HCM Newsletter

Ψ_k Network

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

Number 19 February 1997

Editor: Z. (Dzidka) Szotek
Proposal: ERB4050PL930589
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Coordinator: Walter Temmerman
E-mail: psik-coord@daresbury.ac.uk

Contents

1 Editorial

In this *Newsletter* we publish the annual report for Brussels on the Network activity in 1996. It is in the section **News from the Network**. Additionally, the last section of the *Newsletter* contains scientific highlights of the 1996 collaborations within the *Network*. Please note that the report contains a list of publications that resulted from the collaborations and/or due to a variety of the *Network* activities.

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)*, *M. Finnis (Univ. Belfast)*, *M. Gillan (Univ. Keele)*, *E.K.U. Gross (Univ. Würzburg)*, *B.L. Györffy (Univ. Bristol)*, *M. Heggie (Univ. Sussex)*, *V. Heine (Univ. Cambridge)*, *R. Jones (Univ. Exeter)*, *J. Kübler (TH, Darmstadt)*, *R. Nieminen (TU, Helsinki)*, *J. Nørskov (TU, Lyngby)* with information on CAMP, *M. Scheffler (FHI Berlin)*, *K.-H. Schwarz (TU, Vienna)*, *M. Springborg (University of Konstanz)*, *G.P. Srivastava (Univ. Exeter)*, *W.M. Temmerman (Daresbury Laboratory, UK)*, and *A. Walker (UEA Norwich)*. There also exists a pointer to the WWW home page of the Solid State Theory Group at National Renewable Energy Laboratory, Golden, CO 80401 *(http://www.sst.nrel.gov)*. 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

2.1 Progress Report on the Network Activity in 1996

1 January 1996 - 31 December 1996

HCM ψ_k-Network on
Ab initio (from electronic structure) calculation of
complex processes in materials
Contract Number: CHRXCT930369

2.1.1 Preamble

This Network is characterized by a large number of nodes (over 60) and more than 300 participating researchers. The participating teams of the Network are enumerated in the subsection below. The Network aims to promote excellence in the subject of quantum mechanical calculations for electronic properties of solids through collaborations accross Europe, including helping those in smaller, new or isolated research groups.

Such is the succes of the Network's bimonthly newsletter that more than 500 researchers all over the world receive it electronically. The newsletters are also available through anonymous ftp and on World Wide Web at: **http://www.dl.ac.uk/TCSC/HCM/PSIK/newsletters.html**. The newsletters provide information on abstracts of recently submitted papers, workshops, collaborations, jobs-, books-, and publication-announcements, and scientific highlights.

The culminating point of this year's activity of the Network was the conference that took place in Schwäbisch Gmünd on 17–21 September. It was attended by more than 300 scientists active in the field of *ab initio* electronic structure calculations. Moreover, the amount of collaborations has increased. The number of common publications that explicitly acknowledge the benefits from collaborations within the Network or from attending workshops or due to using computer codes obtained at various 'hands-on computer code' workshops, organized by the Network, has risen this year to 68 as compared to 44 last year.

Teams

Coordinator: *W.M. Temmerman, Daresbury Laboratory, GB tel.: +44 1925 603227, fax: +44 1925 603634*

Other Participants:

O.K. Andersen, MPIF Stuttgart, DE (16 researchers)
A. Andriotis, FORTH, GR (6 researchers)
O. Bisi, Universita degli studi di Trento, IT (3 researchers)
P. Blöchl, IBM-Research Division, CH (2 researchers)
G. Boureau, Universite P.et M. Curie, FR (3 researchers)
J. Braun, Universitat Osnabruck, DE (4 researchers)
N. Christensen, Arhus Universitet, DK (2 researchers)
P. Dederichs, Forschungszentrum Julich, DE (10 researchers)
H. Ebert, Universitat Muenchen, DE (2 researchers)
C. Elsaesser, MPIM Stuttgart, DE (5 researchers)
F. Flores/J. Ortega, Universidad Autonoma de Madrid, ES (7 researchers)
F. Gautier, Universite de Strasbourg, FR (6 researchers)
M. Gillan, University of Keele, GB (9 researchers)
S. Giuliano, Universita degli Studi di Messina, IT (4 researchers)
M. Gupta, Universite de Paris-Sud XI, FR (2 researchers)
B. Gyorffy, University of Bristol, GB (4 researchers)
J. Hafner, Technische Universitat Wien, AT (10 researchers)
V. Heine, University of Cambridge, GB (23 researchers)
R. de Groot, Katholieke Universiteit Nijmegen, NL (8 researchers)
P. Kelly, Nederlandse Philips Bedrijven BV, NL (4 researchers)
C. Koenig, Universite de Rennes I, FR (3 researchers)
J. Kübler, Technische Hochschule Darmstadt, DE (6 researchers)
F. Manghi, Universita degli studi di Modena, IT (6 researchers)
J. Martins, INESC Lisbon, PT (3 researchers)
R. Nieminen, Helsinki University of Technology, FI (10 researchers)
J. Norskov, Danmarks Tekniske Hojskole, DK (10 researchers)
C. Patterson, University of Dublin, IE (4 researchers)
J. Pollmann, Universitat Munster, DE (6 researchers)
H. Potatoglou, University of Thessaloniki, GR (6 researchers)
M. Scheffler, Fritz Haber Institut, DE (20 researchers)
K. Schwarz, Technische Universitat, Wien, Austria (4 researchers)
C. Sommers, Universite de Paris-Sud XI, FR (2 researchers)
M. Springborg, Universitat Konstanz, DE (1 researchers)
J. Staunton, University of Warwick, GB (5 researchers)
N. Stefanou, University of Athens, GR (2 researchers)
V. Van Doren, Universitair Centrum Antwerpen, BE (3 researchers)
A. Walker, University of East Anglia, GB (5 researchers)
P. Weinberger, Technische Universitat Wien, AT (11 researchers)
H. Winter, Kernforschungszentrum Karlsruhe, DE (3 researchers)
F. Gautier, Universite de Strasbourg, FR (10 researchers)
P. Bruno, CNRS, Orsay, FR (2 researchers)
S. Crampin, University of Bath, UK (4 researchers)
O. Eriksson, University of Uppsala, SE (20 researchers)
M. Finnis, University of Belfast, UK (4 researchers)
F. Fiorentini, Universita di Cagliari, IT (4 researchers)
G. Gehring, University of Sheffield, UK (3 researchers)
E. Gross, University of Wuerzburg, DE (8 researchers)
F. Gygi, IRRMA, CH (2 researchers)

W. Hergert, Martin-Luther-University Halle-Wittenberg, DE (2 researchers)
J. Inglesfield, University of Cardiff, GB (2 researchers)
K. Kunc, CNRS Paris, FR (4 researchers)
I. Mertig, Technical University of Dresden, DE (3 researchers)
R. Monnier, ETH Zurich, CH (2 researchers)
N. Papanikolaou, University of Ioannina, GR (3 researchers)
A. Pasturel, CNRS Grenoble, FR (4 researchers)
D. Pettifor, University of Oxford, GB (4 researchers)
M. Richter, MPG Dresden, DE (8 researchers)
E. Sandre, CNRS Grenoble, FR (5 researchers)
W. Schattke, Universitat Kiel, DE (5 researchers)
C. Wijers, University of Twente, NL (3 researchers)
A. Baratoff, University of Basel, CH (1 researchers)
M. Methfessel, Halbleiterphysik Frankfurt/Oder, DE (4 researchers)

2.1.2 Factual Information

This year the Network has funded two Network Management Board Meetings at which current matters of running the Network and organisation of the Network Conference in September 1996 have been discussed and taken care of.

A big conference dealing with all aspects of the 'ab initio electronic structure calculations' was organized by the Network on 17-21 September 1996 in Schwäbisch Gmünd (Germany). In this report we give a brief summary on the Conference and the published book of abstracts is attached to this report.

Five workshops have been organised this year. The workshop on *'The Bogoliubov-de Gennes Equation for Superconductors'*, held in Bristol on 30-31 March 1996, was concerned with new results obtained by means of the above mentioned equation. The workshop on "*Full Potential LAPW Calculations with the WIEN95 Code*", held in Vienna on 9-13 April 1996, was already a second computer course, where use of the latest electronic structure FP-LAPW WIEN95 code for solids was taught. The *Berlin Workshop on 'Molecular Dynamics'*, was already a second computer course on this subject organized by this Network. It was held on 4-8 November, 1996. The workshop 'MNS96', held on 20-21 May in Hallle, was devoted to discussions and exchange of opinions on the subject of "*Magnetic Nanostructures on Surfaces*". The workshop held in Strasbourg on 2-3 June 1996, delt with all research on interface magnetism of Fe/Cr.

This year 20 collaborative visits and long term secondments have taken place, ranging from joint development of computer codes, initiating new collaborative projects, to continuation of established collaborations. This year the number of long term secondments has increased compared to last year. In the following we enumerate most of the established collaborations within the Network. All scientific publications that resulted from a variety of activities within the Network, and which explicitly acknowledge the benefits from the Network, are listed in the section '**Joint publications**'.

- A collaboration between M. Finnis (*MPI-Metalforschung*) and the group of V. Heine (*University of Cambridge, UK*), M. Scheffler (*FHI Berlin*), and M. Gillan (*Keele*) on metal-ceramics interfaces (see Highlights' section, and refs. 5, 11–12, 20 in list of joint publications).

- A collaboration between the groups of M. Parinello and O.K. Andersen (*MPI Stuttgart, Germany*) and the group of V. Heine (*University of Cambridge, UK*) on various aspects of complex processes in materials (see refs. 23-24, 38 and 68 in the list of joint publications).

- A collaboration between the group of N. Stefanou (*Univ. Athens, Greece*) and the group of P. Dederichs in Jülich (*Germany*) on the ab-initio study of dynamical properties of materials (see refs. 35-37 in the joint publications list).

- A collaboration between the group of O.K. Andersen (*MPI Stuttgart, Germany*), the group of W.M. Temmerman (*Daresbury Laboratory, UK*), and B.L. Gyorffy (*Univ. Bristol, UK*) on quasi-particle spectra of high temperature superconductors (see refs. 59-60 in the joint publications list).

- A collaboration between the group of C. Koenig (*Univ. Rennes*) and P.Blöchl (*IBM Zürich*) on molecular materials (see Highlights' section and refs. 15-16 in the joint publications list).

- A collaboration between the group of K.-H. Schwarz (*TU, Vienna*) and P.Blöchl (*IBM Zürich*) on the application of PAW method (see Highlights' section and ref. 49 in the joint publications list).

- A collaboration between J.L. Martins (*INESC Lisbon, Portugal*) and the group of Van Camp and Van Doren (*Univ. Antwerp, Belgium*) on ternary calcium nitrides (see Highlights' section and refs. 62, 65 in the list of joint publications).

- A collaboration between A. Svane (*Univ. Aarhus, Denmark*), H. Winter (*Forschungszentrum Karlsruhe, Germany*), and group of W. Temmerman (*Daresbury Laboratory, UK*) on self-interaction corrected LSD description of rare earth materials (see Highlights' section and refs. 54-55 in the list of joint publications).

- A collaboration between the group of J. Hafner (*TU Vienna, Austria*) and K.P. Bohnen (*Forschungszentrum Karlsruhe, Germany*) on ab-initio calculation of bulk- and surface-phonons for transition metals (see ref. 3 in the list of joint publications).

- A collaboration between the group of J. Hafner (*TU Vienna, Austria*) and the group of M. Gillan (*Univ. Keele, UK*) on ab-initio calculations of energetics, and structural and electronic properties of various materials (see refs. 17 and 41 in the list of joint publications).

- A collaboration between R. Pérez (*Madrid*) and J. Payne (*Cambridge*) on first-principles simulation of nanoindentation on silicon surfaces and on non-contact AFM on reactive surfaces (see refs. 39-40 in the joint publications list).

- A collaboration between B.L. Gyorffy (*Univ. Bristol, UK*) and the group of E.K.U. Gross (*Univ. Würzburg, Germany*) on relativistic approach to dichroism in superconductivity (see Highlights' section and ref. 4 in the joint publications list).

- A collaboration between the group of P. Weinberger (*TU Vienna, Austria*) and C. Sommers (*Univ. Paris, Orsay, France*) on interface exchange coupling (see ref. 56 in the publication list).

- A collaboration between the group of W.M. Temmerman (*Daresbury Lab., UK*) and the group of E.K.U. Gross (*Univ. Würzburg, Germany*) on electronic correlations in the superconducting state (see Highlights' section).

- A collaboration between S. Blügel (*Forschhungszentrum Jülich, Germany*) and G. Bihlmayer and R. Podloucky (*University of Vienna, Austria*) on transition-metal silicides for electronic devices (see Highlights' section and ref. 67 in the joint publications list).

2.1.3 Application of Funding

This year the Network has funded a big conference, two Network Management Board Meetings, five workshops, 20 collaborative visits and secondements, Moreover, 30 visits to the workshops were funded. By far the biggest spending was on the Network Conference in Schwäbisch Gmünd, where 166 members were funded by the Network. The priority has been given to young people. Moreover, the Network funds a half of the salary of the scientific secretary of the Network: Dr. Z. Szotek (Belgian nationality and based in Daresbury Laboratory, UK).
Please note, that collaborative visits and secondments between Austria and Switzerland have been funded by the respective countries, and are not mentioned in this report.

Network's Management Board Meetings

Since this Network is such a large entity, in order to ensure its smooth activity, it is run by the Network Management Board (NMB). The latter consists of spokepersons of all the Working Groups and representatives of all the countries participating in this Network. The NMB meets every half a year. The first NMB of the year was dedicated to the organization of the big Network Conference, and discussions of the proposal for TMR funding for the Network. The second NMB meeting took place the day after the Network Conference in Schwäbisch Gmünd, and was mostly dedicated to the assesment of the Conference, and to finalising the outline of the TMR application. Below we enumerate those present at both NMB meetings.

- *6th Network Management Board's Meeting, University of Paris, 23-24 February, 1996.*
  Present: O.K. Andersen (*vice-chairman*, MPI Stuttgart), O. Bisi (Univ. Trento, Italy), P. Dederichs (IFF-KFA-Jülich, Germany), P.J. Durham (Daresbury Lab., UK), M. Finnis (Univ. Belfast, UK), M. Gillan (Univ. Keele, UK), B.L. Gyorffy (Univ. Bristol, UK), V. Heine (*chairman*, Cavendish Laboratory, UK), C. Koenig (Univ. Rennes, France), J.L. Martins (INESC Lisbon, Portugal), R. Nieminen (TU, Helsinki, Finland), C. Patterson (Univ. Trinity College Dublin, Ireland), R. Podloucky (Univ. Vienna, Austria), M. Scheffler (FHI Berlin, Germany), A. Svane (Univ. Aarhus, Denmark), Z. Szotek (*scientific secretary*, Daresbury Lab., UK), W. M. Temmerman (*coordinator*, Daresbury Lab., UK) E. Wimmer (guest, MSI Paris, France)

- *7th Network Management Board's Meeting, Schwäbisch Gmünd, 22 September, 1996.*
  Present: O. Bisi (Univ. Trento, Italy), S. Blügel (IFF-FA Jülich, Germany), P. Dederichs (IFF-FA-Jülich, Germany), M. Finnis (Univ. Belfast, UK), E.K.U. Gross (Univ. Würzburg), B.L. Gyorffy (Univ. Bristol, UK), J. Hafner (TU, Vienna, Austria), V. Heine (*chairman*, Cavendish Laboratory, UK), J.E. Inglesfield (Univ. Nijmegen, The Netherlands), C. Koenig (Univ. Rennes, France), J.L. Martins (INESC Lisbon, Portugal), R. Nieminen (TU, Helsinki, Finland), C. Patterson (Trinity College, Dublin, Rep. of Ireland), M. Scheffler (Fritz-Haber-Institut Berlin, Germany), N. Stefanou (Univ. Athens, Greece), A. Svane (Univ. Aarhus, Denmark), Z. Szotek (*scientific secretary*, Daresbury Lab., UK), W. M. Temmerman (*coordinator*, Daresbury Lab., UK)

Network's Conference

The $\Psi_{\vec{k}}$−Network Conference, constituting the culminating point of the EU-Human Capital and Mobility $\Psi_{\vec{k}}$−Network on '**Ab initio (from electronic structure) calculation of complex process in materials**', took place in Schwäbisch Gmünd (Germany) on 17–21 September

1996. The conference was attended by 322 participants, 260 participants came from EU countries, 60 from Eastern Europe and overseas. Thanks to important financial contributions from the $\Psi_{\vec{k}}$−Network, the Max-Planck-Gesellschaft, the EU-Commission, and IBM, it was possible to offer financial support not only to the 48 invited speakers, but altogether to 166 mostly young participants. To that, one has to add support for HCM-activities provided out of national sources for nationals of the '*new*' EU-countries (Austria, Finland, Sweden), and Switzerland. The fact that so many young members of our community were able to attend has certainly contributed to the lively and active atmosphere throughout all four conference days - even during the very last sessions no decrease in the attendance could be observed. Moreover the standard of the contributed papers has been excellent, which demonstrates the healthy dynamics of this field. This matter of quality is very important. Of course it is an impossible task to summarise over 200 invited and contributed talks and posters, presented at the conference. Not only was the quality of the calculations high, but they contributed to important areas of mainstream science, being closely joined with experimental results to understand "the phenomena of nature." The focus has shifted from calculating the electronic structure as an end in itself, to calculating various properties or simulating various processes. The list here is endless: magnetic dichroism, ferroelectric behaviour, electric field gradients needed for Nuclear Magnetic Resonance, defects in GaN, and so on. Even transport properties were appearing, sometimes calculated directly from the wave functions with the Kubo-Greenwood formalism. Among simulations we had, for instance, the atomistic effects in polishing a diamond surface. Our work has a growing impact on materials science, for example in the study of optoelectronic properties, semiconductors and grain boundaries. There are a growing number of applications in chemistry, where techniques based on Density Functional Theory are gaining acceptance at last. The calculations include organic materials, even some of biological importance. There were four whole sessions in this conference devoted to surface science, with papers on such practical issues as crystal growth and surface chemical reactions. The gap to industrial applications is closing, or rather has closed at a few points. There were many contributions at the conference of relevance to technological applications, such as for example studies of materials being considered for making a blue laser or as a particular pigment or for optoelectronic devices. There have also been good examples at this conference of well chosen computer experiments designed to elucidate some observed phenomenon. Density Functional Theory (DFT) was the cornerstone of all work presented at the conference. The awareness of its successes and limitations was manifested in a number of sessions devoted to attempts of overcoming the shortcomings: GGA, SIC, OEP, GW, LDA+U, etc. Quantum Monte Carlo techniques play an increasingly important role in providing a testing ground for theories beyond the local density approximation. These activities reflect the committment of our community to find better functionals to make DFT even more useful. Finding an accurate functional is only the first step, the second consists in setting up efficient techniques for solving the Kohn-Sham equations of DFT and to compute total energies and forces for ever more complex systems. The papers presented at the conference demonstrated not only the tremendous progress achieved during the last few years, based on both improved computer performance and better codes (who would have thought only five years ago that we will so soon be able to describe ab-initio not only complex molecular processes at solid surfaces, but even biochemical reactions ?), but also that the development of more performant computational tools remains a very active field of research. The competition is open for a better scaling of the CPU-time with the number of degrees of freedom ($O(N)$-scaling), but we should not forget that to extend the time-scale of our simulations is as necessary as increasing the number of atoms. The development of new codes seems to be characterized by diversification - sometimes one has the impression that a new code should not only be efficient, but also as different as possible from existing codes. Future development could profit from more cooperation and syncretism in the community. However, to make sure that the interesting elements of a code can be put into other codes in an unproblematic way, it is necessary that the codes remain - at least for academic research - within the public domain. Our work derives a good part of its justification from the successful applications of the techniques we are developing to technologically relevant problems. In the conference applications to semiconductors (including novel carbon-based materials), magnetism, superconductors, mechanical properties and phase transitions, surfaces, interfaces and catalysis, and even biological materials were actively discussed. To select highlights among the many results is of course a highly arbitrary decision. If we just pick as an example the modelling of a chemical reaction catalyzed by a transition-metal surface or of the protonization of a molecule by the acid-sites inside a zeolite, we have certainly found convincing examples for the ability of ab-initio simulations to characterize a process in much more detail than possible in a laboratory experiment. This should be of immediate interest not only in academia, but also for industry. Similar conclusions could be drawn from the description of the microscopic magnetic structure of a noncollinear magnet or a thin film, from the modelling of solvation reactions, and from a series of other examples. However, with all the emphasis on application we should not underrate fundamental science - here the encouraging steps towards a pairing-density theory of superconductivity merit special attention.

The most important point of the conference was the aspect of **"the whole family"** of European researchers in electronic structure field, and helping them to do high quality work through interaction with others, and to achieve recognition through presenting their work publicly. The $\Psi_{\vec{k}}-$Network is trying to provide an infrastructure for "the whole family" including running this conference. Previously there was not even an e-mail address list. We had lacked cohesion as a community because firstly we are relatively new, secondly because we tend to identify with the community such as surfaces or magnetism or semiconductors to which our calculations relate, which in a way is a very positive feature, and thirdly because we do not have a central facility to organise around as the neutron scatterers do or those using synchrotron radiation. After this conference it is fair to say that **largely due to the success of the $\Psi_{\vec{k}}-$Network there now exists an active and intensely cooperating electronic-structure community in Europe and that this community has achieved world-wide leadership in this field**. In the long term such co-operation depends on trust, and trust depends on respect, and respect in a scientific community can only ultimately be built on a common pursuit of excellent science. The very high quality of the invited and contributed papers at this conference and the general dynamic of our community are partly due to all the interaction and networking over the last few years. Achieving that high quality depends on knowing about the latest advances made elsewhere, especially in a rapidly developing field such as ours. Owing to this conference many scientists from less developed and less fortunate countries of Eastern and Central Europe could meet the scientists from the West, and benefit from the excellence of science and progress made there. They had the opportunity to discuss their problems and ideas, and to bring up to date their awerness of what has already been accomplished in this dynamically growing field. Many had an opportunity to start scientific collaborations or obtain computer codes which would enable them to compete in science with the most developed EU countries.

This conference was a milestone in our particular community which one can see in the co-operative work that has brought it about, in the scientific excellences of the contributions, and in how a very large fraction of the contributions, presented at the Conference, carried addresses from two or more different countries or involved people whose names indicated different home countries. It will certainly be a very important task to find a way how these fruitful exchanges and cooperations can be supported beyond the expiration date of the HCM $\Psi_{\vec{k}}$−Network at the end of 1997.

Workshops

- **International Workshop on 'The Bogoliubov-de Gennes Equations for Superconductors'**, Bristol, 30-31 March 1996. The Workshop was partially supported by British Computational Project CCP9, and partially by the Network. The outside participants supported by the Network are enumerated below.

Participant	Node	Participant	Node
K. Capelle	Andersen	S. Kurth	Van Doren
M. Lüders	Andersen		

- **2nd Workshop on Full-Potential LAPW calculations with the WIEN95 code:** Vienna 19-22 April 1996
  The scientific programme of this workshop covered a short introduction to Density Functional Theory, band structure methods in general and the LAPW method, with corresponding algorithms in particular. The outline and handling of the new user-friendly program was described in detail, and the participants had also an opportunity to run the WIEN95 code on several workstations in five exercise sessions. Additionally, one day of the workshop was devoted to calculation of forces. Below we include the list of Network funded participants.

Participant	Node	Participant	Node
G. Polanco	Ebert	M. Knecht	Ebert
B. Zellermann	Ebert	F. Wagner	Scheffler
M. Petersen	Scheffler	M. Lüders	Andersen

- **MNS96 Workshop on 'Magnetic Nanostructures on metal and semiconductor surfaces'**, 20-21 May 1996, Halle; partially funded by the Network.

Participant	Node	Participant	Node
P. Dederichs	Dederichs	C. Demangeat	Gautier
H. Dreyssé	Gautier	R. Zeller	Dederichs
K. Wildberger	Dederichs	A. Andriotis	Andriotis

- **Workshop on Fe/Cr interface magnetism-Satellite Meeting of the Symposium of the E-MRS Spring Meeting**, Strasbourg 2-3 June, 1996. This workshop was partially supported by the Network.

Participant	**Node**	**Participant**	**Node**
I. Mertig	Scheffler	W.M. Temmerman	Temmerman
S. Blügel	Dederichs	P.H. Dederichs	Dederichs
K. Wildberger	Dederichs	R. Zeller	Dederichs

- **2nd Berlin Workshop on Molecular Dynamics**, Berlin, 4-8 November, 1996. The course covered the basic concepts of Density Functional Theory, and an introduction to the use of the molecular dynamics '**fhi96md**' computer program. Participants supported by the network are listed below.

Participant	**Node**	**Participant**	**Node**
B. Winkler	Scheffler	L.M. Molina	Ortega/Flores
V. Graschus	Pollmann	H. Herper	Ebert
U. Grossner	Scheffler	O. Pulci	Manghi
P. Senet	Scheffler	D.R. Alfonso	Bisi
J.L. Martins	Martins		

Collaborative Visits and Secondments

Below we enumerate all collaborative visits (less than 10 days) and secondments (longer than 10 days) that have taken place in 1996. This year the Network has funded 3 secondments of more than a month duration.

- **R. Perez** (from *Univ. Madrid, Spain* to *Univ. Cambridge, UK*), 1 January-30 April, 1996
- **C. Katan (Hoerner)** (from *Univ. Rennes, France* to *IBM Zürich, Switzerland*), 17-28 January, 1996
- **E. Hoffmann** (from *Univ. Duisburg, Germany* to *Daresbury Laboratory (UK)*), February 3-March 2, 1996.
- **J.E. Inglesfield** (from *Univ. Cardiff, UK* to *Univ. Nijmegen, The Netherlands*), 14-18 February, 1996
- **J.M. Holender** (from *Univ. Keele, UK* to *TU Vienna, Austria*), 27 February-5 March, 1996
- **U. Schönberger** (from *MPI-Metallforschung, Stuttgart, Germany* to *Univ. Belfast, Northern Ireland*), 10-12 March, 1996
- **P. Vansant** (from {*Univ. Antwerp, Belgium* to *INESC, Lisbon, Portugal*), 10-13 March, 1996
- **M. Lüders** (from *Univ. Würzburg, Germany* to *TU Vienna, Austria*), 9-24 April, 1996.
- **J.E. Inglesfield** (from *Univ. Cardiff, UK* to *Univ. Nijmegen, The Netherlands*), 1-6 May, 1996
- **J.L. Martins** (from *INESC, Lisbon, Portugal* to *Univ. Antwerp, Belgium*), 24-25 June, 1996
- **A. Bieniok** (from *Univ. Frankfurt/M, Germany* to *Univ. Cambridge, UK*), 1-13 July, 1996
- **A. Lichtenstein** (from *Forschungszentrum Jülich, Germany* to *Univ. Oxford, UK*), 7-14 July, 1996
- **C. Katan (Hoerner)** (from *Univ. Rennes, France* to *IBM Zürich, Switzerland*), 22 July-2 August, 1996.

- **J.E. Inglesfield** (from *Univ. Cardiff, UK* to *Univ. Nijmegen, The Netherlands*), 16 August, 1996
- **A. Mujica** (from *Univ. La Laguna, Spain* to *Univ. Cambridge, UK*), 3 July-6 September, 1996
- **K.P. Bohnen** (from *Forzchungszentrum Karlsruhe, Germany* to *TU Vienna, Austria*), 24 August-5 September 1996
- **C. Bekker** (from *Univ. Twente, The Netherlands* to *Univ. Aarhus, Denmark*), 2-29 September, 1996
- **M. Lüders** (from *Univ. Würzburg, Germany* to *Daresbury Laboratory, UK*), 30 September-30 November, 1996
- **P. Slavenburg** (from *Univ. Nijmegen, The Netherlands* to *Univ. Cardiff, UK*), 11-18 November, 1996
- **A. Svane** (from *Univ. Aarhus, Denmark* to *Daresbury Lab., UK*), 15-18 November, 1996

2.1.4 Joint Publications in 1996

This year the following 68 papers have been published or submitted for publication. These acknowledge the benefits from the Network in terms of collaborations, computer codes obtained within the Network individually or at 'hands-on computer code' workshops.

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Newsletters

Moreover, the Network has published 6 Newsletters of both scientific and informative content. They were published in all even months of the past calendar year. These Newsletters are attached to this progress report. Additionally the Conference book of abstracts is also enclosed.

3 News from the Working Groups

3.1 Reports on Collaborative Visits

Report on the collaborative visit of Patrick Slavenburg (Nijmegen) to University of Cardiff

11–18 November 1996

In the period 11-18 November Prof. John Inglesfield and I cooperated on a number of articles. Two articles dealt with the shape memory effect and were follow-ups of two previously submitted articles on that topic. These articles deal with the shape memory effect in Ti-late transition metals such as Fe, Ni, Pd, Pt and Au. We find that the martensitic transformation in these alloys, which forms the basis of the shape memory effect, can be described well by bond order calculations. Bond orders are used in chemistry and by Pettifor and his collaborators to study bonding energies. However we use the bond order concept to study the difference in electronic structure between the high temperature and the low temperature martensitic phase. We find that there is a linear relationship between the size of the difference in bond order in the two crystal structures and the martensitic start temperature. Furthermore our bond order calculations on Ti-3d, 4d and 5d alloys are in agreement with the trends we find in the densities of states and band structures.

We have also studied magnetism in ZrFeCo alloys, related to earlier work on TiFeCo alloys. Our results for the occurrence of magnetism in these systems are in agreement with experiment, and we are able to give an description of the behaviour of the anti-structural atoms occuring in some of these systems.

(Patrick Slavenburg)

Report on the secondment of M. Lüders (University of Würzburg, Germany) to Daresbury Laboratory (UK)

September 30 - November 30, 1996

On the electronic correlations in the superconducting state

M. Lüders
Institut für Theoretische Physik, Universität Würzburg, Germany

Introduction

The aim of the Daresbury - Würzburg collaboration, which was begun 5 months ago, is to gain some insight into the role of electronic correlations in the superconducting state of high T_c materials. To this end the Kohn-Sham-Bogoliubov-de Gennes (KS-BdG) equations [1, 2] are solved on a microscopic level, including exchange-correlation (xc) contributions. These xc-terms are the center of interest of this project. An LDA-type functional for the correlations in the superconducting state is developed from first principles [3, 4] and shall be studied by inserting ab initio densities. The underlying theory was presented in talks by S. Kurth and M. Lüders at the Ψ_k-Network conference in Schwäbisch Gmünd, on 17-21 September 1996.

Scientific Programme

The starting point are the microscopic (KS-BdG) equations [1]

$$\left(\frac{\nabla^2}{2}+v_s(\mathbf{r})-\mu\right)u_i(\mathbf{r})+\int\mathrm{d}^3r'\,\Delta_s(\mathrm{r},\mathrm{r}')v_i(\mathbf{r}) \;=\; E_i\,u_i(\mathbf{r}), \tag{1}$$

$$-\left(\frac{\nabla^2}{2}+v_s(\mathbf{r})-\mu\right)v_i(\mathbf{r})+\int\mathrm{d}^3r'\,\Delta_s^*(\mathrm{r},\mathrm{r}')u_i(\mathbf{r}) \;=\; E_i\,v_i(\mathbf{r}) \tag{2}$$

where u_i and v_i are the particle- and hole-amplitudes of the Kohn-Sham system. The effective potential v_s and the effective pairing potential Δ_s are given by

$$v_s(\mathbf{r}) \;=\; v_0(\mathbf{r})+\int\mathrm{d}^3r'\,\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+v_{xc}[n,\chi](\mathbf{r}), \tag{3}$$

$$\Delta_s(\mathbf{r},\mathbf{r}') \;=\; \Delta_0(\mathbf{r},\mathbf{r}')+\iint\mathrm{d}^3x\,\mathrm{d}^3x'\,w(\mathbf{r},\mathbf{r}',\mathbf{x},\mathbf{x}')\chi(\mathbf{x},\mathbf{x}')+\Delta_{xc}[n,\chi](\mathbf{r},\mathbf{r}') \tag{4}$$

with the xc-potential defined as the functional-derivatives of the xc-free energy with respect to the normal and the anomalous density n and χ. These are given by

$$n(\mathbf{r}) \;=\; 2\sum_i\left(|u_i(\mathbf{r})|^2 f_\beta(E_i)+|v_i(\mathbf{r})|^2 f_\beta(-E_i)\right), \tag{5}$$

$$\chi(\mathbf{r},\mathbf{r}') \;=\; \sum_i\left(v_i^*(\mathbf{r}')u_i(\mathbf{r})f_\beta(-E_i)-v_i^*(\mathbf{r})u_i(\mathbf{r}')f_\beta(E_i)\right) \tag{6}$$

where $f_\beta(E)=1/(1+e^{\beta E})$ is the ordinary Fermi-distribution function and $\beta=1/k_BT$.

The interaction $w(\mathbf{r},\mathbf{r}',\mathbf{x},\mathbf{x}')$ includes both the mutual Coulomb-interaction of the electrons and a phonon-mediated interaction, modeled by the Fröhlich-interaction.

$$\begin{aligned} w(\mathbf{r},\mathbf{r}',\mathbf{x},\mathbf{x}') &= -\frac{\delta(\mathbf{r}-\mathbf{x}')\,\delta(\mathbf{r}'-\mathbf{x})}{|\mathbf{r}-\mathbf{r}'|} \\ &+ \sum_{\substack{\alpha_1\alpha_2\\ \alpha_3\alpha_4}} \sum_{\substack{\mathbf{k}\,\mathbf{k}'\\ \mathbf{q}}} \frac{2\omega_{\mathbf{q}}|V_{\mathbf{q}}|^2}{(\varepsilon_{\alpha_1\mathbf{k}}-\varepsilon_{\alpha_2\mathbf{k}'})^2-\omega_{\mathbf{q}}^2}\,\varphi_{\alpha_3\mathbf{k}'-\mathbf{q}}(\mathbf{r})\,\varphi_{\alpha_2\mathbf{k}+\mathbf{q}}(\mathbf{r}')\,\varphi^*_{\alpha_1\mathbf{k}}(\mathbf{x})\,\varphi^*_{\alpha_4\mathbf{k}'}(\mathbf{x}') \end{aligned} \tag{7}$$

In the Fröhlich interaction, $\omega_{\mathbf{q}}$ are the phonon frequencies and $V_{\mathbf{q}}$ are the electron-phonon coupling constants.

The Würzburg group has developed an approximative scheme [3, 5], which decouples the KS-BdG equations into the normal-state KS Schrödinger equation (8) and a BCS-like gap-equation (9), which, in contrast to the BCS gap-equation, also includes exchange- and correlation-contributions, calculated from first principles:

$$\left(\frac{\nabla^2}{2}+v_s(\mathbf{r})\right)\varphi_{\alpha\mathbf{k}}(\mathbf{r}) = \varepsilon_{\alpha\mathbf{k}}\varphi_{\alpha\mathbf{k}}(\mathbf{r}) \tag{8}$$

$$\Delta_s(\alpha\mathbf{k}) = \Delta_0(\alpha\mathbf{k}) + \frac{1}{2}\sum_{\alpha'\mathbf{k}'}\frac{w(\alpha\mathbf{k},\alpha'\mathbf{k}')\Delta_s(\alpha'\mathbf{k}')}{R_{\alpha'\mathbf{k}'}}\tanh(\frac{\beta}{2}R_{\alpha'\mathbf{k}'}) + \Delta_{xc}[n,\chi](\alpha\mathbf{k}) \tag{9}$$

with

$$\begin{aligned} w(\alpha\mathbf{k},\alpha'\mathbf{k}') &= -w_{Clb}(\alpha\mathbf{k},\alpha'\mathbf{k}') + w_{phonon}(\alpha\mathbf{k},\alpha'\mathbf{k}'), && (10)\\ w_{Clb}(\alpha\mathbf{k},\alpha'\mathbf{k}') &= \iint \mathrm{d}^3x\,\mathrm{d}^3x'\,\frac{\varphi^*_{\alpha\mathbf{k}}(\mathbf{r})\varphi^*_{\alpha-\mathbf{k}}(\mathbf{r}')\varphi_{\alpha'\mathbf{k}'}(\mathbf{r}')\varphi_{\alpha'-\mathbf{k}'}(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}\,, && (11)\\ w_{phonon}(\alpha\mathbf{k},\alpha'\mathbf{k}') &= -\frac{2\omega_{\mathbf{k}-\mathbf{k}'}|V_{\mathbf{k}-\mathbf{k}'}|^2}{(\varepsilon_{\alpha,\mathbf{k}}-\varepsilon_{\alpha',\mathbf{k}'})^2-(\omega_{\mathbf{k}-\mathbf{k}'})^2} && (12) \end{aligned}$$

and

$$R_{\alpha\mathbf{k}} = \sqrt{(\varepsilon_{\alpha\mathbf{k}}-\mu)^2+|\Delta_s(\alpha\mathbf{k})|^2}\,. \tag{13}$$

This decoupling is motivated by the separation of the energy scale of the superconducting gap from that of the electronic band-structure of the normal state. It is based on the physical assumption that the Cooper pairs consist of electrons in time-reversed single-particle states.

An LDA-like functional was derived by KS-perturbation theory *in* the superconducting state [3]. This leads to the xc-pair potential:

$$\begin{aligned} \Delta_{xc}(\alpha,\mathbf{k}) = \frac{1}{2}Z_1(\alpha,\mathbf{k})\Bigg[&\sum_{\alpha_1,\mathbf{k}_1} w(\alpha\mathbf{k},\alpha_1\mathbf{k}_1)\left(1-\frac{\varepsilon_{\alpha_1,\mathbf{k}_1}-\mu}{R_{\alpha_1,\mathbf{k}_1}}\tanh(\frac{\beta}{2}R_{\alpha_1,\mathbf{k}_1})\right) \\ &- \frac{\displaystyle\sum_{\alpha_1,\mathbf{k}_1}\sum_{\alpha_2,\mathbf{k}_2} Z_0(\alpha_1,\mathbf{k}_1)w(\alpha_1\mathbf{k}_1,\alpha_2\mathbf{k}_2)\left(1-\frac{\varepsilon_{\alpha_2,\mathbf{k}_2}-\mu}{R_{\alpha_2,\mathbf{k}_2}}\tanh(\frac{\beta}{2}R_{\alpha_2,\mathbf{k}_2})\right)}{\displaystyle\sum_{\alpha_1,\mathbf{k}_1} Z_0(\alpha_1,\mathbf{k}_1)}\Bigg] \end{aligned} \tag{14}$$

with

$$Z_0(\alpha,\mathbf{k}) = \frac{\beta R_{\alpha,\mathbf{k}}\tanh(\frac{\beta}{2}R_{\alpha,\mathbf{k}})}{2\frac{(\varepsilon_{\alpha,\mathbf{k}}-\mu)^2}{R_{\alpha,\mathbf{k}}}\tanh(\frac{\beta}{2}R_{\alpha,\mathbf{k}})\cosh^2(\frac{\beta}{2}R_{\alpha,\mathbf{k}})+\beta|\Delta_s(\alpha,\mathbf{k})|^2} \tag{15}$$

and

$$Z_1(\alpha,\mathbf{k}) = \frac{(\varepsilon_{\alpha,\mathbf{k}}-\mu)\Delta_s(\alpha,\mathbf{k})\left(\frac{1}{R_{\alpha,\mathbf{k}}}\tanh(\frac{\beta}{2}R_{\alpha,\mathbf{k}}) - \frac{\frac{\beta}{2}}{\cosh^2(\frac{\beta}{2}R_{\alpha,\mathbf{k}})}\right)}{\frac{(\varepsilon_{\alpha,\mathbf{k}}-\mu)^2}{R_{\alpha,\mathbf{k}}}\tanh(\frac{\beta}{2}R_{\alpha,\mathbf{k}}) + \frac{\frac{\beta}{2}|\Delta_s(\alpha,\mathbf{k})|^2}{\cosh^2(\frac{\beta}{2}R_{\alpha,\mathbf{k}})}} \quad . \tag{16}$$

In the vicinity of the transition temperature the gap equation (9) can be linearized in Δ. The xc-contributions can be then interpreted as an "effective interaction", which can be calculated solely from normal-state properties. This effective interaction is studied for both the bare Coulomb interaction and a Fröhlich interaction. In this way we can model also the correlations due to a phonon-mediated interaction. This investigations will be carried out for high-T_c materials as well as for conventional superconductors. The main point of interest will be a comparison of the results between the conventional and the high-T_c materials.

With support from the Ψ_k network M. Lüders, from Würzburg, visited Z. Szotek and W. M. Temmerman in Daresbury for two months, from September 30 to November 30, 1996. The purpose of the visit was to initiate the implementation of the exchange-correlation terms which occur in the above equations. The main ingredients for these terms are the matrix-elements of the mutual Coulomb-interaction between the KS states. These quantities can be expressed within the LMTO-ASA in terms of integrals over the radial functions and the LMTO eigenvectors. For the numerical evaluation of these matrix-elements a code, based on the LMTO-ASA program of the Daresbury group, was developed. Due to the large amount of computer-time the program was converted to a parallel code. A successful optimization of the code now makes the calculations feasible. For the evaluation of the Brillouin-zone integrations, appearing in the gap equation and in the xc-terms, a linear and a quadratic interpolation scheme were devised and investigated for a simple model, showing the same structure as the integration in Eqs. (9) and (14).

During the time in Daresbury M. Lüders also attended two one-day workshops about parallelization- and optimization techniques respectively, which already lead to significant improvements of the code.

Acknowledgments

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3.2 Reports on Workshops

Report on the Workshop on 'Various Aspects of Noncollinear Magnetism'

Darmstadt, January 25–26, 1997

The workshop was held on January 25-26 in Darmstadt, Germany. The aim of the workshop was to bring together researchers from all over Europe active in the field of **non-collinear magnetism**, a field that rapidly developed in the last years. There were 25 participants from outside Darmstadt, coming from Austria, France, Germany, Sweden, UK, Japan, Hungary and USA. Together with scientists and students from the Darmstadt group we had an audience of 35 people. Most of the time allotted for the workshop was reserved for 11 long (invited) talks of 45 minutes duration plus 15 minutes discussion. Additionally 6 short talks (20 mins) and 5 posters were presented.

The following topics were discussed:
Basic formulations (*Capelle, Weinberger*), new technical schemes (*Nordström, Yamagami*), non-collinear magnetism of bulk, surfaces, films and multilayers (*Knöpfle, Kurz, Mohn, Sandratskii, Stoeffler, Ujfalussy*), noncollinear magnetism of non-perfect systems (*Abrikosov, Fleck, Hergert, Hafner, Krey, Lorenz*), non-Stoner thermodynamics of itinerant electron systems (*Entel, Eschrig, Gyorffy, Kübler , Lichtenstein, Uhl*) . Actually, every presentation was devoted to different aspects of non-collinear magnetism and this classification is very approximate. Questions during the talks were allowed and extensive use was made of this by the participants. The 15 minutes reserved for the discussion were never sufficient. A brief additional discussion meeting on non-Stoner thermodynamics was organized spontaneously by the participants in the lunch time.

A few examples for the 'hot' questions are:
Difference between the stability of a magnetic structure in calculation and in experiment; modification of the notion of convergence for the calculation of amorphous systems and spin-glasses; relation between the magnetic spiral and the charge density wave: must one initiate the other?; role of the longitudinal and transversal fluctuations of the magnetic moments. In the next years we expect a further fast increase of the interest in various aspects of the noncollinear magnetism.

The following topics will certainly attract much attention:
Calculations which account for the continuous variation of the direction of the spin and orbital momentum densities; calculation of the complex and non-perfect systems with increasing number of inequivalent atoms; itinerant magnetism at finite temperatures. Dynamical aspects of the problem, especially in studies of finite temperature magnetism and systems with statistical disorder, will receive much more attention than in previous years.

We are not sure if after two years the Vienna, Strasbourg, Bristol, Uppsala or another group will organize a similar meeting. They still will be able to restrict the number of participants to about 40-50, but we are absolutely convinced there will be a great amount of new developments to discuss.

Leonid Sandratskii and Jürgen Kübler

Programme

Saturday, January 25, 1997

8.30 Registration

9.00 Opening: J. Kübler (Darmstadt)

9.10 P. Weinberger (Vienna) *Chairman:* J. Hafner

What is non-collinear magnetism?

10.10 L. Sandratskii (Darmstadt) *Chairman:* H. Eschrig

Stability of magnetic structures: Symmertry principles and first-principles calculations

11.10 Coffee break

11.30 R. Lorenz (Vienna) *Chairman:* J. Kübler

Real-space tight-binding LMTO approach to noncollinear magnetism in complex systems

12.30 U. Krey (Regensburg) *Chairman:* B. Gyorffy

Itinerant noncollinear spin glasses by semi-empirical approach

13.30 Lunch

15.00 D. Stoeffler (Strassburg) *Chairman:* P. Weinberger

Tight binding self-consistent noncollinear magnetic orders in FM/AFM multilayers

16.00 L. Nordström (Uppsala) *Chairman:* L. Sandratskii

Continuous space description of non-collinear magnetism

17.00 Coffee break

17.20 P. Mohn (Vienna) *Chairman:* S. Liechtenstein

Non-collinear spin ordering in selected transition-metal systems

18.20 Poster session

Sunday, January 26, 1997

9.00 B. Gyorffy (Bristol) *Chairman:* P. Entel

LDA and the Disordered Local Moment picture

10.00 J. Kübler (Darmstadt) *Chairman:* P. Mohn

Exchange-coupled spin-fluctuation theory: Application to Fe, Co and Ni

11.00 Coffee break

11.20 H. Eschrig (Dresden) *Chairman:* U. Krey

Finite temperature magnetism of 3d-metals

Short-talks *Chairman:* J. Kübler

12.20 J. Hafner (Vienna)

Noncollinear magnetism in rough fcc Fe/Cu(100) films

12.40 I. Abrikosov (Uppsala)

Magnetism of the 3d transition-metal alloys: mean field description and beyond

13.00 M. Uhl (Darmstadt)

Exchange-coupled spin-fluctuation theory: Application to the Invar problem

13.20 Lunch

14.20 A. Liechtenstein (Jülich) *Chairman:* H. Dreysse

Density functional approach to exchange interactions and spin-fluctuations in solids

Short-talks. *Chairman:* B. Gyorffy

15.20 P. Entel (Duisburg)

First-principles description of Invar and martensitic nucleation in iron-based alloys

15.40 K. Capelle (Würzburg)

New Density Functionals for Magnetic Systems

16.00 B. Ujfalussy (Vienna)

Tilted magnetization in thin films

16.20 Final discussion and closing. J. Kübler (Darmstadt)

Posters

M. Fleck (Stuttgart), A.I. Liechtenstein (Jülich), V.I. Anisimov, A.O. Anokhin, A.I. Poteryaev (Yekaterinenburg), A.M. Oles (Stuttgart)

Dynamical mean field approach for non-collinear doped antiferromagnets

W. Hergert (Halle), V.S. Stepanyuk, P.Rennert, K. Wildberger, R. Zeller, P.H. Dederichs (Jülich)

Influence of Ag impurities on the magnetic properties of Rh and Ru Clusters on Ag(100)

K. Knpfle, L. Sandratskii, J. Kübler (Darmstadt)

Intraatomic magnetic noncollinearity: spin and orbital momentum densities.

P. Kurz (Jülich)

Non-collinear magnetism in the FLAPW method in combination with the frozen potential approximation: Application to ultrathin films

H. Yamagami (Darmstadt)

Non-collinear magnetism in relativistic density-functional theory

4 Job Announcements

Postdoctoral Research Positions in Electronic Structure Theory of Solids

Solid State Theory Group
Basic Sciences Center
National Renewable Energy Laboratory
Golden, Colorado 80401, USA
http://www.sst.nrel.gov

The Solid State Theory Group at the National Renewable Energy Laboratory invites applications for postdoctoral research positions beginning September, 1997. The positions are for two years, renewable upon mutual agreement to a third year. The Solid State Theory Group currently consists of ten Ph.D.'s in condensed matter theory and interacts with a broad range of experimentalists in semiconductor physics at NREL. Areas of particular interest include first-principles electronic structure theory of semiconductor nanostructures and superlattices and the theory of phase-stability of metallic alloys. Candidates should send a curriculum vitae, list of publications (including preprints of unpublished papers, if possible) and list of three references to:

Dr. Alex Zunger
Solid State Theory Group
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado, 80401

NREL is an equal opportunity/affirmative action employer. Clarifications or further details can be obtained via e-mail to **alex_zunger@nrel.gov**.

Post–doctoral Position, University of Aarhus

Theoretical Physics and Chemistry of Clusters

Provided that the necessary funding will be available, a post-doctoral position can be filled at the Institute of Physics and Astronomy at Aarhus University, Denmark. Employment will be limited to two years. The successful applicant is assumed to have a broad knowledge of theoretical solid state physics and/or quantum chemistry, and preferably also to have experience with modern 'ab initio' electronic structure calculations and atomic-scale simulations. (S)he is expected to join research programmes dealing with first-principles studies of atomic clusters, examining structural, dynamical, and optical properties as well as chemical reactions. Although a large part of the computational tools are available, the research still requires the development of new methods, algorithms and codes. There are good opportunities for interactions with experimentalists working in cluster physics at the Institute. Candidates should submit a letter of application, a curriculum vitae, a description of research experience, and arrange for three letters of recommendation to be sent to: **Professor N. E. Christensen, Institute of Physics and Astronomy, Aarhus University, DK-8000 Aarhus C, Denmark**. Applications received before May 1, 1997 will be considered. Further information: e-mail **nec@dfi.aau.dk** and website **http://www.dfi.aau.dk**.

Three 2-year Research Fellowships

Atomistic Simulation Group of Queen's University Belfast

Three post-doctoral positions funded by the EPSRC are available in the Atomistic Simulation Group of Queen's University Belfast working with Dr. Ali Alavi, Dr. Tony Paxton and Professor Mike Finnis. They are for two years from 1/3/97. The research topics are:

Post No. 1 (Ref. 97/F098)
Required to carry out research on new models applied to phases and defects in oxides. Applicants should preferably hold a minimum 2:1 honours degree or equivalent in a relevant discipline. Completion, or near completion of a PhD in solid state physics, chemistry or materials science or, alternatively, relevant postdoctoral research experience is essential. Experience in crystal chemistry, phase transformations or molecular dynamics is desirable.

Post No. 2 (Ref. 97/F099)
Required to carry out research on ab initio calculations of the electronic and atomistic structure of oxide-metal interfaces. Applicants should preferably hold a minimum 2:1 honours degree or equivalent in a relevant discipline. Completion, or near completion of a PhD in solid state physics, chemistry or materials science or, alternatively, relevant postdoctoral research experience is essential. Familiarity with the principles of structure and bonding in metallic and ionic materials, experience of scientific programming in a UNIX environment and familiarity with plane wave or LMTO solutions to the local density functional problem are desirable.

Post No. 3 (Ref. 97/F100)
Required to carry out research on the application of ab initio molecular dynamics to the calculation of free energies. Applicants should preferably hold a minimum 2:1 honours degree or equivalent in a relevant discipline. Completion, or near completion of a PhD with a strong theoretical bias in the areas of solid state physics, chemistry or materials science or, alternatively, relevant postdoctoral research experience is essential as is experience of FORTRAN programming, UNIX environment and parallel computing.

Commencing salary range: 14319 - 15987 UKL per annum, initial placing depending on age, experience and qualifications. Applicants, quoting the relevant reference number(s), may obtain further particulars from the: **Personnel Office, The Queen's University of Belfast, BT7 1NN. Tel.: +44 1232 245133 ext. 3037, fax: +44 1232 324944**. Closing date for applications: 15 February 1997.

The Atomistic Simulation Group participates in the UK Car-Parrinello Grand Challenge Project using the Cray T3D in Edinburgh and in addition has excellent in-house computational facilities.

IMPORTANT:
Please **APPLY ONLY** to the Personnel Office and **AFTER** contacting them for details of how to apply. For informal enquiries, please contact Ali Alavi (A.Alavi@qub.ac.uk) Tony Paxton (Tony.Paxton@qub.ac.uk) or Mike Finnis (M.Finnis@qub.ac.uk).

5 Abstracts

Spin-Multiplet Energies from Time-Dependent Density Functional Theory

M. Petersilka, E.K.U. Gross

Institut für Theoretische Physik, Universität Würzburg

Am Hubland, D-97074 Würzburg, Germany

Abstract

Starting from a formally exact density-functional representation of the frequency-dependent linear density response and exploiting the fact that the latter has poles at the true excitation energies, we develop a density-functional method for the calculation of excitation energies. Simple additive corrections to the Kohn-Sham single-particle transition energies are derived whose actual computation only requires the ordinary static Kohn-Sham orbitals and the corresponding eigenvalues. Numerical results are presented for spin singlet and triplet energies.

(International Journal of Quantum Chemistry, Vol. 60, p. 181 (1996))
Manuscript available from: ptrslka@physik,uni-wuerzburg.de

Many-electron atoms in strong femto-second laser pulses: a density functional study

C.A. Ullrich, E.K.U. Gross

Institut für Theoretische Physik, Universität Würzburg

Am Hubland, D-97074 Würzburg, Germany

Abstract

The fundamental concept of time-dependent density functional theory is to describe the dynamics of an interacting many-particle system exclusively and completely in terms of its time-dependent density. We give a short overview of the basic theorems including an extension of the formalism to a unified treatment of electronic and nuclear motion. The density-functional approach is then applied to describe neon atoms in strong laser fields on a non-perturbative all-electron level, i.e. beyond the so-called single-active electron approximation. We study multiphoton ionization and harmonic generation from 248-nm KrF laser pulses in neon and compare calculated harmonic spectra with recent experimental data.

(to appear in: Comments on Atomic and Molecular Physics)
Manuscript available from: gross@physik,uni-wuerzburg.de

The Optimized Effective Potential Method of Density Functional Theory: Applications to Atomic and Molecular Systems

T. Grabo, E.K.U. Gross

Institut für Theoretische Physik, Universität Würzburg

Am Hubland, D-97074 Würzburg, Germany

Abstract

Using the optimized effective potential method in conjunction with the semi-analytical approximation due to Krieger, Li and Iafrate, we have performed fully self-consistent exact exchange-only density-functional calculations for diatomic molecules with a fully numerical basis-set-free molecular code. The results are very similar to the ones obtained with the Hartree Fock approach. Furthermore we present results for ground states of positive atomic ions including correlation contributions in the approximation of Colle and Salvetti. It is found that the scheme performs significantly better than conventional Kohn-Sham calculations.

(Int. J. Quantum Chem. , in press)
Manuscript available from: toby@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

Am Hubland, D-97074 Würzburg, Germany

Abstract

We describe the optimized effective potential method of density functional theory and the semi-analytical approximation to it 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.

(Submitted to: Molecular Engineering, *Proceedings of "Quantum Systems in Chemistry and Physics", San Miniato, 1996*)
Manuscript available from: toby@physik,uni-wuerzburg.de

Spin-density functionals from current-density functional theory and vice versa: A road towards new approximations

K. Capelle, E.K.U. Gross

Institut für Theoretische Physik, Universität Würzburg

Am Hubland, D-97074 Würzburg, Germany

Abstract

It is shown that the exchange-correlation functional of spin-density functional theory is identical, on a certain set of densities, with the exchange-correlation functional of current-density functional theory. This rigorous connection is used to construct new approximations of the exchange-correlation functionals. These include a conceptually new generalized-gradient spin-density functional and a non-local current-density functional.

(submitted to Phys. Rev. Lett.)
Manuscript available from: capelle@physik,uni-wuerzburg.de

Theoretical prediction of the structure of insulating YH_3

P.J. Kelly

Philips Research Laboratories,

Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands

J.P. Dekker

Faculty of Physics and Astronomy,

Vrije Universiteit Amsterdam, The Netherlands

R. Stumpf

Sandia National Laboratories, Albuquerque, USA

Abstract

Density functional calculations of the total energy have been used to determine minimum energy structures for YH_3. Small, symmetry lowering displacements of the hydrogen atoms lead to a structure with an energy which is lower than that of any other structure considered so far and the opening of a large band gap sufficient to explain the recently observed metal insulator transition in the YH_x system.

(accepted for publication in Physical Review Letters)
Manuscript available from: kelly@natlab.research.philips.com

Applications of Self-Interaction Corrections to Localized States in Solids

W.M. Temmerman[a], A. Svane[b], Z. Szotek[a], and H. Winter[c]

[a]*Daresbury Laboratory, Warrington WA4 4AD, United Kingdom*

[b]*Institute of Physics and Astronomy, University of Aarhus,*

DK-8000 Aarhus C, Denmark

[c]*Karlsruhe, INFP, Postfach 3640, Karlsruhe, Germany*

Abstract

The *ab-initio* self-interaction corrected (SIC) local-spin-density (LSD) approximation is discussed with emphasis on the ability to describe localization phenomena in solids. Two methods for minimizing the SIC–LSD total energy functional are discussed, one using a unified Hamiltonian for all electron states thus having the advantages of Bloch's theorem, the other one employing an iterative scheme in real space. Results for transition metal oxides and cerium compounds are presented. For the transition metal oxides a significant charge transfer gap is produced, in contrast to the vanishing or near vanishing band gap seen in the LSD approximation. Also, the magnetic moment is larger in the SIC–LSD approach than in the LSD approach, and for La_2CuO_4 the correct antiferromagnetic and insulating ground state is found. For the cerium compounds, the intricate isostructural phase transitions in elemental cerium and CeP may be accurately described.

(submitted to Proceedings of the Brisbane Conference on Density Functional Theory, July 1996, Brisbane (Australia))

Manuscript available from: svane@dfi.aau.dk

Calculations of hyperfine parameters in tin compounds

A. Svane [a], N. E. Christensen [a], C. O. Rodriguez [b], and M. Methfessel [c]

[a] *Institute of Physics and Astronomy, University of Aarhus,*

DK-8000 Aarhus C, Denmark

[b] *IFLYSIB, Grupo de Fisica del Solido, C.C. 565,*

La Plata 1900, Argentina

[c] *Institute for Semiconductor Physics, Walter-Korsing-Str. 2,*

D-15230 Frankfurt(Oder), Germany

Abstract

With the aim of calibrating Mössbauer spectroscopic measurements, the electric field gradient and electron contact density is calculated on the Sn nuclear position in a number of Sn compounds representing all kinds of chemical bonding in solids. The full-potential linear-muffin-tin-orbitals method with the local-density-approximation for exchange and correlation effects is used. By comparison with experimental ^{119}Sn Mössbauer data the calibration constants relating measured isomer shifts and quadrupole splittings to the electron contact density and the electric field gradient, respectively, are derived. The difference between the mean square radius of the ^{119}Sn Mössbauer nucleus in its excited isomeric and ground states is found to be $\Delta < r^2 > = (0.0072 \pm 0.0002)$ fm^2, while the quadrupole moment of the excited ^{119}Sn(24 keV,3/2+) nuclear state is obtained as $|Q| = (12.8 \pm 0.7)$ fm^2. The larger database considered and the use of a more accurate band structure calculational scheme than in earlier works makes these numbers more accurate and provides improved calibration for Mössbauer spectroscopy.

(submitted to Phys. Rev. B)
Manuscript available from: svane@dfi.aau.dk

Magnetic order and chemical bonding in the High-T_C molecule-based cyanide magnets $CsM[Cr(CN)_6]$ $(M = Mn, Ni)$ from first principles

V. Eyert

Hahn-Meitner-Institut, Glienicker Straße 100, D-14109 Berlin

B. Siberchicot

CEA/Centre d'études de Limeil-Valenton, F-94195 Villeneuve-St-Georges

M. Verdaguer

Laboratoire de Chimie des Métaux de Transition,

U.R.A. C.N.R.S. 419, 4 place Jussieu, F-75252 Paris

Abstract

We present the results of first principles electronic structure calculations for the molecule-based cyanide high Curie temperature magnetic insulators $CsM[Cr(CN)_6]$, $M = Mn, Ni$. The calculations are based on density functional theory and the local density approximation and employ the augmented spherical waves (ASW) method. The electronic properties are found to be dominated by transition metal $3d$- and ligand $2p$-orbitals. The chemical bonding is analyzed via the first *ab initio* calculation of the crystal orbital overlap population (COOP). The magnetic properties are explained by the orthogonality/overlap of magnetically active orbitals as studied by the COOP. Possible pathways for the exchange interaction are identified. In particular the sign of the exchange integrals between different effective magnetic sites is deduced. Excellent agreement with experimental data is found. While proving essential for the consistent understanding of electronic, magnetic and chemical properties of these materials our first principles approach moreover allows for the prediction as well as the deeper understanding of the type of long-range magnetic order. Thereby it goes beyond the conclusions usually drawn from Goodenough-Kanamori superexchange rules or the model by Kahn and Briat.

(submitted to Phys. Rev. B)

Manuscripts available from: eyert@physik.uni-augsburg.de

Electronic structure of poly-oxadiazoles

G. Brocks and A. Tol

Philips Research Laboratories, Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands

Abstract

The electronic and the geometrical structures of the polymers poly-1,3,4-oxadiazole and poly-(*p*-phenylene-1,3,4-oxadiazole) are studied using density functional calculations. These polymers are fully conjugated, having band widths which are comparable to the more common conjugated polymers. They have however a significantly higher ionization potential, which makes them suitable hole-blocking materials for organic light emitting diodes. In addition poly-1,3,4-oxadiazole is a convenient electron transport material, due to its high electron affinity. Due to the presence of the phenyl rings, the electron affinity of poly-(*p*-phenylene-1,3,4-oxadiazole) is much lower.

(to appear in: *J. Chem. Phys.*)

Preprints available from: brocks@natlab.research.philips.com

Theoretical study of the charge transfer in the organic crystal of dimethylquaterthiophene (DMQtT) and tetrafluoro-tetracyanoquinodimethane (TCNQF$_4$)

G. Brocks

Philips Research Laboratories, Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands

Abstract

The electronic and the geometrical structure of the organic charge transfer crystal of dimethylquaterthiophene (DMQtT) and tetrafluorotetracyanoquinodimethane (TCNQF$_4$) are calculated self-consistently from first principles, using Car-Parrinello techniques. The calculated electronic charge transfer from the DMQtT molecule to the TCNQF$_4$ molecule is $0.46 \pm 0.05\,e$. This charge transfer is accompanied by a structural change in which the DMQtT molecule adopts a more quinoid geometry (compared to the aromatic structure of the neutral DMQtT molecule) and the TCNQF$_4$ becomes from quinoid more aromatic. The electronic structure around the Fermi level is characterized by one-dimensional charge transfer states.

(to appear in: *Phys. Rev. B, March 15*)

Preprints available from: brocks@natlab.research.philips.com

Mott-Hubbard insulators for systems with orbital degeneracy

Olle Gunnarsson[(a)], Erik Koch[(b)], and Richard M. Martin[(b)]

[(a)]*Max-Planck-Institut für Festkörperforschung, D-70506 Stuttgart, Germany*

[(b)]*Department of Physics, University of Illinois at Urbana-Champaign,*

Urbana, Illinois 61801

Abstract

We study how the electron hopping reduces the Mott-Hubbard band gap in the limit of a large Coulomb interaction U and as a function of the orbital degeneracy N. The results support the conclusion that the hopping contribution grows as roughly $\sqrt{N}W$, where W is the one-particle band width, but in certain models a crossover to a $\sim NW$ behavior is found for sufficiently large N.

(submitted to Phys. Rev. B)
Preprints available from: gunnar@and.mpi-stuttgart.mpg.de

Electron self-energy in A_3C_{60} (A=K, Rb): Effects of t_{1u} plasmon in GW approximation

O. Gunnarsson

Max-Planck-Institut für Festkörperforschung, D-70506 Stuttgart, Germany

Abstract

The electron self-energy of the t_{1u} states in A_3C_{60} (A=K, Rb) is calculated using the so-called GW approximation. The calculation is performed within a model which considers the t_{1u} charge carrier plasmon at 0.5 eV and takes into account scattering of the electrons within the t_{1u} band. A moderate reduction (35 %) of the t_{1u} band width is obtained.

(Phys. Rev. B)
Reprints available from: gunnar@and.mpi-stuttgart.mpg.de

Size and structural dependence of the magnetic properties of rhodium clusters

P. Villaseñor-González and J. Dorantes-Dávila
Instituto de Física "Manuel Sandoval Vallarta,"
Universidad Autónoma de San Luis Potosí,
78000 San Luis Potosí, Mexico
H. Dreyssé
Institut de Physique et Chimie des Matériaux de Strasbourg,
Université Louis Pasteur, 23 rue du Loess, F-67037 Strasbourg, France
G. M. Pastor
Laboratoire de Physique Quantique, 118 route de Narbonne,
Université Paul Sabatier, F-31062 Toulouse, France

Abstract

The size and structural dependence of the magnetic properties of Rh_N clusters ($9 \leq N \leq 55$) are studied by using a *d*-electron tight-binding Hamiltonian including Coulomb interactions in the unrestricted Hartree-Fock approximation. Three main different types of cluster geometries are considered (viz., fcc, bcc, and icosahedral). In each case the equilibrium bond-length R is optimized by maximizing the cohesive energy $E_{coh}(N)$. The geometries yielding the largest $E_{coh}(N)$ alternate as a function of N. These structural changes, together with the variation of R, play a crucial role in the determination of the average magnetic moment $\bar{\mu}_N$ of Rh_N. The calculated size dependence of $\bar{\mu}_N$ corresponding to the most stable geometries presents oscillations which are in good qualitative agreement with experiment. The magnetic properties of Rh_N clusters show a remarkable structural dependence which is characteristic of weak (unsaturated) itinerant ferromagnetism. The relation between the observed $\bar{\mu}_N$ and the cluster geometry is analyzed. The role of non-uniform geometry relaxation, *sp* electrons and *sp-d* hybridization effects are quantified for representative examples. Perspectives of extensions of this study are also discussed.

(To appear in Phys. Rev. B)
Manuscripts available from: hugues@Taranis.u-strasbg.fr

Electronic Properties and Magnetic Structure U_3X_4 (X=P,As,Sb)

L.M. Sandratskii and J. Kübler

Institut für Festkörperphysik, Technische Hochschule,

D-64289 Darmstadt, Germany

Abstract

We report results of first-principles calculations of the electronic properties and magnetic structure of U_3X_4 (X=P,As,Sb) which were carried out using a generalization of the local density approximation to density functional theory to apply to the case of noncollinear magnetic configurations which allows a determination of both length and direction of the magnetic moments. Spin-orbit coupling and an effective orbital field responsible for Hund's second rule are taken into account. The calculated trends in the variation of the magnetic anisotropy and the values of the Uranium magnetic moments is in agreement with experimental trends in the series. In particular, the experimentally observed change of the axis of easy magnetization from (111) in U_3P_4 and U_3As_4 to (001) in U_3Sb_4 is born out by our calculations. For all three compounds, our calculations result in a noncollinear magnetic structure. We show that this noncollinearity is a direct consequence of the spin-orbit coupling and supply corresponding symmetry arguments based on the generalized spin-space groups. For U_3P_4 and U_3As_4 our result concerning the noncollinearity of the magnetic structure are in qualitative agreement with experimental findings. However, for U_3Sb_4 our conclusion disagrees with previous treatments of the magnetic structure as collinear. We supply detailed arguments in support of our point of view. For all three compounds we obtained the interesting property that the spin and orbital moments of the same U atom are noncollinear and we formulate the symmetry criterion for the appearance of this effect.

(submitted to Phys. Rev. B)

Latex version can be obtained from: dg5m@mad1.fkp.physik.th-darmstadt.de (L. Sandratskii)

Linear Scaling Solution of the Coulomb problem using wavelets

S. Goedecker† and O. V. Ivanov†‡

†*Max-Planck Institute for Solid State Research, Stuttgart, Germany*

‡*P.N. Lebedev Physical Institute, Moscow, Russia*

Abstract

The Coulomb problem for continuous charge distributions is a central problem in physics. Powerful methods, that scale linearly with system size and that allow us to use different resolutions in different regions of space are therefore highly desirable. Using wavelet based Multi Resolution Analysis we derive for the first time a method which has these properties. The power and accuracy of the method is illustrated by applying it to the calculation of of the electrostatic potential of a full three-dimensional all-electron Uranium dimer.

(submitted to Phys. Rev. Lett.)
Manuscripts available from: ivanov@and.mpi-stuttgart.mpg.de

Angle-Resolved Resonant Photoemission as a Probe of Spatial Localization and Character of Electron States

S.L. Molodtsov[a], M. Richter[b], S. Danzenbächer[a], S. Wieling[a], L. Steinbeck[b,c], and C. Laubschat[a]

[a]*Institut für Oberflächenphysik und Mikrostrukturphysik, TU Dresden,*

D-01062 Dresden, Germany

[b]*Max-Planck-Arbeitsgruppe "Elektronensysteme", TU Dresden,*

D-01062 Dresden, Germany

[c]*Department of Physics, University of York, York YO1 5DD, UK*

Abstract

Resonant photoemission (PE) in angle-resolved mode is proposed as a method to determine the spatial localization and the angular momentum character of valence band states from *on-resonance* PE signals across the Brillouin zone. This technique is applied to study ordered films of La-metal. The obtained experimental data agree well with the results of LCAO band-structure calculations and related eigenvector analysis.

(Phys. Rev. Lett. **78**, 142-5 (1997))
Manuscripts available from: manuel@tmps06.mpg.tu-dresden.de

Amplitude and phase of the oscillatory exchange coupling between Fe-Co-Ni alloy layers across a Cu spacer layer

J. Kudrnovský[a,b], V. Drchal[a,b], R. Coehoorn[c],
M. Šob[d], and P. Weinberger[b]
[a] *Institute of Physics,*
Academy of Sciences of the Czech Republic,
Na Slovance 2, CZ-180 40 Praha 8, Czech Republic
[b] *Institute for Technical Electrochemistry,*
Technical University of Vienna,
Getreidemarkt 9, A-1060 Vienna, Austria
[c] *Philips Research Laboratories, Prof. Holstlaan 4,*
NL-5656 AA Eindhoven, The Netherlands
[d] *Institute of Physics of Materials,*
Academy of Sciences of the Czech Republic,
Žižkova 22, CZ-616 62, Brno, Czech Republic

Abstract

The influence of alloying in ferromagnetic layers on the amplitudes and phases of the oscillations of exchange coupling across Cu layers is studied from first principles. The phases of oscillations vary monotonically with the average number of valence electrons in the alloyed layers and are insensitive to the type of atom from which the layers are formed. We show that in accordance with an RKKY-like description, the exchange coupling energies can be expressed in terms of complex amplitudes characterizing the magnetic subsystems.

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6 Book Announcements

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Contents: Introduction. – Linear Muffin-Tin Orbital (LMTO) Method. – Green Function Method. – Coherent Potential Approximation (CPA). – Selfconsistency within Atomic Sphere Approximation. – Relativistic Theory. – Bulk Systems, Overlayers and Surfaces. – Magnetic Properties. – Effective Interatomic Interactions in Alloys. – Numerical Implementation.

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7 HIGHLIGHTS OF THE 1996 COLLABORATIONS

Highlights of Collaborations on Metal-Ceramic Interfaces

M. W. Finnis

Atomistic Simulation Group, School of Mathematics and Physics,

The Queen's University of Belfast, Belfast BT7 1NN, Northern Ireland

WWW: http://titus.phy.qub.ac.uk

1 Introduction

The importance of the interaction of metals with oxides is ubiquitous in industry, medicine, transport and the home. Protective aluminium oxide scales are a blessing, iron oxide formation is a curse. Medical implants depend on the adherence and longevity of metal-oxide bonds. We are pursuing a programme of basic research in order to understand better the nature of the bonds involved, which do not fit into the neat categories of ionic, covalent or metallic. The network has supported interactions between the Stuttgart node (M.W.Finnis prior to 1.9.95), Belfast (M.W.Finnis since 1.9.95), Berlin (M. Scheffler), Cambridge (M.C. Payne; also V.Y. Milman now with MSI/Biosym) and Keele (M.J.Gillan). The publications cited below acknowledge this support.

The model system Nb/α-Al_2O_3 was chosen for the first *ab initio* study of a metal-alumina interface in which all atomic positions were relaxed to minimise the total energy. The reasons for this choice were partly experimental. It is an interface which can be prepared to a high degree of perfection at the atomic scale, which has enabled detailed studies by high-resolution electron microscopy. The experimental studies suggested a model of the Nb(111)/α-Al_2O_3(0001) interface which has an intriguing construction. The first two layers of Nb atoms appeared to occupy those sites adjacent to the interfacial plane of oxygen atoms which would have been occupied by Al atoms if the Al_2O_3 crystal structure were extended beyond the interface.

2 Calculations

The calculations, which were done in Stuttgart, are described in detail in our recent publication [1]. We used the pseudopotential/plane wave method developed mainly in the Cambridge group and now commercialised by MSI/Biosym in the form of the CASTEP code. We built on previous experience in the Keele group, where the structure and energies of α-Al_2O_2 surfaces had been calculated. These calculations were based on a slab of Al_2O_3 containing three layers of oxygen and fifteen atoms altogether, with an equal thickness of vacuum between the (0001) surfaces.

Preliminary calculations were made with a monolayer of Nb replacing the surface layer of Al. Three different symmetry sites for the Nb were investigated, in each case doing a static relaxation of the total energy. Site A is the observed site which continues the bulk lattice, where the Nb sits in a triangular hollow in the oxygen plane, Sites B and C are also triangular hollows, which differ from A by being vertically above an Al atom in an octahedal site within the plane below. The corresponding octahedral site below the A site is empty.

These calculations were followed by adding further layers of Nb, up to eight altogether, filling the gap between the slabs of Al_2O_3. Finally the effect was calculated of replacing the interfacial layer of Nb with Al.

3 Results for Nb/α-Al_2O_3

The monolayer calculations showed that when Nb is in site A the energy of the system is lowest. In this case the relaxations of the atomic positions are also very small. By contrast, sites B and C are much higher in energy, by more than 3eV, and the relaxations are very pronounced. We observe that when the Nb is on sites B and C there is a strong repulsion between it and the Al atom below it. This is an ionic repulsion. We showed this by plotting the charge density for different energies, which revealedf that the Nb is in the form of an Nb^{3+} ion, a non-spherical ion with an occupied d-orbital perpendicular to the surface.

With five to eight layers of Nb in a multilayer configuration the situation is rather different. There is still charge transfer to the surface layer of oxygen, enabling it to have a full shell of p-electrons. However, the second layer of Nb participates in this bonding too. The overlap of the Nb d-band with the oxygen 2p-band gives rise to a strong hybridisation which does not happen in the monolayer case. Details of the electronic structure are altered very significantly within the Nb even four layers from the interface; notably there is a prominent resonance above the Fermi energy. The Fermi energy itself lies 3eV above the top of the valence band, about half the distance found with the self-consistent tight binding approach. This result is similar to that of other workers who have made calculations on interfaces of Ag, Ti and Al on MgO, in which the Fermi energy is 2.0-2.3eV above the top of the valence band in each case.

The Nb layers at the interface relax quite strongly as a result of the competition of the first two layers of Nb for bonding with the oxygen. The first two layers of Nb pinch together by 0.04nm compared to their bulk spacing. This is just within range of what should be detectable by high resolution transmission electron microscopy, but it has not yet been investigated at the required resolution. When we replace the interfacial layer of Nb by Al, the relaxation is much reduced - it is as if the second Nb layer has given up the competition for O in the presence of the more electropositive Al.

From our predicted atomic positions our colleague G. Moebus in Stuttgart was able to simulate electron microscope images. A surprising result of this was that the difference between an Al-terminated and an O-terminated interface would only just be within the limit of experimental detection by this technique. Other methods, however, such as electron energy loss spectroscopy have been applied which strongly suggest that the Nb termination is the actual one (J. Bruley, private communication).

4 Conclusions and other issues

We have demonstrated the usefulness of pseudopotential calculations for studying metal-ceramic interfaces. The nature of the bonding is complicated and different for a monolayer and a multilayer. Relaxations of the atomic positions, especially in metastable equilibrium geometries, can be very large. The results of this collaboration are set in the context of other theories and models of metal-ceramic bonding in ref. [2].

A frequently asked question has been whether we could predict which of the interfaces between Nb(111) and Al_2O_3(0001) would be more stable, the Nb terminated or the Al terminated one. The answer is yes, in principle we could, but the answer depends on the chemical potentials of the species involved, so it depends on the amount of Al or O dissolved in the Nb. Issues of chemical equilibrium are involved here, which will probably have a bigger role to play in future calculations which attempt to use the elementary energies provided by *ab initio* methods to build a thermodynamic model. Of course, in practice one is not always dealing with the thermodynamically stable structure of an interface, for example if it is prepared at relatively low temperature by molecular beam epitaxy.

Another issue is to try to find simpler models which describe either the atomic interactions or the electronic structure of such interfaces. Real interfaces involve imperfections, defects and roughness, which must affect adhesive energies and other properties. However, with our *ab initio* methods the simulation of all but very simple, atomically flat and coherent, systems is too computationally demanding and there will always be problems for which this remains the case. With a view to tackling such problems, a simple classical interatomic force model has been studied, based on the image interaction between an ion and a metallic surface. Within the framework of the Network we compared the results of this model with *ab initio* calculations for a single external point charge above three low index Al surfaces, and found that it gives a very good account of the differences due to the different corrugations in each case [3]. Work to test and apply it to interfaces is in progress. This work will go hand in hand with detailed *ab initio* calculations of the ideal work of adhesion, which was not addressed in the Nb/Al_2O_3 studies reported here.

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Highlights of Vienna-Zürich Collaboration

Electric Field Gradients using the Projector Augmented Wave Method

H. Petrilli*, P.E. Blöchl *(IBM Research Division, Zürich Research Laboratory)*
K. Schwarz, P. Blaha *(Technical University Vienna)*

Mössbauer experiments and resonance techniques probe quantities such as hyperfine splittings and electric field gradients (EFG), that are sensitive to the local environment of atoms in molecules or solids. Combined with electronic structure calculations, which predict such quantities, these experiments yield most valuable information on the atomic structure and provide a viable test of the approximations underlying electronic structure calculations.

As the measured properties reflect the density in the immediate neighborhood of the nucleus the common pseudopotential approach cannot make such predictions other than through indirect reconstruction techniques. Also the demands on all-electron electronic structure methods are extreme, as the EFGs are dominated by the density in a region that affects the total energy only to a small extent. Currently, the full-potential LAPW method, as used by the Vienna group, is considered most realiable for EFG calculations.

We have now applied the Projector Augmented Wave (PAW) method for the first time to EFG calculations. This work has two goals. First, we hope to extend the range of applications to a wider class of systems by exploiting the flexibility of the PAW method. Secondly, by comparing the results of two independent electronic structure methods, we hope to predict the result for a given density functional independent of numerical errors. This is a nontrivial task, because EFGs have proven to be extremely sensitive to numerical approximations, and variations of up to ten percent are not uncommon.

As a first step we applied our new approach to thirteen different systems including solids and molecules, containing main group elements and transition metal elements. The results have been compared to experiment and LAPW calculations. Our calculations reproduce experiment with an average error of fifteen percent, which is comparable with the experimental error bar. The comparison with LAPW shows an average error of less than ten percent.

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* permanent address: Universidade de Sao Paolo; CP 66318; 05389-970 Sao Paolo, SP; Brasil

Diffusion and Defects using the Projector Augmented Wave Method

J.Sarnthein, K. Schwarz *(Technical University Vienna)*
P.E. Blöchl *(IBM Research Division, Zürich Research Laboratory)*

Li_3N is a superionic conductors with a very high Li conductivity. The diffusion and consequently the conductivity in Li_3N shows a significant anisotropy parallel and perpendicular to the c-axis of the hexagonal structure. In order to understand the microscopic nature of the conductivity we investigated the defects and diffusion by ab-initio molecular dynamics studies using the Projector Augmented Wave (PAW) method.

The barrier for lithium jumps to vacant adjacent sites in the Li_2 plane was found to be very small, namely 0.004 eV, whereas jumps perpendicular to this plane have a barrier of 0.58 eV. Therefore diffusion in the plane is limited by the formation of vacancies, whereas perpendicular to the plane (i.e. parrallel to the c axis) the barrier dominates. A molecular dynamics run at 800 K using the Projector Augmented Wave (PAW) method confirms the anisotropy of diffusion and leads to diffusion coefficients consistent with experiment. From the trajectories of the molecular dynamics run we deduce a microscopic diffusion mechanism and find that mainly isolated rather than correlated jumps take place.

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Highlights of Rennes-Zürich Collaboration

Ab-initio calculations of 1-Dimensional band-structures of mixed-stack molecular compounds: Tetrathiafulvalene-p-benzoquinones derivatives

C. Katan, C. Koenig and P. E. Blöchl*
Groupe Matière Condensée et Matériaux, Université Rennes-1, Campus de Beaulieu, 35042 Rennes-Cedex, France
**IBM Research Division, Zürich Research Laboratory, CH-8803 Rüschlikon, Switzerland*
(Rennes-Zürich Collaboration)

Mixed-stack organic charge-transfer compounds are composed of two types of flat molecules: closed-shell-π electron donors (D) and acceptors (A), which are stacked into linear chains. Members of this class undergo structural phase transitions under pressure, temperature or photoirradiation. Common to all these transitions is the loss of inversion symmetry resulting in a "dimerization" of the chains into D–A pairs. Simultaneously, a more or less abrupt change in the charge transfer is observed.

In the past ten years, these transitions have been studied using 1D models based primarily on Hubbard-like Hamiltonians or free-energy expansions. Qualitatively different transitions can be reproduced within these models by interplay of different parameters, which are usually extracted by fittings to the experimental data.

Recently, first-principles calculations for these systems have become possible, providing the means to determine *ab-initio* values for these parameters and explore the validity of the model assumptions, and thus to arrive at reliable material-specific predictions. We have performed the first ab-initio calculation of the electronic-structure of TTF-CA and TTF-2,5Cl_2BQ. The method used is the projector augmented wave (PAW) method, within the gradient corrected local approximation of the density functional theory.

We first analyzed the electronic and dynamical properties of isolated molecules of TTF, CA and 2,5Cl_2BQ [1]. We provided thus the first theoretical confirmation of the linearity of the variation of some intra-molecular vibrations with ionicity, which is assumed by the experimentalists for the determination of the inter-molecular charge transfer.

Then we investigated the 1D properties of the high symmetry phase of these compounds [2], in order to understand the microscopic nature of the intra-chain coupling between the molecules. Our results led to a visualization at an atomic scale of these interactions and showed especially that, contrary to what has been assumed up to now in 1D model-Hamiltonians, the hybridization between the crystalline states is maximum at the border of the Brillouin zone and not at the Γ point.

In the frame of a 1D tight binding model, these interactions can be expressed by hopping integrals with alternating signs along the chains. Ab-initio values for these integrals and for the charge transfer have been determined from the calculated dispersion, and a clear understanding, at a microscopic level, of the tight relation between symmetry breaking and charge transfer increase has been obtained.

The qualitative features of the 1D behavior result from rather general symmetry arguments. This applies to the entire series of mixed-stack tetrathiafulvalene-p-benzoquinones halogen derivatives. Hence, the large variety of phase transitions in this class of materials must be rooted partly in the different donor and acceptor strengths and partly in the three-dimensional interactions between the chains, which differs greatly from one compound to another. Studies of those interactions are in progress.

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Highlight of the results obtained by the Lisbon-Antwerp collaboration

Structural Optimization of Ternary Calcium Nitrides

P.E. Vansant, P.E. Van Camp, V.E. Van Doren
University of Antwerpen (RUCA), Dept. of Physics,
Groenenborgerlaan 171, B-2020 Antwerpen, Belgium
J.L. Martins, I. Souza
INESC, Rua Alves Redol 9, P-1000 Lisboa, Portugal;
Instituto Superior Tecnico, Avenida Rovisco Pais 1, P-1096 Lisboa, Portugal

An optimization scheme for crystal structure parameters developed recently by Souza and Martins was applied to the study of ternary calcium nitrides. The forces and stresses were calculated with a local-density pseudopotential plane wave method using an iterative matrix diagonalization scheme. The enthalpy at a given pressure is then minimized with respect to the atomic coordinates as well as with respect to the cell metric.

We calculated the zero pressure structure parameters of the perovskite structure Ca_3BiN and of the distorted perovskite structures Ca_3PN and Ca_3AsN. For Ca_3BiN the crystal has cubic symmetry, but for Ca_3AsN and Ca_3PN the crystal has an orthorhombic symmetry with four formula units per cell. The calculated lattice constants shown in the table are in excellent agreement with experiment (values in parenthesis).

The dependence on pressure of the structural parameters of Ca_3AsN was also investigated. We found the orthorhombic symmetry of Ca_3AsN has still a lower enthalpy then the cubic symmetry of Ca_3AsN even when the pressure increases.

Joint Publications:

"Structural Phase Transformations of Aluminum Arsenide". P. E. Van Camp, V. E. Van Doren and J. L. Martins, "Proceedings of the 22nd International Conference on The Physics of Semiconductors", edited by D. J. Lockwood, Vol. 1, p. 181 (World Scientific, Singapore, 1995).

Crystal	a (Å)	b (Å)	c (Å)
Ca$_3$BiN	4.862		
	(4.888)		
Ca$_3$AsN	6.720	6.715	9.526
	(6.725)	(6.720)	(9.534)
Ca$_3$P N	6.710	6.659	9.453
	(6.709)	(6.658)	(9.452)

Table 1: Calculated and measured (in parenthesis) lattice constants of ternary nitrides.

"High Pressure Properties of the Alkaline-Earth Sulphides". P. E. Van Camp, V. E. Van Doren and J. L. Martins, Phys. Stat. Sol. (b) **190**, 193 (1995).

"Electronic Structure and Pressure Dependence for some Ternary Calcium Nitrides". P. R. Vansant, P. E. Van Camp, V. E. Van Doren and J. L. Martins, Phys. Stat. Sol. (b) **198**, 87 – 91 (1996).

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"Structural Optimization of Ternary Calcium Nitrides" P. R. Vansant, P. E. Van Camp, V. E. Van Doren and J. L. Martins, in preparation.

Highlights of Athens–Jülich Collaboration

Towards an ab-initio study of dynamical properties of materials: Calculating forces and lattice distortions

N. Papanikolaou[†], N. Stefanou[†], R. Zeller[‡], P.H. Dederichs[‡]

[†]*University of Athens, Section of Solid State Physics,*
Panepistimioupolis, GR-15784 Athens, Greece
[‡]*Institut für Festkörperforschung, Forschungszentrum Jülich,*
D-52425 Jülich, Germany

The theoretical methods for the study of materials have enormously advanced in recent years. With the help of modern computers we are now able to simulate the microscopic behavior of real materials from first principles and predict experimentally observed properties with a high accuracy. The Korringa-Kohn-Rostoker (KKR) Green function method, which is based on multiple-scattering theory, is a powerful tool to calculate the electronic structure of solids. One of the most important and challenging problems for today's electronic structure methods is the study of the dynamical properties and the diffusion processes in solids. A key issue in such a study is the accurate calculation of the atomic forces. Within the framework of the Jülich-Athens collaboration we have extended the KKR Green function method to calculate reliably the inter-atomic forces and treat lattice relaxation effects. The calculations rely on an exact treatment of the anisotropic potential in each cell, leading to a set of coupled radial equations which are solved iteratively. As a benefit of the full potential KKR-method the forces can be calculated by the Hellmann-Feynmann theorem, since the Pullay corrections vanish.

Using this method we have firstly studied the local lattice distortion around impurities in metals [1,2,3]. For the case of 3d impurities in Cu [1] we found relatively small relaxations of the neighboring atoms, which practically do not effect the local magnetic moments. The results for the local relaxations are in very close agreement with EXAFS measurements, while the predicted volume changes of the dilute alloys agree very well with lattice parameter measurements. The good agreement is however only obtained, if the semi-core states of the impurities are treated as valence states, which is particularly important for the early transitions metal impurities. Calculations for 3d impurities in Al yield a qualitatively different picture, i.e. large relaxations and a drastically increased relaxation energy. Our calculations resolve the long standing problem of the existence or non-existence of a local magnetic moment of 3d impurities in Al [2]. Contrary to the experiment where no local moment was observed for an Fe impurity in Al, previous theoretical calculations predicted a moment of about 1.5 μ_B on the Fe site. This discrepancy was resolved when lattice distortion around the Fe impurity was correctly incorporated into our calculations which then show that the Fe magnetic moment vanishes in the ground-state configuration. We also find that the lattice relaxation is important for the magnetic properties of other impurities, e.g. the magnetic moment of Cr and Mn in Al is strongly reduced. At present we are applying the same method to defects in semiconductors. Here we study the complicated structure of defect complexes and their hyperfine properties which are strongly affected by relaxations.

The success of our method to deal with the lattice distortion has initiated preliminary studies of the lattice dynamics of metals. By shifting one atom and calculating the forces on the neighboring ones, the Born-von Karman coupling parameters can be calculated directly in real space. Calculations of the phonon spectra of several fcc metals are now in progress and give encouraging results. One of our main future aims is the study of structural distortions on surfaces, where these phenomena, due to the more open structures, are more important. Such an extension will allow us to study the relaxations and dynamics of ideal surfaces, as well as surfaces with single adsorbate atoms or small clusters.

One of the main benefits of the Athens-Jülich collaboration was the possibility offered to a young scientist from Greece, N. Papanikolaou, to work in Jülich as a postdoc during 1996 within the TMR-Network "Interface Magnetism".

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Highlights of Aarhus-Daresbury-Karlsruhe Collaboration

Rare Earth Materials studied with the Self-Interaction Corrected Local-Spin-Density Approximation

A. Svane[a], Z. Szotek[b], W.M. Temmerman[b], J. Lægsgaard[a],
S.V. Beiden[c], H. Winter[d] and G. Gehring[c]
[a] *Institute of Physics and Astronomy, University of Aarhus,*
DK-8000 Aarhus C, Denmark
[b] *Daresbury Laboratory, Warrington WA4 4AD, United Kingdom*
[c] *Department of Physics, University of Sheffield,*
Sheffield S3 7RH, United Kingdom
[d] *Forschungszentrum Karlsruhe, INFP, Postfach 3640, Karlsruhe, Germany*

The electronic structures of rare earth compounds are investigated using the self-interaction corrected (SIC) local-spin-density (LSD) approximation to density functional theory implemented with the *ab-initio* linear-muffin-tin orbitals (LMTO) band structure method. This scheme allows a treatment of the rare earth f–electrons as either localized or delocalized, and provides a framework for discussing the phase transitions occurring as the f–electrons change from being predominantly localized to predominantly itinerant as a function of applied pressure. The present collaboration has joined the efforts to: (a) apply the SIC-LSD formalism to more compounds and (b) improve the present computer codes. The current implementations are discussed in Refs. [3,5] below, while recently an extension to a fully relativistic description has been implemented, and the first results are being written up (Ref. [7]).

For cerium metal it is found [1-3] that the two fcc-phases, the low volume α– and the high-volume γ–phase, may well be described by the method, when the f–electrons are treated as delocalized or localized, respectively. The total energy is almost the same in these two phases, in agreement with the experimental fact that transitions between them are observed at moderate changes in temperature or applied pressure. The volume collapse of $\sim 23\%$ is somewhat too large compared with the $\sim 15\%$ observed experimentally, which primarily is caused by a too small theoretical lattice constant for the α–phase. By a simple thermodynamic extension the phase diagram of cerium may qualitatively be reproduced, including the occurrence of a critical point [3].

The cerium monopnictides CeN, CeP, CeAs, CeSb and CeBi exhibit a series of structural phase transitions with accompanying large volume changes, which all may be explained [4-6] by the competitions between the f–electrons being either localized or delocalized and between the B1 and B2 (i.e., the NaCl and CsCl) crystal structures. All crystallize in the B1 structure at ambient conditions, while the B2 structure becomes more favorable either with decreasing crystal volume or with increasing Z (i.e. size) of the ligand atom. In CeP, an isostructural phase transition takes place at 71 kbar, and is found to originate from the f–electrons transferring their weight from localized to delocalized. At a larger pressure of 113 kbar a second phase transition takes place to the B2 structure. In CeAs, only one phase transition is observed, directly from the B1 structure with localized f–electrons to the B2 structure with delocalized f–electrons. In CeSb and CeBi a first phase transtion from B1 to (a distorted) B2 structure, both having localized f–electrons, is seen, at 70 and 88 kbars, respectively, while only at larger pressures the localization-delocalization transitions are found. Experimentally, only the first transitions have been observed. The magnetic structures of the cerium monopnictides is quite complicated. We do find the correct ($T = 0$ and $H = 0$) antiferromagnetic ground state of CeP and CeSb, but with rather small energy differences between various alternatives. This is in accord with the experimental fact that the Nèel temperatures of these compounds are rather small (~ 10 K), but is also a warning that really all relevant energy contributions should be considered, i.e. both spin-orbit coupling [7] and possibly a full-potential treament is called for, before reliable predictions regarding magnetic structures can be made.

Ongoing research applies the SIC-LSD formalism to a number of rare-earth systems, including Yb pnictides, CeB_6 and SmS.

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Highlight of Würzburg-Bristol Collaboration

Relativistic Approach to Dichroism in Superconductors

K. Capelle[†], E.K.U. Gross[†] and B.L. Gyorffy[‡]
[†]*Institut für Theoretische Physik, Universität Würzburg,*
Am Hubland, D-97074 Würzburg, Germany
[‡]*H.H. Wills Physics Laboratory, University of Bristol, Bristol, UK*

The collaboration between the groups of Prof. B.L. Györffy, Bristol, UK, and Prof. E.K.U. Gross, Würzburg, FRG, focuses on applying the relativistic theory of superconductivity to study dichroism in superconductors.

A system is said to exhibit dichroism if the absorption of light depends on its polarization [1]. Usually dichroism occurs if time reversal symmetry is broken through external or internal ('exchange') magnetic fields. The former case corresponds to the Faraday or Kerr effect, depending on whether it is observed in transmission or reflection, while the latter case is referred to as spontaneous dichroism. Instead of broken time reversal symmetry, dichroism can also result from lack of inversion symmetry. In normal metals and ferromagnets these phenomena have been the subject of many theoretical and experimental investigations [1, 2]. For superconductors, on the other hand, very little is known about mechanisms and consequences of dichroism. The objective of the collaboration is to develop a systematic theory of dichroism in superconductors.

We use the Bogolubov-de Gennes (BdG) approach to inhomogeneous superconductors in magnetic fields [3], including relativistic effects [4], and employ perturbation theory to incorporate a variety of potential sources for dichroism. As a measure of dichroism we use the difference, $\Delta P = P_{LHP} - P_{RHP}$, in the power absorption of light with left-handed polarization (LHP) and right-handed polarization (RHP). ΔP is proportional to $\mathrm{Im}[\sigma_{xy}(\omega)]$, the imaginary part of the offdiagonal elements of the conductivity tensor [5] which govern all magneto-optical phenomena.

Recently the BdG equations were generalized to include relativistic effects on the single-particle level [4]. ¿From this generalization, the full form of the spin-orbit operator in superconductors is known to have offdiagonal elements involving the pair potential (anomalous spin-orbit coupling), in addition to the well-known diagonal spin-orbit terms which contain the lattice potential. We include the spin-orbit terms, as well as orbital currents and order parameter inhomogeneities via stationary perturbation theory.

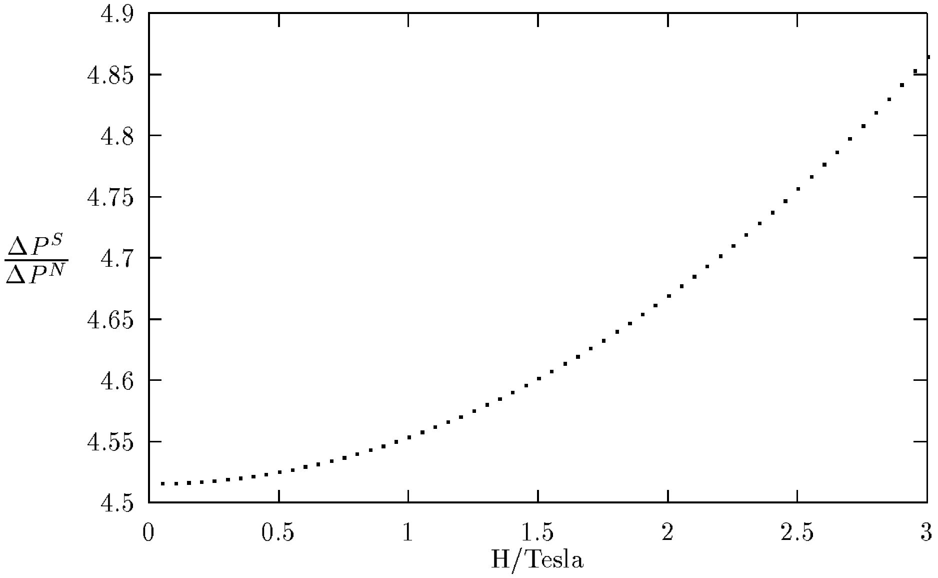

Figure 1: Dichroism ratio vs. magnetic field at $T = 3K$ for $\omega = 3meV$ and an energy gap at $T = 0$ of $2meV$.

Five distinct mechanisms which can give rise to a nonvanishing ΔP in superconductors were identified and interpreted in this way.

Mechanism 1: The conventional spin-orbit coupling (SOC) can, just as in normal metals, produce dichroism, provided that an (external or internal) magnetic field is present.

Mechanism 2: Anomalous spin-orbit coupling, too, can give rise to dichroism if magnetic fields are present. This term has a very different temperature behaviour compared to conventional SOC.

Mechanism 3: Orbital currents produced by $\mathbf{A}$, such as screening currents, can lead to a finite ΔP, without SOC. In normal metals this is usually smaller than the effects due to SOC. In superconductors, where the screening currents responsible for the Meissner effect are particularly large, this need not be the case any more.

Mechanism 4: Even in the absence of magnetic fields and SOC, $\mathbf{r}$-dependent pair potentials are a possible source of dichroism if they are either complex (i.e. break time reversal symmetry), or break inversion-symmetry. This is particularly interesting because it makes dichroism a potential tool to investigate unconventional order parameters.

Mechanism 5: A material which lacks a center of inversion already displays dichroism in the normal state. Such a material in general also displays dichroism in the superconducting phase.

What all mechanisms have in common, is that time reversal symmetry or inversion symmetry is broken, by magnetic fields, by the pair potential or by the lattice potential. Mechanisms 1 and 3, which were investigated thoroughly for normal metals, are present in superconductors as well. However, we find that they are strongly modified by the superconducting coherence. This is illustrated by the figures to be discussed below. Mechanisms 2 and 4 are special to superconductors and not present at all in the normal state.

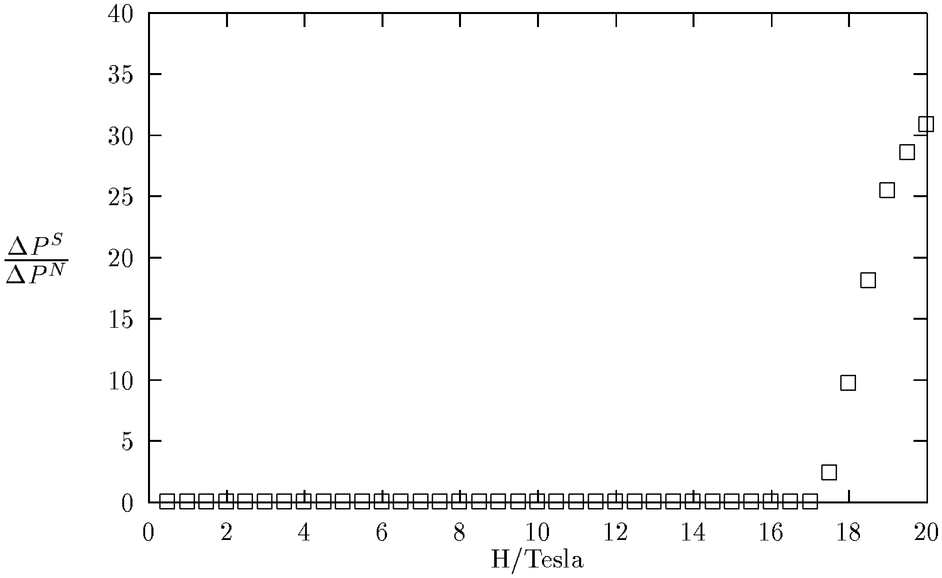

Figure 2: Same as in Fig. 1, but for $T = 0$ and fields up to the paramagnetic limit of superconductivity.

Those mechanisms requiring magnetic fields in the superconductor, namely 1, 2 and 3, cannot take place in the bulk of the material, as long as it is in the Meissner phase. They can be active in three different situations: (a) at surfaces, within the penetration depth, (b) in the vortex phase and (c) in superconductors displaying coexistence of magnetism and superconductivity. Mechanisms 1 and 2 are of relativistic origin. In particular, mechanism 2 constitutes the first potentially observable consequence of the anomalous spin-orbit coupling, predicted in [4].

Using simple approximations for the relevant matrix elements, we calculated ΔP for a model superconductor in which mechanism 1 is dominant. (Different model systems in which the other mechanisms dominate are currently under study.) In the plots we display the ratio of ΔP in the superconductor to ΔP in the normal conductor, $\Delta P^S/\Delta P^N$. This ratio is a direct measure for the interplay of relativistic symmetry breaking, due to mechanism 1, and superconducting coherence.

In Fig. 1 we plot $\Delta P^S/\Delta P^N$ versus the applied magnetic field. Both, numerator and denominator are almost linear functions of B and vanish for $B = 0$. Their ratio, however, is an increasing function of B because superconductors are more susceptible to magnetic fields than normal conductors. Repeating this calculation at $T = 0$, we find that the superconductor does not display dichroism for the fields in Fig. 1. This is physically reasonable, because at $T = 0$ a magnetic field will not produce spin polarization in a superconductor, since all electrons are paired. On the other hand it is known from normal state calculations that a finite spin magnetization is a necessary condition for SOC to produce dichroism. An alternative point of view is, that at $T = 0$ all paired electrons occupy mutually time conjugate states, so that the ground state is invariant under time reversal. Breaking this invariance, however, is mandatory for SOC induced dichroism.

In Fig. 2 we consider a superconductor with high upper critical field, H_{c2}. At zero temperature, we find, as before, $\Delta P^S \equiv 0$, until $B \approx 17.5T$. This is the field at which the Zeeman energy of

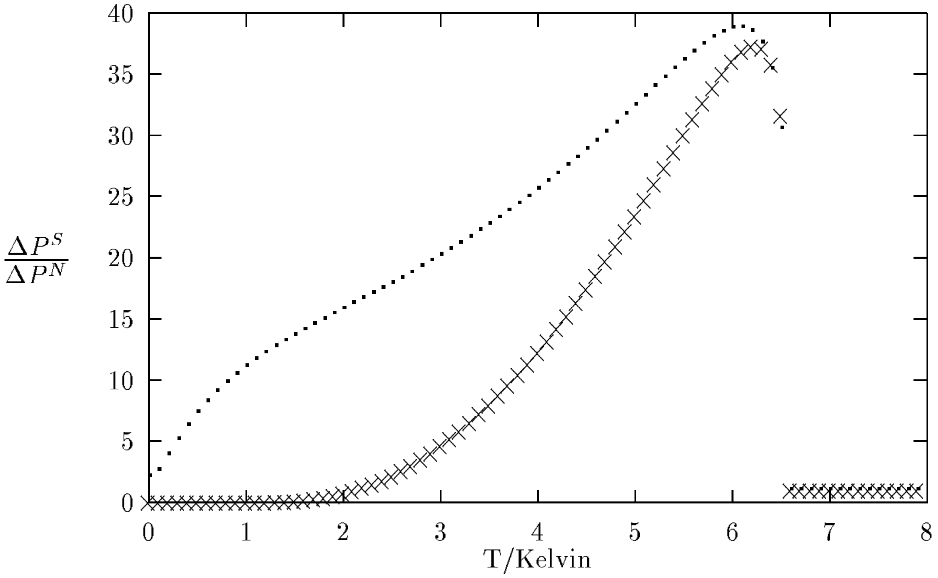

Figure 3: Dichroism ratio vs. temperature for $\omega = 4meV$ and $B = 0.1T$ (crosses) and $B = 17.5T$ (dots). T_c is at $6.6K$. Hebel-Slichter- and gap-enhancement are seen.

the electron spins equals the energy gap. At this strength the magnetic field can break Cooper pairs paramagnetically. Once there are unpaired electrons, the magnetic field will immediately produce a net spin magnetization (hence break time reversal invariance) and dichroism results. Interestingly, this effect could lead to a very direct experimental identification of paramagnetic limiting as the cause of the upper critical field.

In Fig. 3 we keep the field fixed and vary the temperature. Above T_c the ratio is unity. Right below T_c we find a drastic increase in dichroism in the superconductor [6]. This increase can be partly traced back to a Hebel-Slichter like effect, due to a novel combination of coherence factors. A second amplifying mechanism is due to the presence of the superconducting gap, [9, 10].

The second graph in Fig. 3 is for $B > \Delta$, i.e. for the paramagnetic limit of superconductivity. The peak below T_c is not affected much, but at $T = 0$ the curve for small fields goes to zero, while the curve for the paramagnetic limit approaches a finite value. This is in accordance with our discussion of Figs. 1 and 2.

In Fig. 4, finally, we display the frequency dependence of the absorption. There is an absorption edge at $\omega = 2meV$, which corresponds to the energy gap. This edge occurs because we considered only pair breaking processes [7]. The behaviour right above the edge is usually classified phenomenologically, according to the shape of the peak to be of type I or II [8], a classification which reflects the symmetry under time reversal of the perturbation (type I: odd, type II: even). The shape of the peak in Fig. 4 is of a mixed type, reflecting the fact that our model contains two perturbations, the polarized light (which is odd under time reversal) and the SOC (which is even).

The various plots demonstrate that even in the simple model many characteristics of the physics of dichroism and of superconductivity can be found. The exact numbers depend, of course, on the detailed parameters of the model. We believe, however, that the qualitative behaviour is generic, and constitutes a definite signature of the SOC mechanism.

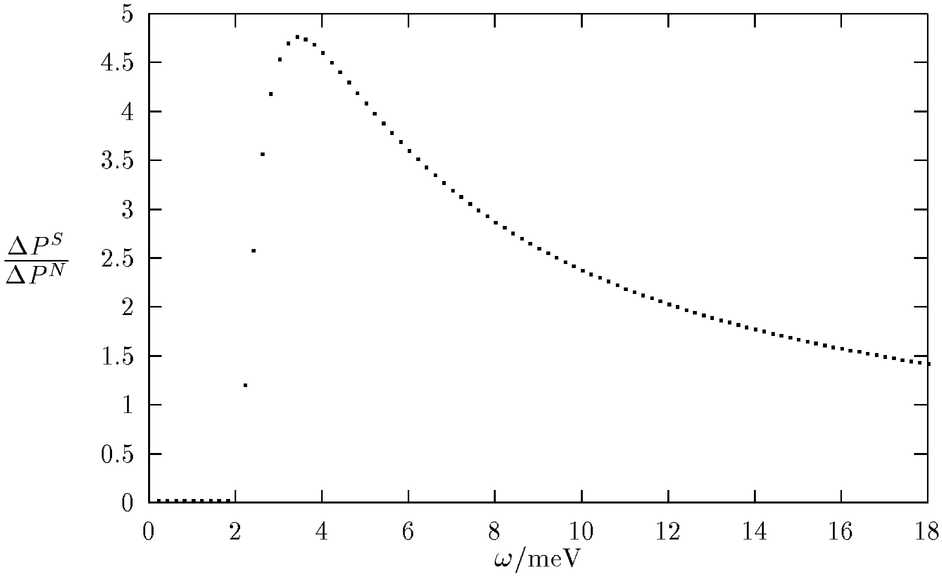

Figure 4: Dichroism ratio vs. frequency, at $T = 3K$ and for $B = 0.1T$. A mixed type I-II absorption edge at the gap energy of 2meV is present.

The above results have recently been submitted for publication [9]. A more detailed account of this work is currently being written [10].

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Highlight of Bristol-Daresbury-Stuttgart Collaboration

On the semi-phenomenological quasi-particle spectra of high T$_c$ superconductors

B.L. Gyorffy[†], Z. Szotek[‡], W.M. Temmerman[‡], O.K. Andersen[§], and O. Jepsen[§]

[†]*H.H. Wills Physics Laboratory, University of Bristol, Bristol, UK*
[‡]*Daresbury Laboratory, Warrington, WA4 4AD, UK*
[§]*Max-Planck-Institut für Festkörperforschung, Postfach 80 06 65, D-70506 Stuttgart, Germany*

Recently, a new semi-phenomenological approach to the problem of calculating the electronic structure in the superconducting state has been proposed [1]. It is based on a physically appealing, and very economical, parametrization of a phenomenological attractive interaction between the electrons afforded by the Density Functional Theory (DFT) of superconductivity [2] and the powerful LMTO-ASA methodology for solving self-consistent field problems for normal electrons [3, 4]. Preliminary calculations highlighted in the Ψ_k−Newsletter No. 13 (February 1996), indicated that the dramatic variation of the superconducting gap across the Fermi surface, as deduced from photoemission experiments, can be quantitatively reproduced with just one interaction constant. Here we report on some encouraging results of our first calculations of the specific heat [5] for YBCO, based on the same parametrization and without any further adjustable parameters.

The Kohn-Sham type Euler-Lagrange equations of the DFT for superconductors is of Bogoliubov-de Gennes, two-component, form and features the non-local pairing potential $\Delta(\mathbf{r},\mathbf{r}')$. This latter quantity is related to the pairing amplitude $\chi(\mathbf{r},\mathbf{r}')$, the order parameter of the problem, by the interaction kernel $\lambda^{(2)}(\mathbf{r},\mathbf{r}';\mathbf{r_1},\mathbf{r'_1})$, which may be interpreted as an effective pairing potential. To make progress, it is expanded in terms of LMTO orbitals. In the present calculation these are those of the eight-band model of Andersen et al. [4]. The corresponding expansion coefficients are the parameters of the method. In the present calculation only one inequivalent expansion coefficient $\lambda_{\mu\mu';\mu\mu'}=\lambda_{\mu,\mu'}$, which describes the interaction of an electron in orbital labeled by μ and another in orbital μ' when the two electrons form a singlet, is kept and all the other coefficients were set equal to zero. In particular, the μ and μ' states were chosen to be $d_{x^2-y^2}$ orbitals on the nearest neighbour Cu sites of a CuO$_2$ bilayer. The corresponding λ was determined by the requirement that the calculated T$_c$ agreed with experiments on optimally oxygenated YBCO. These were taken to imply that T$_c$=91.5 K.

In Fig. 1 we display the gap on the two main sheets of the Fermi surface as determined in the calculation described above. Evidently, it is highly anisotropic and it can be interpreted as having 'd-wave' symmetry [6]. Moreover, it agrees quantitatively as well as qualitatively with the gap deduced from photoemission experiments on optimally doped YBCO [7]. Given that only the experimentally measured T_c was used to fit λ, this is an encouraging, if not altogether decisive, result.

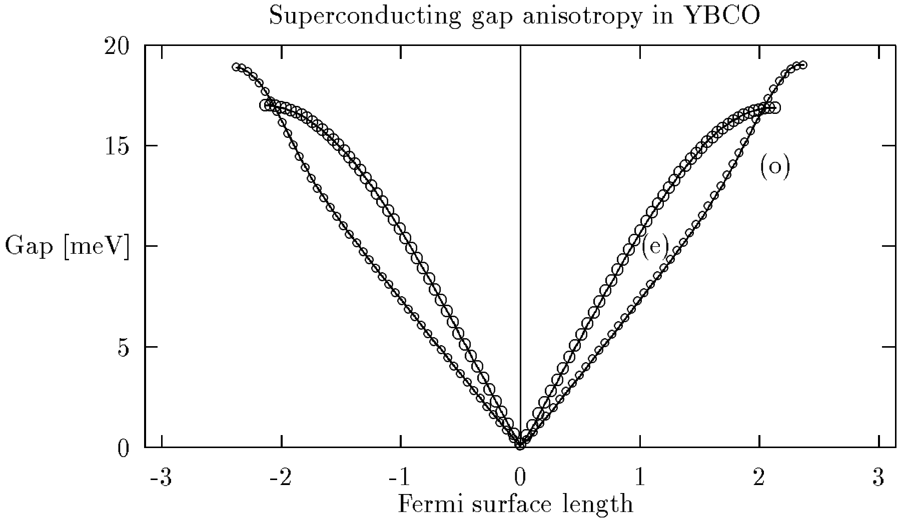

Figure 1: Superconducting gap for the nearest neighbour Cu d–Cu d interaction, as a function of Fermi surface length for even (e) and odd (o) sheets of the YBCO Fermi surface.

Having obtained the quasi-particle spectra in the superconducting state we can now calculate the specific heat without further adjustable parameters. The zero in $\Delta(\mathbf{k_F})$ on the (π,π) line implies a line of nodes on the full three-dimensional Fermi surface. This implies without numerical calculations, that at sufficiently low temperature the specific heat $C_v \approx T^2$, in dramatic contrast to exponential decay which is the prediction of the BCS model [6]. Whilst this power law behaviour is a general consequence of a line of nodes in $\Delta(\mathbf{k_F})$ on the Fermi surface, the coefficient of the T^2 contribution depends quantitatively on the quasi-particle spectra. Thus it is of interest to use $E_{\mathbf{k},\nu}$, which agreed with the photoemission experiments, to calculate C_v (T). The general formula for the specific heat due to independent quasi-particles is

$$C_v(T) = T\frac{dS}{dT} = \frac{1}{2}k_B\beta^2\sum_{\mathbf{k},\nu}(E_{\mathbf{k},\nu} + \beta\frac{\partial E_{\mathbf{k},\nu}}{\partial\beta})E_{\mathbf{k},\nu}sech^2(\frac{1}{2}\beta E_{\mathbf{k},\nu}). \tag{17}$$

Here S is the entropy, k_B is the Boltzmann constant, and β=1/k_BT. As is readily appreciated in the asymptotically small temperature T limit, the dominant contribution to the Brillouin zone integral in the above formula comes from the close vicinity of the node. We have developed a flexible method of integration which preferentially samples this relevant region. In the limit T $\rightarrow$ 0 we find

$$C_v(T) = 0.93(\frac{T}{T_c})^2(\frac{mJ}{molK}). \tag{18}$$

In measurements of the low temperature heat capacity for all the high T_c materials one finds large linear and cubic contributions which are not due to the superconducting electrons. Nevertheless, Moler et al. [8] have succeeded in extracting a quadratic contribution which in general supports the emerging consensus [6] that the Cooper pairs in these materials have 'd-wave' internal symmetry. Moreover, they find

$$C_v(T) = 0.11T^2 = 0.91(\frac{T}{T_c})^2(\frac{mJ}{molK}) \tag{19}$$

which, to our pleasant surprise, is in good quantitative agreement with our semi-phenomenological calculations. Obviously, further work is required before the significance of these interesting developments are fully appreciated. Nevertheless, for the time being they point to the conclusion that whatever the physical pairing mechanism is, it operates between electrons of opposite spins on nearest neighbour Cu sites.

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Highlights of Cambridge Collaborations in the Network

The active sites of microporous (zeolite) solid acid catalysts

Volker Heine and Rajiv Shah

TCM, Cavendish Laboratory, Cambridge, UK

The calculations described here were done in collaboration with Drs. J. Gale and M.C. Payne, connecting with the Highlight of 1995 reported by Dr. E. Nusterer et al. (Vienna) and the research on zeolite flexibility by Dr. A. Bieniok (Frankfurt), and benefiting from discussions with Prof. J. Sauer (Berlin).

As is well known, zeolites are microporous structures consisting of SiO_4 and $AlO_3(OH)$ tetrahedra joined into a three-dimensional framework by the shared oxygen atoms at the corners. They are important chemicals for various purposes, one of which is the catalytic activity of what are called Bronsted acid sites. At an aluminium containing tetrahedron, the extra proton needed for charge balance is attached to one of the four oxygens. It is available for creating a hydrogen bond to an adsorbed molecule, or for transfer to the molecule thus hydrogenating it. In the latter case it may result in splitting off an -OH group from the adsorbed molecule in the form of a water molecule.

The calculations were for the zeolite chabazite containing a methanol molecule in each unit cell. Chabazite has 36 atoms per unit cell, and contains rings of 8 tetrahedra (8-rings).

The first finding was that there are substantial differences amounting to 15 kJ/mol between the binding energies of the proton to the four sites, much larger than kT at ambient temperatures. We already see here the importance of the specific structure of the zeolite. A zeolite's structure is important in making it catalyse very specific reactions and not others, referred to as selectivity.

It was found that the methanol molecule is not physisorbed, as had been suggested by some previous cluster calculations. It is chemisorbed held by two hydrogen bonds. The proton from the Bronsted acid site is transferred to the methanol molecule, apparently without any energy barrier, forming an -OHH group at its end. This forms two hydrogen bonds to two oxygen atoms of the zeolite framework, with H-O distances of 1.38 $\AA$ and 1.54 $\AA$ respectively. The first of these is particularly close, indicating a very strong hydrogen bond, which explains the large hydroxyl stretching frequency shifts observed in the infrared spectrum. The molecule then lies snugly within the 8-ring, presumably held additionally by electrostatic and Van der Waals forces to the ring structure.

A similar calculation was carried out for a methanol molecule in a sodalite framework, the simplest model of a zeolite. It only has 6-rings which are not large enough to accommodate the molecule. The latter has to point into the body of the sodalite cage. In this situation the calculations found the methanol only physisorbed, with no proton transfer from the Bronsted acid site of the framework to the molecule.

Clearly the energetics of proton transfer are finely balanced. The above and other results suggest that in ZSM-5 both protonated and unprotonated species may be present at ambient temperature. This is the commercial catalyst for methanol to gasoline, but it has a unit cell too large currently for ab initio calculations. It contains 10-rings, intermediate between the 8-rings of chabazite and the cage voids of sodalite referred to above.

Another issue arising from the calculations and being researched further is the role of zeolite flexibility. Zeolites are rather flexible structures, in fact they are extremely flexible in one or more very specific ways which are characteristic of the particular zeolite structures. One can expect such flexibility to be important in matching the shape of a corner of the framework to the need for bonding to the adsorbed molecule, and perhaps in letting go again in the chemical process.

The behaviour of gallium atoms in a grain boundary in aluminium

David Thomson and Volker Heine

TCM, Cavendish Laboratory, Cambridge, UK

This project (with Dr. M. C. Payne) is a collaboration with Prof. M. Finnis, started when he was in Stuttgart.

The project was motivated distantly by the phenomenon of grain boundary embrittlement, but understanding that is still some distance away since we do not know how impurity atoms behave in a grain boundary in a metal. In some cases they severely embrittle the metal, of which Ga is Al is a spectacular example, while in other cases they strengthen it.

The present study concerns various concentrations of Ga in one particular boundary, namely a $\Sigma = 11$ (113) tilt boundary in Al. Although it is only one specific case, a picture emerges of the energetics of Ga in different situations that we believe will have a wider applicability.

In this boundary the two grains really fit very well together. Of the two types of atomic site on the boundary, one (A) has 12 nearest neighbours as in bulk Al and the other (B) has 11. To be precise, the B site lies on the boundary plane and two A sites opposite to one another on either side. There are 44 atoms in a unit cell containing two boundaries with three atomic layers between them, and the system is always relaxed in the z direction taken perpendicular to the boundary plane. Various checks were carried out, e.g. the pure Al grain boundary energy compared with a previous calculation, and the heat of solution of Ga in bulk Al compared with experiment. The Al pseudopotential had previously been tested on the Al elastic constants, and the Ga pseudopotential had been tested and used in an extensive computational study of Ga.

The greatest possible care was taken with convergence in the number of k-points and correcting the energies to zero broadening at the Fermi level.

Ten calculations were carried out with between zero and 6 Ga atoms in each boundary placed on various sites on and near the boundary. The energy was compared with the same number of Ga atoms in bulk solid solution in Al. A regression analysis showed that Ga atoms are strongly attracted to the A sites (relative to bulk solid solution), but hardly at all to the B sites and to the C sites, the next adjacent on either side of the boundary. To be precise, a Ga atom is bound by 78 meV to an A site when the other A site of the pair is an Al atom. Another Ga atom is then attracted by 51 meV to the second A site of the pair.

To make sense of all this we have to look carefully at the local stresses as measured by the interatomic distances and the extension of the system perpendicular to the boundary (when fully relaxed), and at the changes in these as more Ga atoms are added to the boundary. In the pure Al boundary the B atoms are locally under some tension, balanced by an equal but opposite compression between the two A atoms in a pair. It is this compression which is relaxed by Ga atoms moving into the A sites. It is not that the A sites are particularly favourable for Ga atoms: rather the compression makes them unfavourable sites for the Al atoms.

The strange fact is that Ga in an (unstable computed) fcc structure has an atomic volume 10% larger than that of Al, and a Ga atom in bulk solid solution in Al expands the lattice by less than 1%. Hence Ga is certainly not a small atom. So how can it relax the tight A sites? The answer lies in the unusual structure of pure Ga with 7 near neighbours and the pseudopotential understanding of this fact. In metallurgy the sizes of atoms are the predominant determinant of alloy structures, but there used to be much discussion about how to define 'size': should it be based on the atomic volume or the nearest neighbour distance? The pseudopotential theory of the 1960's (and elaborated since then) shows that both are relevant, e.g. it is the interplay between them that accounts for the crystal structure of Ga. In an Al environment the Ga atom has a volume equal to that of an Al atom, but a hard-core radius determining the nearest neighbour distance smaller than that of Al. (This point is verified by calculating the restoring force constants for a Ga atom in bulk Al solid solution which are found to be weakened.) Thus in the A sites, Ga atoms are quite happy with the unusually short nearest neighbour distance between the pair of A sites. This picture is further supported by a calculation of the energy barrier for migration of the grain boundary, which involves short displacements by two A atoms each squeezing through a hole between three other atoms. The energy barrier is halved if the moving atoms are Ga, compared with Al, because again their smaller hard-core radius allows them to squeeze by more easily.

Other grain boundaries appear to be considerably less well fitting than the one studied here. We may therefore expect even stronger local compressions at some sites, which will therefore be even more attractive to Ga atoms. It remains to apply this principle to the behaviour of dislocations near the boundaries leading to embrittlement.

Highlights of Jülich-Vienna Collaboration

Transition-Metal Silicides for Electronic Devices

G. Bihlmayer *(Uni. Wien)*, S. Blügel *(Forschungszentrum Jülich)*,
and R. Podloucky *(Uni. Wien)*

Transition-metal (TM) silicides are widely used in very large scale integrated microelectronic and optoelectronic devices. The large variety of applications are due to a large variability in the electronic structure due to numerous different compounds and their match to a silicon-based technology. Most of these compounds are conductors. Some of them are used as interconnects, wires and contacts ($CoSi_2$ and $FeSi_2$). Some of them are semiconducting and are used for example as infrared sensors in infrared cameras. In order to build TM silicide structures at the Si wafer several techniques have been developed. One is the epitaxial growth of TM silicides on Si, an other one is TM ion implantation into Si followed by tempering which leads to buried TM silicides structures. With the rise of the glasfiber technology, it becomes necessary to match the silicon technology to the optoelectronic suitable for this technology. On demand is a silicide with a direct band-gap of 0.8eV with a large oscillatory strength. Motivated by the many material problems, last year the Vienna group and S. Blügel from Jülich teamed up to perform *ab initio* calculations of the electronic structure using the FLAPW method based on density functional theory in the local density approximation to look at several of the above problems.

(i) **$CoSi_2$/Si interface**:

First as a step towards understanding of the TM silicide/Si interface we investigated the clean $CoSi_2(110)$ surface [1], studying the electronic structure and surface relaxation effects. As a second point, it was found that the $CoSi_2$ grown on Si(100) shows a c(2×2) reconstruction, and it was not clear whether this reconstruction is due to the termination of the $CoSi_2$ surface by Co or Si. Recently carried out voltage dependent scanning tunneling microscopy (STM) experiments found that certainly both, the Co as well as the Si atoms terminate the $CoSi_2$, but due to the lack of chemical resolution of the STM, it was not clear which of the atoms are Co or Si. Calculating the STM image on the basis of the Tersoff-Hamann model [2] and comparing the theoretical images with the experimental ones led to the identification of the atom types.

(ii) **Buried layers of $FeSi_2$**:

Nowadays one is able to grow buried layers of $FeSi_2$ by ion-beam synthesis. The problem is that $FeSi_2$ exists in at least two phases: (a) the $\alpha-$ (high temperature) phase of $FeSi_2$. In this phase $FeSi_2$ is metallic. (b) the $\beta-$ (low temperature) phase, which is semiconducting with a band gap of 0.8 eV. A metastable $\gamma-$ phase was also found which is metallic and crystallizes in the CaF_2 structure. We found a strong influence of the crystallographic parameters on the size of the gap and, indeed, the transformation from $\gamma-$ to $\beta-$phase $FeSi_2$ can be viewed as an opening of a band gap due to a Jahn-Teller-like distortion. The basic problem is, that it is not *a priori* clear, which silicide is formed for a particular process condition. The electronic structure of the buried silicide was investigated by a novel technique called soft x-ray emission spectroscopy. We calculated the electronic structure of $\alpha-FeSi_2$ and $\beta-FeSi_2$ with and without core-hole and compared them with the experimental data [3] to unambiguously identify which phase was formed.

(iii) **TM silicide for the optoelectronics**:
Most investigated silicides show metallic conductivity. An exception is for example $CrSi_2$, which has 14 valence electrons per formula unit. Most semiconducting TM silicides show a hybridization gap in the *d*-band region of the TM atoms. Since the band gaps are not direct gaps, the oscillator strength for *d*–*d* transitions is tiny and the *d*–bands rather flat and the mobility of the carriers rather low, most silicides have little potential for optoelectronic applications. On searching for new optoelectronic silicides we found the little investigated, but a large class of Nowotny-chimney-ladder silicides, characterized by the magic number of 14 valence electrons per formula unit. In this case the Fermi energy is located at the hybridization gap between *p* and *d* states. We suggested a promising new silicide for applications in the optoelectronic: Ru_2Si_3 [4]. We found a direct $p - d$ gap of 0.45 eV, opened by a strong Si (*p*) - Ru (*d*) hybridization and a *p*-band of high dispersion at the top of the valence band. Taking into account that the band gap is usually underestimated by LDA calculations, the true gap might be larger and may approach the 0.8eV needed for the glasfiber technology.

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