides. The large spatial extent of the 5f wavefunctions means a general tendency to a more delocalized behaviour, which is manifest in the participation of the 5f states in bonding in the case of light actinides (Th-Pu). The broad-band situation observed in the pure elements can be modified by alloying or forming a compound, in which the 5f-5f overlap is reduced due to increasing inter-actinide spacing. Prominent correlation effects in such situation can give rise to e.g. heavy-fermion behaviour, and analogies can be found to lanthanides with the 4f instability. Strong spin-orbit interaction in actinides can lead to induced orbital moments even in strongly itinerant systems. Magnetic order in light actinides can be at a first glance understood as due to the fulfillment of the Stoner criterion (leading to spin-up-spin-down subband splitting), but once the net spin moment is formed, an antiparallel orbital magnetic moment can be induced compensating (in some cases) or even overcompensating (in most of cases) the spin magnetic moment. Appreciable orbital moments mean strong mutual influence of magnetism and bonding geometry (enormous magnetic anisotropy). Other mechanism leading to the 5f instability even in cases of large inter-actinide spacing is the hybridization with non-f states of ligand atoms. The model of two-ion hybridization-induced exchange interaction can explain why ordering temperatures are in actinides typically higher than in corresponding lanthanide materials, in which the RKKY interaction dominates. The strengthening of the hybridization accounts for an anomalous large increase of ordering temperatures, observed in some cases with increasing pressure.Important issues to be solved include the degree of the 5f-localization in particular cases, description of the dynamics of magnetic moments, especially in the vicinity of the quantum critical point, or ratio of spin and orbital moments under various circumstances.

Orbital Magnetism in Itinerant Magnets

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Moment formation and stable magnetic moments are fairly well understood for 3d magnets in terms of the local spin density approximation. The rare earth magnets, with their localized 4f electrons and large orbital and spin magnetic moments, are better handled by more traditional atomic theory. The 5f electrons in the actinides frequently appear to be itinerant although the exact nature of the 5f states depends upon environment - in particular the actinide-actinide spacing. Density functional theory has been applied to actinide magnets and spin polarized energy band calculations yield large orbital moments when spin-orbit coupling is included among the interactions. The physical reason for this is that the spin-orbit splitting is far larger relative to the bandwidth in actinides than in the 3d transition metals. The consequences of the existence of large orbital moments in actinides with itinerant 5f electrons may be observed in several types of experiment. The orbital moments are anti-parallel to the spin moments which leads to major changes in the shape of the magnetic form factor compared with spin-only magnets: the Kerr angles and magnetic anisotropy are very large at low temperature, even in cubic systems; the xray magnetic circular dichroism is also large. Recent calculations of orbital magnetic moments, neutron form factors, Kerr effect and dichroism spectra for several actinide magnets are reported. The dichroism sum rules, and the influence of the dipole operator upon them, is investigated as a function of spin-orbit interaction and compared with results for 3d magnets.

Strong Pressure Effects on the Resistivity of PuTe

V. Ichas, J. Rebizant, J.C. Spirlet and J.C. Griveau

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The Pu monochalcogenides (NaCl structure) have a special place among the actinide chalcogenides, because they do not order magnetically and display anomalous properties. The lattice parameter of PuTe is consistent with a trivalent Pu ion. It has been shown however, that the induced magnetic moment is dominated by the spin contribution which is incompatible with Pu^{2+} or Pu^{3+} ions [1]. The ambient pressure resistivity displays an up-turn as temperature is decreased. This was interpreted as a semi-conductor behaviour with 2 different gaps [2]. However, the electronic contribution of the specific heat (˜30mJmol-1K-2 [3]) seems to be in contradiction with a classical semi-conductor behaviour.A number of models have been proposed to explain the electronic structure of the Pu monochalcogenides [4,5,6]. From density of states calculations within the one-electron band model [7], dramatic changes in resistivity were expected in PuTe at the NaCl-CsCl structural transition observed in X-Ray experiments [8].

We have therefore performed a high-pressure resistivity study up to around 24 GPa, from 300K down to 1.5K, on a single crystal of PuTe. At low-pressure, the resistance R displays the expected up-turn as found at ambient pressure. Surprisingly, the resistance at 1.5K is enhanced with pressure. This is contrary to the effect which might be expected upon any semi-conducting gap. Between 10.7 GPa and 12.7 GPa, R strongly decreases over the whole temperature range. We attribute the collapse of the resistance to the NaCl-CsCl structural transition. Above 12.7 GPa, the up-turn tends to disappear and the temperature variation of R progressively approaches that of a metal. Moreover, we observed interesting features in the derivative of the resistance which might be a signature of magnetic order. This should be confirmed by other experiments.

Our study showed that the transport properties of PuTe are strongly affected by the application of pressure. In the hybridization-gap model, it is suggested that the spin-orbit coupling has a strong influence on the lattice constant [6].

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X-ray magneto-optical effects in Rare-Earth and Actinide Compounds

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The description of the electronic structure of Rare-Earth and Actinide compounds is still a major problem today because of the f-electrons involved. We are using the relativistic version of multiple scattering theory for spin-polarized systems (SPR-KKR) that without doubt assumes the f-electrons to be essentially itinerant. Within this framework X-ray magneto-optical effects in absorption and scattering have been investigated for various Rare-Earth and Actinide compounds. Results, in particular for magnetic EXAFS (MEXAFS), will be presented and discussed in comparison with available experimental data. Emphasize will be put on the decomposition of the magnetic moment of the absorbing atom into a spin and orbital part on the basis of the so-called sum rules as well as the interpretation of the Fourier transformed MEXAFS-spectra in terms of the magnetization distribution around the absorber. Finally, we will present results of investigations on the influence of non-collinear spin structures for magnetic dichroic spectra.

Spin and orbital moments by neutron diffraction

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The neutron scattering cross section is proportional to the sum of the spin and orbital moments. Unlike the scattering of photons, there is no direct method to separate these contributions. However, the scattering from the orbital moment (μ_L) and spin moment (μ_S) have a i*different* dependence on the momentum transfer, **Q**. Within the dipole approximation (valid for small Q) the spin moment varies as $< j_0 >$ and the orbital moment varies as $(< j_0 >+< j_2 >)$, where $< j_l >$ are Bessel transforms of the single electron density, and are well known. For the light rare earths and actinides, Hund's rules dictate that μ_L and μ_S are oppositely directed. In this favourable situation (which includes some of the most interesting *f* magnetic elements) the dominant contribution of $< j_0 >$ in the form factor is strongly reduced, and the amount $< j_2 >$ of observed allows us to derive the quantity μ_L/μ_S with an uncertainty of about ±10%. In addition, the intercept of the form factor with Q=0 gives the total moment $\mu_L + \mu_S$. To obtain the necessary data, single crystals are necessary, and, in the case of ferromagnets or paramagnetic systems, so is the use of polarized beams. For the moment, these experiments are performed only at reactor sources.

I shall review some of the data already published on materials containing U, Np, and Pu ions, including the well-known case of UFe_2, and conclude with our latest results on UGa_3. In this system we clearly see a change in f(Q) from the para- to antiferromagnetic states, as has been predicted by LDA + orbital polarization calculations.

An understanding of orbital magnetism from magneto-optical spectra.

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The description of orbital magnetism in actinides is complicated by the correlated nature of the 5f-shell, in which the f electrons are not fully localized, neither well delocalized. The local spin-density theory leads in most cases to an underestimation of the orbital moment. Magneto-optical (MO) spectroscopy˜– dichroism, MO Kerr effect, or Faraday effect – probes the orbital moment, as, e.g., can be recognized from the recently derived sum rule $\int \sigma^2_{xy}(\omega) d\omega \propto < l_z > +R$ in which σ^2_{xy} is the absorptive part of the off-diagonal optical conductivity, and R is a small remainder. The orbital magnetism in a number of uranium compounds is discussed in the light of this sum rule. While one would expect to find similar deviations in the MO spectrum as in the orbital moment, this is surprisingly not often the case. Even for several uranium compounds that where categorized to have localized 5f's, e.g., UAsSe, URhAl, the MO spectrum is rather well described by the itinerant LSDA-approach, although the calculated orbital moments are too small. This indicates that the energy bands and their orbital magnetism are reasonably given by the LSDA, and the pertinent question is, which improvement is needed to obtain both the proper MO spectrum and orbital moment.

Are the sum rules letting US down?

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http://srs.dl.ac.uk/msg

Whereas the sum rules have proven to be reliable allies in attacking the spin and orbital polarization of transition metal and lanthanide systems, in conquering the actinides they appear to be less faithful. The actinides differ from all other elements in that spin and orbit are firmly coupled in the ground state, which necessitates the employ of a relativistic approach. The strong spin-orbit interaction prompts to a large value of the magnetic dipole term T_z, even for compounds with cubic symmetry such as ferromagnetic US [1] . For some materials the combined results from neutron scattering and x-ray magnetic circular dichroism (XMCD) results merely in a modest consent about the magnitude of the spin and orbital magnetic moments. It is shown how the XMCD sum rules can be developed to take care of the large spin-orbit coupling of the 5f's. Whereas j = 5/2 and 7/2 states provide a good basis for quantities that are diagonal in j, such as the density and the spin-orbit operator, a cross-term has to be included to enable a proper description of the magnetic properties. [2] The jj-coupled tensors are a linear combination of the LS coupled tensors, L_z, S_z and T_z, and provide the underlying fabric of the relativistic sum rules. [3] Hybridization and diffuse magnetism play an important role in the spectral shape of the U 3d → 5f ($M_{4,5}$) XMCD of uranium compounds. It is shown that the current understanding is insufficient to explain fully the electronic and magnetic structure of the varied scalar of actinides. Some compounds conform to neither a localized nor a delocalized description of the 5f electrons. Furthermore, it is disputed whether under all circumstances neutron and x-ray data are consistent with each other. The presence of crystal field interaction, indicated by the breaking of the proportionality rule for L_z, S_z and T_z, does not seem to be confirmed in neutron scattering.

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XANES and XMCD study of US: new results

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Recent results of high resolution XAFS experiments at both U M-edges and S K-edge in Uranium sulphide single crystal are presented. A comparison of S K-edge XANES spectrum with the element projected partial density of states calculated using LMTO method revealed a rather good agreement. Our analysis suggest that there is a strong hybridization of the 5f orbitals of U with 3p orbitals of the sulphur, which also contributes to the conduction band. This f-p hybridization in US may also be revealed from the comparison with S K-edge XANES spectra of isostructural EuS and GdS crystals. The strong f-p interaction results in a large sulphur p-band polarization which is unambiguously confirmed by the detection of a huge XMCD signal at the Sulphur K-edge. The structure in the U M4,5- and S K-XMCD spectra are discussed on the basis of the differential magneto-optical sum rules.

Should Ce be considered an honorary actinide?

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$CeFe_2$ and UFe_2 are isostructural ferromagnets, which order at 230 K and 160K respectively, temperatures which are significantly lower than the ordering temperatures of ˜550 and ˜600 K for the isostrucural compounds YFe_2 (which has no f electrons) and $LuFe_2$ (with 4f shell full). It is now generally accepted that the 4f and 5f electrons (of Ce and U) are responsible for the observed depression of the ordering temperatures as well as in the reduction of the Fe moment from ˜1.7 in YFe_2 (and $LuFe_2$) to ˜1.2and 0.6 in $CeFe_2$ and UFe_2, respectively. It is, therefore, not surprising that Ce is often considered to be similar to U and that the 4f-electrons of Ce are treated theoretically as itinerant 4f-bands, in a manner analogous to 5f bands of U. While the magnetic form factor of U in UFe_2 was shown to be in good agreement with band theory predictions, measurements on $CeFe_2$ have revealed considerable discrepancies yielding relatively small 4f spin and negligibly small orbital moment on Ce, almost an order of magnitude smaller than predicted by band theories. We argue that this discrepancy may be associated with the fact that 4f electron in $CeFe_2$ does not constitute a fully itinerant 4f band, but may do so only partially while remaining bound within a broadened, localised state for a significant temporal fraction. A systematic investigation of a number of systems reviewed here such as $CeNi_2$, $CeRh_2$, $CeRu_2$ as well as $CeFe_2$ using high energy neutrons on the spallation neutron source (ISIS) indicate that bulk of the magnetic moment of Ce in such systems is associated with high energy paramagnetic scattering which is single-ion inform and whose integrated intensity represents a substantial fraction (70 - 80 %) of the magnetic moment of the J=5/2 state of Ce. These observations constitute the magnetic manifestation of the fractional charge occupancy of the f1 state (also of similar magnitude) observed from X-ray LIII absorption measurements. For the U-based intermetallic compounds no such well defined charge occupancies of the 5f state from X-ray absorption or photo-emission have been clearly established, nor have neutron inelastic studies demonstrated unambiguously the localised character of the 5f response, except in a relatively few cases. It is hoped that our results of neutron inelastic scattering measurements on the Ce systems will stimulate measurements on isostructural U-based compounds to permit better comparision and understanding of the two ionic species.

DIAMOND, a source for the next millennium

R.J. Cernik

Daresbury Laboratory

The United Kingdom will have a new third generation light source for the next millennium. The design details are currently being discussed in a series of workshops that will extend beyond the summer of 1999. The final design will be a balance between biologists and physical scientists but it now seems clear that a design close to 3 GeV with 20 cells will satisfy 95% of the UK user community. For research into magnetism soft X-rays have become an indispensable tool. DIAMOND will perform at its best in this energy range. In addition the range of helical, variable polarisation or crossed undulators will deliver orders of magnitude extra flux with circular polarisation. The opportunities for research in magnetism using soft and hard X-rays will be discussed. Options for insertion devices and beamline optics will also be covered along with developments in detector technology that will enable experimenters to gain maximum benefit from the new source.

Magnetic, Structural and Electronic Relationships between the Lanthanide and Actinide Elements

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The similarity and difference between the solid state properties of the 4f and 5f transition metals are pointed out. The later 5f elements show properties which have direct correspondence to the early 4f transition metals, suggesting a localized behaviour of the 5f electrons for those metals. The fact that Pu metal has a 30% lower volume than its neighbour heavier element, Am, suggests a tremendous difference in the properties of the 5f electrons for this element relative to the heavier actinides. This change in behaviour can be viewed as a Mott transition as a function of the atomic number Z. On the metallic side of the Mott transition, the elements show most unusual crystal structures, the common feature being their low symmetry, and relatively inefficient filling of space. An analogous behaviour for the lanthanides is found in cerium metal under compression, where structures typical for the light actinides have been found experimentally. A generalized phase diagram for the actinides is shown to contain features comparable to the individual phase diagram of Ce metal. The crystal structure behaviour of the lanthanides and heavier actinides originates from the number of 5d (or 6d) electrons in the metallic state. Electronic structure calculations account very well for the ground state crystal structures of the actinides. The distorted structures can be understood as Peierls distortions away from the symmetric bcc structure and originate from strongly bonding 5f electrons occupying relatively narrow 5f states.

X-ray absorption near-edge structure studies of actinide compounds

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The x-ray absorption near-edge structure (XANES) at the L-thresholds of actinide elements offers a practicable way for studying the electronic structure of actinide compounds, despite

of their radioactivity. By employing safely incapsulated samples, early results were obtained at HASYLAB/Hamburg for compounds of U, Np, Pu, and Am. In combination with diamond-anvil pressure cells, the technique allows also to study changes of the electronic structure as a function of external pressure. The $L_{2,3}$ XANES spectra are characterized by relatively strong white lines, in addition to absorption thresholds, which shift in terms of the occupancy and localization of the 5f states. In the Np case, a comparison of the white-line shifts with Moessbauer isomer shifts of the 59-keV Moessbauer resonance of Np-237 is possible, providing further insight into the information contained in the XANES spectra. We further discuss the prospects of this spectroscopy in view of the availability of intense x-ray beams at third-generation synchrotron-radiation facilities.

This work was supported by the Bundesminister fuer Bildung und Forschung as well as the Deutsche Forschungsgemeinschaft.

Resonant magnetic X-ray scattering at the M4,5 edges of Np0.5U0.5Ru2Si2

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Numerical crystal-field calculations will be presented for resonant magnetic diffraction at the $M_{4,5}$ edges of $Np_{0.5}U_{0.5}Ru_2Si_2$. Spectra obtained from a simple localised model, consisting of a coherent superposition of U^{4+} and Np^{3+} ions, will be discussed and compared to experimental data.

Itinerant f-electron antiferromagnetism in UGa_3

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We shall present a review of all known to date bulk physical properties of UGa_3, studied on both poly- and monocrystalline specimens by means of dc- and ac-magnetic, electrical transport, thermal transport, heat capacity and dilatometric measurements. Some reference will also be made to the findings of neutron and synchrotron X-ray scattering experiments.

It will be argued that UGa_3 is a unique example of itinerant 5f-electron antiferromagnet with the magnetic behaviour governed mainly by hybridisation between the U 5f- and Ga 4p-electronic states. In this context our review of the experimental data will be supplemented by a brief presentation of the recent results of band structure calculations.

Resonant Scattering Effects in U and Np Compounds

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Resonant X-ray magnetic scattering gained significant momentum when colossal resonant enhancements were observed in UAs by tuning the photon energy near the $M_{4,5}$ edges of Uranium. At these edges the resonant process arises from strong dipole electric transitions to the polarized 5f states which carry most of the magnetization. Since then, the large resonant intensities at the M edges have been exploited first to investigate either weak 5f moment systems or small scattering volumes, such as micro-crystals, thin films and even surfaces. In particular, resonant scattering has allowed studies of magnetic structure in minute samples of materials such as transuranium actinides or thin films, which are too small to be looked at with neutrons. Examples will taken from studies on UAs and NpO_2. In addition to large intensity enhancements, resonant x-ray scattering has three characteristics: species selectivity, electronic shell selectivity and energy lineshape. The species selectivity has been exploited when studying solid solutions such as $U_xNp_{1-x}RuSi_2$. The shell selectivity is obtained by tuning the photon energy near the $L_{2,3}$ edges where it is possible to observe the contributions from the 6d levels to the total magnetization. Finally, the energy profile of the resonance coupled to the properties of the synchrotron x-ray sources provide information on the spatial distribution of magnetic moments. Recent experimental examples will be given.

The speaker is indebted to his collaborators, especially N. Bernhoeft, S. Langridge, E. Lidstrvm, D. Mannix, D. Wermeille and G.H. Lander.

Noncollinear spin and orbital magnetism in actinide compounds

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The physical interactions responsible for the noncollinearity of the magnetic structure in the Uranium compounds are analyzed on the basis of the first-principles calculations. The following compounds are considered: noncollinear ferromagnets U_3X_4 (X=P, AS, Sb) and UFe_4Al_8 and noncollinear antiferromagnets U_2Pd_2Sn, UPdSn and UPtGe. Special attention is given to the UFe_4Al_8 where two different types of the noncollinearity are obtained both experimentally and theoretically. First type of the noncollinearity is almost orthogonal directions of the Fe and U magnetic moments, second type is a small canting of the Fe magnetic moments from the crystallographic a axis. It is shown that both types of the noncollinearity are closely connected and have the same physical origin. It is stressed that the spin-orbit coupling is crucial for the appearance of the noncollinearity of the magnetic structure. Additionally it is shown that the hybridization of the U states and the states of other atoms is essential for the noncollinearity of the magnetic structure in a number of compounds. The last property allows to use the noncollinearity of the magnetic structure as indirect measure of the hybridization of the U 5f and other electron states. The orbital polarization is used to improve the agreement between theory and experiment. Systematic comparison of the experimental and theoretical values of the magnetic moments is given and discussed.

X-ray magnetic Compton and magnetic circular dichroism on uranium compounds.

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With the advent of the third generation synchrotron radiation sources, it is now relatively easy to carry out experiments by x-ray magnetic compton scattering (MCS) and magnetic circular dichroism (XMCD) at the $M_{4,5}$ uranium edges. We report the results of such experiments performed on uranium compounds at the European Synchrotron Radiation Facility in Grenoble. Combining the results of MCS with previously published neutron and bulk magnetic measurements, we determine the spin and orbital magnetic moments of the 5f and conduction electrons for US. Using previously published Compton, neutron and magnetization data on USe and UTe, we establish how the spin and orbital moments vary along the uranium chalcogenide series. We get the remarkable result that while the orbital magnetic moment of the conduction electrons in US is unexpectively large, it decreases as the lattice parameter of the uranium chalcogenide increases and becomes negligible in UTe. The shapes of our XMCD spectra are nicely described by the recently published theoretical Hartree-Fock treatment of an extended Hubbard model by Shishidou et al. (Phys. Rev. B. 59, 6813 (1999)). We determine experimentally for US the mean value of the operator T_z which appears in one of the dichroism sum rule. We report a systematic XMCD investigation at the $M_{4,5}$ uranium edges of eight uranium compounds, including heavy fermion superconductors. While a single lobe is always observed for the dichroic signal at the M_4 edge, one or two lobes are detected at the M_5 edge. This is not an obvious relation between the macroscopic physical properties of a compound and its dichroic lobe structure at the M_5 edge. We will argue that this structure provides information on the polarized density of states above the Fermi level. Finally, we report the first measurements by XCMD on uranium multilayers.

High Resolution Photoelectron Spectroscopy of Pu at the Advanced Light Source

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In collaboration with teams from LANL (J. Terry, R. Schultze, J. Lashley, D. Farr, and T. Zocco) and LBNL (D. Shuh and E. Rotenberg), high resolution photoelectron spectroscopy of Pu has been performed at the Spectromicroscopy Facility (Beamline 7.0) at the Advanced Light Source in Berkeley. Based upon an initial analysis of the data, two key results are immediately obvious.

1. The 5d-5f ResonantPhotoemission of the Pu 5f levels exhibits a dependence upon the Pu phase and structure. For example, the results from and Pu differ significantly. This strongly suggests that electronic behavior is linked to atomic ordering and structure in Pu.

2. Contamination with oxygen and carbon may be more insidious and subtle than initially believed. Photoemission measurements at a photon energy of 800eV exhibit oxygen and carbon

core level peaks, while the same sample shows no contamination utilizing a photon energy of 1253eV, a typical laboratory source energy used in ECSA machines (i.e., Mg k-). In other words, what was thought to be "clean" may not have been. Furthermore, contamination issues like these have a crucial impact upon interpretation of Pu core level spectra, e.g. localized and delocalized screening by 5f electrons. Additionally, 5f-6p Resonant Photoemission, core level spectra (particularly the Pu 4f's) and X-Ray absorption data, all from the Pu will be presented and discussed. Future plans, including ideas about studying magnetic effects in Pu, will also be described.

Low-temperature specific heat and resistivity of UAsSe ferromagnet

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UAsSe is a ferromagnet (T_C=113K) for stoichiometric compound) which shows an unusual increase of resistivity at low temperatures. It was shown that such kind of behaviour can be described on the assumption of a single-ion Kondo-like component to the resistivity. The Kondo component includes less than one quarter of the total resistivity at room temperature. In spite of this, the resistivity at the lowest temperatures, which is governed almost only by the Kondo contribution (its value extrapolated to 0 K is order of hundreds of mWcm). Very recently, it was shown that that the resistivity of $UAs_{1-x}Se_{1+x}$ system can be scaled with x and T_K (T_K is Kondo temperature) in very similar way to non-Fermi liquid $Y_{1-x}U_xPd_3$ system, which is described as the quadrupolar two-channel Kondo ones. A source of the Kondo impurities in UAsSe ferromagnet is presumably a disorder in the anion sublattice, which is the most likely due to the very small difference in the ionic radius between As and Se. It is worth to add that the decrease in the As/Se content ratio lowers T_C and enhances the incoherent Kondo resistivity in the ferromagnetic state.

We present results of the systematic investigations of the low-temperature specific heat of non-stoichiometric UAsSe single crystals. A variation of the Sommerfeld coefficient, g, with the As/Se ratio (controlled by T_C) is consistent both with the literature data (g=41 mJ/molK^2) and with our preliminary results (g=24 mJ/molK^2). There are two regions of the g (T_C) dependence; in the first, for samples with constant b, the dependence is consistent with the resistivity data. However, in the second one, b decreases with increasing T_C, what can be considered as the change of the Debye temperature, q_D. It is worth to add that a region boundary is located in the vicinity of T_C=113 K founded for stoichiometric compound.

Magnetism and Metamagnetism of Ternary UTX (T=Fe,Rh,Pt; X=Si,Ge) compounds

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The electronic structure of actinide intermetallic compounds is mainly determined by partially occupied f-electron states. So far a general theory does not exist for the description and understanding of all physical properties of uranium intermetallics. A partial description at the first principle level can be obtained from density functional theory (DFT), which treats exchange and correlation effects for the ground state in a mean-field approach. The actual calculations are usually performed using the local spin density approximation (LSDA). There are many uranium intermetallic compounds which show spin-fluctuation effects. To obtain a quantitative microscopic picture of the influence of the spin fluctuations on magnetic ordering in the 5f-systems we performed DFT electronic structure calculations on a selected group of UTX ternary compounds, which are paramagnetic (UFeSi, UFeGe) or exhibit ferromagnetic ordering with a small value of magnetic moment but still strong magnetocrystalline anisotropy effects (URhSi, URhGe). To complete the representative choice of UTX compounds we have also studied the UPtGe, which can be classified as a more localized 5f system with larger uranium moment and very interesting antiferromagnetic ground state. In the present study we used three different computational methods, namely fully relativistic optimized linear combinations of atomic orbitals (OLCAO), general potential linearized augmented plane wave (LAPW) and scalar relativistic augmented spherical wave (ASW). We have found a reasonable account for ground state minimal volumes can be obtained in the framework of LSDA. The tendency to ferromagnetic instability was investigated (Stoner product) and the ferromagnetic instability was found for URhSi, URhGe and UPtGe. The total energy calculations (fixed spin moment method) show that the paramagnetic ground state of UFeGe is stable but in the case of UFeSi band metamagnetism is suggested. Results of extended relativistic spin-polarized calculations revealed that both URhSi and URhGe exhibit an almost complete cancellation of spin and orbital magnetic moments, which explains the small values found by experiment. Assuming fluctuations of the total (small) magnetic moment, Curie temperatures of about 38 K can be expected which should be compared with the experimental result of about 9 K. UPtGe was found to have a larger spin and orbital moment than URhX. Moreover the topology of the E(V,m,q) space is quite complicated.

Resonant Magnetic X-ray Scattering Spectroscopy from Actinide Compounds

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Resonant x-ray magnetic scattering (RXMS) is an element specific spectroscopy occurring when the incident photon energy matches roughly that of an absorption edge [1, 2]. The enhancement of the magnetic intensity was explained by Hannon et al [3] as arising from multipole transitions (dipole or quadrupole) to available magnetic states through spin orbit coupling in either the core or intermediate levels. The magnetic sensitivity is related to the spin polarisation and exchange splitting of the intermediate states. In this model, strong RXMS effects were predicted and subsequently observed [4] at the M absorption edges of actinide compounds, where strong dipole transitions couple directly to the 5f magnetic states. Weaker resonant effects may also be observed arising from the finite polarisation of d and p bands. Actinide compounds are of special interest here due to the large hybridisation of the 5f wavefunctions with conduction and anion p states. Because of the small beam spot size used in x-ray experiments, small ˜mg quantities of transuranium compounds can be studied using this technique.

This poster briefly previews some results from our on going resonant x-ray magnetic scattering investigations of actinide compounds. Magnetic diffraction at the actinide M edges of UGa_3, NpO_2, and PuSb together with results at the neptunium L edges of NpP are discussed. In addition, recent and unusual resonant scattering effects are demonstrated at the L and K edges of the anion species in the antiferromagnetic compounds UGa_3 and UPtGe.

All these investigations were undertaken at the ID20 magnetic scattering beamline of the ESRF, with the exception of PuSb, studied the X22C of the NSLS, Brook haven National Laboratory. Although most of the work is still in progress, this presentation should generate some interesting discussion at this meeting.

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6 General Job Announcements

Lecturer in Ab-Initio Condensed Matter Theory

University of Paris VI

Applications are invited for a lecturer permanent position (Matre de Confrence) to start in September 2000 upon final approval of the University and of the MENRT. The successful candidate will teach in french. Ph.D. in Physics, fluency in French, and previous teaching experience are required. The successful candidate will join the Laboratory "Physique des Milieux Condenss". The research topics of the Laboratory are experimental high pressure Physics and Physical Chemistry (see http://argon.pmc.jussieu.fr). The successful candidate will develop a research program in electronic-structure-based ab-initio Condensed Matter Theory in conjunction with the experimental activity of the laboratory. He will also collaborate with the theoreticians of other laboratories of the Physics Department. Candidates should send, ASAP and before October 15th 1999, a CV and the names for at least three references to:

Philippe Pruzan, Physique des Milieux Condenss, B77, Universit Paris VI, 75252 PARIS Cedex 05, France

or by e-mail to:

philippe.pruzan@pmc.jussieu.fr or francesco.mauri@lmcp.jussieu.fr

POSTDOCTORAL and PhD POSITION in SOLID STATE THEORY (Magneto-electronics)

IFF, Forschungszentrum Jülich, Germany

Magneto-electronics develops rapidly to a new field in solid state physics with future perspective in information technology: e.g. (i) novel storage concepts such as non-volatile memories based on the tunneling of spin-polarized electrons from ferromagnets through an oxide barrier or, (ii) the development of a spin-transistor based on metal-semiconductor junctions which use in addition to the transport of charge also the information of the spin of an electron to develop more complex active elements.

Magneto-electronics is a field where electronic structure, magnetism, atomic structure, correlation effects and transport properties of magnetic metal/semiconductor and magnetic metal/oxide junctions meet in applications. Those junctions are largely unexplored.

In this context we invite applications for two research positions:

1. a postdoctoral position for one year, renewable upon mutual agreement for two years
2. a PhD position for three years.

The salaries will be based on

1. BAT IIa, annual net income is about 40-45 kDM, depending on age and social status
2. BAT IIa/2 annual net income about 22 kDM.

Both positions are devoted to the field of electronic structure theory of magnet/semiconductor and magnet/oxide junctions relevant for magneto-electronics. The work includes ab-initio calculations of the electronic structure, magnetism, the atomic structure and the relation to the spin-polarization of the electrons in these junctions, the development of a screened exchange LDA formulation to describe the oxide and semiconducting materials, the description of the complex band structure and the transmission matrix elements, which enter the formulation of the transport properties of electrons.

The work will be carried out, and the methodological developments will be made with our recently developed bulk and film FLAPW code: FLEUR. The work will benefit from a strong interaction with a broad range of experimentalists at the Forschungszentrum Jülich and there is an active exchange program with other groups outside of Germany.

The Institut für Festkörperforschung (IFF) has access to outstanding computational facilities (CRAY J90, T90, and two 512 processor T3Es) and provides an excellent basic-research atmosphere. Due to the discoveries of Prof. Grünberg, Jülich is the birthplace of magneto-electronics and is one of leading institutions in the world in the area related to this work. It is located close to two old cities (Köln and Aachen) which have a rich cultural and student life.

Interested candidates should immediately send a curriculum vitae, a list of publications or current research activities, and should arrange for 1-2 reference letters to be sent directly to:

Dr. Stefan Blügel
IFF
Forschungszentrum Jülich
D-52425 Jülich
Germany

or via email to: s.bluegel@fz-juelich.de

Additional information are availlable at the webpage:
`http://www.fz-juelich.de/iff/personen/S.Bluegel/`

Postdoctoral Positions in Solid State Theory Group

National Renewable Energy Laboratory

http://www.sst.nrel.gov

The Solid State Theory Group at the National Renewable Energy Laboratory invites applications for a postdoctoral research positions to start immediately. The position is for two years, renewable upon mutual agreement to a third year, and is specifically in the area of first-principles theory of defects in semiconductors and insulators. Details of this project are described in http://www.sst.nrel.gov/funding/doping.html. The starting salary is US$ 42-52 K/year depending on qualification. The Solid State Theory Group currently consists of ten Ph.D.'s in condensed matter theory and interacts with a broad range of experimentalists at NREL. The group has outstanding computational facilities, an excellent basic-research atmosphere, and is located near the beautiful Rocky Mountains. For more information about the group research activities, publications and personnel, see http://www.sst.nrel.gov. Interested candidates should immediately send a curriculum vitae, list of publications and should arrange for 2-3 reference letters to be sent directly to:

Dr. Su-Huai Wei
Solid State Theory Group
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado, 80401
swei@nrel.gov

NREL is an equal opportunity/affirmative action employer.

Postdoctoral Positions
MIT, Cambridge, MA, USA
Department of Chemical Engineering

Wanted: A Post-Doc with experience in plane-wave based first-principles methods to work on systems of both scientific and industrial interest. Applications include catalytic systems, such as zeolites and transition metal catalysts and aqueous systems, including solvated species, order-disorder transitions, and systems of relevance to energy needs. A major focus is on applications with environmental emphasis. Most of this work is done in collaboration with experimentalists.

The salary will depend on level of experience, and the starting date is negotiable.

Please send a CV with contact information of references to:

Bernhardt Trout
trout@mit.edu
77 Massachusetts Avenue, 66-556
Cambridge, MA 02139
USA

Appointment as Scientific Collaborator
Department of Physics, University of Antwerp, Belgium

A vacancy exists from January 1, 2000 at the Department of Physics, University of Antwerp, for a scientific collaborator to work with Profs. V.E. Van Doren and N.H. March on the exchange-correlation potential in density functional theory (DFT) via density matrices.

Interested workers may contact Prof. V.E. Van Doren at any time for further details. A good Bachelor's degree in Physical Sciences or Materials is required, supplemented by high performance in Mathematics or a specialist branch of Theoretical Science. Some knowledge of electronic computation would be an advantage. Application of DFT in (a) simple atoms Be and Ne (b) metal surfaces and (c) low-dimensional systems like graphite and BN, as well as helical systems, is planned.

The appointment would be for a period of two years in the first instance, but the possibility of ongoing support exists (e.g. for applicants who would desire to submit a Doctorate as a result of their research at the University of Antwerp).

The annual salary would be about 670.000 BEF after taxes (about US$ 16,800).

Candidates should send a curriculum vitae to:

V.E. Van Doren
Department of Physics
University of Antwerp (RUCA)
Groenenborgerlaan 171
B-2020 Antwerpen, Belgium

Ph. D. Position in Condensed Matter Theory

Max-Planck-Institut für Mikrostrukturphysik
Halle (Saale), Germany

A Ph. D. position is available in the theory department of the Max-Planck-Institut für Mikrostrukturphysik in Halle (Saale), Germany, for up to three years.

The successful candidate is expected to work on the theory of scanning tunneling microscopy of magnetic systems. A diploma degree (or equivalent) as well as a strong background in solid state theory are required for this position. Knowledge of multiple-scattering theory and experiences in computer programming (C++) would be advantageous.

Candidates should send their application including a curriculum vitae, copies of examination certificates and names of two referees to Dr. Jürgen Henk, Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D–06120 Halle (Saale). For further information please mail to henk@mpi-halle.de or visit our WWW-page http://www.mpi-halle.de. Applications from women, minorities, and disabled persons are encouraged.

Ph. D. Student in Condensed Matter Theory

Max-Planck-Institute of Microstructure Physics at Halle, Germany

The Max-Planck-Institute of Microstructure Physics at Halle, Germany, has a position for a **Ph. D. student in Condensed Matter Theory** available for up to three years. The candidate for this position will develop an electronic theory of **Femtosecond Dynamics** in metallic nanoparticles using non-perturbative methods. The theory envisages the ultrafast laser control of nano-optics, which has recently started to attract a lot of interest from both the scientific as well as the technological points of view. A diploma (or equivalent M.A.) degree as well as a strong background in solid state theory and/or optical control formalisms is required for this position. Applications from women, minorities, and disabled persons are encouraged.

Candidates for the position, which is open to all nationalities, should send their application including a CV and the names of two references to:

Dr. W. Hübner,
Max-Planck-Institut für Mikrostrukturphysik Halle,
Weinberg 2, D – 06120 Halle, Germany
Fax: +49-345-5511 223,
email:huebner@mpi-halle.de

Postdoctoral Position in the Chemistry Department, UCLA

Los Angeles, CA

At least one postdoctoral position will be available in the research group of Professor Emily A. Carter in the Chemistry Department at UCLA, commencing January 2000 or before. In addition to applications research on materials science problems (e.g., ion diffusion and phase transitions in bulk ceramics, metal-ceramic and ceramic-ceramic interface adhesion, and oxidation and embrittlement of metals), the ideal candidate would be interested in and capable of continuing recent development work on embedding methods (a local CI or MP treatment embedded in periodic DFT - c.f. N. Govind, Y. A. Wang, and E. A. Carter., J. Chem. Phys., 110, 7677 (1999)), ab initio molecular dynamics (c.f. M. R. Radeke and E. A. Carter, Ann. Rev. Phys. Chem., 48, 243 (1997)), and/or a newly funded collaborative project on bridging length scales from the atomistic to the microstructural. The ideal candidate would be either a physicist or a physical chemist with superior skills in applied mathematics and programming, as well as knowledge of solid state physics, density functional theory, and/or configuration interaction theory. For further information about the Carter group, go to http://www.chem.ucla.edu/carter/. The salary will be at least US$29K/yr for the first year (depending on level of experience). Medical, dental, and vision benefits are provided. Interested parties should send a curriculum vitae and arrange to have three letters of recommendation sent to:

Prof. Emily A. Carter,
Dept. of Chemistry and Biochemistry,
Box 951569, UCLA, Los Angeles, CA 90095-1569 USA

Inquiries may also be sent to: eac@chem.ucla.edu.

Faculty Position in Computational Materials Science
Department of Materials Science and Engineering
University of Virginia

Applications are solicited for a tenure-track faculty position at the assistant professor level in the field of computational materials science. Candidates in all areas of computational materials science will be considered. They should demonstrate the potential for excellence in teaching at both the graduate and undergraduate levels and for establishing an outstanding program of sponsored research. Applications from women and minority candidates are strongly encouraged.

Qualified candidates should send a letter of application with a detailed curriculum vitae, statement of research plans and teaching interests, and contact information for four or more references to:

Professor William C. Johnson
Department of Materials Science and Engineering
University of Virginia
Charlottesville, VA 22903-2442
e-mail: wcj2c@virginia.edu

TWO POSITIONS IN GROUP FOR THEORETICAL SOLID STATE PHYSICS

Institute for Solid State and Materials Research (IFW), Dresden

http://www.ifw-dresden.de

The Group for Theoretical Solid State Physics at the Institute for Solid State and Materials Research Dresden invites appliations for two research positions:

1. a postdoctoral position for one year, renewable upon mutual agreement for a second year and
2. a PhD position for three years.

Both positions are devoted to the field of electronic structure theory. In particular, the following topics are addressed in the project:
- interpretation of spectroscopic data on metals and compounds;
- intrinsic properties of highly anisotropic magnetic materials;
- valence stability of rare earth compounds.

The project will be carried out in close collaboration with experimental groups at IFW, University of Technology Dresden, and Max-Planck-Institute for Chemical Physics of Solids. Salaries will be based on BAT IIa (position (i), annual net income about 34-40 kDM, depending on age and social status) and BAT IIa/2 (position (ii), annual net income about 20 kDM).

The Group for Theoretical Solid State Physics consists of twelve PhD's in solid state theory, six PhD students, and several guest scientists. The group has up-to-date computer facilities, daily coffee meetings, and a lively exchange with a number of other groups inside and outside of Dresden (theoretical and experimental, physics and chemistry).

The city of Dresden is situated mid-way between Berlin and Prague, in the valley of river Elbe. With a population of about 500,000, it is known for a rich cultural live and for its baroque silhouette.

Interested candidates should send a curriculum vitae, a list of publications or current research activities, and 1-2 reference letters to:

Prof. Dr. Helmut Eschrig
Institute for Solid State and Materials Research
P.O. box 270 016
D-01171 Dresden
Germany

7 Abstracts

Magnetic behavior of thin Cr layers sandwiched by Fe

A. B. Klautau[11], S. B. Legoas[1], R. B. Muniz[2] and S. Frota-Pessôa[1]
[1] *Instituto de Física, Universidade de São Paulo,*
Caixa Postal 66318, 05315-970 São Paulo, SP, Brazil
[2] *Departamento de Física, Universidade Federal Fluminense, Niteroi, RJ, Brazil*

Abstract

The magnetic behavior of thin layers of Cr in Fe/Cr/Fe(001) trilayers and superlattices is studied using the first principles self-consistent RS-LMTO-ASA (Real Space - Linear Muffin-tin Orbital - Atomic Sphere Approximation) method. The effects of lattice compression and interface mixing are investigated, and it is shown that they can cause large reductions of the Cr magnetic moments.

(Phys. Rev. B, accepted)
Manuscripts available from: aklautau@usp.br

Chiral Magnetic Domain Structures in Ultrathin FePd Films

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Gerrit van der Laan[1], M. Belakhovsky[4], C. Mocuta[4], A. Marty[4],
Y. Samson[4]
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Daresbury Laboratory, Warrington WA4 4AD, UK
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[3] *University of Amsterdam, Valckenierstraat 65, NL 1018 XE Amsterdam, Netherlands*
[4] *CEA-Grenoble, Service de Physique des Matériaux et Microstructures,*
17 rue des Martyrs, 38054 Grenoble cedex 9, France

Abstract

The magnetization profile of magnetically ordered patterns in ultrathin films was determined by circular dichroism in x-ray resonant magnetic scattering (CDXRMS). When this technique was applied to single crystalline iron palladium alloy layers, magnetic flux closure domains were found whose thickness can constitute a large fraction (∼25 percent) of the total film.

(SCIENCE 284, 2166 - 2168 (1999))
Reprints available from: g.vanderlaan@dl.ac.uk

Understanding the valency of rare earths from first-principles theory

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Institute of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus C, Denmark
W.M. Temmerman and Z. Szotek
Daresbury Laboratory, Daresbury, Warrington WA4 4AD, United Kingdom
H. Winter
INFP,Forschungszentrum Karlsruhe GmbH, Postfach 3640, D-76021 Karlsruhe, Germany

Abstract

The rare-earth metals have high magnetic moments and a diverse range of magnetic structures. Their magnetic properties are determined by the occupancy of the strongly localized $4f$ electronic shells, while the outer $s-d$ electrons determine the bonding and other electronic properties. Most of the rare earth atoms are divalent, but generally become trivalent in the metallic state. In some materials, the energy difference between these valence states is small and, by changing some external parameters (such as pressure), a transition from one to the other occurs. But the mechanism underlying this transition and the reason for the differing valence states are not well understood. Here we report first-principles electronic-structure calculations that enable us to determine both the valency and the lattice size as a function of atomic number, and hence understand the valence transitions. We find that there are two types of f electrons: localized core-like f electrons that determine the valency, and delocalized band-like f electrons that are formed through hybridization with $s-d$ bands and which participate in bonding. The latter are found only in the trivalent systems; if their number exceeds a certain threshold, it becomes energetically favourable for these electrons to localize, causing a transition to a divalent ground state.

(Nature **399**, 756 (1999))
Reprints available from: P.Strange@phys.keele.ac.uk

Electronic Configuration of Yb Compounds

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Box 530, 75121 Uppsala, Sweden
[6]*Center of Materials Science and Theoretical Division, Los Alamos National Laboratory,*
Los Alamos, New Mexico 87544

Abstract

We study for Yb and a number of its compounds the lattice constant and the total energy difference between their so-called divalent and trivalent states. In particular, we want to verify if band theory can describe the valency changes that occur as a function of ligand and pressure in these Yb compounds. Two different band theoretical approaches, which differ in the treatment of the localized f states, are used in this study. The first approach calculates the energy difference of trivalent and divalent Yb compounds by combining a band structure approach for the *spd* electrons with experimental atomic data for the f electrons. The second approach calculates the energy difference for the scenarios with 13 and 14 localized f electrons using self-interaction corrections. By combining the results of these two theories, we find that in all trivalent Yb monopnictides the energy difference between their trivalent and the hypothetical divalent state is nothing else than the energy to localize an f electron. For divalent Yb chalcogenides our study shows that the pressure induced delocalization of an f electron does not imply a change of valency to trivalent, but rather implies an intermediate valency.

(Submitted to Phys. Rev. Lett.)
Manuscripts available from: svane@ifa.au.dk

Theoretical study of the (3×2) reconstruction of β-SiC(001)

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A. Catellani
CNR-MASPEC, Parma, Italy
G. Galli and F. Gygi
LLNL, Livermore, USA
A. Baratoff
Department of Physics and Astronomy, Basel University, Switzerland

Abstract

By means of *ab initio* molecular dynamics and band structure calculations, as well as using calculated STM images, we have singled out one structural model for the (3×2) reconstruction of the Si-terminated (001) surface of cubic SiC, amongst several proposed in the literature. This is an alternate dimer-row model, with an excess Si coverage of $\frac{1}{3}$, yielding STM images in good accord with recent measurements [F.Semond et al. Phys. Rev. Lett. **77**, 2013 (1996)].

(Submitted to Phys. Rev. B, Rapid Comm.)
Postscript file available from http://xxx.lanl.gov/ps/cond-mat/9906380

STM TUNNELING INTO A SINGLE MAGNETIC ATOM: A NON PERTURBATIVE AB-INITIO CALCULATION

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Avenida del Libertador 8250, 1429 Buenos Aires, Argentina

Abstract

We report a non perturbative ab-initio calculation of the tunneling current between a Co adatom on Au(111) and a Au tip. This was performed by obtaining first the band structure of a model periodic system and after that the conductivity using linear response theory. A strong decay of the current with probe-tip separation is observed, as in the experiments. In the tunneling regime we find that the current is mostly due to s electrons. The more localized d electrons from the Co atom, that contribute with a large density of states at the Fermi energy, have a negative effect on the conductivity. They give rise to its decrease due both to direct and indirect interactions (hybridization and spin-orbit terms respectively).

(Submitted to Phys. Rev. B)

Manuscripts available from: weissman@cnea.gov.ar

First-Principles Calculations of the Self-Interstitial Cluster I_4 in Si

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Department of Material Physics, Osaka National Research Institute,
Agency of Industrial Science and Technology,
1-8-31, Midorigaoka, Ikeda, Osaka 563-8577, Japan
S. Takeda
Department of Physics, Graduate School of Science, Osaka University, 1-16,
Machikane-yama, Toyonaka, Osaka 560-0043, Japan

Abstract

The I_4 cluster model, which is recently proposed as primaly self-interstitial clustering in Si (N. Arai *et al.*, Phys. Rev. Lett. **78**, 4265 (1997)), has been examined using the *ab initio* pseudopotential method based on the local density-functional theory. All the bonds are well reconstructed with enough bond charge and relatively small bond distortions. The formation energy per self-interstitial is 1.5 eV. This value is less than one half of that of isolated self-interstitials, although this is fairly larger than that of extended self-interstitial agglomerates such as {113} planar defects. The I_4 cluster has no electronic states inside the minimum band gap, which is consistent with no previous experimental identification. The present results quantitatively support the possible existence of the I_4 clusters as primary clusters or embryos of extended agglomerates.

(To appear in Phys. Rev. B)
Manuscripts available from: kohyama@onri.go.jp

Tensile strength and fracture of a tilt grain boundary in cubic SiC: a first-principles study

Masanori Kohyama
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Agency of Industrial Science and Technology,
1-8-31, Midorigaoka, Ikeda, Osaka 563-8577, Japan

Abstract

The *ab initio* tensile test has been applied to the non-polar interface of the $\{122\}\Sigma=9$ tilt boundary in cubic SiC, where the tensile strength and mechanical behaviour at zero temperature are examined using the *ab initio* pseudopotential method based on the local density-functional theory. This interface is strong because of the reconstruction of interfacial bonds. The maximum tensile stress in the unaxial extension normal to the interface is about 42 GPa, which is about 80% of the theoretical and experimental values of the strength of bulk crystal along the $\langle 111\rangle$ direction. The Young's modulus and the fracture toughness are also comparable to the values of bulk crystal. The back Si–C bond of the interfacial C–C bond is broken first because the C–C bond has large strength and short bond length like a diamond bond. Then the interfacial Si–C bonds are broken, and the Si–Si bond is broken. The Si–C bonds are rapidly stretched and broken if the bond stretching once exceeds about 20%, and the bond charge clearly disappears when the bond stretching exceeds about 30%. The changes in the electronic structure associated with the bond breaking are analysed.

(To appear in Phil. Mag. Lett.)
Manuscripts available from: kohyama@onri.go.jp

Perturbative approach to orbital magnetism in density-functional theory

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Instituto de Física de São Carlos, Universidade de São Paulo
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and
Institut für Theoretische Physik, Universität Würzburg
Am Hubland, D-97074 Würzburg, Germany

Abstract

It is shown how to calculate the total energy, the single-particle energies, and the current density of an interacting current-carrying many-body system, from solutions of the Kohn-Sham equation of conventional density-functional theory. On the conceptual side, this procedure, which applies both in the presence and absence of external magnetic fields, sheds light on the role of orbital magnetism in density-functional theory and the interrelation of conventional and current-density functional theory. On the practical side it provides a computationally simple many-body approach to the interplay of orbital magnetism and electron-electron interactions in atoms, molecules, and solids

(Physical Review A, accepted as a Rapid Communication)
Manuscripts available from: capelle@if.sc.usp.br

Theory of Relativistic Effects in Superconductors

M. Marques (1), K. Capelle (1,2) and E.K.U. Gross (1)
(1) Institut für Theoretische Physik, Universität Würzburg
Am Hubland, D-97074 Würzburg, Germany
(2) Instituto de Física de São Carlos, Universidade de São Paulo
Caixa Postal 369, 13560-970 São Carlos, SP, Brazil

Abstract

We develop a relativistic generalization of the Bogoliubov-de Gennes equations where the particle and hole amplitudes are Dirac spinors. In the weakly relativistic limit we find, besides the usual spin-orbit, Darwin and kinetic energy corrections, additional 'spin-orbit' and 'Darwin' terms. These new terms are present in superconductors only and involve the pairing field in place of the electrostatic potential. They become relevant for superconductors such as the heavy-fermions and high-T_c compounds, which are characterized by a short coherence lenght and heavy elements in the lattice.

(Physica C, accepted)
Manuscripts available from: marques@physik.uni-wuerzburg.de

Search for Antiferromagnetism in Homogeneous Electron Systems

K. Capelle and L.N. Oliveira
Instituto de Física de São Carlos, Universidade de São Paulo
Caixa Postal 369, 13560-970 São Carlos, SP, Brazil

Abstract

We present numerical and analytical evidence for the absence of a second-order phase transition of homogeneous electron systems into an antiferromagnetic state. Our results are based on numerical data extending from the extreme high-density regime ($r_s \to 0$) to the extreme low-density regime ($r_s = 100$). The particle-particle interaction is treated within the random-phase approximation, augmented by various types of local-field corrections. The latter turn out to be crucial for a correct description of the screening of spin-density waves. Our results indicate the absence of a second-order transition of the three-dimensional homogeneous electron gas, the two-dimensional homogeneous electron gas, and laterally homogeneous electron layers, into a collinear antiferromagnetic state.

(European Physical Journal B, accepted)
Manuscripts available from: capelle@if.sc.usp.br

Novel Density-Functional Approach to Non-Collinear Spin-Density Waves

K. Capelle and L.N. Oliveira
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Caixa Postal 369, 13560-970 São Carlos, SP, Brazil

Abstract

We propose a new density-functional approach to antiferromagnetism and non-collinear spin-density waves. Antiferromagnetic correlations and non-collinear spin configurations are incorporated via a staggered density, which enters the formalism on the same footing as the particle density. We establish the pertinent generalization of the Hohenberg-Kohn theorem, derive the associated Kohn-Sham equations, outline the construction of several approximations for the corresponding exchange and correlation functional, discuss the relation of the present method to other density-functional approaches, and report a first application to a simple model system.

(To be submitted) Manuscripts available from: capelle@if.sc.usp.br

Magnetic behavior of thin Cr layers sandwiched by Fe

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05315-970 São Paulo, SP, Brazil
R. B. Muniz
Departamento de Física, Universidade Federal Fluminense, Niteroi, RJ, Brazil

Abstract

The magnetic behavior of thin layers of Cr in Fe/Cr/Fe(001) trilayers and superlattices is studied using the first principles self-consistent RS-LMTO-ASA (Real Space - Linear Muffin-tin Orbital - Atomic Sphere Approximation) method. The effects of lattice compression and interface mixing are investigated, and it is shown that they can cause large reductions of the Cr magnetic moments.

(Accepted to Phys. Rev. B)
Manuscripts available from: aklautau@usp.br

Phonon- versus electron-mediated surface reactions: Femtosecond laser-induced desorption and oxidation of CO on Ru(0001)

Mischa Bonn, Stephan Funk, Christian Hess, Daniel N. Denzler, Catherine Stampfl*,
Matthias Scheffler, Martin Wolf, and Gerhard Ertl
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6,
D-14195 Berlin-Dahlem, Germany
*Present address: *Department of Physics and Astronomy, Northwestern*
University, 2145 Sheridan Road, Evanston, Illinois, 60208-3112

Abstract

Heating of a Ruthenium surface on which carbon monoxide and atomic oxygen are co-adsorbed leads exclusively to desorption of CO. Yet excitation with femtosecond infrared laser pulses enables also the formation of CO_2. While the desorption is caused by coupling of the adsorbate to the phonon bath of the Ru substrate, the oxidation reaction is initiated by hot substrate electrons, as is evident from the observed sub-picosecond reaction dynamics and from density functional calculations. The presence of this laser-induced novel reaction pathway allows us to elucidate the microscopic mechanism and the dynamics of the CO oxidation reaction.

Science (to be published).
Contact person: bonn@fhi-berlin.mpg.de

Density-functional theory study of the catalytic oxidation of CO over transition metal surfaces

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Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6,
D-14195 Berlin-Dahlem, Germany
*Present address: *Department of Physics and Astronomy, Northwestern*
University, 2145 Sheridan Road, Evanston, Illinois, 60208-3112

Abstract

In recent years due to improvements in calculation methods and increased computer power, it has become possible to perform first-principles investigations for "simple" chemical reactions at surfaces. We have carried out such studies for the catalytic oxidation of CO at transition metal surfaces, in particular, at the ruthenium surface for which unusual behavior compared to other transition metal catalysts has been reported. High gas pressure catalytic reactor experiments have revealed that the reaction rate over Ru for oxidizing conditions is the highest of the transition metals considered – in contrast, under ultra high vacuum conditions, the rate is by far the lowest. We find that important for understanding the pressure dependence of the reaction is the fact that Ru (0001) can support high concentrations of oxygen at the surface. Under these conditions, the O-metal bond is atypically weak compared to that at lower coverages. We have investigated a number of possible reaction pathways for CO oxidation for the conditions of high oxygen coverages, including scattering reactions of *gas-phase* CO at the oxygen covered surface (Eley-Rideal mechanism) as well as the Langmuir-Hinshelwood mechanism involving reaction between *adsorbed* CO molecules and O atoms.

cond-mat/9905341, Surf. Sci. (to be published).
Contact person: stampflc@fhi-berlin.mpg.de

Theory of adsorption on metal substrates

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Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6,
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University, 2145 Sheridan Road, Evanston, Illinois, 60208-3112

Contents

In *Handbook of Surface Science, Vol. 2: Electronic structure of metal surfaces*, edited by K. Horn and M. Scheffler (Elsevier, Amsterdam, 1999).

Contact person: scheffler@fhi-berlin.mpg.de

A Novel STM Imaging Mechanism Used to Resolve the Atomic Structure of the As-Rich GaAs(001)-(2×4) Surface

V. P. LaBella, H. Yang, D. W. Bullock, and P. M. Thibado
The University of Arkansas, Department of Physics, Fayetteville, AR 72701
Peter Kratzer and Matthias Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6,
D-14195 Berlin-Dahlem, Germany

Abstract

The atomic arrangement of the technologically important GaAs(001)-(2×4) reconstructed surface is determined using scanning tunneling microscopy (STM) and first-principles, electronic structure calculations. The bias-dependent STM images reveal the relative position and depth of atomic-scale features within the trenches between the top layer As dimers, which are in agreement with the $\beta2(2\times4)$ structural model. The bias-dependent simulated STM images reveal that a retraction of the top most dangling bond orbitals is the unique mechanism that enables the STM tip to image the trench structure.

(submitted to: Phys. Rev. Lett.)

Direct Exchange and Interaction of 3d impurities on the (001) Surface of Iron

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Department of Physics, Florida Atlantic University, Boca Raton, Florida 33431, USA
H. Dreyssé
Institut de Physique et Chimie des Matériaux de Strasbourg, BP 20 CR 67037, France

Abstract

We present a detailed ab-initio study of direct exchange and interaction processes of 3d atoms on the Fe(001) surface. The calculations are based on local density functional theory and apply a KKR-Green's function method for impurities on surfaces. For practically all 3d transition metal impurities on Fe(001) we find a strong tendency for a direct exchange mechanism into the first surface layer. The early 3d impurities V, Cr and Mn strongly repel each other on neighboring positions within the first layer, while Ni and Cu atoms show a moderate repulsion. The ab-initio results are in good agreement with STM studies for Cr/Fe(001) by the NIST group and present valuable predictions for all 3d/Fe(001) systems.

(J. Magn. Magn Mater. **198-199** (1999) 548-550)

The work has benefited from collaborations within the TMR-Network 'Interface Magnetism' (Contract No. EMRX-CT96-0089)

Interface reflectivity of magnetic layers in Cu: effects of adlayers

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D-52425 Jülich, Germany
A. Rampe, G. Guentherodt
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Abstract

We study the reflection and transmission of a spacer Bloch-wave at a magnetic layer of finite thickness. The layer has a composite structure obtained by attaching an adlayer to the magnetic layer. The emphasis of this paper will lay on the change of the reflectivity induced by the adlayer. In particular, we calculate the reflection coefficients for (001) layers of Fe, Co and Ni in Cu as well as such layers with one or more admonolayers of 3d elements. The calculations are performed by the KKR-Green's function method for layered systems. We discuss in detail the relation between the $q_{\|}$-dependent density of states of the composite magnetic layer and the reflectivity. We show that the reflectivity of a magnetic layer in Cu can change considerably due to the introduction of adlayers.

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Unusual magnetic behavior in imperfect 4d and 5d clusters on the Ag (001) surface

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Abstract

Small mixed 4d and 5d clusters on Ag (001) are investigated by means of the KKR Green's function method. It is shown that the mixture of pure transition metal clusters with substrate atoms or the creation of defects in the cluster leads to an unexpected enhancement of the magnetic moments. The results are discussed in the framework of a tight binding model.

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First-principles calculations for vacancy formation energies in Cu and Al; non-local effect beyond the LSDA and lattice distortion

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Abstract

We show ab initio calculations for vacancy formation energies in Cu and Al. The calculations are based on density-functional theory and the full-potential Korringa-Kohn-Rostoker Green's function method for impurities. The non-local effect beyond the local-spin-density approximation (LSDA) for density-functional theory is taken into account within the generalized-gradient approximation (GGA) of Perdew and Wang. The lattice relaxation around a vacancy is also investigated using calculated Hellmann-Feynman forces exerted on atoms in the vicinity of a vacancy. We show that the GGA calculations reproduce very well the experimental values of vacancy formation energies and bulk properties of Cu and Al, as they correct the deficiency of LSDA results (underestimation of equilibrium lattice parameters, overestimation of bulk moduli, and vacancy formation energies). It is also shown that the GGA calculations reduce the LSDA results for the lattice relaxation energy for a vacancy in Cu.

(Comput. Mater. Science **14** (1999) 56-61)

Unusual magnetic behavior in imperfect 4d and 5d clusters on the Ag (001) surface

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Abstract

Ab initio calculations are presented for magnetic properties of small islands of 3d, 4d, and 5d adatoms on the Ag(001) surface, intermixed with Ag substrate atoms. We show that the intermixing of small 4d and 5d clusters can lead to an unexpected enhancement of the local moments and is very different from the intermixing behavior found in the monolayer regime.

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Full Potential KKR-calculations for Metals and Semiconductors

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Abstract

We present systematic total energy calculations for metals (Al, Fe, Ni, Cu, Rh, Pd, Ag) and semiconductors (C, Si, Ge, GaAs, InSb, ZnSe, CdTe), based on the all-electron full-potential (FP) Korringa-Kohn-Rostoker (KKR) Green's function (GF) method, using density functional theory. We show that the calculated lattice parameters and bulk moduli are in an excellent agreement with calculated results obtained by other FP methods, in particular the full potential LAPW method. We also investigate the difference between the local-spin-density approximation (LSDA) and the generalized-gradient approximation (GGA) of Perdew and Wang (PW91), and find that the GGA corrects the deficiencies of LSDA for metals, *i.e.* the underestimation of equilibrium lattice parameters and the overestimation of bulk moduli. On the other hand, for semiconductors the GGA gives no significant improvement over the LSDA. We also discuss that a perturbative GGA treatment based on FP-LSDA spin-densities gives very accurate total energies. Further we demonstrate that the accuracy of structural properties obtained by FP-LSDA and FP-GGA calculations can also be achieved in the calculations with spherical potentials, provided that the full spin-densities are calculated and all Coulomb and exchange integrals over the Wigner-Seitz cell, occuring in the double-counting contributions of the total energy, are correctly evaluated.

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A Parallelized Ab Initio Molecular Dynamics Code for the Investigation of Atomistic Growth Processes

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Abstract

We developed a parallelized *ab initio* molecular dynamics code for the investigation of materials properties and processes based on the local density approximation to the density functional theory, using separable, norm-conserving pseudo-potentials and a plane-wave representation of the wave functions. We briefly describe the methodological formulation of the many-body potential of interacting atoms generated by a quantum mechanical treatment of the valence electrons and discuss the parallelization strategies and speed-ups. Two different parallelization strategies are discussed. It is shown, that distributing the wave-function representations in real and reciprocal space to computing nodes leads to a flexible approach where many computing nodes can be efficiently used in parallel. We found that the degree of parallelization of the program is 99.5% which permits very efficient calculations on 128 computing nodes for unit cells containing up to 400 atoms. As a physical application we present results of calculations of reaction rates of ad-atoms on As-terminated Si(111).

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An Ab-Initio Study of Acceptor-Donor Complexes in Silicon and Germanium

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Abstract

The electronic and geometrical structures, in particular the electric field gradients (EFGs), of $[\mathrm{CdD}]^-$ (D=P, As, Sb) acceptor-donor pairs in Si and Ge are studied using the full potential Korringa-Kohn-Rostoker Green's function method. It is shown that the EFG of Cd depends very sensitively on the large lattice relaxations induced by the pair complex and can be understood by a simple hybridisation model. It is demonstrated that due to a reloading of a deep level also neutral pairs $[\mathrm{CdD}]^0$ in silicon exist, exhibiting a change of the Cd EFG being almost independent of the donor type. In addition, also trimer complexes $[\mathrm{CdD}_2]^0$ are investigated. In general, our calculations are in good agreement with the available experimental information and provide a consistent picture of the behavior of acceptor-donor complexes in Si and Ge.

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In-Donor Complexes in Si and Ge: Structure and Electric Field Gradients

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Abstract

The electronic and geometrical structure of neutral InD (D=P, As, Sb) acceptor-donor pairs in silicon and germanium is studied using two complementary ab-initio methods, i.e. the all-electron Korringa-Kohn-Rostoker (KKR) Green's function method and the pseudopotential ab-initio molecular dynamics method. Furthermore the electric field gradients are predicted at the In sites, which can be measured by PAC experiments using the ^{119}In probe. The results for the InD pairs are compared with the geometrical structures and in particular with the electric field gradients of the isoelectronic $[\mathrm{CdD}]^-$ complexes in silicon and germanium. The lattice relaxations calculated by both theoretical methods for the InD complexes agree quite well and are similar to the relaxations for the $[\mathrm{CdD}]^-$ complexes, which have been studied extensively in PAC experiments using the ^{111}In/^{111}Cd probe. In contrast to this the calculated In electric field gradients are, however, considerably larger than the Cd ones.

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Magnetic spin origin of the charge-ordered phase in manganites

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Abstract

We argue that the charge ordering observed in 50% doped manganites is a manifestation of the peculiar antiferromagnetic spin ordering. The latter, combined with the large Hund's rule physics in manganites, divides the whole system into the quasi-one-dimensional zig-zag objects, which exhibit a very unique electronic structure and behave as band insulators. This results in a strong anisotropy of short-range double-exchange interactions, which is responsible for the local stability of the antiferromagnetic state.

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8 SCIENTIFIC HIGHLIGHT OF THE MONTH

Industrial Use of Electronic Structure Methods

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8.1 Introduction

It is exciting and satisfying to see that electronic structure methods are becoming an integral part of industrial research. In addition to the intrinsic scientific and intellectual values, this methodology is now creating direct economic benefits. The vision of the founders of computational materials science developed earlier in this century is thus becoming a reality. Of course, such a development occurs gradually and it is probably hard to determine when the industrial acceptance of electronic structure methods actually started. In fact, the chemical and pharmaceutical companies were probably first to employ molecular orbital calculations to help in solving problems of molecular structures and chemical reactivity. Today all major chemical companies in Europe, the US, and Japan are using quantum chemical methods in their daily work.

Except for companies with a long tradition in fundamental research such as Bell Labs, IBM and NEC, the majority of materials science related industries, most notably the microelectronics companies such as Intel, Motorola, and Infineon (Siemens) have started only recently to use electronic structure methods. This applies also to diversified companies and catalyst manufacturers. Hence it is timely to discuss highlights from the use of electronic structure methods in the area of industrial materials science. In trying to do so, however, one is confronted with the problem of confidentiality. Often, important industrial discoveries and inventions become generally known in the form of patents and publications only years after they were made or they are kept as trade secrets and are never publicly disclosed. The authors of this contribution in their work in the private industry are confronted with this problem daily. Therefore, the following discussions and illustrative examples are perhaps in some cases more vague then the reader would like. The authors apologise for this in advance!

Reflecting the major research efforts within the Psi-k Network, the focus of this article is on inorganic solid state materials. Within this field, the following sections present a selection of recent industrial cases where electronic structure methods have been used.

8.2 Improvement of Iron Oxide Catalyst

The use of electronic structure methods in heterogeneous catalysis immediately triggers the thought that the main problem is related to surface reactivity. One thinks of surface structures and surface reactions, of adsorption and dissociation pathways, and the associated energy hypersurface with its local minima, energy barriers, and transition states. Once this information is known, one might conclude, then the problem of catalyst design is essentially solved. In practice, this line of reasoning is flawed in several ways. First, the surface of a real catalyst is not a property which can be determined from knowing just the chemical composition. It depends on the history of the preparation of the catalyst and the conditions within the chemical process including all changes in feedstock and operating variables. Second, even if one could determine the surface structure in each stage (a combination of advanced experimental methods including high-resolution transmission electron microscopy, x-ray photoemission spectroscopy, scanning tunnelling microscopy, and Raman spectroscopy might allow that in principle) and if one had a complete chemical inventory of reactants, intermediates, and products, there would be such a large multitude of possible reactions and intermediate steps that the shear number of systems to be considered would be overwhelming. Third, if one could narrow the number of relevant reactions to only a few, then current electronic structure methods are not accurate enough to determine the energies of an energy barrier of a transition state of a surface reaction with chemical accuracy. An error of 4 kcal/mol in the barrier height (which is not easy to achieve computationally) causes an order of magnitude error in a reaction rate! Given this situation, it is not surprising that technology managers of catalyst manufacturers are highly sceptic about the potential benefits of computational approaches. From a computational materials scientist's point of view, the above reality is challenging indeed.

Nevertheless, the situation is not as bad if one considers the alternatives. If we imagine a discussion between a sceptical technology manager of a catalyst manufacturer and a computational materials scientist eager to show the usefulness of electronic structure methods, the arguments could go as follows. The computational scientist would admit that the theoretical and computational tools are by no means perfect and ask the technology manager, what approaches and tools are currently used to improve existing catalysts or to develop new ones. The answer would be that a large number of experiments are made and evaluated based on the experience present in the companies. In other words, the approach is essentially the same as at the beginning of the century when A. Mittasch developed the catalyst for the ammonia synthesis [2]. The computational scientist would ask how many experiments would be needed and how one would decide which ones to perform first. He could also confirm that the cost of an industrial researcher and

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[2] The catalyst introduced by A. Mittasch and coworkers in 1910 is made from iron oxides and contains Al_2O_3, K_2O and CaO. It is estimated that at least 10 000 experiments, but probably many more (perhaps 70 000) were made to find and optimise this system

engineer in the European chemical industry runs at about 300 000 euros or more per year. Then the technology manager would say that in addition to a range of experimental techniques for materials characterisation there are now wonderful techniques called combinatorial chemistry and high-throughput experimentation which are being applied to catalysis. In fact, companies such as Symyx are receiving industrial contracts valued in the tens of millions of dollars to perform such work. At that point, the computational materials scientist would propose a little analysis: consider a catalyst containing only 5 elements including transition metals, rare-earth atoms, some promoters like alkali atoms, and some main-group elements like Al or Ga. If one would select a total of 12 elements as possible candidates (perhaps based on prior experience) and choose three concentrations for each element, one would end up with about 50 000 combinations. Then one would need to consider a range of possible preparation methods, for example calcination at different temperatures under reductive or oxidative conditions and one would have to test the performance of the catalysts for a range of reaction conditions (e.g. high and low temperature). One could easily end up with about one million experiments. When this is all set and done, which is clearly a major effort even with very sophisticated high-throughput synthesis and screening methods, another practical problem will have to be addressed as well, namely the degradation of the catalyst in the reactor. Thermostability is a critical factor in catalyst technology. One would probably have to address this design requirement through long-term tests once a set of promising candidates has been found. All in all, this represents a formidable task and one begins to appreciate the enormous accomplishments of scientists and technologists that have lead to the present generation of successful catalytic systems. By analysing this problem, one could also come to the conclusion that intuition and serendipity have lead to useful materials but that the majority of materials have never been synthesised or tested. Real treasures may still await their discovery!

Without developing this scenario further, it is clear that the experimental efforts to develop new catalytic systems are enormous and in today's economic conditions are simply becoming too expensive and time consuming if done in a brute-force manner. At this point, the technology manager and computational materials scientists may stop arguing with each other and bring up the real issue. We simply don't understand most of the structure, function, and degradation mechanisms of a catalyst system. Experimental screening guided by experience and vague models provides solutions, but they are very tedious to obtain and even if they work, one still does not have a good way to optimise the system in a rational manner.

Obviously, any approach is welcome that would help to rank possible candidates before any experiments are made, thereby increasing the chances for finding a good solution sooner. It is probably safe to say that computational methods, in particular *ab initio* electronic structure methods, are starting to fill that role and thus are truly valuable. In this sense, computational materials science together with experiment can make a real difference. The aim of computations is not the design of a material solely by simulations, but the goal is much more humble and realistic. Computations simply add more relevant information, they provide insight and understanding, they help in the interpretation of experimental data, assist in asserting or eliminating mechanistic hypotheses, and can help in the design of experimental training sets. With this in mind, theoretical and computational approaches are making real contributions to industrial research.

As an example, let's take iron-oxide based catalysts. These catalysts are used in the important water-gas shift reaction, which yields hydrogen from carbon monoxide and water. Another major use of iron-based catalysts is the conversion of ethylbenzene to styrene, the precursor of polystyrene. Styrene is a commodity product with an annual world consumption of more than 15 million metric tons representing a commercial value of approximately 20 billion euros. Chemical producers such as BASF, Dow and BP Amoco need to keep the production cost as low as possible in order to compete on the world market while maintaining clean and safe processes. Equipment in the chemical plant is expensive and each unit such as a reactor or separation unit needs to run as long as possible without interruption because of the links to other processes. Any down-time of a reactor is very expensive. If a catalyst manufacturer introduces a new catalyst which gives higher yields and higher selectivity, but needs to be replaced more frequently than the old catalyst, then this may be a disaster for the catalyst producers as well as their users! The introduction of a new catalyst brings another risk: the performance of a catalyst depends on its synthesis. Unless the catalyst can be manufactured with fully reproducible and predictable performance, it cannot be brought to the market. There is yet another threat lurking. If during the life time of the catalyst in the reactor toxic compounds are formed (certain metal compounds can be a serious environmental hazard), then the catalyst user or manufacturer has a nasty problem at hand concerning the safe disposal of the used catalyst.

In fact, a major producer of iron oxide catalysts was faced with the problem of replacing Cr because of environmental issues. During the life time of the catalyst material, Cr was oxidized to Cr(VI). This made the disposal of the used catalyst material very costly and the catalyst manufacturer was asked to replace Cr without altering the other properties of the system too much. Early attempts lead to a system with good catalytic properties, but the material tended to sinter much faster than the original one. This would have reduced the time in the reactor necessitating a more frequent maintenance shut-down of the reactor unit in the chemical plant. Furthermore, the synthesis needed to be better understood in order to ensure reproducible quality and performance of the catalyst. To help with these problems, the particular catalyst manufacturer decided to explore the use of computational methods.

It would have been fairly hopeless trying to simulate the sintering process directly using quantum mechanical and atomistic models. Therefore, a simpler approach was taken. It is reasonable to assume that diffusion of atoms in the bulk and at the surface combined with changes in the local chemical composition are related to sintering. Therefore, it was decided to develop a better understanding of the solubility, diffusion, possible clustering and surface segregation of Cr. The situation was complicated. These catalysts are typically prepared by dissolving metal salts in water and precipitation by alkali hydroxides. The precipitates are filtered, dried, and then calcinated. This leads to the formation of a hematite phase, Fe_2O_3 with elements such as Cr substituting some Fe atoms in the lattice. The reactor is loaded with this form and then the catalyst is activated by reduction with hydrogen to a magnetite phase,

Fe_3O_4. This phase becomes the active catalyst. Total energy calculations revealed that Cr had a tendency towards clustering and formation of super-structures, but the energy difference between the energetically most and least stable Cr distributions was quite small [1]. In contrast, some of the candidates considered for the replacement of Cr either showed tendencies for clustering in the bulk or exhibited surface segregation. By carrying out electronic structure calculations of the original Cr-containing system and possible replacements of Cr, information was gained on the changes in the charge distribution (oxidation state) of the Fe atoms surrounding the substitutional site, which allowed a ranking among possible Cr substitutes. This insight provided a screening tool for the pre-selection of possible candidates, thereby reducing the number of systems that had to be tested experimentally.

In the actual theoretical and computational studies, methods based on empirical potentials were used in conjunction with quantum mechanical methods, since a great number of cases needed to be screened. This use of theoretical and computational methodology is reducing the development time for the Cr-free catalyst and it increases the knowledge-base of the catalyst manufacturer thus benefiting other development projects as well. It was gratifying to see that at the completion of this computational study the catalyst manufacturers announced a new position for a scientist with modelling experience to join their research team.

8.3 CVD reaction mechanisms

In contrast to practical heterogeneous catalysts, which are "dirty" systems, materials for electronic devices are extremely well controlled and characterised. Therefore, microelectronic materials offer interesting possibilities for electronic structure methods. One of the key competitive advantages in the microelectronics industry comes from the rapid introduction of a new generation of microprocessors or memory chips. In practice this means that the manufacturing plant needs to become fully operational as fast as possible. The set-up of a manufacturing plant for devices such as memory chips costs approximately one billion euros. This means that every day lost in getting the production up to full capacity (i.e. achieving a yield of 80 or 90%) causes a shortfall in revenues of several million euros. In addition, markets strongly favour those companies who are able to introduce their products such as a new memory chip first. Therefore, being late in production penalises the producer even further. Needless to say that major efforts are made to shorten the time of developing and tuning the production process. Yet at the same time this industry is very conservative in setting up the production facility. Nobody wants to take high risks by using unproven technologies such as electronic structure calculations in establishing the manufacturing process.

In chemical vapour deposition (CVD), which is the predominant technology used in the production of microelectronic devices such as processors or memory chips, the key operational parameters are reactor geometry, concentrations and flow rates of reactants, and temperature profiles. These parameters need to be selected and tuned such that optimal uniformity is achieved over the entire wafer (300 mm in the new generation). Furthermore, the process conditions have to be chosen such as to ensure robustness of the process with respect to slight variations in any of the parameters. Another major concern is the control of impurities in the reactants. This is primarily the problem of the CVD gas suppliers such as Air Liquide.

For the above reasons, one needs a reliable and predictive model for the CVD processes. Traditionally, simplified reaction schemes were used and parameterised by control experiments. In many cases, this approach works sufficiently well, at least for the current generation of microelectronic devices. However, if the chemical mechanisms of the deposition process are not properly captured, the model is reliable only in the range for which it has been parameterised. This is dangerous. For this reason there is an urgent need in the microelectronics industry to have tools which can help in the determination of reaction mechanisms. To this end, quantum mechanical methods offer unique capabilities.

An illustrative example has recently been presented by M. Hierlemann from Infineon (the microelectronics company created by Siemens) [2]. In the CVD growth of Si-Ge alloys it has been observed that small amounts of Ge significantly enhance the deposition rate of Si. This is a rather surprising observation and one can easily imagine that a kinetic model would be seriously flawed if it does not properly take this effect into account. Two possible mechanisms were considered as explanation for this effect, namely (i) a collective rearrangement of the surface atoms in the presence of Ge atoms thus leading to enhanced reactivity of the surface Si atoms and (ii) a local change of the surface reactivity near the Ge atoms.

It is well known that the desorption of hydrogen is the rate determining step in the CVD growth of pure Si from dimethylchlorosilane. It is also known that the desorption of molecular hydrogen from a germanium surface has a smaller barrier than for a silicon surface. If this property of Ge is maintained also in the case of Si-Ge alloys, then this property could explain the increased growth rate of Si provided that the lateral diffusion barrier of hydrogen atoms is smaller than the desorption barrier. In this case, hydrogen atoms could diffuse from Si sites to a surface Ge atom, recombine to form molecular hydrogen and desorb. At a finite temperature this diffusion process would free more Si sites from hydrogen thus enabling the faster deposition of fresh Si atoms.

This problem was treated by researchers at Siemens using *ab initio* quantum mechanical methods. As validation of the computational model, the desorption energies of hydrogen from Si and Ge surfaces were determined and the results were found to be in very good agreement with experiment, thus lending credibility to the computational approach. Encouraged by these results, the energetics of lateral diffusion of hydrogen on models of Si and Si-Ge surfaces was investigated. The results clearly demonstrated that the lateral diffusion barriers were lower than the desorption barrier, thus giving strong support for the diffusion mechanism rather than a cooperative surface reconstruction. In fact, earlier studies of molecular adsorption on a (4x2) reconstructed Si(001) surface with its alternating tilted Si surface dimers showed that the structural and electronic changes induced by the adsorption on one dimer did not alter the geometry of the neighbouring dimer [3]. This provides a further indication of the local nature of the surface processes on a Si(001) surface and casts doubts on a cooperative model.

Using this information gained from *ab initio* quantum mechanical calculations, researchers at Siemens developed a kinetic model based on the hydrogen diffusion mechanism, tuned it with available experimental data, and achieved an excellent description of observed deposition rates. This kinetic model thus provides a sound basis for predictions in a parameter space where no experiments are available.

A. Korkin from Motorola and coworkers reported similar studies on CVD growth of silicon nitride [4]. In this case, the situation is complicated by the fact that silicon nitride grows as an amorphous layer. This makes the construction of structural models quite difficult. However, the previous case as well as other studies on covalent semiconductor surfaces show a fairly local nature of the surface reactions. Therefore, a cluster model containing a rather modest number of atoms (about 10 to 30 atoms), with hydrogen atoms terminating bonds towards the bulk is sufficient to capture the major effects of adsorption. Such an approach is valuable, but it is hard to make an assessment of the errors introduced by the structural model. In fact, any engineering application requires first and foremost reliable estimates of errors rather than automatically the highest possible accuracy. However, all factors need to be taken into account which can cause differences between predictions and real systems.

8.4 Optoelectronic materials

The third example is taken from a particular area of optoelectronics, namely thermophotovoltaics. The technological objective is the direct conversion of heat into electricity. Specifically, one envisions radiation sources emitting predominantly in the infrared with a photon energy of about 0.5 eV. In order to capture this energy by photovoltaic devices, one obviously needs narrow band gap semiconducting materials which absorb in the above energy range. Quaternary III-V materials containing Ga, In, As, and Sb meet this requirement. In order to achieve a long life time of the electron-hole pair one needs to grow device materials with low defect concentrations (e. g. dislocations). This requires a very good epitaxial lattice match with the substrate. In fact, InP is a convenient substrate for this type of III-V semiconductors. By using a quaternary alloy, it is possible to tune the energy band gap independently of the lattice parameter. However, different substrates could be considered if there are good reasons.

III-V alloys containing four or more atomic species can form local ordering on the sub-lattices which can be driven thermodynamically or kinetically. It is known that such effects can have significant impact on the optoelectronic properties.

In order to gain a deeper understanding of the delicate relationship between chemical composition, crystallographic structure, alloy ordering effects, doping, electronic structures and optoelectronic properties, one needs a robust and reliable theoretical and computational approach that can provide structural as well as electronic and energetic information. The key requirements for an appropriate theoretical and computational approach are therefore: (i) accurate prediction of ground state structures of pure, alloyed, and doped III-V semiconductors, (ii) calculation of relative energies accurate enough to predict local ordering effects in alloys, (iii) calculations of optical excitation energies (band gaps) with an absolute accuracy of a few tenths of one eV, (iv) inclusion of relativistic effects for the accurate description of systems containing heavy elements such as In and Sb, and (v) ability to treat unit cells (super cells) of up to about 30 atoms.

Considering a number of possible options, the choice was made to build on the proven all-electron full-potential linearised augmented plane wave (FLAPW) method. On the LDA level, this method provides very good structural properties as well as relative energies as needed, for example, to investigate local ordering effects in alloys. For the calculation of optical excitation energies, the screened-exchange LDA approach was implemented self-consistently in the FLAPW method [5]. Spin-orbit relativistic effects are included as well thus resulting in a comprehensive methodology to tackle narrow band gap semiconductors meeting the requirements specified above.

The capability of this methodology has been tested on a range of elemental and compound semiconductors with small and large band gaps. Compared with the LDA Kohn-Sham eigenvalues, it is remarkable that the sX-FLAPW approach consistently improves the absolute as well as relative accuracy in computed energy band gaps. In particular, narrow band gap semiconductors such as InSb are well described whereas LDA wrongly predicts these materials to be metallic. The calculated optical absorption spectrum of GaAs demonstrates that this methodology, as applied to III-V semiconductors, achieves "engineering quality". In fact, optical absorption spectra calculated with this methodology are now being used as input into macroscopic device models.

8.5 Perspectives and Conclusions

Electronic structure methods are becoming an integral part of research and development of materials related industries such as catalyst manufacturers and electronics companies. This development is taking place about 10 to 15 years after the chemical and pharmaceutical industries started to adopt electronic structure methodology. The sequence is remarkable as it reflects the pace of methodological developments in the areas of quantum chemistry and solid state physics. The principal theoretical approach for organic molecules is based on Hartree-Fock theory as implemented in programs such as Gaussian, GAMESS and Turbomole. Automatic geometry optimisations and hence the calculation of relative molecular energies based on Hartree-Fock theory with Gaussian-type orbitals were developed around 1970, i.e. about 10 to 15 years earlier than the same capabilities with DFT methods. Since the reliable calculation of structural properties and related energies are critical for most practical applications of *ab initio* methods, this capability appears to have been a key enabling factor. The other factor is the availability and ease of use of electronic structure programs. Programs such as Gaussian and the semiempirical MOPAC program were successful because of these features. In addition, industrial organisations want to use commercially supported programs in order to save the costly time of industrial research scientists. Thus, the introduction of commercial software products is a third factor in the successful industrial deployment of a novel technology. (The same is true for experimental techniques and equipment such as the scanning tunnelling microscope.) At present, commercially supported solid state programs coexist with programs available from academic sources. This is characteristic for the early phase of a growing field. Experience in other areas of simulation technology such as structural analysis and computational fluid dynamics show that commercial software eventually dominates as particular methodologies mature and academic research focuses on new areas.

The examples discussed in this article give a glimpse on the type of industrial problems where electronic structure methods can make a difference. These cases show that one needs to be very careful in setting expectations. If one positions electronic structure methods as a tool that can make a useful contribution in solving a variety of problems, then success can be achieved. If, on the other hand, the claim is made that this approach will suddenly change industrial research and development and replace experiment, then the harsh economic realities can cause deep disappointment and thus damage the field. Unfortunately, there were cases where this happened and it takes almost a decade to demonstrate the true value of this methodology and to rebuild confidence.

Given the incredible reduction in the cost of computing, the development of reliable and powerful electronic structure programs, and the steady progress on the fundamental theoretical level, it is safe to say that the industrial acceptance and usefulness of this methodology will grow and will become a significant part of industrial research.

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