HCM Newsletter

Ψ_k Network

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

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Editor: Z. (Dzidka) Szotek
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Coordinator: Walter Temmerman
E-mail: psik-coord@daresbury.ac.uk

Contents

1 Editorial

The **Editorial** is followed by the section **News from the Network**, where we write about important Network matters and give some information on changing the structure of future newsletters.

In the section **News from the Working Groups** readers will find reports on recent collaborative visits, and past workshops. Especially, the report on the October CECAM/PSIK Workshop in Lyon, on **'Ab initio Calculation in Relation to Modelling Constitutive Relations and Fracture Toughness of Metals'**, is very detailed and contains also abstracts of talks and posters. Additionally we have reports on the recent Workshop in Aarhus, on **'Quantum Theory of Solids'**, and a very focused meeting on **'Ab initio modelling program (AIMPRO)'** in Exeter.

The **Highlight of the Month** Section contains an interesting article by Franca Manghi and Massimo Rontani (*University of Modena*) on **'3-Body Scattering Theory of On-site Correlation in Narrow Band Materials'**. We would also like to turn readers' attention to the contribution by Meb Alouani (*Strasbourg*) on **benchmarking computer codes**, just before the **Highlight of the Month** Section. It is important for the benefit of all of us to get involved in this initiative.

The *Network* has a home page on World Wide Web (WWW). Its *Uniform Resource Locator* (URL) is:
http://www.dl.ac.uk/TCSC/HCM/PSIK/main.html

The above contains pointers to several other nodes: *O.K. Andersen (Stuttgart)*, *P. Blöchl (IBM, Zürich)*, *S. Crampin (Univ. Bath)*, *M. Finnis (Univ. Belfast)*, *M. Gillan (Univ. Keele)*, *E.K.U. Gross (Univ. Würzburg)*, *B.L. Györffy (Bristol)*, *V. Heine (Univ. Cambridge)*, *M. Heggie (Univ. Sussex)*, *B. Johansson (Univ. Uppsala)*, *R. Jones (Univ. Exeter)*, *J. Kübler (TH, Darmstadt)*, *J.L. Martins (INESC, LISBON)*, *R. Nieminen (TU, Helsinki)*, *J. Nørskov (TU, Lyngby)* with information on CAMP, *M. Scheffler (FHI Berlin)*, *K.-H. Schwarz (TU, Vienna)*, *M. Springborg (Univ. Konstanz)*, *G.P. Srivastava (Univ. Exeter)*, *W.M. Temmerman (Daresbury Laboratory)*, and *A. Walker (UEA Norwich)*. There are also pointers to the WWW home pages of the Solid State Theory Group at National Renewable Energy Laboratory, Golden, CO 80401 *(http://www.sst.nrel.gov)*, and to the home page of Prof. David Vanderbilt, Department of Physics and Astronomy, Rutgers University *http://www.physics.rutgers.edu/ dhv.* If you maintain a home page on your activities we will be happy to include a pointer from the *Network's* home page to your home page.

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

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

	function
psik-coord@daresbury.ac.uk	**messages to the coordinator & newsletter**
psik-management@daresbury.ac.uk	**messages to the NMB**
psik-network@daresbury.ac.uk	**messages to the whole Network**

Dzidka Szotek & Walter Temmerman
e-mail: psik-coord@daresbury.ac.uk

2 News from the Network

As was mentioned in previous Newsletters, at the end of December the HCM Network comes to its end, being replaced by two new TMR networks and one ESF Programme. As a result, the Newsletter will change accordingly to accommodate all these networks. We intend to run separate sections for each of the networks to make their individual activities more visible. Of course, as we are one big community, we want to keep everything united in the same Newsletter. We hope that you do agree with us concerning this point, but if you have different views or new suggestions for improvements we would be very happy to hear from you. Our e-mail addresses remain as they used to be, although they will involve more people responsible for running these networks. One of these networks, namely the TMR Network on 'Interface Magnetism', has been in operation for over a year now, and the other two are expected to start in January 1998 (ESF Programme) and March/April 1998 (second TMR Network). As before, we are counting very much on your contributions to the Newsletters, and would be glad to introduce new concepts to improve their contents.

To finalize the HCM Network's activity we have to submit a detailed report to the European Commission in Brussels in early January. For this we need your help. We asked for it specifically in the previous Newsletter, unfortunately we did not get much response to that. To make the report, we need detailed information of all original **forty** nodes who participated to the HCM Network by signing the associate member contracts. Of course, we would also appreciate contributions from those of you who have not been among those original forty, but would like to make a contribution. Some of the nodes have done this, but many have not. We need to know details of all your papers acknowledging the Network, the activities in which you have participated within the Network, we want to know how you have benefited from the Network, its workshops, the Conference, collaborative visits, and computer codes. We would also want to know how the Network has benefited from you. Moreover, we would need a short scientific highlight of your research that has in any way resulted from your involvement with the Network. As in previous years, we shall publish the final report in the first Newsletter of 1998 (February issue). We would like to put all the scientific highlights together into the **Highlight of the Month** Section. The report, containing the scientific highlights, and all the Newsletters of this year will be submitted to Brussels to fulfil the requirements of the EU Commission. We hope, that as in previous years, you will help us to make this report and the next Newsletter a success. Finally, we would like to thank all of those who have already done their bit.

Below please find enumerated what your individual reports should contain.

- **Benefits from the Network**–list all activities that the members of your node participated in (workshops, the Conference, computer codes received within the Network,

collaborative visits, etc.)

- **How has the Network benefited from your node**–what have you done for the Network in terms of contributions (organizing workshops, the Conference, computer codes, etc.)

- **Give details of all papers that your node has published, and that acknowledge the Network**

- **Scientific highlight of your research** that in any way benefited from the Network (this need not be long, and should have a format of a short scientific article; if it is to contain figures, they should be in the latex format! The past February issues can serve as examples for highlights)

Dzidka Szotek
(The Editor)

3 News from the Working Groups

3.1 Reports on Collaborative Visits

Report on a Collaborative Visit of J.C.L. Hageman (University of Nijmegen) to the Theory Department of the Fritz-Haber-Institute of the Max-Planck-Gesellschaft in Berlin.

21 September - 4 October

I visited the group of Prof. Dr. Matthias Scheffler at the Fritz-Haber-Institute of the Max-Planck-Gesellschaft in Berlin from 21 September to 4 October 1997.

In Nijmegen the fhi96md code, the pseudopotential code which is developed at the Fritz-Haber-Institute, is used to study polymers. These consist mainly of first row elements, which require large numbers of plane waves. Thorough knowledge of features of the fhi96md is necessary to make the planned calculations feasible and the goal of this visit was to improve my knowledge, especially on the new features.

Special attention was payed to the reduction of the number of timesteps to converge the electronic structure. The initialization procedure with a mixed basis set to get good trial wave functions was discussed as well as the possible integration schemes to get convergence. Insight in both these topics makes it possible to speed up electronic convergence for the large polymer systems.

Also discussions on the treatment of charged defects were useful for future research in conducting polymers.

I think my future research will greatly benefit from this visit and I am grateful for the support of the Ψ_k-Network.

(Joost Hageman)

Report on a Collaborative Visit of S.S.A. Razee (Warwick) to University of Messina in Italy

October 26-November 3, 1997

I visited Professor B. Ginatempo and his group in the University of Messina between October 26 and November 3, 1997. The purpose of the visit was to develop a computer code to study the magnetocrystalline anisotropy of ferromagnetic matrials with *any* Bravais lattice using the spin-polarised relativistic Korringa-Kohn-Rostoker coherent-potential approximation (SPR-KKR-CPA). At Warwick, myself and Dr. J. B. Staunton have been working on the magnetocrystalline anisotropy of disordered alloys using the SPR-KKR-CPA scheme but our study was limited to cubic systems only. Prof. Ginatempo and his coworkers have developed the computer code to study the electronic structure of solids with any Bravais lattice but within the non-spin-polarised relativistic KKR-CPA scheme. Also, their code uses an innovative hybrid method to perform the Brillouin zone integration accurately and efficiently. During my visit to Messina we were successful in combining the two codes. Now with this code we can study the magnetocrystalline anisotropy of ferromagnetic solids - pure elements, ordered compounds, disordered alloys - with any Bravais lattice. We plan to study the effects of lattice distortions, such as from cubic to tetragonal, on the magnetic anisotropy of solids and hope to find answers to many outstanding problems in this area.

During this time, we were also successful in developing the computer code to calculate the Bloch spectral density function (BSF) within the SPR-KKR-CPA. This will be used to study Fermi surface (FS) and other $\mathbf{k}$-dependent properties of solids and to interprete various experimental and theoretical data. In particular, we will be using this code to calculate the FS of disordered Co-Pt alloys and interprete our results on the effect of compositional order on the magnetocrystalline anisotropy of alloys.

It was a fruitful visit and now we are planning several publications together.

(Sayed S.A. Razee)

3.2 Reports on Workshops

Report on the CECAM/PSIK Workshop: Ab Initio Calculation in Relation to Modelling Constitutive Relations and Fracture Toughness of Metals

Lyon, France, 20-22 October 1997

FORMAT

The final program can be seen in
http://titus.phy.qub.ac.uk/group/Mike/CECAM/CECAM_program.html.
About thirty five scientists took part, including experimentalists, mesoscopic modellers and atomistic simulators besides specialists in ab initio calculation. Below is the list of participants. There were several participants who stayed on for the subsequent workshop, which provided some useful continuity of discussion between the closely related themes.

To help focus the discussion, the 13 talks were grouped into four sessions. The first posed a number of challenges (session ch), the second concentrated on atomistic modelling (session at), the third on mesoscopic modelling (session me) and the fourth on ab initio applications (session ab). Four half-hour discussion sessions, indicated by disc1-disc5 in the program, focussed on the group of talks which preceded them. The poster sessions with coffee on Monday and Tuesday afternoon were a focus of lively discussion which must remain unreported. The abstracts of the nine posters, besides those of the talks, are included in the program.

It is not possible or desirable to compartmentalise discussion, one wants merely to focus it, so it will be clear that the session headings are not exclusive. The talks themselves lasted about 40 minutes, with 10 minutes of discussion after each talk. The final discussion session, disc5, recapped and summarised some of the outstanding problems. The following summarise the outcome of these sessions, and has been prepared with the help of the discussion leaders. MWF takes responsibility and apologises for errors and omissions.

CHALLENGES

The first challenge to ab initio calculaters, but not only to them, was Steve Roberts' general one: how can we identify at each scale of length and time a set of rules that provide input for models operating on the next highest level of length and time. Engineers use what he referred to as 'non knowledge-based' modelling, and the aim should be to inject knowledge (literally science) into the empiricism. It is well known that extrapolation based on empirical rules can either be life threatening or it can build in an unnecessary margin of safety. In the same spirit, ab initio calculations might be useful to mesoscopic modellers if they provided certain parameters for them. This raised the important question, returned to later, as to who are the customers for ab

initio calculations. What is their role, if any, in developing constitutive relations. The problem of bridging length scales permeated the meeting and was of course the focus of the subsequent CECAM workshop.

Nevertheless, ab initio calculations were not only seen in terms of providing input for modelling at the next larger length scale. From Mick Brown's talk, it was clear that ab initio calculation can have a direct role to play in understanding electronic structure of impurities at grain boundaries, by enabling the interpretation of Electron Energy Loss spectra (EELS) in terms of the type of local bonding. The specific challenge was to determine the behaviour of impurities at grain boundaries, in particular, their possible function as 'anodic' or 'cathodic' centres setting up electrical circuits that cause corrosion.

Ulrich Messerchmidt's challenges related specifically to questions of interpreting what is seen in in situ micrographs of strained specimens.

1) What is the atomic structure of ZrO2 - Y2O3 alloys?
2) How do moving dislocations in these alloys react with each other?
3) What is the Peierls stress of the slip systems in ZrO2.
4) What is the nature of the coupling between the microstructure and the ferroelastic deformation in partially stabilized ZrO2?
5) What are the anti-phase boundary energies for (100) and (110) planes.

Such specific questions are very helpful to the theoretical communities. One of conclusions from the discussion were that there were challenges here, such as the EELS, and 3) and 5) above, which could be met (and in general are being met) directly by present ab initio technology. By *ab initio* we tend to mean here LDA calculations or small extensions of them. Someone stressed the importance of formulating the right question! On the one hand, the problem has to be technically doable. But even if it is, one should ask 'What advance will have resulted if we provide an answer'. The value of large-scale model potential simulations in this context was discussed briefly, with no firm or universal agreement. Opinions ranged widely from 'valueless' to 'potentially of great value in understanding mechanisms, for example for the interaction of dislocations '. The range of opinions was due perhaps to the tendency in published work to focus unduly on the size of the computation rather than its intrinsic information content. This was addressed further in the subsequent discussions.

ATOMISTIC MODELLING

The preceding discussion had focused on the use of multiscale approaches to getting useful results, i.e. using atomic-level calculations as input for mesoscale simulations, which in turn should yield directly applicable results such as constitutive relations and fracture toughness. The discussion following the three atomic-level simulation talks focused instead on whether one could get useful information directly from atomic-level simulations, without going through the mesoscale simulations as an intermediary. Vitek argued that simulations of the core structure in bcc metals can give the yield strength of a materials fairly directly, and this is probably true in general for high-Peierls stress materials. The effect of dissociated cores in bcc metals also

gives rise to a variety of other phenomena, including unexpected deformation modes and slip geometries, and strong and unusual dependence of the flow stress on crystal orientation and temperatures, which can thus be predicted to some extent via atomic-level simulations. (In fcc metals, the Peierls stress is generally so low that its contribution to the stress-strain curve is small). The yield stress is only one point on the stress-strain curve, but nevertheless a useful start. However, strain-hardening effects are usually quite important, and cannot be ignored - it was pointed out that in bcc metals, they can exceed the yield strength by an order of magnitude. Vitek argued that the strain-hardening effects have been studied intensively by workers such as Kocks, and that one might be able to include them in a constitutive relation without doing the "full-blown" simulation. The issue of dislocation interactions with impurities was also raised. The blocking stress associated with these also often exceeds the Peierls stress. However, these types of interactions are still within the realm of atomic-level theory.

The practicality of these types of calculations was also discussed to some extent. It was generally agreed that an accurate Peierls stress calculation requires a simulation cell on the order of more than 1000 atoms. Such calculations are thus on the edge of possibility with ab-initio methods, although quite straightforward with semiempirical potentials. One can expect sufficient progress in ab-initio methods and CPU power over the next few years that ab-initio Peierls stress calculations will become widespread, and the compilation of a database of such numbers would be very useful.

Another issue that was raised regarding having an impact right now, rather than in ten years, was the treatment of deformation textures. This actually involves stepping completely away from atomic-level calculations, and instead using a much more coarse-grained starting point. Approximate but useful theories of texture development exist, and, unlike atomic-level theories, they are having an impact in manufacturing, specifically in the metal plate used for automobiles. But no way for ab-initio calculations to enter this type of analysis was given.

Nanostructures provide a field where atomistic methods may find direct applications, since the length scales are right. Jacobsen demonstrated this with nanocrystaline materials. A major problem is always to obtain physically meaningful results in, at most, nanosecond simulation times. Jacobsen's approach, which involved continous static relaxation under applied stress rather than molecular dynamics per se, offered a useful solution to this difficulty which engendered lively discussion.

MESOSCOPIC MODELLING

There have been significant advances in mesoscale modelling over the past few years, as the talks made evident. One reason for this is that the basic object responsible for behaviour is known to be the dislocation. A material could be simulated reasonably faithfully in principle if we knew how isolated dislocations behave, how they interact with each other and with objects such as point defects, grain boundaries and precipitate particles.

The discussion after the talks first clarified that there are actually several simulation techniques which are all described as 'meso', i.e. between other levels of approximation and discretization. Furthermore it revealed that it is probably somewhat overamibitious to directly aim at

quantitative results from these simulations, since many of the critical ingredients for mesoscale simulations are still based on more or less empirical rules, instead of physically sound understanding of the underlaying processes. This is especially true for the discrete dislocation dynamics, (also referred to as DDD, or spaghetti) simulations of crystal plasticity.

A list of issues has been identified where atomistic input could be very helpful in providing a better justified physical basis for the DDD simulations. This includes:

(1) The mobility law for the motion of the dislocations. More or less undisputed is how to calculate the forces on individual segments of a dislocation, whereas how this force translates into a (temperature dependent) velocity law for the motion of the dislocation is less clear. Information on this question can directly be obtained from etch-pit experiments but these are very tedious and almost impossible for materials with a high stress exponent n. In principle, atomistic simulations can provide all the necessary data for these velocity laws, which are (stress dependent) kink pair formation enthalpies and kink mobilies. Unfortunately these calculations appear generally somewhat too demanding for ab-initio methods, at least in the near future, since they are geometrically very complex and therefore require very large system sizes. For some specific and geometrically simple cases, however, it may nevertheless be possible to obtain at least part of this information.

(2) Dislocation nucleation criteria, cross slip probabilities, dislocation annihilation criteria and properties of dislocation junctions and jogs. All these quantities are not only quantitatively but also qualitatively poorly understood and will require atomistic input. However, the simulations at present seem to be too demanding for general application of ab-initio methods and must be treated by simple atomistic interaction models.

(3) The interaction of dislocations with other defects. It was recognized that we are still very far from understanding chemical variations, interaction with precipitates or grain boundaries and from seeing how to implement these aspects into DDD simulations.

The importance of entropies was repeatedly mentioned, especially in connection with chemical effects but also in connection with dislocation mobility. The audience reached consensus that entropies are indeed very difficult to get at by ab-initio methods except in a very case such as vacancy migration.

It was recognized that ab initio calculations are very useful in providing information on the stability of different faults and therefore on the possibilities of dislocation dissociation processes, which play a very important part in mechanical properties. Furthermore, ab-initio calculations are the only way of clearly discriminating between different materials.

The importance of ab initio calculations for the development of our understanding of the bonding characteristics was also repeatedly mentioned. Ab initio calculations are in this context not only useful in order to provide material specific data to adjust empirical potentials, but even more for the insight they bring to the construction of improved models of the atomic interaction. They are needed to discriminate between materials within a class, such as specific nickel based intermetallic alloys, which can possibly be treated by the various simpler methods.

AB INITIO APPLICATIONS

Speakers had applied ab initio methods either to develop simpler interatomic force models or to calculate planar fault energies and gamma surfaces. For example Fähnle highlighted the way that good quality ab initio calculations of planar fault energies can help in the explanation of experimental results when there is controversy, eg. whether dislocations dissociate into one or more stacking faults. Gamma surfaces could be used in generalised Peierls-Nabarro models to explain, for example, improved ductility (the example of MoSi2 was given by Kaxiras).

The usefulness of even carefully fitted interatomic force models (eg. embedded atom or effective medium) was pointed out in discussion to be erratic. NiAl can be reasonably well represented by an embedded atom type potential whereas FeAl cannot (Fähnle), but in any case quantitative predictions are risky. However, it was noted that even ab initio does not mean exact, and as an example errors of disturbing size in alumina were reported (about 0.2eV) between different ab initio total structural energy differences. There was quite lengthy discussion as to how useful would be a wide ranging database of ab initio calculations, covering the periodic table, using state of the art methods (a sort of updated and greatly extended Morruzi, Janak and Williams). While several people thought such a database would be very useful for reference purposes, benchmarking and so on, it was also considered that there is little chance of obtaining funding for this kind of work.

Molteni's calculations of grain boundary sliding, while not predictive for real materials in a quantitative sense, showed how insights can be obtained. They showed in particular how ab initio calculations may be interpreted to discuss effects which are essentially dependent on thermal excitation. The discussion widened into the need for calculations of activation energies and volumes. A particular problem was posed by Mick Brown - is their a critical distance for the spontaneous cross-slip to mutual annihilation of a pair of screw dislocations, and if so what is it. Experimentally it seems to be about 30nm in Cu. This was another challenge which seems to be aimed mainly at large scale atomistic simulation. The annihilation of edge dislocation dipoles is a similar problem which appears to be equally mysterious in terms of the barrier heights and atomistic processes.

GENERAL REMARKS

Some further general comments were made which are worth reporting. We have seen that there are customers for particular ab initio calculations in the atomistic and mesoscale communities, and that there are particular quantities which are worth calculating. Nevertheless, the models considered at our workshop will not suffice to determine the constitutive behaviour of the vast majority of industrially interesting materials. If we pose the question 'What will happen if we solve the problems of mesoscale (dislocation) modelling?', one can be reasonably sure that we will still not be able to predict constitutive laws for steels or other complex alloys that are routinely used in industrial applications. It is possible to isolate some of the important factors, such as grain size, and to construct 'kinetic' models based on the notion that the material's properties are determined by the various 'phase transformations' that occur during processing. There are many groups of metallurgists working on macro-models of constitutive behaviour (eg.

at Ecole des Mines, Nancy), but this kind of modelling is currently completely disconnected from the kind of mesoscale modelling referred to above. The disconnect also refers to the scales of length and time involved. Simulation of materials behaviour and processing is done with finite element methods (FEM) which require as input a macromodel (on a node by node basis) of the constitutive behaviour. Knowledge of the critical parameters that go into this kind of modelling could be very helpful in steering ab initio/mesoscale simulations to 'Ask the right questions', namely questions which, if successfully answered, would foster FEM simulations having truly predictive capability (the 'knowledge based' approach). A recommendation was that the next 'connecting the length scales' program should involve macroscale modellers in a very integral way.

Activation energies and the energies of thermally excited processes such as point defect formation and the cross slip or climb of dislocations can be significantly temperature dependent. This temperature dependence of parameters is additional to the role of vibrational entropy terms which enter rate theory. The quasiharmonic approximation and methods of thermodynamic integration will have to be applied increasingly in conjunction with ab initio calculations for making quantitative predictions.

LIST OF PARTICIPANTS

Dr Gianluigi A. Botton, Department of Materials Science and Metallurgy, University of Cambridge, Pembroke St., Cambridge, CB3 3QZ, U.K. gb10003@cus.cam.ac.uk

Prof. L. M. Brown, Cavendish Laboratory, University of Cambridge, Madingley Rd., Cambridge CB3 OHE, UK, lmb12@hermes.cam.ac.uk

Prof. A. E. Carlsson, Department of Physics, Washington University, One Brookings Drive, St. Louis, MO 63130, U.S.A., aec@howdy.wust1.edu

Prof. Bernard R. Cooper, West Virginia University, Dept. of Physics, P.O.Box 6315, Morgantown WV 26506-6315, USA, brcoop@wvnvm.wvnet.edu

Dr. Benoit Devincre, Laboratoire d'Etudes des microstructures CNRS-ONERA (LEM), ONERA, BP72, 92322 Chatillon Cedex, France, http://zig.onera.fr/lem/staff/devincre.html, devincre@zig.onera.fr

Dr. Christophe Domain, EDF, Departement Etude des Materiaux, Les Renardieres, F-77250 Moret sur Loing, France, Christophe.Domain@der.edf.fr

Dr. Francois Ducastelle, Laboratoire d'Etudes des microstructures CNRS-ONERA (LEM), ONERA, BP72, 92322 Chatillon Cedex, France, ducastelle@onera.fr

Dr. Christian Elsässer, Max-Planck-Institut für Metallforschung, Seestraße 92, D-70174 Stuttgart, Germany, elsae@marvin.mpi-stuttgart.mpg.de

Prof. Manfred Fähnle, Max-Planck-Institut für Metallforschung, Heisenbergstraße 1, D-70569 Stuttgart, Germany, faehn@physix.mpi-stuttgart.mpg.de

Prof. Michael W. Finnis, Atomistic Simulation Group, School of Mathematics and Physics, Queen's University of Belfast, Belfast BT7 1NN, Northern Ireland. m.finnis@qub.ac.uk

Dr. Peter Gumbsch, Max-Planck-Institut für Metallforschung, D-70174 Stuttgart, Germany, gumbsch@finix.mpi-stuttgart.mpg.de

Dr. John Harris, MSI/Biosym, 9685 Scranton Road, San Diego CA 92121-3752, USA, jfh@msi.com

Prof. Kai-Min Ho, Ames Laboratory - U.S. Department of Energy, Department of Physics and Astronomy, Iowa State University, Ames IA 50011, USA, KMH@ameslab.gov

Prof. Richard G. Hoagland, Department of M&ME, Washington State University, Pulman, Washington 99164, (USA), hoagland@hombre.mme.wsu.edu

Prof. Karsten W. Jacobsen, Dept. of Physics, Building 307, DTU, DK-2800 Lyngby, Denmark, kwj@fysik.dtu.dk Web Address: http://www.fysik.dtu.dk/persons/kwj.html

Prof. Efthimios Kaxiras, Harvard University, Dept. of Physics, 324A Lyman Lab., 9 Oxford Street, Cambridge MA 02138, USA. kaxiras@cmt.harvard.edu

Dr. Timo Korhonen, Institut fuer Festkoerperforschung, Forschungszentrum Juelich, D-52425 Juelich, Germany, t.korhonen@fz-juelich.de

Dr. Ladislas Kubin, Laboratoire d'Etudes des microstructures CNRS-ONERA (LEM), ONERA, BP72, 92322 Chatillon Cedex, France kubin@onera.fr

Mr. Alejandro Legris, URA CNRS 234, Laboratoire de Mtallurgie Physique, Universit de Lille 1, 59655 Villeneuve d'Ascq Cedex, France, legris@lulla.univ-lille1.fr

Prof. Jose L. Martins, INESC, Rua Alves Redol 9, P-1000 Lisboa, Portugal. jlm@pseudo.inesc.pt

Prof. Ulrich Messerschmidt, Max Planck Institute of Microstructure Physics, Weinberg 2, Halle/Saale, D-06120, um@mpi-halle.mpg.de

Dr. Carla Molteni, Max-Planck-Institut für Metallforschung, Heisenbergstraße 1, D-70569 Stuttgart, Germany. molteni@prr.mpi-stuttgart.mpg.de

Dr. Elio G. Moroni, Institut fur Theoretische Physik, Technische Universität Wien, Wiedner Hauptstrasse 8-10 A 1040 Wien, Austria. elio@betty.tssc.univie.ac.at

Dr. Duc Nguyen-Manh, Materials Modelling Laboratory, Department of Materials, University of Oxford, Oxford, Parks Road, OX1 3PH, UK. manh.nguyen@materials.ox.ac.uk

Dr. Alain Pasturel, Experimentation Numérique, Maison des Magistères, CNRS, BP 166, 38042 Grenoble Cedex, France. pasturel@belledonne.polycnrs-gre.fr

Prof. David G. Pettifor, University of Oxford, Department of Materials, Parks Road, Oxford OX1 3PH, UK. david.pettifor@materials.oxford.ac.uk

Prof. Rob Phillips, Brown University, Division of Engineering, Box D, Providence RI 02912, USA. phillips@alpha1.engin.brown.edu

Dr. Steve Roberts, University of Oxford, Department of Materials, Parks Road, Oxford OX1 3PH, UK, steve.roberts@materials.ox.ac.uk

Dr. Jacky Ruste, EDF, Departement Etude des Materiaux, Les Renardieres, F-77250 Moret sur Loing, France

Dr. Klaus Schwarz, IBM Thomas J. Watson Research Center, PO Box 218, Yorktown Heights,

NY 10598, USA. schwarz@watson.ibm.com

Dr. Don Siegel, 105 S. Goodwin Ave, Urbana, IL 61801, USA. d-siegel@uiuc.edu

Dr. Mojmir Šob, Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Brno, Czech Republic, mojmir@ipm.cz or mojmir@sol1.lrsm.upenn.edu

Dr. Adrian P. Sutton, University of Oxford, Department of Materials, Parks Road, Oxford OX1 3PH, UK. adrian.sutton@materials.ox.ac.uk

Prof. Vaclav Vitek, Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA 19104, USA. vitek@lrsm.upenn.edu

Prof. Göran Wahnström, Department of Applied Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden. wahnstrom@fy.chalmers.se

Mike Finnis
Belfast mail to: M.Finnis@qub.ac.uk

LIST OF TALKS

Session 1: CHALLENGES

S. Roberts
Oxford University
"Appropriate length and time scales for modelling 'real' fracture problems"

I will discuss length scales, time scales, scaling laws and (what I regard as) the most appropriate type and level of modelling for phenomena connected with fracture and brittle-ductile transitions. I will argue that while atomistic and large-scale (FEM) modelling can be useful for understanding some aspects of these phenomena, there are intrinsic reasons why the most effective, and possibly the only practicable approach is at the mesoscopic (dislocation network) scale.

L.M. Brown
Cavendish Laboratory, Cambridge
"Electron energy loss spectroscopy and cohesion of grain boundaries, or: are theories of defects in metals at last directly testable?"

Many laboratories are now equipped with electron microscopes incorporating electron spectrometers, giving about 0.3 V energy resolution in spectra of energy lost by electrons traversing a thin foil while focussed to a sub-nanometre probe. It is therefore now possible in principle to investigate changes caused locally by defects to the site-projected and angular-momentum projected density of unoccupied states. In special cases, particularly in transition metals, where the bonding is dominated by d-bands which can contain a fixed number of electrons, changes

in cohesion at grain boundaries can be estimated directly from spectra, and compared with experiment. Effects associated with surfaces and dislocations can also be seen. How accurate are these estimates? Much more systematic work needs to be done to generate sound data; such data, however, should have a direct impact on the solution of engineering problems of great importance. A review will be given of the results obtained so far, their implications for possible charge transfer effects at boundaries, and changes in the electron potential there.

U. Messerschmidt
Max Planck Institute of Microstructure Physics, Halle/Saale

"Questions put to theory arising from results of in situ straining experiments in the transmission electron microscope"

In situ experiments in a transmission electron microscope allow the direct observation of the dynamic behaviour of individual dislocations. Some examples are described, with open questions being discussed, e.g.: In gamma TiAl, the flow stress anomaly is usually explained in terms of the core structure of superdislocations. However, ordinary dislocations dominate at all temperatures. The mechanism controlling their mobility is changing from a precipitation hardening mechanism at room temperature to a diffusion-controlled mechanism at high temperatures. What are the details of this mechanism and why does the latter increase the flow stress?

The dynamic behaviour of dislocations in cubic zirconia strongly depends on the type of the slip plane. We need calculations of the Peierls stresses for the different slip planes. Obviously, there are two types of antiphase boundary-like defects on different planes in tetragonal zirconia. What are the energies of these defects? The question is important for the models of precipitation hardening in partially stabilized zirconia.

The dislocations in quasicrystals move in a viscous way pointing at the action of an intrinsic friction mechanism. Details of a possible mechanism are discussed and questions are put regarding the energy and entropy of the process.

Session 2: ATOMISTIC SIMULATION

C. Molteni(1), N. Marzari(2), M.C. Payne(3) and V. Heine(3)

"Modelling grain boundary sliding from first principles"

Grain boundary sliding (i.e. the sliding of one grain over another parallel to the boundary interface that occurs in response to applied forces) is an important process in the deformation and fracture of polycrystalline materials. We have used density functional theory simulations to investigate the microscopic mechanisms that accompany sliding at twist and tilt boundaries in germanium, a typical brittle semiconductor, and aluminium, a typical ductile metal. We find a variety of sliding behaviours, that depend not only on the covalent or metallic character of the bonding, but also on the boundary geometry, the local order and the presence of defects. While in germanium sliding is controlled by local stick-slip events involving rebonding of a few atoms,

in aluminium larger numbers of atoms act in concert over extended areas, ultimately limited by by boundary defects.

(1) Max Planck Institut fuer Festkoerperforschung, Stuttgart (Germany)
(2) Department of Physics and Astronomy, Rutgers University, NJ (USA)
(3) Cavendish Laboratory, Cambridge (UK)

V. Vitek
University of Pennsylvania

"Structure of dislocation cores and relation to macroscopic plasticity"

Ample evidence now exists for a broad range of crystalline materials that the influence of dislocation core structures on macroscopic plastic flow is significant. Common signatures of core effects are unexpected deformation modes and slip geometries, strong and unusual dependence of the flow stress on crystal orientation and temperature, and, most commonly and significantly, a break-down of the Schmid's law. The non-Schmid behavior, which we will discuss in more detail, may critically affect macroscopic flow it influences significantly the formation of shear bands under both single- and multiple-slip conditions. In this talk we first discuss the concept of the energy-displacement surfaces, i.e. g-surfaces, and the simplest dislocation core model employing this concept, the Peierls-Nabarro model. The limitations of this model will be emphasized, in particular the fact that it is applicable only to planar cores. It will then be argued that non-planar cores are common in a wide variety of materials and the core phenomena are particularly important in this case. However, while the Peierls-Nabarro model cannot then be applied straightforwardly, the g-surfaces combined with crystallographic considerations can still provide information sufficient for understanding the essential features of these cores. This will be demonstrated for bcc transition metals. In particular we concentrate on differences in plastic properties and core structures between Vb and VIb transition metals. The first distinction is seen in the values of elastic moduli. This then projects to g-surfaces and further to the core structures and distinct differences in non-Schmid behavior in these two groups. This line of argument provides an excellent opportunity for linking ab initio calculations with studies of macroscopic deformation behavior: g-surfaces can be studied by ab initio calculations relatively simply. Link with the core can then be established either via atomistic calculations using suitably constructed empirical potentials or using semi-continuum models. The continuum mechanics then provides link to macroscopic phenomena.

K.W. Jacobsen
Technical University of Denmark

"Mechanical response of nanophase metals: a reverse Hall-Petch effect"

Nanocrystalline metals are known to exhibit mechanical properties that are different from (and often superior to) conventional metals, e.g. increased hardness and fracture toughness. We present atomic-scale simulations of the deformation process in nanocrystalline copper using molecular dynamics and effective medium potentials. Since we can follow the positions and

motion of dislocations and grain boundaries, we are able to observe the deformation process directly.

In conventional materials the hardness and yield stress is known to increase with decreasing grain size (the Hall-Petch effect). We observe a *reverse* Hall-Petch effect in our simulations, in agreement with some experiments at very small grain sizes. However, the experimental situation is not completely unambiguous mainly due to the difficulties of preparing samples without microscopic voids. In our simulations the reverse Hall-Petch effect is caused by increased deformation in the grain boundaries as the grains get smaller. The grain sizes examined are comparable to the smallest grains studied experimentally.

Session 3: APPROACHING THE MESOSCALE

R. Philips
Brown University

"Locality vs. Nonlocality: Linking Quantum Mechanics and the Finite Element Method"

Mixed atomistic and continuum methods attempt to remain faithful to the microscopic underpinnings of a given process while at the same time exploiting the degree of freedom reduction that attends the use of continuum approaches. This talk will describe one such method (i.e. the quasicontinuum method) with special emphasis on the way in which a finite element description of the deformation of a solid may be built around explicit atomistic calculations. The role of constitutive nonlinearity and nonlocality will be highlighted by way of illustrating how dislocations emerge in this setting.

K.W. Schwarz
IBM Research, Yorktown Heights

"Simulation of dislocation motion on the mesoscopic scale — relaxation of a strained layer"

Because the interaction of dislocations is complicated, little is known about the effects that individual dislocations have on each other when they come into proximity, and, more generally, about the evolution of collections of strongly interacting dislocations. In order to address this issue, we have implemented the full Peach-Koehler formalism for a parallel-computing, distributed-memory environment. The code, which allows the 3D modelling of interacting dislocations on arbitrary glide planes, has been applied to study the relaxation of a strained layer containing a low density of Frank-Read sources. We find that the dislocations generated by these sources interact to form characteristic patterns. The computed dislocation patterns are remarkably similar to those observed experimentally in epitaxially grown SiGe films.

B. Devincre

CNRS-ONERA

"Mesoscopic simulation of the complex dislocation dynamics in Ni3Al alloys"

Ni3Al crystals are known to exhibit plastic strain anomalies like an increase of the yield stress between 200 and 800K. The purpose of the present work is to examine the basic properties at the origin of such anomalies by means of computer models at a mesoscopic scale. The simulation basic rules are derived from the elastic theory and theoretical computations at the microscopic scale on dislocation core properties. The outcomes of simulations are discussed in relation with experimental observations and the existing constitutive relations of the flow stress.

Session 4: AB INITIO APPLICATIONS

E. Kaxiras

Harvard University

"On the use of first-principles calculations to model the brittle/ductile behavior and dislocation motion in solids"

Phenomenological models based on continuum approaches provide a framework for addressing complex processes in solids, such as dislocation motion and brittle versus ductile response. Examples are the Peierls-Nabarro model for dislocation motion and the Rice model for dislocation nucleation at a crack tip. We discuss how first principles calculations provide accurate determination of key quantities that enter in these phenomenological models. Even more importantly, these calculations are able to provide guidance on how the phenomenological models should be extended and improved to yield a more realistic description of the phenomena under consideration, by investigating simple model systems. We will give examples of how these ideas apply to dislocations in Silicon, Aluminum and Molybdenum Disilicide.

B.R. Cooper

West Virginia University

"Interface, grain boundary, and coarsening studies: ab initio electronic structure and dynamic simulations"

I will present a survey of our work that relates to microstructure development in metallic systems. this work uses a number of our technical capabilities: our in-house-developed ab initio full-potential (with true interstitial) LMTO (including force routine for lattice relaxation) electronic structure capabilities, ab-initio-based atomistic potentials extracted from such LMTO calculations, molecular dynamics and monte-carlo simulations, grain boundary modeling, ab inito vacancy and vacancy-complex creation energy calculations. We have used these capabilities for treating such problems as: (1) an integrated treatment of coarsening including vacancy-diffusion effects; this is based on a combination of ab initio precipitate/matrix interface energy and three-dimensional monte-carlo; (2) preferential location of additive species at grain boundaries-using ab-inito-based atomistic potentials; (3) vacancy clustering affecting fracture in intermetallics-

based on large-scale ab-initio full-potential LMTO including force routine for lattice relaxation.

Jan Hartford, Björn von Sydow and Göran Wahnström
Department of Applied Physics, Chalmers University of Technology and Göteborg University, S-412 96 Göteborg, Sweden

"Peierls barriers and stresses for dissociated partial dislocations in Pd and Al based on first principle calculations"

A combination of first principle total energy calculations and atomistic simulation techniques are used to investigate the motion of Schockley partials in close-packed fcc metals.

First principle calculations of generalized stacking fault curves are performed along the 110 and 121 directions for Al and Pd using the density functional theory (DFT) together with the pseudo-potential approximation. The accuracy of the plane-wave calculations is checked by comparing with previous DFT calculations of the stacking fault energy and some experimental numbers. We find good agreement.

The generalized stacking fault curves are applied in the classical Peierls-Nabarro model to calculate the Peierls barriers and stresses and we find stresses of the order $10^{-5}\mu - 10^{-6}\mu$, where μ is the shear modulus.

The first principle data are used to construct a many-body model potential of the 'pair-functional' form for Pd used in atomistic simulations. We study two edge dislocations, which dissociate into two pairs of Schockley partials, using a supercell with about 100 000 atoms with a combination av free and periodic boundary conditions. With a constraint technique and energy minimization we study the motion of the dislocation over the Peierls barrier and we find that the two Schockley partials move jointly to minimize the elastic interaction. By comparing with the classical Peierls-Nabarro model with superposition of two partial dislocations we find a considerable wider core region caused by interaction between the two partial dislocations.

M. Faehnle, J. Ehmann and S. Kohlhammer
Max-Planck-Institut fuer Metallforschung, Heisenbergstr. 1, 70569 Stuttgart, Germany

"Determination of dislocation-dissociations by the generalized Peierls-Nabarro model in connection with ab-initio calculations"

The plastic behaviour of metals and intermetallic compounds, especially the sometimes anomalous temperature dependence of the yield stress, is strongly influenced by the dissociation of dislocations into partial dislocations. Within the framework of the generalized Peierls-Nabarro model /1/ the ener- getics of dislocation dissociations may be investigated for straight dis- locations with arbitrary Burgers vector in an arbitrary glide plane in a crystal with arbitrary anisotropy. The atomistic input information for this mesoscopic model is the generalized stacking-fault energy which is the energy required to move the upper part of the crystal with respect to the lower part by an arbitrary translation vector. In systems with complicated electronic structure it is indispensable to calculate this generalized stacking-fault energy by the ab-initio electron theory.

Examples are given for TiAl, Ni3Al and Al3Ti. It is shown that in TiAl the antiphase boundary configuration is very high in energy and mechanically unstable, and the consequences for the discussion of the anomalous yield stress are outlined. Ni3Al also exhibits an anomalous yield stress, in contrast to Al3Ti which may crystallize in the same crystal structure. It is discussed whether this may be understood within the framework of different energetics for the generalized stacking-fault ener- gies. /1/ G. Schoeck, Phil Mag. A**69** (1994) 1085

LIST OF POSTERS

p1

G.A. Botton, G.Y. Guo*, W.M. Temmerman* and C.J. Humphreys
University of Cambridge

"Electron Energy Loss Spectroscopy Near Edge Structure Studies of Intermetallic Alloys: Comparison With Ab-Initio Methods"

Electron energy loss spectroscopy has now become a powerful method to characterise materials at very high spatial resolution while providing both chemical composition and electronic structure information. The technique is therefore potentially useful to measure the changes in the electronic properties induced by microstructures and defects. With this perspective on the technique, the method can be considered as an experimental link between the electronic structure effects and the macroscopic properties. A detailed interpretation of the spectra, with the aim of retrieving quantitative information, requires a comparison of the spectra with simulations based on ab-initio methods. In this poster, we present experimental results obtained on binary intermetallic alloys with and without ternary alloying additions and show the remarkable agreement with calculations. From this comparison, we discuss the effects of these alloying additions on the macroscopic properties. We compare results obtained with the coherent potential approximation and supercell calculations and discuss the sensitivity of the method of comparison to retrieve information about the defect structure and the properties.
Daresbury Laboratory, Warrington, Cheshire, W4A 4AD, U.K.

p2

C. Elsaesser
Max-Planck-Institut fuer Metallforschung

"Ab-initio determination of the atomic structure of symmetrical tilt grain boundaries in body-centered cubic transition metals"

Atomistic simulations of grain-boundary structures in body-centered cubic transition metals have revealed that angle-dependent contributions to interatomic interactions are essential (see, e.g., [1,2]). Unfortunately the results of presently available empirical potentials are not yet always sufficiently accurate or unique for quantitative theoretical predictions of grain-boundary structures, which are consistent with experimental observations, e.g., by HRTEM. Ab-initio local-density- functional calculations offer the possibility to determine accurately the structure

of some special high-symmetry grain boundaries, which can be further used as a data base for the development of empirical potentials. Results of such calculations, using a mixed-basis pseudopotential method and grain-boundary supercells, are presented for the symmetrical Sigma 5 (310) [001] twin grain boundaries in Nb and Mo.

(1) G. H. Campbell et al., Phys. Rev. Lett. **70**, 449 (1993).
(2) A. G. Marinopoulos et al., Phil. Mag. A **72**, 1311 (1995).

p3

T. Korhonen, N. Papanikolaou, R. Zeller, and P.H. Dederichs
IFF Juelich, Germany

"Lattice Relaxations and Phonons in bcc Iron"

We present first-principles calculations of forces and lattice relaxations in bcc Fe. Firstly, the relaxations around transition metal impurity in iron are calculated and compared with experimental data. Secondly, we calculate the Born-von Karman coupling parameters of bcc iron in real space and from these the phonon dispersion and frequency spectrum. In particular we discuss the importance of magnetism on stabilizing the bcc structure. The calculations are based on a full-potential Korringa-Kohn-Rostoker Green's function method for defects and employ the local spin density approximation for the exchange and correlation effects. The non-spherical parts of the potential and the charge density are treated correctly, while the forces are calculated by the Hellmann-Feynman theorem.

p4

J.L. Martins
INESC, Lisboa

"Metric as the dynamical variable for variable cell-shape molecular dynamics"

We are using a new variable cell-shape molecular dynamics algorithm where the dynamical variables associated with the cell are the six independent dot products between the vectors defining the cell instead of the nine cartesian components of those vectors. We can perform molecular dynamics simulations under the conditions of constant external pressure or constant thermodynamic tension. We can also optimize the structure under those two conditions. We will present applications of the method to a simulation of pressure induced phase transition in Si with forces and stresses calculated from first-principles of density functional theory, optimization of ternary calcium nitride perovskites, also from first principles, and a simulations for Ar with Lennard-Jones parameters under uniaxial stress, where yielding can be observed during the simulation.

p5

D. Nguyen-Manh and D.G. Pettifor
University of Oxford

"Origin of the O-phase and Pseudo-Twinning Deformation in the Nb-Ti-Al systems"

A new structural instability with respect to two kinds of shuffle-type displacive operations from the B2 structure has been investigated in (Ti,Zr,V,Nb)Al intermetallics by mean of a systematic first-principle total energy calculations. In a difference to the conventional tetragonal distortions which transform the bcc into an fcc lattice, these coherent phase transformations give rise to a compound with an orthorhombic structure (referred as the O-phase) related to the B2 phase through an intermediate B19 structure. Moreover, it has been demonstrated also that the B2 high temperature phase may transform along other paths to low temperature orthorhombic phase involving a homogeneous twinning deformation. The latter transformation mode is directly correlated to a negative value of the cubic elastic constant $C''=(2C'+ C_{44})/3$ (the Lamé shear modulus in the isotropic limit). The structural relationships between these phases and twinning variants are analysed, the theoretical results strongly supporting the observed microstructural evolution in the advanced intermetallic Nb-Ti-Al materials.

p6

A. Pasturel

LPMMC, Maison des Magisteres, CNRS, Grenoble

"First-principles calculations to describe the energetics of Zr-O system"

We have investigated the energies of a number of phases in Zr-O system using the ab initio plane wave approach with ultra-soft pseudopotentials. In a first step, we have studied the four structures of zirconia compound which are observed with increasing temperature and pressure. We show that gradient corrections are necessary to reproduce the experimental structural sequence. We have also studied the defects using a supercell approach and the main result is that the presence of charged vacancies of oxygen is able to modify the structural sequence in agreement with experimental results obtained for irradiated materials.In a second step, we have studied the oxygen absorption in Zr bulk and on the Zr (0001) surface . We show that the heat of absorption displays similar values for both bcc and hcp zirconium structures and the energetically most favorable occupation sites for oxygen are the octahedral sites. For the adsorption of oxygen on Zr (0001), we found that the energetically most favorable sites for oxygen are subsurface octahedral sites. Tha adsorption is found to be strongly exothermic and the oxygen atoms at subsurface adsorption sites are energetically more favorable than those in bulk oxides. The initial oxidation process of Zr surface is discussed in the framework of our ab initio results.

p7

M.Šob(1)(2), L.G. Wang(1) and V. Vitek(2)

"Study of the Structural Stability in Intermetallics Using Displacive Transformation Paths"

Relative structural stability of TiAl, FeAl, NiAl and NiTi is studied by investigating displacive phase transformation paths. These include the well known tetragonal (Bain's) and trigonal deformation paths which correspond to large homogeneous straining, and also more complex paths that include the shuffling of atomic planes. The results of full-potential APW total energy cal-

culations show that all higher-energy cubic structures studied are locally unstable with respect to some deformation modes. There may or may not be symmetry-dictated energy extrema corresponding to cubic lattices depending on the atomic ordering. However, other energy extrema that are not imposed by symmetry requirements occur along the transformation paths. Configurations corresponding to energy minima may represent metastable structures that can play an important role in interfaces and other extended defects. (1)Institute of Physics of Materials,
Academy of Sciences of the Czech Republic,Brno, Czech Republic
(2)Department of Materials Science and Engineering,
University of Pennsylvania, Philadelphia, PA, U.S.A.

p8

Elio G. Moroni and J. Hafner
Institut für Theoretische Physik, Technische Universität Wien, A 1040 Wien

"Structural and Magnetic Effects in Epitaxial Metallic Films"

The epitaxy of metallic films is investigated ab-initio using ultrasoft pseudopotentials and using simple continuum elasticity model along various deformation direction, for various crystal structures and substrate lattice dimension. For Mn, Fe, Co and Ni we analyse the stability of various magnetic configurations and we discuss the accuracy of the numerical calculations using different approximation for the exchange-correlation functional. To go beyond the local-spin-density-approximation (LSDA), generalized gradient approximations (GGA) for the exchange-correlation functional have been included. Application are also given for compounds and multilayers. The epitaxial stabilisation of bulk-unstable structure and the electronic modification of coherent epitaxy are discussed for Fe-Si compounds and for artificial FeSi/Fe and FeSi/Si multilayer. The potential electronic applications of these epitaxial material are discussed in the context of their novel properties.

p9

H. Schweiger, E.G. Moroni, W. Wolf, and R. Podloucky
Institute of Physical Chemistry, Univ. Vienna
Institute of Theoretical Physics TU Wien, A 1040 Wien

Residual resistometry revealed two processes of the order-order relaxation in the $L1_2$ ordering kinetics of $Ni_3Al(+0.19\%B)$. We computed formation energies of vacancies and antisites using pseudopotential as well as all electron full-potential methods to find an interpretation for the experimental results. From the calculated formation and activation energies we can ascribe the process with an unusual high activation energy of 4.2 eV with the creation of an Al-vacancy.

Report on the

Workshop on Quantum Theory of Solids, 'QTS-4'

Aarhus, November 12 - 15, 1997

Organized by: **Niels E. Christensen** (nec@dfi.aau.dk)

The workshop was held at the Institute of Physics and Astronomy, University of Aarhus. Approximately 37 participants, the majority invited, took active part in the meeting which consisted of invited talks, posters and discussions. A variety of subjects were treated, new LMTO formalisms (O.K. Andersen) and new way of implementing the LMTO (M. Methfessel and M. van Schilfgaarde), applications of FP-LAPW to phonon and structural properties of H-T_c materials (C. Ambrosch-Draxl) and to perovskites (A. Postnikov, M. Stachiotti, C.O. Rodriguez). The connection between the theoretical calculations for H-T_c materials and experiments was critically reviewed (M. Cardona). New developments of O(N)-methods were presented by J. Soler who illustrated his thechniques by application to several examples, including DNA. Very impressing. Applications of the PAW method to complex systems were presented by C. Koenig and M. Alouani.

Just a few examples of very interesting presentations are give above. Further details follow from the program (see below) and the abstracts which can be obtained from the web:

http://www.dfi.aau.dk/~nec/qts4.html

(a tar file of 'gzipped' abstract can be accessed and downloaded).

In summary, it was a scientifically very useful meeting with many very lively discussions.

(Niels E. Christensen.)

PROGRAM:

Wednesday November 12-th, 1997

10:00	10:25	Opening of meeting.	N.E. Christensen	Aarhus
10:30	11:15	"Theoretical High Pressure Crystal Structure Structure Studies of Ce, Th, Ca and the Anomalous Large Void CoSn Structure."	B. Johansson	Uppsala
11:30	13:30	**Lunch.**		
13:30	14:15	"Low-Energy One-Electron Hamiltonians from the LMTO Method. Applications to High-Temperature Superconductors"	O.K. Andersen	Stuttgart
14:30	15:15	"A new FP-LMTO method for crystals"	M. Methfessel	Frankfurt/O
15:30	16:00	**Coffee.**		
16.00	16.45	"Sublinear scaling in layered systems"	M. van Schilfgaarde	Stanford
17:00	17:45	"LAPW Investigations of Vibronic and Optical Properties of Y-Ba-Cu-O Compounds"	C Ambrosch-Draxl	Graz

Thursday, November 13-th, 1997

10:00	10:45	"Raman Spectra of High-Temperature Superconductors Above and Below T_c"	M. Cardona	Stuttgart
11:00	11:45	"First principles theoretical study of the electric-field gradients in high-temperature superconductors"	C.O. Rodriguez	La Plata
12:00	13:30	**Lunch**		

13:30	14.15	"Dynamical properties and structural transitions in perovskites"	R.L. Migoni	Rosario
14:30	15:15	"First-principles Supported Atomistic Modelling of Ferroelectric Perovskites"	M. Stachiotti	Rosario
15:30	16:00	**Coffee.**		
16:00	16:45	"Structural Instabilities and Lattice Vibrations in Perovskites"	A. Postnikov	Osnabrück
17:00	17:45	"Electronic and Dynamical properties of SrHfO3. Comparison with SrTiO3"	G. Fabricius	Madrid

Friday, November 14-th, 1997

10:00	10:45	"Recent Developments in ab initio O(N) Methods"	J. Soler	Madrid
11:00	11:45	"Structural Transformations and Charge Transfer in Mixed-Stack Organic Compounds: Ab-Initio Calculations Versus Experiments"	C. Koenig	Rennes
12:00	13:30	**Lunch**		
13:30	14.15	"Self-Interaction Corrected Electronic Structure Calculations of Lanthanides"	A. Svane	Aarhus
14:30	15:15	"Crystal-Structure Contribution to the Solid Solubility in Transition Metal Alloys"	H.L. Skriver	Lyngby
15:30	16:15	"LDA simulation of pressure induced anomalies in c/a and EFG for Zn and Cd"	D.L. Novikov	Evanston
16:30	??:??	Poster session + reception	see WWW	

Saturday, November 15-th, 1997

10:00	10:45	"Hartree-Fock Simulations of silver film adhesion on Al_2O_3(0001) and MgO(001) Surfaces"	E.A. Kotomin	Riga
11:00	11:45	"Soft Pseudopotentials and their Applications in Surface Science"	W.W. Schulz	Cambridge
12:00	14:30	**Lunch**		
14:30	15.15	"Ab-Initio PAW Calculation of Binding and Diffusion of a Ga Adatom on the GaAs (001)-c(4x4) Surface"	M. Alouani	Strasbourg
15:30	16:15	"Anisotropic Thermal Expansion in Silicate Systems"	A.I. Lichtenstein	Jülich
16:30	16:35	**Closing.**		

Invited Speakers:

M. Alouani, *Strasbourg (France)*
C. Ambrosch-Draxl, *Graz (Austria)*
O.K. Andersen, *Stuttgart (Germany)*
M. Cardona, *Stuttgart (Germany)*
G. Fabricius, *Madrid (Spain)*
B. Johansson, *Uppsala (Sweden)*
C. Koenig, *Rennes (France)*
E.A. Kotomin, *Riga (Latvia)*
A.I. Lichtenstein, *Juelich (Germany)*
M. Methfessel, *Frankfurt/O (Germany)*
R.L. Migoni, *Rosario (Argentina)*
D. Novikov, *Evanston (USA)*
A. Postnikov, *Osnabrueck (Germany)*
C.O. Rodriguez, *La Plata (Argentina)*
M. van Schilfgaarde, *Stanford (USA)*
W.W. Schulz, *Cambridge (UK)*
H. Skriver, *Lyngby (Denmark)*
J. Soler, *Madrid (Spain)*
M. Stachiotti, *Rosario (Argentina)*

A. Svane, *Aarhus (Denmark)*

Further Invited Participants:

R.E. Eglitis, *Riga, (November: Osnabrueck)*
R. Alonso, *La Plata (Argentina)*
F. Aryasetiawan, *Lund (Sweden)*
R. Weht, *Buenos Aires (Argentina)*
M. Weissman, *Buenos Aires (Argentina)(Nov.: France)*
I. Gorczyca, *Warsaw (Poland)*
T. Strohm, *Stuttgart (Germany)*
D. Munzar, *Stuttgart (Germany)*
E. Peltzer y Blanca, *La Plata (Argentina)*
M. Šob, *Brno (Czech Republic)*

Report on

Ab Initio Modelling Program (AIMPRO) Meeting

The meeting began on the evening of October 30, 1997 and continued until late on Friday. It was attended by 16 people.

Dr. Patrick Briddon from Newcastle described some recent developments in the AIMPRO package, a LDA program in which the Kohn–Sham equations are solved in real space using a localised basis. Various new feature were discussed, including modifications to improve the accuracy and stability of the charge density fitting procedure and its relevance to a number of problems currently being studied by the group. It is hoped that the improved stability in this latest version may enable more rapid progress to be made in a number of areas, for example the standard approach has not always worked for complexes of transition metal atoms with native lattice defects in diamond, a system in which correlation effects are particularly important and for which progress has been slower than anticipated.

In addition, a new code was introduced, also using localised basis of Gaussian orbitals of arbitrarily high angular momenta $s, p, d, f, \ldots$, but this time working within periodic boundary conditions rather than with the framework of a cluster as discussed in the previous paragraph. The program uses either an LDA or GGA treatment of exchange–correlation and pseudopotentials can be specified, either in the BHS parametrised form or on a radial grid. The program gives all the standard properties of bulk solids such as lattice constant, bulk modulus, phonon spectra to the same accuracy as other LDA codes, mostly using plane waves.

For example, the GaAs phonon frequencies (in cm^{-1}) at the zone edge points are trivially obtained from a 16 atom unit cell calculation and are presented in the following table for a number of different basis sets (using 4, 5 and 6 Gaussian functions to expand the s and $p-$ orbitals).

Mode	4 exp	5 exp	6 exp	expt
LO/TO(Γ)	292	278	276	267/285
TA(X)	88	88	90	79
LA(X)	232	224	225	227
TO(X)	268	256	255	252
LO(X)	255	246	244	241
TA(L)	66	66	66	62
LA(L)	224	217	216	209
TO(L)	280	267	265	261
LO(L)	247	238	239	238

We have calculated some properties of defects with the new code, and obtain the localised vibrational mode of the carbon interstitial in silicon to within 30 wave-numbers of the experimental

value, a result slightly better than the cluster result but using a smaller number of atoms. The relative stabilities of a number of structures involving gold in silicon has also been investigated.

The use of localised orbitals as opposed to the plane waves, more commonly used for unit-cell calculations makes this code more compatible with our previous methodologies and is especially efficient when we are dealing with problems such as transition metal ions in semiconductors, where a large basis has to be used in one part of the unit cell with a smaller basis elsewhere. The use of a supercell complements the cluster approach we have used previously, broadening the range of problems which the group can study.

There was a lengthy discussion of the details of how this can be used of this to help with a number of projects currently under way. These include dislocations and extended defects (in which periodic boundary conditions may be applied in one or two dimensions only, and hydrogen termination in the remainder) (*Phys.Rev.Lett.*, in press); oxygen complexes in silicon where it is hoped that the total energies found may converge more rapidly than is the case in clusters (for more details see (*Phys.Rev.Lett.* **77**, 865-8, (1996)) ; and formation energies and stabilities of lattice defects and solubilities of dopants, which it is very much more straightforward to calculate in the absence of an additional element acting as a terminator as is the case in a cluster approach. This will feed into a number of projects (see *Phys.Rev.Lett.*, **77**, 4812-5 (1996); *Phys.Rev.B*, **53**, 16289 (1996). We will be producing a detailed comparison between the cluster and supercell treatments in the future.

The new code is written in FORTRAN90 using full dynamic memory allocation, and the group also held a technical discussion as to whether this should also be done with AIMPRO, and what the best approach would be. The code was installed on a number of hardware platforms including serial versions for workstations and a fully parallelised version on the T3E at Edinburgh.

Further technical details concerning the program or the meeting can be obtained from Patrick Briddon (patrick.briddon@ncl.ac.uk) or Bob Jones (jones@excc.ex.ac.uk).

4 Workshop/Conference Announcements

4.1 ICTP Workshop on LAPW

ICTP WORKSHOP ON

THE PHYSICS OF THE ELECTRONIC BEHAVIOUR IN THE CORE REGION: ALL-ELECTRON LAPW ELECTRONIC STRUCTURE CALCULATIONS

22 June - 4 July 1998

(Miramare - Trieste, Italy)

An international Workshop on LAPW electronic structure calculations will be held at the International Centre for Theoretical Physics, Trieste, from 22 June to 4 July 1998. This Bulletin contains the preliminary programme of the Workshop, request for participation form and miscellaneous information.

ORGANIZERS:

P. Blaha (Technische Universitaet Vienna, Austria)
J. Kohanoff (ICTP, Trieste, Italy)
C.O. Rodriguez (IFLYSIB, La Plata, Argentina)
K. Schwarz (Technische Universitaet Vienna, Austria).

I. PURPOSE AND NATURE

The workshop will be focused on the recent progress in density functional calculations using the all-electron full-potential Linearized Augmented Plane Wave (FP-LAPW) method as embodied in the WIEN97 code. This all-electron methodology is presently considered to be one of the most precise electronic structure tools in condensed matter physics. The scientific programme will cover an introduction to Density Functional Theory (DFT), band structure methods, in general, and the LAPW method with corresponding algorithms and features, in particular. A second part will deal with applications directly or indirectly related to the WIEN97 package. Oral and poster presentations will illustrate interesting topics related to the physics of core electrons, namely spin-orbit splitting, electric field gradients, crystal field parameters, photoemission and X-ray emission/absorption spectra. Also more general topics such as molecular dynamics, phonons and phase stability will be included in the programme.

Mainly during the first week but continued in the second, the Research Leaders, in collaboration with a group of tutors, will coach the participants in the actual implementation and usage of the WIEN97 package, using ICTP's computing facilities. It is expected that, during this fortnight, specific small projects will be carried out by the participants.

In addition to the scheduled lectures there will be formal and informal seminars on a variety of research topics by lecturers, participants and visiting experts.

II. PROGRAMME

A preliminary list of Research Leaders includes:

P. Blaha (Vienna, Austria): Concepts and fundamentals of LAPW and the WIEN97 code.

C. A. Draxl (Graz, Austria): Applications of the LAPW method to phonons and optics.

J. Luitz (Vienna, Austria): The graphical user interface of WIEN97.

P. Novak (Prague, Czech Republic): Calculation of spin-orbit coupling.

C. O. Rodriguez (La Plata, Argentina): Electric field gradient calculations.

M. Scheffler (Berlin, Germany): Applications of the LAPW method to chemical reactions at metal and semiconductor surfaces.

K. Schwarz (Vienna, Austria): Fundamentals of DFT and applications of the LAPW code.

D. Singh (Washington, U.S.A.): Applications of the LAPW code to perovskites.

III. RELATED ACTIVITY

Coinciding with the last three days of the Workshop (2 - 4 July 1998) ICTP will hold a related Conference on "Hyperfine Interactions in the Solid State: Experiments and First-principles Electronic Structure Calculations". As this activity has its own separate Bulletin/Request for Participation Form, anyone wishing to apply must request and fill in the relevant form which may be obtained via e-mail: smr1100@ictp.trieste.it or addressing your requests to ICTP quoting the exact title of the Conference.

IV. PARTICIPATION

The Workshop is open to research workers from all countries that are members of the United Nations, UNESCO or IAEA. As the Workshop will be conducted in English, participants should have an adequate working knowledge of that language. Applications from graduate students about to finish their PhD, fresh post-docs and young, active faculty members are encouraged. A background in solid state theory, electronic structure and density functional theory is required. Knowledge of FORTRAN and UNIX is a necessary condition.

For logistic reasons, due to the number of PCs available, the total number of participants in the Workshop is limited.

As a rule, travel and subsistence expenses of the participants are borne by the home institution.

However, some funds are available which permit the Centre to grant a subsistence allowance to a limited number of people from developing countries who will be selected by the Organizers. As scarcity of funds allows travel to be granted only in few exceptional cases, every effort should be made by candidates to secure support for their fares (or at least partial fare) by their home country. Such financial support is available only to those attending the entire Workshop. Scientists from developed countries are welcome to join on their own funds. There is no registration fee for attending the Workshop.

Deadline for the RECEIPT of request for participation form:
28 February 1998

The "Request for Participation" form can be obtained via e-mail:

smr1085@ictp.trieste.it, using as subject **"get bulletin"**

or via WWW Server:

http://www.ictp.trieste.it/cgi-bin/ICTPsmr/mkhtml/smr2html.pl?smr1085/Bulletin

and should be sent to:

International Centre for Theoretical Physics
Workshop on "The Physics of the Electronic Behaviour in the Core Region"
P.O. Box 586 (Strada Costiera 11: for courier delivery)
I-34100 Trieste
Italy

or via e-mail to:

smr1085@ictp.trieste.it, followed by hard copy via regular mail.

Please note that no LATEX/TEX files are accepted.

Any attachments to the request for participation, relevant to extra information for selection purposes, should not exceed 6 pages.

The decision of the Organizing Committee will be communicated to all candidates as soon as possible.

VERY IMPORTANT:

If you have obtained the following form via e-mail or gopher, please follow these instructions:

1) ABSOLUTELY do NOT modify the form at all;
2) PRINT it in portrait mode (A4 lengthwise);
3) Fill in the HARD copy of the form,sign it and post it as indicated above.

4.2 ICTP Conference on Hyperfine Interactions

ICTP CONFERENCE ON

HYPERFINE INTERACTIONS IN THE SOLID STATE: EXPERIMENTS AND FIRST-PRINCIPLES ELECTRONIC STRUCTURE CALCULATIONS

2 - 4 July 1998

(Miramare - Trieste, Italy)

An international Conference on: "Hyperfine interactions in the solid state: Experiments and first-principles electronic structure calculations" will be held at the International Centre for Theoretical Physics, Trieste, from 2 to 4 July 1998, within the ICTP Workshop on The Physics of the Electronic Behaviour in the Core Region: All-electron LAPW Electronic Structure Calculations (22 June - 4 July 1998). Organizers of the Conference will be: P. Blaha (Technische Universitaet Vienna, Austria), A. Lopez Garcia (Universidad Nacional de La Plata, Argentina), R.C. Mercader (Universidad Nacional de La Plata, Argentina), C.O. Rodriguez (IFLYSIB, La Plata, Argentina) and W. Steiner (Technische Universitaet Vienna, Austria). The local organizer will be: J. Kohanoff (ICTP, Trieste, Italy).

Experiments that make use of nuclear hyperfine interactions to investigate solid-state properties, such as Mossbauer Spectroscopy, Perturbed Angular Correlations, Nuclear Magnetic Resonance, Nuclear Quadrupole Resonance, or Muon Spin Resonance, have traditionally found an almost unsurmountable barrier when comparing their results with the predictions of available models, which could even lead to wrong interpretation of the experimental results. In all cases it has been, up to now, impossible to assess reliably the influence that the electrons - in particular their behaviour in the core region - have on the nuclear splittings sensed by those techniques. Only recently has a reliable solid-state theoretical description of the behaviour of the core electrons been achieved through all-electron full-potential methodologies. The advances in the efficiency of the computational methods and computing power have also allowed very complex systems to be studied successfully. The precision reached by state-of-the-art codes has since then drawn great attention from experimentalists, who find a new momentum to the interpretation of their results.

With this Conference we would like to call the attention of the large experimentalist community who use hyperfine interactions as their main research tool, to get them acquainted with the new possibilities offered by theoretical calculations currently available. At the same time, it is intended that theoreticians working in this area meet members of the hyperfine community to get first-hand knowledge of which are the open problems experimentalists face in their laboratories, and to try to find together new strategies to tackle the difficult problems that arise in many

of the systems under study. To know the current possibilities and limitations will be of great benefit for both communities attending the conference.

Invited Speakers:

P. Blaha (Vienna, Austria): Theory of hyperfine parameters.

P. Boolchand (Cincinnati, U.S.A.): Experimental measurements of electric field gradients in HTSCs and glasses.

T. Butz (Leipzig, Germany): Nuclear quadrupole interactions in molecules and crystals: experiments and theory.

N.E. Christensen (Aarhus, Denmark): Ab-initio studies of iron-silicides.

P.H. Dederichs (Juelich, Germany): Hyperfine interaction parameters calculated by KKR-Green's function method.

M. Faehnle (Stuttgart, Germany): Electric field gradients as fingerprints of atomic defects in crystals: the impact of ab-initio calculations.

M. Forker (Bonn, Germany): Electric quadrupole interactions in metal-hydrogen systems.

A. Lopez Garcia (La Plata, Argentina): Electric field gradients in perovskites.

H. Haas (Berlin, Germany): The electric field gradient in simple solids: experiments, calculations and models.

R.C. Mercader (La Plata, Argentina): Mossbauer determination of electric field gradients and hyperfine fields in small particles systems.

D.L. Nagy (Budapest, Hungary): Mossbauer effect methodology: energy and time domain experiments.

H. Petrilli (Sao Paulo, Brazil): The PAW method and calculations of hyperfine parameters.

P. Riedi (St. Andrews, U.K.): Experimental nuclear resonance with particular application to correlated electron and ordered magnetic systems.

C.O. Rodriguez (La Plata, Argentina): Ab initio determination of electric field gradients in HTSCs.

R.B. Scorzelli (Rio de Janeiro, Brazil): Phase transformations in Fe-Ni Invar-type alloys in meteorites, thin films and mechanically alloyed samples.

W. Steiner (Vienna, Austria): Dynamics of hyperfine interactions determined by Mossbauer spectroscopy.

H. Winkler (Luebeck, Germany): Precision measurements of hyperfine parameters by nuclear resonant forward scattering of synchrotron radiation.

The Conference is open to research workers from all countries that are members of the United Nations, UNESCO or IAEA. As a rule, travel and subsistence expenses of the participants are borne by the home institutions. However, some funds are available which permit the Centre to grant a subsistence allowance to a limited number of people from developing countries who will be selected by the Organizers. As scarcity of funds allows travel to be granted only in few exceptional cases, every effort should be made by candidates to secure support for their fares

(or at least partial fare) by their home country. Scientists from developed countries are welcome to join on their own funds. There is no registration fee for attending the Conference.

Deadline for receipt of requests for participation:

28 February 1998

Scientists not requesting financial support may apply by:

31 March 1998

The "request for participation" form can be obtained via e-mail:

smr1100@ictp.trieste.it, using as subject **"get bulletin"**

or via WWW Server:

http://www.ictp.trieste.it/cgi-bin/ICTPsmr/mkhtml/smr2html.pl?smr1100/Bulletin

and should be sent to:

Conference on "Hyperfine Interactions in the Solid State"
International Centre for Theoretical Physics
P.O. Box 586 (Strada Costiera 11: for courier delivery),
I-34100 Trieste, Italy

or via e-mail to:

smr1100@ictp.trieste.it, followed by hard copy via regular mail.

Telephone: +39-40-2240111
E-mail: smr1100@ictp.trieste.it
Telex: 460392 ICTP I
Telefax: +39-40-224163

Please note that no LATEX/TEX files are accepted.

Any attachments to the request for participation, relevant to extra information for selection purposes, should not exceed 6 pages.

The decision of the Organizing Committee will be communicated to all candidates as soon as possible.

VERY IMPORTANT:

If you have obtained the following form via e-mail or gopher, please follow these instructions:

1) ABSOLUTELY do NOT modify the form at all!;
2) PRINT it in portrait mode (A4 lengthwise);
3) Fill in the HARD copy of the form,sign it and post it as indicated above.

4.3 1998 CONFERENCE ON COMPUTATIONAL PHYSICS - CCP 1998

September 2-5 1998, GRANADA (Spain)

Sponsored by the European Physical Society, the International Union of Pure and Applied Physics, and the American Physical Society

Organized by the EPS Computational Physics Board and the Institute Carlos I for Theoretical and Computational Physics of the University of Granada

The CCP 1998, to he held at the Exhibition and Conference Centre in Granada, initiates a new series that continues the tradition of both the APS-EPS Physics Computing conferences (Boston 1989, Amsterdam 1990, San Josi 1991, Prague 1992, Albuquerque 1993, Lugano 1994, Pittsburgh 1995, Krakow 1996, Santa Cruz 1997), and the Asian ICCP conferences (Beijing 1988 and 1993, Taiwan 1995 and Singapore 1997), some of which have also been supported by the IUPAP.

PROGRAMME

The methods developed to deal with the computational aspects of physical problems are useful in an increasing number of situations, from chemistry and geology to engineering and communications. Computational Physics has thus evolved into a trans-disciplinary field now concerned with the creative use of computers in all fields of scientific research. This is partly because Computational Physics is very well suited to study cooperativity. Cooperative and collective phenomena, a main concern of Statistical Physics, occur and often determine the emergent, observable behavior at the interfaces between physics and biology, economy, sociology, environmental sciences, etc. The CCP 1998 is planned to focus at this interface, so that contacts and the exchange of ideas and methods between these different fields of science are favoured. With this aim, abstract submissions are strongly encouraged not only from these interfaces but from all areas of Computational Physics, and the final programme is expected to consist of invited lectures and other contributions on

Computer-aided Simulation and Modelling

Novel Monte Carlo Methods, Novel Methods in Fluid Dynamics, Quantum Computing Methods, High Performance Visualization, Large Scale Computing Systems, Symbolic Modelling, ...

And their Applications to

Condensed Matter and Materials Science, Statistical Physics, Nonlinear and Adaptive Systems, Astronomy and Cosmology, High Energy Physics and Accelerators, Nuclear and Plasma Physics, Atomic, Molecular and Optical Physics, Environmental and Geological Phenomena, Pattern

Recognition and Classification, Artificial Intelligence and Neural nets, Industry such as Modeling Industrial Devices, Materials and Processes, ...

Speakers are to be confirmed.

In addition to invited lectures and oral and poster contributions, we are planning industrial and commercial exhibits and technical presentations, e.g., educational and scientific software, computers and workstations, and emerging technologies concerning computing and networking.

Science is expected to meet computation at the CCP 1998!

A social programme, and post conference tours, will be offered.

Full details, including the call for papers, are available at **http://dalila.ugr.es/ ccp1998.**

5 Job Announcements

Announcement: Post-doc position in electronic structure theory and perpendicular anisotropy

Partner Sweden of the TMR network

A postdoctoral position is available at The Condensed Matter Theory Group, Uppsala University, Sweden. Interested applicants should contact: Professor Borje Johansson (email:borje.johansson@fysik.uu.se), Dr. M.S.S. Brooks (email:brooks@ituprag.fzk.de), Dr. Olle Eriksson (email:olle.eriksson@fysik.uu.se), Dr. Lars Nordström (lars.nordstrom@fysik.uu.se) or Dr. Igor Abrikosov (abrikos@fysik.uu.se). Only citizens of the countries belonging to the European Community, with the exception of Sweden, are eligible.

Two Postdoctoral Positions in Condensed Matter Theory

Max–Planck–Institute Halle

The Max-Planck-Institute for Microstructure Physics at Halle, Germany, has **two postdoctoral positions in Condensed Matter Theory** available for up to three years. The candidate for the first position will carry out calculations on **Nonlinear Optics** of low-dimensional systems using both density-functional theory (FLAPW) and electrodynamic methods. A strong background in electronic bandstructure calculations based on first-principles theory is expected. The candidate for the second position will develop a many-body theory of **Femtosecond Spin-Dynamics** in thin magnetic films using non-perturbative methods. Experience with many-body techniques (exact diagonalization, quantum chemical methods, or Green's function techniques) is required for this position. The gross salary of the positions amounts to approx $ 45,000 depending on age, experience, and marital status (BAT IIa according to German Salary Scale). The Max-Planck Society is an Affirmative Action/Equal Opportunity employer. Applications from women, minorities, and disabled persons are encouraged.

Candidates for one of the positions, which must be non-German citizens of the European Union or an Associated State (Associated States are Iceland, Israel, Liechtenstein, and Norway) should send an application including a CV and the names of three references to **Dr. W. Hübner, Max-Planck-Institut für Mikrostrukturphysik Halle, Weinberg 2, D – 06120 Halle, Fax: ++49-345-5511 223, email:huebner@mpi-halle.mpg.de**

POST-DOCTORAL POSITIONS
SISSA/ISAS TRIESTE

The International School for Advanced Studies (SISSA/ISAS) in Trieste expects to offer 3 post-doctoral positions in the field Theory of Condensed Matter

Research lines include electronic structure, empirical and ab-initio molecular dynamics simulations of solids, liquids, and surfaces, strongly correlated systems, quantum fluids, surface phenomena, phase transitions, statistical mechanics and nonequilibrium phenomena. The present research group includes faculty members: S. Baroni, G.C. Chiarotti, S. de Gironcoli, F. Ercolessi, M. Fabrizio, S. Fantoni, A. Maritan, M. Marsili, G. Santoro, S. Sorella, E. Tosatti, plus about 8 postdocs and long-term visitors, plus 20 Ph.D. students.

You can find more details on the activities of the group at the URL:
http://www.sissa.it/cm

These positions will be available from the Fall of 1998 for one year and renewable for a second year. Candidates, who must not be over 36 years of age, should submit their applications by 31 December 1997 with their Curriculum Vitae, list of papers and preprints, and a tentative non committal research programme. They should arrange for at least 2 letters of reference to be sent by the same date. Email applications are welcome, but a hardcopy should also reach the School anyway before the deadline.

Applications and correspondence should be sent to:

Postdoc Programme
International School for Advanced Studies
Via Beirut, 2-4
34013 TRIESTE - ITALY
email: postdoc@sissa.it
fax (+39) 40 3787528

Claudia PARMA - S.I.S.S.A. Scientific Secretariat
Phone no.: +39-40-3787453 - Fax no.: +39-40-3787528 - Telex 460269 - SISSA

NEW POST-DOC POSITION IN COMPUTATIONAL

CONDENSED-MATTER PHYSICS

A new Post-Doc position will be soon opened in my group at the Department of Materials Science - University of Milano (Italy).

The position will be funded by the Italian Institute for the Physics of Matter (INFM). The candidate will operate within the INFM research network on Silicon Physics (SiNET). The position is for 1 year, renewable for 1 more year. The gross salary will be fixed according to INFM rules and candidate's qualifications (see below). A Ph.D. in Condensed Matter Physics, Materials Science, or Theoretical Chemistry is requested. Italian students that have successfully completed their three-year Ph.D. curriculum will be considered as regular Ph.D. candidates.

For this position the candidate is expected to work on theoretical and computational aspects of defect physics in silicon, by means of quantum (tight-binding) and classical (empirical) molecular dynamics simulations.

The candidate should be familiar with the use and application of atomistic simulation tools to general materials science problems. In addition, priority will be given to those candidates with a background in parallel computing and/or tight-binding molecular dynamics.

More details on the Post-Doc position can be found on the INFM Web page:

http:/www.infm.it.

Deadline: **30 December, 1997**

Requests of further information could be forwarded directly to:

Dr. Luciano Colombo
Department of Materials Science
University of Milano
via Emanueli 15
20126 Milano
Italy
Phone : +39 2 66174218
Fax : +39 2 66174403 E-mail: luciano.colombo@mater.unimi.it

Postdoctoral Position in

Theory of Atomic and Molecular Manipulation

Department of Applied Physics,
Chalmers/Göteborg University,
Göteborg, Sweden

A postdoctoral position within the TMR network on "Atomic/Molecular Manipulation" is open in the theory group of Materials and Surface Physics. The successful applicant will work on the theoretical description and modeling of manipulation of individual atoms and molecules with the scanning tunneling microscope under supervision of S. Gao and M. Persson and in collaboration with the theory and experimental groups of the network. Candidates should have a Ph. D and a strong background in the theoretical and computational methods of condensed matter physics such as electronic structure methods based on density functional theory and many-body techniques. The post is up to three years and starting date will be as soon as possible. Further details about the position can be obtained from Mats Persson. (See, e.g. **http://fy.chalmers.se/ap/msp/** and **http://fy.chalmers.se/ap/TMR/** for some information about our group and the network, respectively).

Applicants should send a CV, a list of publications and names of a few reference persons with phone numbers to:

Prof. Mats Persson,
Department of Applied Physics,
Chalmers/Göteborg University,
S-412 96 Göteborg, SWEDEN
e-mail: tfymp@fy.chalmers.se
phone: +46-31-7723666

6 Abstracts

A Relativistic Framework for Microscopic Theories of Superconductivity
Part One: The Dirac Equation for Superconductors

K. Capelle and E.K.U. Gross
Institut für Theoretische Physik, Universität Würzburg,
D-97074 Würzburg, Germany

Abstract

We present a unified treatment of relativistic effects in superconductors. The relativistically correct (Dirac-type) single-particle Hamiltonian describing the quasi-particle spectrum of superconductors is deduced from symmetry considerations and the requirement of the correct non-relativistic limit. We provide a complete list of all order parameters consistent with the requirement of Lorentz covariance. This list contains the relativistic generalizations of both the BCS and the triplet order parameters, as well as new types of order parameters which were previously unknown. Furthermore, we present a symmetry classification of the order parameters according to their behaviour under the Lorentz group, generalizing previous treatments that were based on the Galilei group.

(Submitted to Phys. Rev. B)
Manuscripts available from: gross@physik.uni-wuerzburg.de

A Relativistic Framework for Microscopic Theories of Superconductivity
Part Two: The Pauli Equation for Superconductors

K. Capelle and E.K.U. Gross
Institut für Theoretische Physik, Universität Würzburg,
D-97074 Würzburg, Germany

Abstract

It is shown that the interplay between relativity and coherence, found in superconductors with heavy elements, leads to a number of interesting and previously unknown effects. These include several types of spin-orbit coupling present only in superconductors. Explicit expressions describing these effects are derived using a covariant formulation of the theory of superconductivity. It is demonstrated that relativistic effects can become relevant, e.g., in high-temperature and heavy-fermion superconductors, but the theory is just as well applicable to any other situation in which pairing takes place.

(Submitted to Phys. Rev. B)
Manuscripts available from: gross@physik.uni-wuerzburg.de

Approximate Relativistic Optimized Potential Method

T. Kreibich[(a)], E.K.U. Gross[(a)] and E. Engel[(b)]
[(a)] *Institut für Theoretische Physik, Universität Würzburg,*
D-97074 Würzburg, Germany
[(b)] *Institut für Theoretische Physik, Universität Frankfurt,*
Robert Mayer Straße 8-10, D-60054 Frankfurt/Main, Germany

Abstract

Approximate semianalytical solutions of the integral equation for the relativistic optimized potential are constructed by extending a method recently proposed by Krieger, Li, and Iafrate [Phys. Lett. A **146**, 256 (1990)] to the relativistic regime. The quality of the approximation is tested in the longitudinal x-only limit where fully numerical solutions of the relativistic optimized effective potential integral equation are available for spherical atoms. The results obtained turn out to be in excellent agreement with the exact x-only values. The proposed method provides significant improvement over the conventional relativistic local density approximation and generalized gradient approximation schemes.

(Phys. Rev. A 56, (1997), in press)
Manuscripts available from: kreibich@physik.uni-wuerzburg.de

Analysis of Dichroism in the Electromagnetic Response of Superconductors

K. Capelle[(a)], E.K.U. Gross[(a)] and B.L. Gyorffy[(b)]
[(a)] *Institut für Theoretische Physik, Universität Würzburg, D-97074 Würzburg, Germany*
[(b)] *University of Bristol, Tyndall Avenue, Bristol, BS8 1TL, UK*

Abstract

The absorption of polarized light in superconductors is studied within the framework of the Bogolubov-de Gennes approach to inhomogeneous superconductors in magnetic fields. Several mechanisms which give rise to a polarisation dependent absorption (i.e., dichroism) in superconductors are analysed in detail. The relation to the absorption of unpolarized light in superconductors and to the absorption of polarized light in normal conductors is investigated and several new effects, not known from either of these cases, are found. These effects arise from the interplay of broken chiral symmetry, which produces dichroism, with the superconducting coherence. One potential source for dichroism, namely spin-orbit coupling, is investigated numerically for a simple model superconductor.

(Submitted to Phys. Rev. B)
Manuscripts available from: gross@physik.uni-wuerzburg.de

Asymptotic Properties of the Optimized Effective Potential

T. Kreibich[(a)], S. Kurth[(b)], T. Grabo[(a)] and E.K.U. Gross[(a)]
[(a)] *Institut für Theoretische Physik, Universität Würzburg, D-97074 Würzburg, Germany*
[(b)] *Dept. of Physics, University of Antwerpen (RUCA), Groenenborgerlaan 171, 2020 Antwerpen, Belgium*

Abstract

Rigorous properties of the optimized effective potential (OEP) are derived. We present a detailed analysis of the asymptotic form of the OEP, going beyond the leading term. Furthermore, the asymptotic properties of the approximate OEP scheme of Krieger, Li and Iafrate [Phys. Lett. A **146**, 256 (10990)] are analysed, showing that the leading asymptotic behavior is preserved by this approximation.

(Advances in Quantum Chemistry, in press)
Manuscripts available from: kreibich@physik.uni-wuerzburg.de

Optimized Effective Potential for Atoms and Molecules

T. Grabo, T. Kreibich and E.K.U. Gross
Institut für Theoretische Physik, Universität Würzburg, D-97074 Würzburg, Germany

Abstract

We describe the optimized effective potential method of density functional theory and the semi-analytical approximation due to Krieger, Li and Iafrate. Results for atomic and molecular systems including correlation contributions are presented and compared with conventional Kohn-Sham methods. The combination of the exact exchange energy functional with the correlation energy functional of Colle and Salvetti works extremely well for atomic systems, while further improvement is required for molecular systems.

(Molecular Engineering (1997), in press)
Manuscripts available from: kreibich@physik.uni-wuerzburg.de

The electronic structure and optical properties of $\beta-FeSi_2$

V.N. Antonov, O. Jepsen
Max–Planck–Institut für Festkörperforschung,
D-70569 Stuttgart, Federal Republic of Germany
W. Henrion, M. Rebien, P. Stauß, H. Lange
Hahn–Meitner–Institut Berlin GmbH, Abteilung Photovoltaik,
Rudower Chaussee 5, D-12489 Berlin, Federal Republic of Germany

Abstract

We have investigated the optical properties of $\beta-FeSi_2$ experimentally and theoretically. The measured optical functions were compared with those calculated using the local density functional (LDA) theory and the linear muffin-tin orbital (LMTO) method. The calculated electronic structure is analysed using orbital projected densities of states (DOS) and the optical functions are interpreted in terms of interband transitions. We find generally excellent agreement between theory and experiment.

(Submitted to Phys. Rev. B)
Manuscripts available from: jepsen@and.mpi-stuttgart.mpg.de

Buckling and d–Wave Pairing in HiTc–Superconductors

O. Jepsen, O.K. Andersen, I. Dasgupta, and S. Savrasov
Max–Planck–Institut für Festkörperforschung,
D-70569 Stuttgart, Federal Republic of Germany

Abstract

We have investigated whether the electron-phonon interaction can support a d–wave gap–anisotropy. On the basis of models derived from LDA calculations, as well as LDA linear-response calculations we argue that this is the case, for materials with buckled or dimpled CuO_2 planes, for the so–called buckling modes, which involve out–of–plane movements of the plane oxygens.

(Submitted to J. Chem. Phys. Sol.)
Manuscripts available from: jepsen@and.mpi-stuttgart.mpg.de

Overlayer–dependent magnetic moment and anisotropy of a Co monolayer on Cu(100)

L. Szunyogh[a,b], B. Újfalussy[a,c], U. Pustogowa[a], and P. Weinberger[a,d]
[a] *Center for Computational Materials Science, Gumpendorferstr. 1a, A-1060, Vienna, Austria*
[b] *Department of Theoretical Physics, Technical University Budapest, Budafoki út 8, H-1521, Budapest, Hungary*
[c] *Research Institute for Solid State Physics, Hungarian Academy of Sciences, H-1525 Budapest, PO Box 49, Hungary*
[d] *Institut für Technische Elektrochemie, Technische Universität Wien, Getreidemarkt 9/158, A-1060, Vienna, Austria*

Abstract

An extensive study of the magnetic moment and of the magnetic anisotropy of a Co monolayer on a Cu(100) substrate capped by an additional $3d$, $4d$ or $5d$ monolayer is presented in terms of first–principles calculations. While for the magnetic moment of the Co and the cap layer systematic trends can be traced which seem to be consistent with the Stoner model, the dependence of the magnetic anisotropy energy on the type of overlayer is found to be less straight–forward. However, in some selected cases a correlation of the magnetic anisotropy with the specific features in the electronic structure of the Co and the cap layer can be pin–pointed.

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Manuscripts available from: pw@ws1.cms.tuwien.ac.at

Is there 'superlattice' symmetry in magnetic multilayer systems?

J. Zabloudil
Center for Computational Materials Science, Vienna, Austria
C. Uiberacker, C. Blaas
Institute for Technical Electrochemistry, Technical University of Vienna, Austria
U. Pustogowa
Center for Computational Materials Science, Vienna, Austria
L. Szunyogh
Center for Computational Materials Science, Vienna, Austria
and Department of Theoretical Physics, Technical University of Budapest, Budapest, Hungary
C. Sommers
Laboratoire de Physique des Solides, Campus d'Orsay, Orsay, France
P. Weinberger
Center for Computational Materials Science, Vienna, Austria
and
Institute for Technical Electrochemistry, Technical University of Vienna, Austria

Abstract

The problem of 'superlattice' symmetry, i.e., the question of periodicity along the growth direction (surface normal) in magnetic multilayer systems is discussed using discrete Fourier transformations for the anisotropy energy, as well as for the antiparallel and perpendicular interface exchange coupling. We analyse the system Cu(100)/$(Cu_3Ni_3)_n$, where n is the number of repetitions, for the case of free surfaces and surfaces capped semi-infinitely by Cu(100). It will be shown that for some magnetic properties, and only in certain situations (almost) periodic behavior with respect to n applies, while for other properties an oscillatory behavior is characteristic. Also discussed are implications with respect to typical experimental situations and with respect to traditional 'supercell' approaches.

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Oscillatory behavior of the magnetic anisotropy energy in Cu(100)/Co_n multilayer systems

L. Szunyogh[a,b], B. Újfalussy[a], C. Blaas[c], U. Pustogowa[a], C. Sommers[d], and P. Weinberger[a,c]

[a] *Center for Computational Materials Science, Vienna, Austria*

[b] *Department of Theoretical Physics, Technical University of Budapest, Budapest, Hungary*

[c] *Institut für Technische Elektrochemie, Technische Universität Wien, Vienna, Austria*

[d] *Laboratoire de Physique des Solides, Campus d'Orsay, Orsay, France*

Abstract

The oscillatory behavior of the magnetic anisotropy energy in different types of Co_n multilayers on a Cu(100) substrate, including free surfaces, capped surfaces, and Co/Cu spacer systems, is shown in terms of ab-initio like calculations using the selfconsistent fully relativistic spin-polarized Screened Korringa-Kohn-Rostoker method. Deduced from direct representations and discrete (linear) Fourier transformations with respect to the number of Co layers, a period of two monolayers seems to be characteristic for these oscillations, whereas for a given number of Co layers and viewed with respect to the number of Cu-spacer layers they rapidly approach the value of the magnetic anisotropy energy for the corresponding Co_n multilayer on Cu(100) with a semi-infinite Cu cap, the so-called biased value. By excluding the so-called preasymptotic regime a short and a long period of 2.5 and 5.5 monolayers, respectively, can be traced for the oscillations with respect to the number of Cu-spacer layers.

All types of oscillations, namely either with respect to the number of Co layers or with respect to the number of Cu-spacer layers, are analyzed in terms of layer-resolved band energy contributions to the magnetic anisotropy energy. Such a layer-wise distribution of the magnetic anisotropy energy not only allows one to characterize different regimes of thicknesses, but also to discuss the effect of the actual interface on the absolute values of the magnetic anisotropy energy, shown in particular by considering a system with Co/Au interfaces.

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Real Space Approach to the calculation of Magnetocrystalline Anisotropy in Metals

S.V. Beiden*, W.M. Temmerman†, Z. Szotek†, G.A. Gehring*,
G.M. Stocks‡, Yang Wang‡, D.M.C. Nicholson‡, W.A. Shelton‡,
and H. Ebert§

Department of Physics, University of Sheffield, Sheffield, U.K.
†*Daresbury Laboratory, Daresbury, Warrington, WA4 4AD, U.K.*
‡*Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA*
§*Institute for Physical Chemistry, University of München,*
Theresienstr. 37, D-80333 München, Germany

Abstract

We have implemented the fully relativistic and spin-polarized extension of the locally self-consistent multiple scattering method. We have calculated the spin and orbital magnetic moments and magneto-crystalline anisotropy energy of Fe, Ni, and Co in the face centered cubic (fcc) and hexagonal close packed (hcp) crystal structures. We have obtained fast convergence of these quantities in real space. Moreover, these results compare favourably with the results of conventional **k**-space methods.

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Manuscripts available from: W.M.Temmerman@dl.ac.uk

First-principles spin-polarised calculations on the reduced and reconstructed TiO2 (110) surface

P. J. D. Lindan and N. M. Harrison
Daresbury Laboratory, Warrington WA4 4AD, U.K.
M. J. Gillan
Physics Department, Keele University, Staffordshire ST5 5BG, U.K.
and J. A. White
Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, U.K.

Abstract

We have performed plane-wave pseudopotential density-functional theory calculations on the stoichiometric and reduced TiO_2 (110) surface, the 2×1 and 1×2 reconstructions of the surface formed by the removal of bridging oxygen atoms, and on the oxygen vacancy in the bulk. The effect of including spin-polarisation is investigated, and it is found to give a qualitatively different electronic structure compared with a spin-paired description. In the spin-polarised solutions, the excess electrons generated by oxygen reduction occupy localised band-gap states formed from Ti (3d) orbitals, in agreement with experimental findings. In addition, the inclusion of spin polarisation substantially lowers the energy of all the systems studied, when compared with spin-paired solutions. However, spin-polarisation does not change the relative stability of the two reconstructions, which remain energetically equivalent.

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Paper available from: P.J.D.Lindan@dl.ac.uk

Ab initio studies of the (100), (110) and (111) surfaces of $CoSi_2$

R. Stadler[1], R. Podloucky[1], G. Kresse[2] and J. Hafner[2]
[1] *Institute for Physical Chemistry, Univ. of Vienna,*
Liechtensteinstrasse 22A/1/3, A-1090 Vienna, Austria
[2] *Institute for Theoretical Physics, Technical Univ. of Vienna,*
Wiedner Hauptstrasse 8-10/136, A-1040 Vienna, Austria

Abstract

Based on the ultrasoft pseudopotential technique of the Vienna *ab initio* simulation package we performed *ab initio* calculations for the (100), (110) and (111) surfaces of $CoSi_2$ within the framework of the generalized gradient approximation. Surface energies were derived from the total energies as well as estimated from simple models. Relaxed surface geometries were determined for the (1x1) surfaces by force minimization. For the (100) surface a proposed $\sqrt{2} \times \sqrt{2}$ reconstruction was investigated which however is not stable. Energetical results as well as simulated scanning tunneling images strongly indicate that the reconstruction does not exist. The band structures show a number of surface states, in particular in gaps of the projected bulk bands at and above Fermi energy for the (100) and (110) surface. For the Si-Co-Si terminated (111) surface, however, only two Si-like surface bands are found. Some surface states are analyzed in terms of density contours revealing covalent Co-Si bonding and coupling to deeper layers. Work functions are also provided.

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Manuscripts available from: robert@calvin.tssc.univie.ac.at

Hydrogen molecules in silicon located at interstitial sites and trapped in voids

B. Hourahine, R. Jones
Department of Physics, The University of Exeter, Exeter, EX4 4QL, UK
S. Öberg
Department of Mathematics, University of Luleå, Luleå, S-97187, Sweden
R. C. Newman
Semiconductor IRC, Imperial College, Prince Consort Road, London, SW7 2BZ, UK
P. R. Briddon
Department of Physics, The University of Newcastle upon Tyne, Newcastle upon Tyne, NE1 7RU, UK
E. Roduner
Institut für Physikalische Chemie, Pfaffenwaldring 55, D-70569, Stuttgart, Germany

Abstract

The vibrational modes of H_2 molecules in Si are found using a first principles method and compared with recent experimental investigations. The isolated molecule is found to lie at a T_d interstitial site, oriented along [011] and is infra-red active. The rotational barrier is at least 0.17 eV. The molecular frequency is a sensitive function of cage size and increases to the gas value for cages about 40% larger than the T_d site. It is suggested that Raman active modes around 4158 cm^{-1} are due to molecules within voids.

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Latex-file available from: bh@excc.ex.ac.uk

Fractional occupancies and temperature in electronic-structure calculations

Michael Springborg[a], R. C. Albers[b], and Karla Schmidt[a]
[a] *Department of Chemistry, University of Konstanz,*
D - 78457 Konstanz, Germany
[b] *Theoretical Division, Los Alamos National Laboratory*
Los Alamos, New Mexico 87545, U.S.A.

Abstract

Fractional occupancies are often used in electronic-structure calculations. We use a simple model that contains the essential elements of more elaborate first-principles techniques in order to evaluate the effects of four typical fractional occupancy schemes on a system's calculated physical properties. We find that when the broadenings used in such a scheme are not significantly larger than the characteristic energies of the system of interest, the results depend only marginally on the type of broadening function that is used, except for Lorentzian broadening. We have also studied differences between free-energy and total-energy formulations. Finally, we present closed formulas for those parts of the forces that originate from the fractional occupancies, both for our model and for electronic-structure calculations within the density-functional formalism. Based on our results, we recommend using a simple step-function broadening scheme, which, unlike some more common methods, does not require a highly non-linear equation to be iteratively solved for the Fermi energy.

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Latex-file available from Michael Springborg (mcs@chclu.chemie.uni-konstanz.de) (figures only as hard copies).

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A simple model for calculating the $P-T$ phase diagram of Ti

S.A.Ostanin,V.Yu.Trubitsin
Physico-Technical Institute,
Ural Branch ofRussian Academy of Sciences,
132 Kirov Str.,426001 Izhevsk,Russia

Abstract

$FP-LMTO$ method is used to calculate the total energy and equilibrium lattice properties for the observed phases of Ti. The temperature dependences of the free energy, specific volume, bulk modulus, Debye temperature, and Grüneisen constant are found for these structures within the Debye model. For most quantities a good quantitative agreement with the experiment is obtained. The $P-T$ phase diagram constructed from the calculated thermodynamical Gibbs potentials fits well the available room-temperature data on the $\alpha \to \omega$ transition. The model suggested predicts the formation of a high-pressure $\beta-$ phase in Ti at $P^{\omega\to\beta}_{T=300K} = 950kbar$, which pressure is still not gained experimentally.

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Calculation of the $P-T$ phase diagram of Zr in different approximations for the exchange-correlation energy

S.A.Ostanin,V.Yu.Trubitsin
Physico-Technical Institute,
Ural Branch ofRussian Academy of Sciences,
132 Kirov Str.,426001 Izhevsk,Russia

Abstract

The FP-LMTO method is used within the LDA and GGA to calculate the total energy and equilibrium lattice properties for the observed phases of Zr. The temperature dependences of the free energy, specific volume, bulk modulus, Debye temperature, and Grüneisen constant are found for these structures within the Debye model. For most quantities, a good quantitative agreement with experiment is obtained. The $P-T$ phase diagram constructed from the calculated thermodynamical Gibbs potentials within the GGA fits well the available room-temperature data on the $\alpha \to \omega$ and $\omega \to \beta$ transitions. At ambient pressure, we get $T_{\beta\to\alpha} = 1193K$, which is close to the observed value.

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An anharmonic model of instability evolution near the $bcc \rightarrow hcp$ phase transition in Zr

S.A.Ostanin, E.I.Salamatov,V.Yu.Trubitsin
Physico-Technical Institute,
Ural Branch ofRussian Academy of Sciences,
132 Kirov Str.,426001 Izhevsk,Russia

Abstract

A local minimum is observed on the FP-LMTO curve of total energy versus the amplitude of atomic displacements corresponding to transverse $[1\bar{1}0]$ vibrations at the N point of the Brillouin zone in Zr. The temperature dependence of the inelastic one-phonon neutron scattering spectra is calculated within the framework of a modified pseudoharmonic approximation. The appearance of the spectrum fine structure with decreasing temperature is associated with the intermediate phase phonon whose frequency is close to that of the -phonon of *hcp* Zr.

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Latex manuscripts available from: ost@otf.fti.udmurtia.su

Calculation of the phase diagram of Zr in a simple model

S.A.Ostanin, V.Yu.Trubitsin
Physico-Technical Institute,
Ural Branch ofRussian Academy of Sciences,
132 Kirov Str.,426001 Izhevsk,Russia

Abstract

We have calculated the lattice properties and the phase diagram (P,T) of Zr within the Debye model using the FP-LMTO method with GGA for the exchange-correlation energy. The $P-T$ phase diagram constructed from the calculated thermodynamical Gibbs potentials fits well the available room-temperature

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Latex manuscripts available from: ost@otf.fti.udmurtia.su

Magnetism of epitaxial monolayers on graphite

P. Krüger, A. Rakotomahevitra, J. C. Parlebas, and C. Demangeat
IPCMS-GEMME, UMR46 CNRS, 23, rue du Loess, 67037 Strasbourg, France

Abstract

We have investigated the magnetism of hexagonal $3d$ metal monolayers, epitaxially adsorbed on the graphite (0001) surface, by spin-polarized electronic structure calculations using the tight-binding linear-muffin-tin orbitals method. The calculations have been carried in the ferromagnetic, an antiferromagnetic, and a ferrimagnetic configuration for both adsorbed and unsupported monolayers. We find that the V monolayers are nonmagnetic, and that the Fe, Co and Ni monolayers are ferromagnetic. For the Mn monolayers, the antiferromagnetic and ferrimagnetic configurations are more stable than the ferromagnetic one. For the unsupported Cr monolayer, the antiferromagnetic and a ferrimagnetic configuration exist, but they are almost degenerate with the non-magnetic solution. This is due to the frustration of the antiferromagnetic nearest neighbor coupling on the hexagonal lattice. The magnetic moments of the adsorbed monolayers are substantially reduced from their unsupported monolayer values and vanish completely in the case of Cr.

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Manuscripts available from: kruger@belenus.u-strasbg.fr

The adsorption of thiophene on the catalytically active edge-surface of MoS_2: An ab-initio local-density-functional study

P. Raybaud[a,b], J. Hafner[a], G. Kresse[a] and H. Toulhoat[b]

[a] *Institut für Theoretische Physik,*
and Center for Computational Material Science
TU Wien, Wiedner Hauptstraße 8 - 10,
A-1040 Wien, Austria

[b] *Institut Français du Pétrole,*
Groupe de Modélisation Moléculaire, B.P. 311,
F-92852 Rueil-Malmaison, France

Abstract

The adsorption of thiophene on the catalytically active $MoS_2(010)$ edge-surfaces has been studied using ab-initio local-density-functional molecular-dynamics, including generalized gradient corrections to the exchange-correlation functional. It is shown that thiophene adsorbs in an η^5-configuration with the molecular ring parallel to the surface, centered above a coordinatively unsaturated Mo-atom, and with the sulfur atom in a binding position between two Mo-surface atoms. This configuration provides not only the highest adsorption energy, but activates in addition the thiophene molecule with respect to both C-S bond-cleavage (and hence desulfurization) and hydrogenation. Hence it represents a realistic scenario for the first step in catalytic hydrodesulfurization.

(Physical Review Letters, submitted)
Preprints from: jhafner@tph.tuwien.ac.at

Ab-initio density-functional studies of transition-metal sulfides: I. Crystal structure and cohesive properties

P. Raybaud[a,b], G. Kresse[a], J. Hafner[a] and H. Toulhoat[b]
[a] *Institut für Theoretische Physik,*
and Center for Computational Material Science,
Technische Universität Wien, Wiedner Hauptstraße 8 - 10,
A-1040 Wien, Austria
[b] *Institut Français du Pétrole, Groupe de Modélisation Moléculaire,*
B.P. 311, F-92852 Rueil-Malmaison, France

Abstract

The structural and cohesive properties of more than thirty transition-metal sulfides of various stoichiometries and crystal structures have been investigated using density functional theory, with the aim of establishing a correlation between strength of the metal-sulfur bond and catalytic activities of these materials. It is shown that the local-density approximation has a tendency to overestimate the strength of the bonding. The overbinding manifests itself in the prediction of too small atomic volumes and too large cohesive energies. Nonlocal corrections to the local exchange-correlation functional in the form of a generalized gradient approximation correct the overbinding (albeit with a certain tendency to overcorrect, especially for the sulfides of the heavy transition metals) and result in accurate structural prediction and cohesive energies. A correlation between the sulfur-metal bond-strenght and the catalytic activities is established.

(J. Phys.: Condensed Matter (in print))
Preprints from jhafner@tph.tuwien.ac.at

Ab-initio density-functional studies of transition-metal sulfides: II. Electronic structure

P. Raybaud[a,b], J. Hafner[a], G. Kresse[a] and H. Toulhoat[b]
[a] *Institut für Theoretische Physik,*
and Center for Computational Material Science,
Technische Universität Wien, Wiedner Hauptstraße 8 - 10,
A-1040 Wien, Austria
[b] *Institut Français du Pétrole, Groupe de Modélisation Moléculaire,*
B.P. 311, F-92852 Rueil-Malmaison, France

Abstract

A study of the electronic structure of about thirty transition-metal sulfides (TMS) of various stoichiometries and crystal structures is presented, supplementing recent studies of their structural and cohesive properties (P. Raybaud, G. Kresse, J. Hafner, and H. Toulhoat, preceding paper). The electronic structure of the TMS is found to be determined by short-range interactions in the S-3p–TM-d band complex, with the ligand-field splitting of the TM-d states in the environment of the S-atoms determining the structure of d-band. For the layered group VI disulfides, for ReS_2 and for the group VIII-pyrites this leads to the formation of a gap at the Fermi surface. Semiconducting properties are predicted also for the monosulfides PtS and PdS and for Rh_2S_3 and Ir_2S_3. We show that the semiconducting TMS have a higher catalytic activity for hydrodesulfurization than the metallic sulfides. We suggest a correlation between the catalytic activity and the characters of the highest occupied states (the frontier orbitals).

(J. Phys.: Condensed Matter (in print))
Preprints from jhafner@tph.tuwien.ac.at

Molecular precursors in the dissociative adsorption of O_2 on Pt(111)

A. Eichler and J. Hafner
Institut für Theoretische Physik,
and Center for Computational Material Science,
Technische Universität Wien, Wiedner Hauptstraße 8 - 10,
A-1040 Wien, Austria

Abstract

Ab-initio local-spin-density calculations for the adsorption of O_2 on Pt(111) are presented. We identify two distinct, but energetically almost degenerate chemisorbed precursors. A superoxo-like paramagnetic precursor is formed at the bridge-site, with the molecule parallel to the surface. A second peroxo-like nonmagnetic precursor is formed in the threefold hollow, with the atom slightly canted in a top-hollow-bridge geometry. The nature of the barrier for dissociation into atoms adsorbed in the hollows is explored.

(Physical Review Letters, in print)
Preprints from: jhafner@tph.tuwien.ac.at

Ab Initio Calculations of the $\beta-$SiC(001)/Al Interface

J. Hoekstra and M. Kohyama
Department of Material Physics, Osaka National Research Institute, AIST,
1-8-31, Midorigaoka, Ikeda, Osaka 563, Japan

Abstract

The $\beta-$SiC/Al interface has been studied using the ab initio pseudopotential method, with the conjugate-gradient technique proposed by Bylander-Kleinman-Lee, and Troullier-Martins soft pseudopotentials. Ionic and electronic structure at the interface, local density of states, Schottky-barrier heights, and bond adhesion between the two materials were determined for both the silicon terminated and carbon terminated interfaces. Results show a distinct difference between the Al-Si and the Al-C interactions effecting all aspects of the chemical bond, as well as bond adhesion. However, bond adhesion for both the Si-terminated and C-terminated interfaces is substantially greater than for non-reactive interfaces such as MgO/Al.

(Phys. Rev. B, in press)
Manuscripts available from: hoekstra@onri.go.jp

Structural and electronic properties of the $MoS_2(10\bar{1}0)$ edge-surface

P. Raybaud[a,b], J. Hafner[a], G. Kresse[a] and H. Toulhoat[b]
[a] *Institut für Theoretische Physik,*
and Center for Computational Material Science,
Technische Universität Wien, Wiedner Hauptstraße 8 - 10,
A-1040 Wien, Austria
[b] *Institut Français du Pétrole, Groupe de Modélisation Moléculaire,*
B.P. 311, F-92852 Rueil-Malmaison, France

Abstract

Ab-initio investigations of the structural and electronic properties of the clean $MoS_2(010)$ edge-surface are presented. It is shown that the bulk-terminated surface remains stable in vacuum up to temperatures of $T \sim 700$ K, with only modest relaxations of the surface atoms. In contrast to the semiconducting bulk, the (010) surface shows a finite density of states at the Fermi level. On the unsaturated Mo-surface atoms the most intense surface states are empty d_{yz} and $d_{x^2-y^2}$-type states just above the Fermilevel, demonstrating the acceptor-properties of the surfaces. On the unsaturated S-sites, ($p_y p_z$) states at the Fermi-level promote a tendency to S-S pairing.

(Submitted to Surface Science)
Preprints from: jhafner@tph.tuwien.ac.at

Face-centered icosahedral Al-Mg-Li alloys: a free-electron quasicrystal

G. Dell'Acqua[a,b], M. Krajčí[a,c] and J. Hafner[a]
[a] *Institut für Theoretische Physik,*
and Center for Computational Material Science,
Technische Universität Wien, Wiedner Hauptstraße 8 - 10,
A-1040 Wien, Austria
[b] *Dipartimento di Fisica, Università degli Studi di Padova,*
I-35131 Padova, Italy

Abstract

We present detailed studies of the atomic and electronic structure of quasicrystalline Al-Mg-Li alloys. The face-centered icosahedral structure is described by decorating the even and odd twelvefold vertices of a canonical-cell-tiling with $Al_{24}Mg_{20}$ and $Al_{24}Li_{20}$ Bergman-clusters, respectively. The electronic structure has been calculated using a real-space tight-binding linear-muffin-tin orbital method. The electronic spectrum is characterized by a deep, structure-induced pseudogap just below the Fermi-level and similar structures at higher binding energies associated with the face-centered icosahedral order.

(J. Phys.: Condensed Matter (in print))
Preprints from jhafner@tph.tuwien.ac.at

Unusual behavior and its origin of the alkali metal adsorbed W(001) surface

H. W. Kim[1], J. R. Ahn[1] and J. W. Chung[1] B. D. Yu[2] and M. Scheffler[2]
[1]*Department of Physics, and Basic Science Research Institute,*
Pohang University of Science and Technology, Pohang, 790-784, Korea
[2]*Fritz-Haber-Institut der Max-Planck-Gesellschaft,*
Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany

Abstract

Remarkable differences between Li and K adsorbed on W (001) surface are observed in the surface core level shifts of W $4f$ and in the changes of transition temperature for the reconstruction of the clean surface. The data strongly suggest that Li and K occupy different binding sites, namely the hollow and bridge geometry, respectively. Based on results from density functional theory calculations, we argue that the unusual binding site for K apparently violating the general preference for the highest coordination site in metallic bonding is stabilized by the reconstruction of surface W atoms. In addition, we show that the reconstruction is driven essentially by a Kohn anomaly as for the clean W (001) surface.
PACS numbers: 79.60.Gs,73.40.-c,71.45.Nt

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

Density-Functional Theory Calculations of Hopping Rates of Surface Diffusion

C. Ratsch[1] and M. Scheffler[2]
[1] *Hughes Research Laboratories,*
3011 Malibu Canyon Road, Malibu, CA 90265
[2] *Fritz-Haber-Institut der Max-Planck-Gesellschaft,*
Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany

Abstract

Using density-functional theory with the local-density approximation we compute the energy barriers and the attempt frequencies for surface diffusion for Ag on Pt(111), Ag on one monolayer of Ag on Pt(111), and Ag on Ag(111). We find that the attempt frequency is of the order of 1 THz for all the systems studied, and that in contrast to the so-called compensation effect the attempt frequency decreases slightly when the barrier increases. This is also at variance with experimental studies, where for the same system a very large compensation effect has been claimed. Analyzing the applicability of simple commonly used scaling laws we conclude that the determination of parameters for diffusion and growth is not as straightforward as it is typically assumed.
PACS numbers: 68.55.Jk, 68.35.Bs, 68.35.Fx

(submitted to Phys. Rev. Lett. , October 1997)
Contact person: scheffler@fhi-berlin.mpg.de

Ab initio calculation of the potential energy surface for the dissociation of H_2 on the sulfur covered Pd(100) surface

C. M. Wei[1], A. Groß[2], and M. Scheffler[2]
[1] *Institute of Physics, Academia Sinica,*
Nankang, Taipei, Taiwan 11529, Republic of China.
[2] *Fritz-Haber-Institut der Max-Planck-Gesellschaft,*
Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany

Abstract

The presence of sulfur atoms on the Pd(100) surface is known to hinder the dissociative adsorption of hydrogen. Using density-functional theory and the full-potential linear augmented plane-wave method, we investigate the potential energy surface (PES) of the dissociative adsorption of H_2 on the sulfur covered Pd(100) surface. The PES is changed significantly compared to the dissociation on the clean Pd(100) surface, in particular for hydrogen close to the S atoms. While the hydrogen dissociation at the clean Pd(100) surface is non-activated, for the (2×2) sulfur adlayer (coverage Θ_S= 0.25) the dissociation of H_2 is inhibited by energy barriers. Their heights strongly depend on the distance between the hydrogen and sulfur atoms leading to a highly corrugated PES. The largest barriers are in the vicinity of the sulfur atoms due to the strong repulsion between sulfur and hydrogen. Still the hydrogen dissociation on the (2×2) sulfur covered Pd(100) surface is exothermic. Thus the poisoning effect of sulfur adatoms for H_2 dissociation at low sulfur coverage ($\Theta_S \leq 0.25$) is mainly governed by the formation of energy barriers, not by blocking of the adsorption sites. For the c(2×2) sulfur adlayer (Θ_S= 0.5), the PES for hydrogen dissociation is purely repulsive. This is due to the fact that for all different possible adsorption geometries the hydrogen molecules come too close to the sulfur adatoms before the dissociation is completed.
PACS numbers: 68.45.Da, 73.20.At, 82.65.Jv

(submitted to Phys. Rev. B , November 1997)
Contact person: axel@theo22.rz-berlin.mpg.de

Electronic and structural properties of vacancies on and below the GaP(110) surface

G. Schwarz, A. Kley, J. Neugebauer, and M. Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft,
Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany

Abstract

We have performed total-energy density-functional calculations using first-principles pseudopotentials to determine the atomic and electronic structure of neutral surface and subsurface vacancies at the GaP (110) surface. The cation as well as the anion surface vacancy show a pronounced inward relaxation of the three nearest neighbor atoms towards the vacancy while the surface point-group symmetry is maintained. For both types of vacancies we find a singly occupied level at mid gap. Subsurface vacancies below the second layer display essentially the same properties as bulk defects. Our results for vacancies in the second layer show features not observed for either surface or bulk vacancies: Large relaxations occur and both defects are unstable against the formation of antisite vacancy complexes. Simulating scanning tunneling microscope pictures of the different vacancies we find excellent agreement with experimental data for the surface vacancies and predict the signatures of subsurface vacancies.

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(submitted to Phys. Rev. B , November 1997)

Contact person: schwarz@theo23.rz-berlin.mpg.de

Clean and As covered zinc-blende GaN (001) surfaces: Novel surface structures and surfactant behavior

Jörg Neugebauer[1], Tosja Zywietz[1], Matthias Scheffler[1],
John E. Northrup[2] and Chris G. Van de Walle[2]
[1]*Fritz-Haber-Institut der Max-Planck-Gesellschaft,*
Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany
[1]*Xerox Palo Alto Research Center,*
3333 Coyote Hill Road, Palo Alto, California 94304

Abstract

We have investigated clean and As-covered zinc-blende GaN (001) surfaces employing first-principles total-energy calculations. For clean GaN surfaces our results reveal a novel surface structure very different to the well-established dimer structures commonly observed on polar III-V (001) surfaces: The energetically most stable surface is achieved by a Peierls distortion of the truncated (1×1) surface rather than through addition or removal of atoms. This surface exhibits a (1×4) reconstruction consisting of *linear Ga tetramers*. Furthermore, we find that a submonolayer of arsenic significantly lowers the surface energy indicating that As might be a good surfactant. Analyzing surface energies and band structures we identify the mechanisms which govern these unusual structures and discuss how they might affect growth properties.

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Contact person: zywietz@FHI-Berlin.mpg.de

Conceptual and computational advances in multiple-scattering electronic-structure calculations

Rudolf Zeller
Institut für Festkörperforschung, Forschungszentrum Jülich GmbH,
D-52425 Jülich, Federal Republic of Germany

Abstract

A physically transparent transformation of the Korringa-Kohn-Rostoker (KKR or multiple-scattering) method into a tight-binding form is described. The transformation replaces the complicated, slowly decaying, traditional KKR structure constants by exponentially decaying "tight-binding" parameters. The main computational effort consists in the inversion of sparse matrices and scales for surfaces and interfaces, i.e. for systems with two-dimensional periodicity, linearly with the number of layers. This gives the opportunity to treat high-indexed surfaces as an approximation for almost isolated surface steps. Additional adatoms on surfaces and at steps can also be treated and it is discussed that reliable atomic forces and geometric arrangements can be obtained. (PACS No.: 71.15.-m, 71.20.-b).

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Preprints available from: Ru.Zeller@fz-juelich.de

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7 Presenting Other Initiatives

BENCHMARK OF AB-INITIO ELECTRONIC STRUCTURE CODES

Mebarek Alouani
Université Louis Pasteur, Strasbourg, France

The success of computer technology (supercomputer CPU speed is now beyond 100 Mflops per node) allows all-electron ab-initio methods to approach the exact LDA limit. To get to this limit many shape approximations to the potential or the charge density are being removed. The continuous effort of building new and accurate computer codes, in this last decade, produced great advances in the computation of material properties from first principles. It is now possible to compute accurately ground-state electronic structure, geometries, cohesive energies, and linear response functions for solids containing a large number of atoms per unit cell.

Therefore, to continue this effort, I would like to invite everyone of you (out there) to contribute to a construction of a data base which contains benchmark reference data for typical electronic structure calculations. This data base could be used to implement new computational methods and algorithms, and to test their results against data of known numerical accuracy. We need results for atomic and solid state total energies, high accurate calculations of eigenvalues, density of states, and linear response functions. We could provide data for spin-restricted, spin-polarized LDA, and for various relativistic effects (semi-relativistic or spin-orbit coupling).

We invite all code developers or users to benchmark their codes in various computer platforms. We can then put the results on a web page which should be accessible to all the electronic structure communities.

Here is the first list which should be discussed.

Elements:
Cu, Fe, Si, and Gd.

Compounds:
GaAs, FeAl (CsCl structure), and Fe/Cu (001) 1 layer of Fe on 5layers of Cu.

We should agree on the experimental lattice parameters, the number of k-points, the type of exchange and correlation potential ... etc.

I would like to have your first reactions to this suggestion. Please e-mail me at: mea@taranis.u-strasbg.fr.

8 HIGHLIGHT OF THE MONTH

3-Body Scattering (3BS) theory of on-site correlation in narrow band materials

Franca Manghi and Massimo Rontani
Istituto Nazionale per la Fisica della Materia - Dipartimento di Fisica, Università di Modena
Via Campi 213/a I-4110 Modena Italy

Abstract

We present the results of a recently developed approach where the interplay between the itinerant and localized character of electrons in narrow band materials is described by adding on-site correlation effects to a first principle band calculation: the single particle band states are treated as mean field solutions of a multi-orbital Hubbard Hamiltonian and the many-body term associated to localized e-e interaction is described in a configuration-interaction scheme. The method allows to calculate hole and electron spectral functions which can be directly compared with spectroscopical results.

8.1 Introduction

The Hubbard model, dominated by the competition between inter-site hopping and on-site electron-electron repulsion, is believed to describe the physics of narrow band materials such as transition metals, transition metal oxides, cuprates, etc. [1]. In these systems the itinerant character of valence electrons - clearly shown by the **k**-dispersion observed in photoemission - coexists with strong local correlations responsible of other spectroscopical features - satellites, band-narrowing, and opening, in some cases, of a Mott-Hubbard gap.

In spite of the enormous amount of theoretical and experimental work which has been done on cuprates since the discovery of high T_c superconductors, an unified theoretical description of the whole valence spectrum, from the high binding energy region characterized by satellites, up to the valence band top, including both unperturbed single particle like and strongly correlated Cu derived structures, is still missing; this is due to the difficulty to combine an accurate treatment of many body terms with a realistic description of the band structure.

Most of the work on this subject has been based on a drastic simplification of either the band structure or the e-e interaction; if the complex structure of these systems is reduced to a model description involving only CuO planes, the e-e interaction can be treated accurately, for instance by exact diagonalization techniques of finite (and small) CuO clusters [1], by refined mean-field solutions of a two dimensional t-J Hamiltonian [2] etc. . However, in this search for the simplest model containing the relevant physics of superconductors one may miss some important effects, related for instance to the coupling between adjacent CuO planes [3], and the possibility of a quantitative comparison with spectroscopical results.

Photoemission data of highly correlated materials have been also interpreted using theoretical approaches based on impurity and cluster configuration-interaction models which assume a strong wave function localization and adopt a rather simplified description of the band structure, with a considerable number of adjusting parameters. They have been widely used to describe the main structures and satellite peaks observed in the angle-integrated photoemission spectra of CuO [4] and of cuprate superconductors [5]. Other approaches have been proposed based on the density functional approximation (self-interaction corrected [6] and LDA+U [7] functionals) which fully include the itinerant character of electron states but describe the electron-electron interaction as a mean-field effective single-particle potential.

A theoretical approach is then needed which includes both the hybridization between Cu and the ligands (or between *sp* and *d* states in the case of transition metals) accounted for by first principle band theory, and a treatment of e-e interaction which must be non-perturbative - to deal with systems which are in the high correlation regime - and beyond mean field - to include finite life-time excitations.

The 3BS method [8, 9, 10, 11] can be seen as an extension to the solid state of the configuration-interaction scheme used for finite systems: the Hubbard Hamiltonian is projected on a set of states obtained by adding a finite number of e-h pairs to the ground state of the single-particle Hamiltonian and this expansion is truncated to include one e-h pair. The effect of electron correlation on one electron removal energies from a partially filled band is then described as hole-hole and hole-electron interaction. The 3BS theory corresponds to the solution of a 3-body scattering problem involving two holes and one electron and has been originally formulated by Igarashi [8]. Self-energy corrections, spectral functions and quasi-particle band structure can be calculated for systems in different correlation regimes, getting a complete picture of the whole valence spectrum, including both long-lived coherent quasiparticle structures and incoherent short-lived ones.

8.2 Hamiltonians

Since we want to augment band theory with the inclusion of on-site correlation it is essential to define the relationship between band and Hubbard Hamiltonian in order to avoid double counting of e-e interaction. The exact many body Hamiltonian in second quantization is

$$\hat{H} = \sum_{i\alpha\sigma} \epsilon_{i\alpha} \hat{n}_{i\alpha\sigma} + \sum_{\alpha\beta\sigma} \sum_{ij}{}' t_{i\alpha,j\beta} \hat{c}^{\dagger}_{i\alpha\sigma} \hat{c}_{j\beta\sigma}$$

$$
\begin{aligned}
&+ \quad \frac{1}{2}\sum_{\alpha\beta}\left[\sum_i (U_{\alpha\beta}-J_{\alpha\beta})\sum_\sigma \hat{n}_{i\alpha\sigma}\hat{n}_{i\beta\sigma} + \sum_i U_{\alpha\beta}\sum_\sigma \hat{n}_{i\alpha\sigma}\hat{n}_{i\beta-\sigma}\right] \\
&+ \quad ...(\text{multi-center terms}), \qquad (1)
\end{aligned}
$$

with $\hat{n}_{i\alpha\sigma} = \hat{c}^\dagger_{i\alpha\sigma}\hat{c}_{i\alpha\sigma}$ and $\hat{c}_{i\alpha\sigma}, \hat{c}^\dagger_{i\alpha\sigma}$ destruction and creation operators.

Here $\epsilon_{i\alpha}$ and $t_{i\alpha,j\beta}$ are the intra- and inter-atomic matrix elements of the one-particle Hamiltonian and $U_{\alpha\beta}$, $J_{\alpha\beta}$ are on-site Coulomb and exchange terms:

$$U_{\alpha\beta} = V_{i\alpha\sigma,i\beta\sigma,i\beta\sigma,i\alpha\sigma} = V_{i\alpha\sigma,i\beta-\sigma,i\beta-\sigma,i\alpha\sigma},$$

$$J_{\alpha\beta} = V_{i\alpha\sigma,i\beta\sigma,i\alpha\sigma,i\beta\sigma},$$

with

$$V_{i\alpha\sigma,j\beta\sigma',l\gamma\sigma',m\delta\sigma} = \sum_{ss'}\int \phi^*_{i\alpha\sigma}(\mathbf{r},s)\phi^*_{j\beta\sigma'}(\mathbf{r}',s')\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\phi_{l\gamma\sigma'}(\mathbf{r}',s')\phi_{m\delta\sigma}(\mathbf{r},s)\mathrm{d}\,\mathbf{r}\mathrm{d}\,\mathbf{r}'.$$

Different approximations to the exact Hamiltonian (1) can be obtained using a mean field approach which amounts to neglect fluctuations in the electron occupation

$$
\begin{aligned}
\hat{n}_{i\alpha\sigma}\hat{n}_{i\beta\sigma'} &= \hat{n}_{i\alpha\sigma}\left\langle \hat{n}_{i\beta\sigma'}\right\rangle + \hat{n}_{i\beta\sigma'}\left\langle \hat{n}_{i\alpha\sigma}\right\rangle - \left\langle \hat{n}_{i\alpha\sigma}\right\rangle\left\langle \hat{n}_{i\beta\sigma'}\right\rangle \\
&+ \left(\hat{n}_{i\alpha\sigma} - \left\langle \hat{n}_{i\alpha\sigma}\right\rangle\right)\left(\hat{n}_{i\beta\sigma'} - \left\langle \hat{n}_{i\beta\sigma'}\right\rangle\right) \\
&\simeq \hat{n}_{i\alpha\sigma}\left\langle \hat{n}_{i\beta\sigma'}\right\rangle + \hat{n}_{i\beta\sigma'}\left\langle \hat{n}_{i\alpha\sigma}\right\rangle - \left\langle \hat{n}_{i\alpha\sigma}\right\rangle\left\langle \hat{n}_{i\beta\sigma'}\right\rangle.
\end{aligned}
$$

The mean field approximation can be applied to all the many body terms of (1) transforming it into a single particle Hamiltonian

$$\hat{H}^{MF} = \sum_{i\alpha\sigma}\epsilon^{MF}_{i\alpha\sigma}\hat{n}_{i\alpha\sigma} + \sum_{\alpha\beta\sigma}{\sum_{ij}}' t_{i\alpha,j\beta}\hat{c}^\dagger_{i\alpha\sigma}\hat{c}_{j\beta\sigma}, \qquad (2)$$

or selectively to the multi-center integrals, keeping the full many body character in the one-center terms; in this way one gets the generalized Hubbard model

$$
\begin{aligned}
\hat{H}^H &= \sum_{i\alpha\sigma}\epsilon^H_{i\alpha\sigma}\hat{n}_{i\alpha\sigma} + \sum_{\alpha\beta\sigma}{\sum_{ij}}' t_{i\alpha,j\beta}\hat{c}^\dagger_{i\alpha\sigma}\hat{c}_{j\beta\sigma} \\
&+ \frac{1}{2}\sum_{\alpha\beta}\left[\sum_i (U_{\alpha\beta}-J_{\alpha\beta})\sum_\sigma \hat{n}_{i\alpha\sigma}\hat{n}_{i\beta\sigma} + \sum_i U_{\alpha\beta}\sum_\sigma \hat{n}_{i\alpha\sigma}\hat{n}_{i\beta-\sigma}\right]. \qquad (3)
\end{aligned}
$$

Since $\hat{H}^{MF}$ and $\hat{H}^H$ differ only for the treatment of the on-site correlation - included in $\hat{H}^{MF}$ as a mean field and treated as a many body term in $\hat{H}^H$ - it is easy to show that

$$\epsilon^{MF}_{i\alpha\sigma} = \epsilon^H_{i\alpha\sigma} + \sum_\beta\left[(U_{\alpha\beta}-J_{\alpha\beta})\left\langle \hat{n}_{i\beta\sigma}\right\rangle + U_{\alpha\beta}\left\langle \hat{n}_{i\beta-\sigma}\right\rangle\right]. \qquad (4)$$

Using a Bloch basis set the two approximate Hamiltonians become

$$
\begin{aligned}
\hat{H}^H &= \sum_{\mathbf{k}n\sigma}\epsilon^H_{\mathbf{k}n\sigma}\hat{a}^{n\dagger}_{\mathbf{k}\sigma}\hat{a}^n_{\mathbf{k}\sigma} + \sum_{\alpha\beta}\sum_{\mathbf{k}\mathbf{k}'\mathbf{p}}\sum_{nn'}\sum_{mm'}\sum_\sigma \frac{1}{2N} \\
&\times\Big[U_{\alpha\beta}C^n_{\alpha\sigma}(\mathbf{k})^*C^{n'}_{\alpha\sigma}(\mathbf{k}+\mathbf{p})C^m_{\beta-\sigma}(\mathbf{k}')^*C^{m'}_{\beta-\sigma}(\mathbf{k}'-\mathbf{p})\hat{a}^{n\dagger}_{\mathbf{k}\sigma}\hat{a}^{n'}_{\mathbf{k}+\mathbf{p}\sigma}\hat{a}^{m\dagger}_{\mathbf{k}'-\sigma}\hat{a}^{m'}_{\mathbf{k}'-\mathbf{p}-\sigma} \\
&+ (U_{\alpha\beta}-J_{\alpha\beta})\,C^n_{\alpha\sigma}(\mathbf{k})^*C^{n'}_{\alpha\sigma}(\mathbf{k}+\mathbf{p})C^m_{\beta\sigma}(\mathbf{k}')^*C^{m'}_{\beta\sigma}(\mathbf{k}'-\mathbf{p})\hat{a}^{n\dagger}_{\mathbf{k}\sigma}\hat{a}^{n'}_{\mathbf{k}+\mathbf{p}\sigma}\hat{a}^{m\dagger}_{\mathbf{k}'\sigma}\hat{a}^{m'}_{\mathbf{k}'-\mathbf{p}\sigma}\Big], \qquad (5)
\end{aligned}
$$

$$\hat{H}^{MF} = \sum_{\mathbf{k}n\sigma} \epsilon^{MF}_{\mathbf{k}n\sigma} \hat{a}^{n\dagger}_{\mathbf{k}\sigma} \hat{a}^{n}_{\mathbf{k}\sigma}; \tag{6}$$

here $\hat{a}^{n}_{\mathbf{k}\sigma}$,$\hat{a}^{n\dagger}_{\mathbf{k}\sigma}$ are destruction/creation operators of electrons with wave vector $\mathbf{k}$, spin σ, band index n and $C^{n}_{\alpha}(\mathbf{k}\sigma)$ are the expansion coefficients of Bloch states in terms of localized orbitals. The relationship between single particle eigenvalues $\epsilon^{MF}_{\mathbf{k}n\sigma}$ and $\epsilon^{H}_{\mathbf{k}n\sigma}$ appearing in the two Hamiltonians is now

$$\epsilon^{MF}_{\mathbf{k}n\sigma} = \epsilon^{H}_{\mathbf{k}n\sigma} + Q^{n}_{\mathbf{k}\sigma}, \tag{7}$$

$$Q^{n}_{\mathbf{k}\sigma} = \sum_{\alpha\beta} |C^{n}_{\alpha\sigma}(\mathbf{k})|^2 \left[U_{\alpha\beta} \frac{1}{N} \sum_{\mathbf{k}'n'}^{occ} |C^{n'}_{\beta-\sigma}(\mathbf{k}')|^2 + (U_{\alpha\beta} - J_{\alpha\beta}) \frac{1}{N} \sum_{\mathbf{k}'n'}^{occ} |C^{n'}_{\beta\sigma}(\mathbf{k}')|^2 \right], \tag{8}$$

which is the analogue of eq. (4) for Bloch states. Any band structure calculation corresponds to the solution of some $\hat{H}^{MF}$ describing the interacting system as an effective single particle problem and equations (7,8) contain the correct recipe to include Hubbard correlation starting from band structure eigenvalues, avoiding e-e interaction double counting.

8.3 Hole spectral function, self-energy and the Faddeev method

We are interested in the hole spectral function

$$D^{-}_{\mathbf{k}\sigma}(\omega) = \frac{1}{\pi} \sum_{n} \mathrm{Im}\, \mathcal{G}^{-}(\mathbf{k}n\sigma, \omega)\,, \tag{9}$$

which describes the removal of one electron of wave-vector $\mathbf{k}$, band index n and spin σ and is related to the hole-propagator

$$\mathcal{G}^{-}(\mathbf{k}n\sigma, \omega) \quad = \quad -\langle \Psi_0 |\, \hat{a}^{n\dagger}_{\mathbf{k}\sigma} \hat{G}\,(z)\, \hat{a}^{n}_{\mathbf{k}\sigma} |\Psi_0\rangle\,, \qquad\qquad z = -\omega + E_0\,(N_e) + \mathrm{i}\delta; \tag{10}$$

$E_0\,(N_e)$ and $|\Psi_0\rangle$ define the ground state of the N_e particle system and

$$\hat{G}\,(z) = \frac{1}{z - \hat{H}^{H}} \tag{11}$$

is the resolvent operator. By projecting the Hamiltonian (5) over a complete set appropriate for the $N_e - 1$ particle system one gets an expression for $\hat{H}^{H}$ appropriate to describe one electron removal. The key approximation is to choose a subset of all the excited states of the *non-interacting* system and assume it to be complete. Any N particle non-interacting state can be obtained by repeated applications of creation/destruction operators to the ground state Slater determinant $|\Phi_0\rangle$ i.e. by adding e-h pairs to it; according to 3BS the *interacting* state with one removed electron of momentum $\mathbf{k}$ and spin σ is expanded in terms of the basis set including 1-hole and 3-particle configurations

$$|s\rangle \equiv \hat{a}_{\mathbf{k}n\sigma}\,|\Phi_0\rangle\,, \qquad |t\rangle \equiv \hat{a}^{\dagger}_{\mathbf{q}_3 n_3 \sigma_3} \hat{a}_{\mathbf{q}_2 n_2 \sigma_2} \hat{a}_{\mathbf{q}_1 n_1 \sigma_1}\,|\Phi_0\rangle\,, \tag{12}$$

with

$$\mathbf{q}_1 + \mathbf{q}_2 - \mathbf{q}_3 = \mathbf{k}, \qquad\qquad \sigma_1 + \sigma_2 - \sigma_3 = \sigma.$$

The effective Hamiltonian for the N-1 particle system is then

$$\hat{H}^{H}_{N_e-1} \simeq \hat{H}_1 + \hat{H}_3 + \hat{V}, \tag{13}$$

where $\hat{H}_1$ is associated to one-hole configurations

$$\hat{H}_1 = \langle s| \hat{H}^H |s\rangle |s\rangle \langle s| ,$$

$\hat{H}_3$ describes the contribution of 3-particle configurations

$$\hat{H}_3 = \sum_{tt'} \langle t| \hat{H}^H |t'\rangle |t\rangle \langle t'| ,$$

and $\hat{V}$ is the coupling between 1- and 3-particle states

$$\hat{V} = \sum_{t} \langle s| \hat{H}^H |t\rangle |s\rangle \langle t| + h.c. \quad .$$

We can now calculate the resolvent (11). We define the 3-particle resolvent, that is the resolvent associated to the 3-particle interaction

$$\hat{F}_3(z) = \frac{1}{z - \hat{H}_3},$$

and the Dyson equation which relates $\hat{G}(z)$ to it

$$\hat{G}(z) = \hat{F}_3(z) + \hat{F}_3(z)[\hat{H}_1 + \hat{V}]\hat{G}(z). \tag{14}$$

The Faddeev scattering theory allows to determine $\hat{F}_3(z)$ by separating the 3-body Hamiltonian in diagonal and non-diagonal parts

$$\hat{H}_3^D = \sum_{t} \langle t| \hat{H}^H |t\rangle |t\rangle \langle t| ,$$

$$\hat{H}_3^{ND} = \sum_{tt'}{}' \langle t| \hat{H}^H |t'\rangle |t\rangle \langle t'| ,$$

defining the *diagonal* 3-body resolvent

$$\hat{F}_3^D(z) = \frac{1}{z - \hat{H}_3^D},$$

and the scattering operator

$$\hat{S} = \hat{H}_3^{ND} + \hat{H}_3^{ND}\hat{F}_3^D\hat{S}.$$

The *full* 3-body resolvent can be written in terms of the diagonal one and of the scattering operator as

$$\hat{F}_3 = \hat{F}_3^D + \hat{F}_3^D\hat{S}\hat{F}_3^D. \tag{15}$$

As shown in references [9, 10] the non-diagonal 3-body interaction is the sum of two potentials

$$\hat{H}_3^{ND} = \hat{V}_{h-h} + \hat{V}_{h-e},$$

which describe h-h and h-e multiple scattering. We define partial scattering operators $\hat{S}_{h-h}$,$\hat{S}_{h-e}$ such that $\hat{S} = \hat{S}_{h-h} + \hat{S}_{h-e}$, i.e.

$$\begin{aligned} \hat{S}_{h-h} &= \hat{V}_{h-h} + \hat{V}_{h-h}\hat{F}_3^D\hat{S}, \\ \hat{S}_{h-e} &= \hat{V}_{h-e} + \hat{V}_{h-e}\hat{F}_3^D\hat{S}, \end{aligned}$$

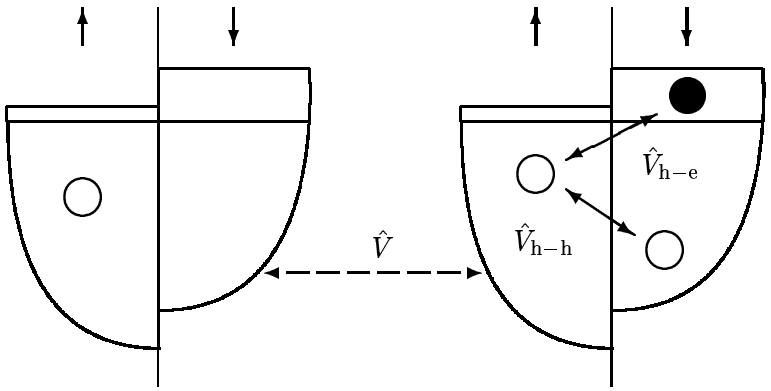

Figure 1: Pictorial representation of non-diagonal terms in the effective hole Hamiltonian: $\hat{V}$ couples one- and three-particle configurations while $\hat{V}_{h-h}$ and $\hat{V}_{h-e}$ describe scattering between three-particle states, namely hole-hole and hole-electron scattering respectively.

which are related to the scattering T-matrices

$$\hat{T}_{h-h} = \hat{V}_{h-h} + \hat{V}_{h-h}\hat{F}_3^D\hat{T}_{h-h}, \tag{16}$$

$$\hat{T}_{h-e} = \hat{V}_{h-e} + \hat{V}_{h-e}\hat{F}_3^D\hat{T}_{h-e}, \tag{17}$$

through the Faddeev equations [12]

$$\hat{S}_{h-h} = \hat{T}_{h-h} + \hat{T}_{h-h}\hat{F}_3^D\hat{S}_{h-e},$$

$$\hat{S}_{h-e} = \hat{T}_{h-e} + \hat{T}_{h-e}\hat{F}_3^D\hat{S}_{h-h}. \tag{18}$$

Inserting (18) into (15) one gets the expression for the 3-particle resolvent in terms of scattering operators S_{h-e} and T_{h-h}

$$\hat{F}_3 = \hat{F}_3^D + \hat{F}_3^D\left(\hat{T}_{h-h} + \hat{T}_{h-h}\hat{F}_3^D\hat{S}_{h-e} + S_{h-e}\right)\hat{F}_3^D. \tag{19}$$

In this expression $\hat{F}_3^D$ and $\hat{T}$-operators -or rather their matrix elements between three-particle states- have an analytical expression, while the inclusion of scattering operator $\hat{S}_{h-e}$ will require the solution of an integral equation.

After some algebra the hole propagator becomes

$$\mathcal{G}^-(\mathbf{k}n\sigma,\omega) = -G_{ss}(z) = \frac{1}{\omega - E_0\left(N_e\right) + H_{ss}^H + \sum\limits_{tt'} F_{3tt'}V_{t's}V_{st}}; \tag{20}$$

with the notation $G_{ss} \equiv \langle s|\,\hat{G}\,|s\rangle$, $F_{3tt'} \equiv \langle t|\,\hat{F}_3\,|t'\rangle$ etc.. Since the difference between the ground state energy of the N_e-particle system $E_0(N_e)$ and the average of $\hat{H}^H$ over $|s\rangle$ states turns out to be

$$E_0(N_e) - H_{ss}^H = \epsilon_{\mathbf{k}n\sigma}^H + Q_{\mathbf{k}\sigma}^n = \epsilon_{\mathbf{k}n\sigma}^{MF},$$

the mean field band eigenvalues appear naturally in the denominator of the hole propagator. Comparing eq. (20) with the usual expression

$$\mathcal{G}^-(\mathbf{k}n\sigma,\omega) = \frac{1}{\omega - \epsilon^{MF}_{\mathbf{k}n\sigma} - \Sigma^-_{\mathbf{k}n\sigma}(\omega)}, \tag{21}$$

we can identify the self-energy correction to band eigenvalues as

$$\Sigma^-(\mathbf{k}n\sigma,\omega) = -\sum_{tt'} F_{3tt'} V_{t's} V_{st}. \tag{22}$$

The procedure we have outlined ends up with a result which has a simple physical interpretation: the creation of one hole in an unfilled valence band is followed by multiple h-h and h-e scattering which is responsible of a renormalization - through self-energy corrections - of the energy states. The efficiency of the scattering processes depends a) on the strength of the screened on-site e-e interaction and b) on the available empty states (i.e. on the number of *initial* valence holes). This explains the well known differences between various transition metals (Ni and Cu, for instance) and possibly those arising in cuprates as a consequence of hole doping.

The self-energy Σ^+ and spectral function D^+ for electron addition can be calculated in the same way as described above just exchanging empty states with filled ones and vice versa, as described in detail in ref. [9].

8.4 3BS at work

In order to calculate the self-energy $\Sigma^-(\mathbf{k}n\sigma,\omega)$ according to (22) one has to perform summations over the 3-particle states $|t\rangle$ involving $\mathbf{k}$-vector conservation; this is done within the so called *local* approximation [13]

$$\delta_{\mathbf{k}=\mathbf{k}'} = \frac{1}{N}\sum_{\mathbf{R}} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}} \simeq \frac{1}{N}.$$

This approximation allows to transform the $\mathbf{k}$-vector summations into integrals involving the orbital density of states $n_\alpha(\epsilon)$ and to calculate T-matrices, scattering operators, resolvents, self-energy and finally spectral functions according to the computational strategy discussed in detail in ref. [9, 10] which can be summarized as follows:

- `Input: band structure` $(\epsilon^n_k, C^n_{\alpha\uparrow}(k), n_{\alpha\uparrow}(\epsilon))$ `and` U`;`
- `free propagators`

$$g^{\alpha\beta}_{h-h}(\omega) = \int_{-\infty}^{E_f} \mathrm{d}\,\epsilon' \int_{-\infty}^{E_f} \mathrm{d}\,\epsilon \frac{n_{\alpha\downarrow}(\epsilon) n_{\beta\uparrow}(\epsilon')}{\omega - \epsilon' - \epsilon - i\delta},$$

$$g^{\alpha\beta}_{h-e}(\omega) = \int_{-\infty}^{E_f} \mathrm{d}\,\epsilon' \int_{E_f}^{\infty} \mathrm{d}\,\epsilon \frac{n_{\alpha\downarrow}(\epsilon) n_{\beta\uparrow}(\epsilon')}{\omega - \epsilon' + \epsilon - i\delta}, \qquad g^{\beta}(\omega) = \int_{-\infty}^{E_f} \mathrm{d}\,\epsilon' \frac{n_{\beta\uparrow}(\epsilon')}{\omega - \epsilon' - i\delta};$$

- `T-matrices`

$$T^{\alpha\beta}_{h-h}(\omega) = \frac{U}{1 + U g^{\alpha\beta}_{h-h}(\omega)}, \qquad T^{\alpha\beta}_{h-e}(\omega) = \frac{-U}{1 - U g^{\alpha\beta}_{h-e}(\omega)};$$

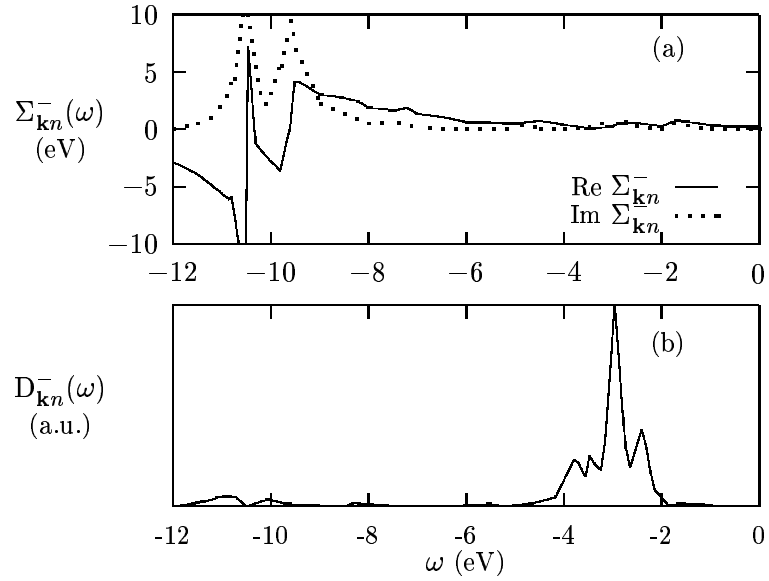

Figure 2: Real (solid line) and imaginary (dotted line) part of self-energy $\Sigma^-_{\mathbf{k}n}(\omega)$ (a) and spectral function (b) in paramagnetic $CuGeO_3$ for the creation of a hole at the Γ point corresponding to the single particle band energy $\epsilon^n_{\mathbf{k}}$ = -3.58 eV. Energies are referred to E_f.

- `kernel`

$$K^{\alpha\beta}(\omega,\epsilon,\epsilon') = \int_{-\infty}^{E_f} \mathrm{d}\,\epsilon'' n_{\alpha\downarrow}(\epsilon'') g^{\beta}(\omega+\epsilon''-\epsilon) g^{\beta}(\omega+\epsilon''-\epsilon') T^{\alpha\beta}_{h-e}(\omega+\epsilon'') T^{\alpha\beta}_{h-h}(\omega-\epsilon''),$$

`and`

$$\begin{aligned} B^{\alpha\beta}(\omega,\epsilon) &= \int_{-\infty}^{E_f} \mathrm{d}\,\epsilon' n_{\alpha\downarrow}(\epsilon') g^{\beta}(\omega+\epsilon'-\epsilon) T^{\alpha\beta}_{h-e}(\omega+\epsilon') \\ &\times \left[g^{\alpha\beta}_{h-e}(\omega-\epsilon') + \int_{E_f}^{\infty} \mathrm{d}\,\epsilon'' n_{\alpha\downarrow}(\epsilon'') g^{\beta}(\omega+\epsilon'-\epsilon'') g^{\alpha\beta}_{h-h}(\omega-\epsilon'') T^{\alpha\beta}_{h-h}(\omega-\epsilon'') \right]; \end{aligned}$$

- `solve the integral equation`

$$A^{\alpha\beta}(\omega,\epsilon) = B^{\alpha\beta}(\omega,\epsilon) + \int_{E_f}^{\infty} \mathrm{d}\,\epsilon' n_{\alpha\downarrow}(\epsilon') K^{\alpha\beta}(\omega,\epsilon,\epsilon') A^{\alpha\beta}(\omega,\epsilon');$$

- `orbital self-energy`

$$\Sigma^-_{\beta\uparrow}(\omega) = \sum_{\alpha} \int_{E_f}^{\infty} \mathrm{d}\,\epsilon\, n_{\alpha\downarrow}(\epsilon) T^{\alpha\beta}_{h-h}(\omega-\epsilon) \left[1 + U A^{\alpha\beta}(\omega\epsilon)\right];$$

- **K**`- and band-index dependent self-energy`

$$\Sigma^-(kn\uparrow,\omega) = U \sum_{\beta} |C^n_{\beta\uparrow}(k)|^2 \left[\sum_{\alpha} \int_{-\infty}^{E_f} \mathrm{d}\,\epsilon\, n_{\alpha\downarrow}(\epsilon) \Sigma^-_{\beta\uparrow}(\omega) \right];$$

- `spectral function`

$$D^{(-)}_{\uparrow}(\omega) = \frac{1}{\pi} \sum_{kn} \mathrm{Im} \frac{1}{\omega - \epsilon^n_k - \Sigma^-(kn\uparrow,\omega)}.$$

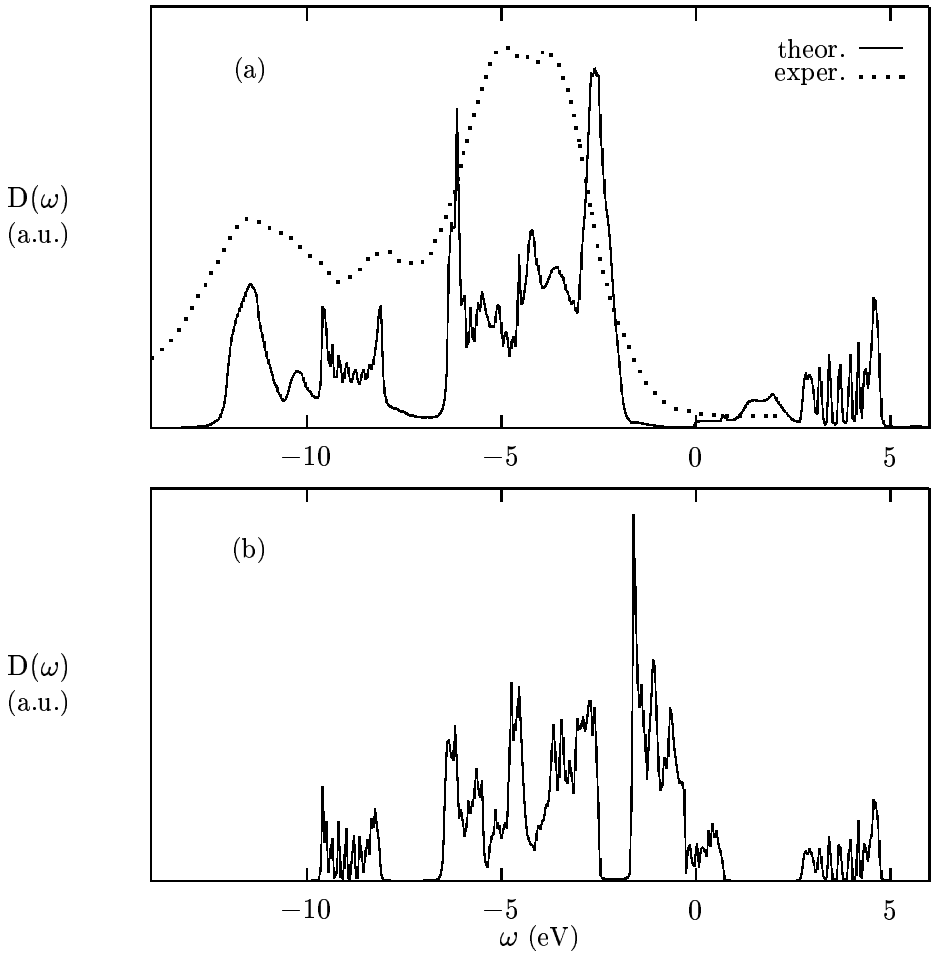

Figure 3: Total spectral function $D(\omega) = D^-(\omega) + D^+(\omega)$ for $CuGeO_3$ calculated by (a) 3BS theory with U=8 eV; (b) single particle density of states ref. [14]. E_f corresponds to $\omega = 0$ eV.

We report the results for a transition metal (nickel) and a cuprate ($CuGeO_3$) obtained by considering the interaction between opposite spin electrons localized on the transition metal sites as the dominant contribution, i.e.

$$U_{\alpha\beta} = \begin{cases} U_{dd} & \text{for } \alpha, \beta = d \text{ orbitals} \\ 0 & \text{elsewhere;} \end{cases}$$

$$U_{\alpha\beta} - J_{\alpha\beta} \simeq 0.$$

To apply this method to $CuGeO_3$ we have used the eigenstates/eigenvalues of ref. [14] and assumed $U_{dd} = 8$ eV. Fig. 2 shows the hole spectral function and self-energy for a particular eigenstate ($\epsilon^n_{\mathbf{k}}$=-3.58 eV at the Γ point). The peaks in the spectral function can be classified either as quasiparticle excitations or as satellites, according to the value of the imaginary part of the self-energy in the region of the peak: quasi-particle excitations correspond to small imaginary part, and give rise to the coherent part of the spectral function. Satellites occur where the imaginary part of self-energy is large and correspond to short-lived excitations with a large intrinsic line-width; we refer to them as to the incoherent part of the spectral function.

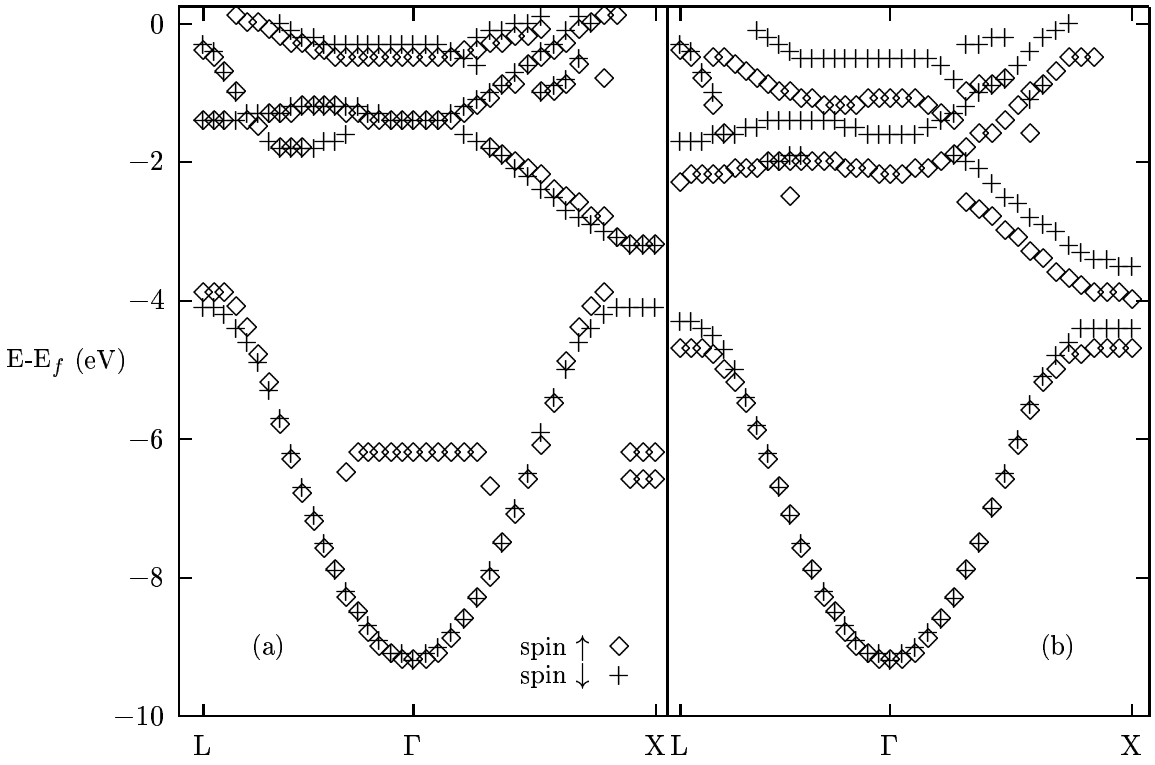

Figure 4: (a) Energy position of the peaks of nickel in the spectral function at **k**-points along high symmetry lines of the Brillouin Zone. (b) Single particle band structure of ref. [10].

The hole and electron spectral functions are plotted in fig. 3 and compared with single particle results. The effect of electron correlation on single-particle states is dramatic: some bands are shifted to higher binding energies, spectral weight is removed from the upper part of the spectrum, and many new states (satellites) appear; only states around $-8 \div -9$ eV and $-5 \div -6$ eV are practically unaffected being mainly Ge and O derived. $CuGeO_3$ is an insulator but it is predicted to be a metal by single particle band calculation; the inclusion of electron correlation reproduces this insulating behavior and the energy gap, calculated as the energy separation between electron removal and electron addition spectra, reproduces the experimental one [15]. The same was proven to be true also in the case of NiO, where a 3BS description of Hubbard correlation was able to reproduced both the complex satellite structure and the measured value of the insulating gap [16].

The ability of 3BS approach to open up Hubbard gaps, i.e. to reproduce an insulating behaviour in a system which is metallic according to band theory, is related to its non-perturbative character; the method can be applied in any correlation regime and it has been shown [8, 16, 17] to reproduce for U much larger than the band width W ($\frac{U}{W} \to \infty$) the so called "Hubbard I" solution [18] of Hubbard Hamiltonian, i.e. the *atomic limit* where hole and electron states are separated by a Mott-Hubbard gap equal to U [19].

We describe now the results of the application of 3BS to nickel. In this case the on-site e-e repulsion is more effectively screened and the estimated value of U_{dd} is $\simeq$ 2 eV [20]. Fig. 4, reporting the comparison between quasi-particle states and single particle ones, shows that e-e

correlation effects are still sizable and they are actually essential in order to to reproduce the observed spectroscopical features, i.e. satellite structure at 6 eV binding energy, correct band width (overestimated in LDA), exchange splitting [21], and energy dispersion [10].

8.5 Summary and outlook

We have described a method to include on-site interactions in the description of hole and electrons states: ab-initio single-particle band states are used as input mean-field eigenstates for the calculation of self-energy corrections according to a 3-body scattering (3BS) solution of a multi-orbital Hubbard Hamiltonian. When applied to valence states of ferromagnetic nickel it allows to get a quasiparticle band structure which compares much more favorably with the experimental observation than conventional mean-field LDA, reproducing the observed band width, the energy dispersion, the satellite structure and the exchange splitting. Since the method does not rely on a perturbation expansion it has a wide range of application, including any correlation regime. In the case of a highly correlated system such as $CuGeO_3$, 3BS is able to reproduce both the insulating behaviour and a correct overall picture of photoemission experiments.

Our present choice of empirically determining the parameter U of the Hubbard Hamiltonian - which has been fixed to reproduce the satellite binding energy - ensures that we obtain a good agreement with experiments; however the possibility of reproducing both the satellite structures and other spectroscopical features such as energy dispersion and spin dependence in nickel and the insulating gap in $CuGeO_3$ can be seen as a non trivial result and a success of the method itself: previous methods based on a simplified description of the scattering channels [22, 23] in fact have not been able to reproduce at the same time the satellite energy position and the valence band width which turned out to be systematically overestimated for values of the Coulomb integral fixed to reproduce the satellite binding energy. The problem of extracting Hubbard U from ab-initio calculation, either in the so called Constrained-Density Functional scheme [24] or as screened Coulomb interaction [20, 25], is an important issue which goes in the direction of a full match between model Hamiltonians and realistic systems and that we are presently considering as an implementation of our approach.

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