Ψ_k Newsletter

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

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

Contents

1 Editorial

As mentioned in the previous Newsletter, from this Newsletter onwards we are going to cover several networks. At present only the TMR1 Network on 'Interface Magnetism' is in operation, but the two other networks are to start soon. Consequently, we have replaced the name 'HCM Newsletter' on the front page by 'Ψ_k−Newsletter'. The change is to reflect the spirit of our community and to ensure continuity. Also, since the HCM Network expired last December, and the section 'News from the Working Groups' lost its relevance, it has been replaced by the following sections: **'News from the HCM Network'** (only in the present Newsletter to accomodate the final HCM report to Brussels and the reports of recent collaborative visits and workshops), **'News from the TMR1 Network'**, **'News from the TMR2 Network'** and **'News from the ESF Programme'**. Of course, the section 'News from the Network' has also lost its meaning, and therefore, when communicating news concerning all the networks, we shall place it under the heading **'General News'**. In this Newsletter, it contains some preliminary information on the next big conference of all networks. In the section **'Workshop/Conference Announcements'**, we shall only advertise the events that are not organized by the specific networks. However, meetings, workshops and/or conferences, organized by the respective networks will be announced in the subsections of the sections devoted to the news from the respective networks, depending on which network is to organize the event.

In this Newsletter, in the section **'News from the HCM Network'**, we have reports of collaborative visits and a report and abstracts of the recent workshop in Halle on *'Electronic and Magnetic Properties of Oxides and their Surfaces – Theory and Experiment'*. There, we also publish a draft of the final report on the activity of the HCM Ψ_k−Network, that will be submitted to the European Commission in Brussels. Moreover, in this Newsletter, the **Highlight of the Month** section, has been replaced by the **Scientific Highlights** section, and in there we present a few scientific highlights of the HCM Network activity in the reporting period. In the section **'News from the TMR1 Network'** we have a short report on its scientific accomplishments in the past year or so. In the section **'News from the TMR2 Network'** readers can find some information on this new network, which together with the ESF Programme, described in the section **'News from the ESF Programme'**, represents a continuation of the HCM Network.

We hope, that the Newsletter will continue to generate interest in our community, and that all readers will find it worth their while to contribute to it, so that it maintains high scientific and informational standards.

The *Networks* have 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. Gillan (Keele)*, *E.K.U. Gross (Univ. Würzburg)*, *B.L. Györffy (Bristol)*, *V. Heine (Univ. Cambridge)*, *R. Jones (Univ. Exeter)*, *J. Kübler (TH, Darmstadt)*, *J.L. Martins (IN-*

ESC, LISBON), *R. Nieminen (TU, Helsinki)*, *J. Nørskov (TU, Lyngby)* with information on CAMP, *M. Scheffler (FHI Berlin)*, *K.-H. Schwarz (TU, Vienna)*, *G.P. Srivastava (Univ. Exeter)*, and *A. Walker (UEA Norwich)*. There are also pointers to the WWW home page of the Solid State Theory Group at National Renewable Energy Laboratory, Golden, CO 80401 *(http://www.sst.nrel.gov)*, and to the home page of Prof. David Vanderbilt, Department of Physics and Astronomy, Rutgers University *http://www.physics.rutgers.edu/ dhv.* If you maintain a home page on your activities we will be happy to include a pointer from the *Networks'* home page to your home page.

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

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

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

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

2 General News

Follow-up of the Schwäbisch Gmünd Conference

Since the 1996 Conference in Schwäbisch Gmünd was very succesful and widely appreciated, we have started thinking of the next conference of the same kind. As the Schwäbisch Gmünd Conference, the next one will focus on all aspects of the 'Ab initio calculations of complex processes in materials'. This conference is to be organized by the Daresbury Laboratory team with Dr. Paul Durham as its chairman. The considered dates for the conference are the end of 1999 and the early spring of 2000. The conference is to take place in England and at present we are busy looking for a suitable conference centre which would resemble the one in Schwäbisch Gmünd, providing right atmosphere for lively and constructive scientific discussion. We would appreciate any suggestions especially concerning the most suitable date for the conference as well as any information on other major conferences already planned for the above mentioned dates. Please send any comments and suggestions to: psik-coord@dl.ac.uk.

3 News from the HCM Network

3.1 Reports on Collaborative Visits

Report on a Collaborative Visit of E. Artacho (Madrid) to the University of Kiel in Germany

November 24 - December 1, 1997

I visited Dr. Björn Winkler and his group in the Mineralogy Institut at the Kiel University between November 24 and December 1, 1997. The purpose of the visit was to apply the SIESTA program developed by Daniel Sánchez-Portal, Pablo Ordejón, Joseé M. Soler and myself, to specific problems in mineralogy under study in Winkler's group. SIESTA is a code for first-principles calculations based on standard Density Functional approximations (LDA, LSD, GGA) and norm-conserving pseudopotentials, for which the computational effort scales linearly with the size of the system. It allows the ab initio computation of properties of systems of unprecedented size, very well suited for the complex structures of many minerals. This collaboration is, therefore, a very natural one, and three projects have already been started at Kiel during this week:

(i) The study of the structure, equation of state, and stability of sodalite, a relatively simple zeolite of both mineralogical and chemical interest. Calculations will be performed with and without molecules of dioxolan in the cage. It was demonstrated that it is realistic to study properties as a function of dioxolan content. During this week first results have been already obtained, and a phase transition has been already obverved for tensile strains.

(ii) Clustering of Mg or Ca atoms in garnets. A first calculation of pure Ca garnet (grossular) was already performed with a full relaxation of the inner degrees of freedom. Calculations of the same structure with two Ca atoms substituted by Mg in different positions of the unit cell are underway. The aim of this study is to quantify the short-range interactions between the cations, which is important for the understanding of the solid solutions encountered in nature.

(iii) Magnetic structure of azurite (copper carbonate) at zero temperature. Azurite is most probably a Mott antiferromagnet below 1.8 K. In our first, prelimenary, calculations at Kiel a ferromagnetic structure has been already computed. The project continues now by obtaining different spin arrangements in supercells and comparing their energies.

It has been a very fruitful visit, the start of a promising collaboration. Publications of results coming out of the mentioned projects are planned for the short term, especially in projects (i) and (iii).

(Emilio Artacho)

Report on a Collaborative Visit of Pablo Ordejón (Universidad de Oviedo) to Giulia Galli (IRRMA, Lausanne)

24 - 28 November, 1997

I visited Dr. Giulia Galli at the IRRMA in Lausanne, from 24 November to 28 November 1997. This visit has served to continue an ongoing collaboration, which was started in 1996. Both of us have been involved in the last years in the development of schemes for the calculation of the properties of large scale systems from the electronic structure, and the application to real, complex materials. In particular, we have worked on the development of Order-N techniques.

During this visit, we have worked on two different issues:

(a) Study of the vibrational properties of small fullerene-assembled thin films.

Cluster-assembled carbon thin films have been the subject of increasing interest in the last years. The presence of fullerenic structures embedded in an amorphous matrix could give rise to disordered carbon systems with novel mechanical properties; furthermore, the control of the deposition energy and the mass distribution of the clusters can open the way to building materials with a tunable sp^2 to sp^3 site ratio. Recently, Raman spectroscopy has been used to characterize cluster-assembled thin films[1]. However, the interpretation of measured spectra in terms of the microscopic structure is far from being clear, and usually is based on prior knowledge of diamond-like and graphitic films. No interpretation in terms of the microscopic cage structure has been provided so far.

In order to gain insight about the relationship between vibrational and structural properties, we have computed the phonon spectrum and the Raman activity of a thin film model with 812 atoms, obtained with a computer simulation by assembling small fullerenes [2]. The calculations have been performed using the Tight-Binding hamiltonian of Xu *et al.* [3]. In order to handle the large number of atoms in the model, we have used an Order-N technique developed recently [4] for the calculation of phonons in large systems, from the electronic structure. Our results have allowed us to correlate the various features of the Raman spectrum to different local bonding configurations in the computer generated model, and to suggest an interpretation of recent experimental data. In particular, we have been able to identify the Raman features steaming from the presence of sp^2 and sp^3 bonding configurations in the cages network, as well as the disorder in the film. Our results may also provide a way to identify the existence of different size cages in the films, in terms of the frequency shift of certain Raman peaks.

We will present the results of this work in the next March Meeting of the APS, and are writing a paper which we will submit shortly.

(b) Organization of a CECAM workshop on "Local Orbital Methods for Large Scale Atomistic Simulations"

This workshop has been approved by the CECAM scientific commitee, and will take place in July 1998. We are two of the organizers, together with David Pettifor (Oxford) and Luis

Seijo (Universidad Autónoma de Madrid). During this visit we have worked on several aspects of the organization of the workshop: scientific program, financial issues, etc.

References

[1] P. Milani et al. J. Appl. Phys. (in press), and references therein.

[2] A. Canning, G. Galli and J. Kim, Phys. Rev. Lett. **78**, 4442 (1997).

[3] C. Xu *et al.*, J. Phys. Condensed Matter **4**, 6047 (1992).

[4] P. Ordejón, D. Drabold, R. Martin and S. Itoh, Phys Rev. Lett. **75**, 1324 (1995).

(Pablo Ordejón)

3.2 Reports on Workshops

Report on the Workshop

Electronic and Magnetic Properties of Oxides and their Surfaces - Theory and Experiment -

Supported in part by the EU HCM Ψ_k-Network on "Ab-initio (from electronic structure) calculation of complex processes in materials"

General Information on the Halle Workshop

The workshop was held from December 4 to December 6 in Halle, Germany. The workshop was organized by the Department of Physics, Martin-Luther-University Halle-Wittenberg (*W. Hergert*) and the Max-Planck-Institut für Mikrostrukturphysik Halle (*W. Hübner*).

The aim of the workshop was to bring together theorists and experimentalists, working in this field, to discuss the state of the art in calculating electronic, magnetic and optical properties of clean and modified oxide surfaces as well as the present status of experimental studies of such systems. The main topics of the workshop have been:

- magnetic and magneto-optic properties of transition metal (TM) oxide surfaces
- real structure of TM oxide surfaces
- electronic structure and correlation effects
- properties of TM oxide clusters
- ultrafast electron and spin dynamics in TM oxides
- ferroelectricity

24 colleagues from outside of Halle took part in the workshop coming from Germany, France, UK, USA, Italy, Finland, Spain and Russia. About 60 physicists attended the workshop. 22 talks have been given (10 talks about experimental techniques and results, 12 talks about theory).

H.-J. Freund discussed the geometric and electronic structure of oxide surfaces. The problems of the application of standard surface analysis techniques like electron scattering and electron spectroscopy have been discussed in detail.

Central topic of the discussion in the thoretical talks was the correct description of correlation effects in oxides.(*Lichtenstein, Manghi, Temmerman, Terakura*) The LDA-SIC approach as well as the LDA+U approach have been discussed and compared.

An overview about the magnetic properties of transition metal clusters and oxide clusters has been given at the beginning of the workshop (*P. Jena*). The relationship of properties of free and supported clusters has been discussed in detail by *S. Nayak*. Ab initio molecular dynamics methods have been used to study systems containing boron, carbon, nitrogen, oxygen, silicon and mixtures of them (*G. Seifert*). The modification of oxide electronic structure with its stoichiometry ($Li_{4+p}O_2$) has been reported by *C. Noguera*.

Bulk properties (lattice instabilities, *A. Postnikov*) and surface properties (reconstruction, magnetism *Wang*) of perovskite type crystals have been investigated. *Wang* presented an extensive study of the surface geometry of the Fe_2O_3 (0001) surface. The calculations are done in the framework of DFT-GGA using the FP-LAPW method. Differently terminated surfaces are compared.

Experimental techniques have been discussed from the theoretical point of view (spin-pol. photoelectron diffraction, *P. Rennert*) or with respect to the application to special systems. The use of magneto-optic effects (*Fröhlich, Oepen Veenstra*), spin polarization analysis (*Oepen*) and x-ray spectroscopy (*Dräger*) has been discussed in special talks.

STM investigations of oxide surfaces have been repoted by (*M. Heiler*) (CoO on Ag(100) and Au(100) and (*G. Schmitz*) (β-Ga_2O_3 on CoGa(001)).

Problems of spin dynamics have been addressed in a theoretical talk by *W. Hübner*. *J.-Y. Bigot* has shown experimental results about an optically induced demagnetization of ferromagnetic systems in the subpicosecond timescale.

Ferroelectric properties have been discussed in two talks. The properties of epitaxial ferroelectric thin films have been discussed by *A. Pignolet*. *H. Beige* has demonstrated how methods of nonlinear dynamics can be used to study structural phase transitions in ferroelectric materials.

The success of the workshop and the increasing interest in the magnetic properties of oxide surfaces at the MPI für Mikrostrukturphysik Halle and the Martin-Luther-University Halle-Wittenberg encourage the organizers to organize such workshops also in the future.

(W. Hergert)

Abstracts of the Talks

- **Magnetism at the Nanoscale**

  Puru Jena, Virginia Commonwealth University, Richmond

  Materials at the nanoscale possess many unique structural, electronic and magnetic properties. This is brought about by their reduced size, unique geometry, low coordination and large surface-to volume ratio. Atomic clusters constitute the ultimate nanostructured materials. The ability of researchers to synthesize and characterize atomic clusters and nanoparticles with precise size and composition has given rise to the possibility that a new class of materials with tailored properties could be made by assembling these particles in ordered arrays. This talk will provide a brief overview of the salient parameters that govern magnetism at the nanoscale. We will ilustrate not only how magnetic moments of clusters of ferromagnetic transition metal elements get enhanced over their bulk value, but also how otherwise paramagnetic and antiferromagnetic systems exhibit ferromagnetism in the cluster phase. Examples will include clusters of V, Mn, Fe, Co and Ni as well as oxides of Mn and Ni. We will also demonstrate that interaction of clusters and multilayers with hydrogen, nitrogen, and substrate can influence their ambient magnetic order. All our results are based on first priciples state-of-the-art calculations that have predictive capability. It is argued that an indepth understanding of the evolution of magnetism from clusters to crystals can lead to the synthesis of new nanoscale magnetic materials. This can have potential impact on the technology of the future as man strives to build small and faster electronic, magnetic and optical devices.

- ### Geometric and Electronic Structure of Oxide Surfaces

  H.-J. Freund, Fritz-Haber-Institut der Max-Plack-Gesellchaft, Berlin

  The surfaces of various oxides, such as $Cr_2O_3(0001)$ and NiO(100), has been investigated with electron scattering to probe the geometric structure and with electron spectroscopy to study the electronic structure. While the work has mainly been performed on epitaxially grown thin metal oxide films, some properties of the thin films have been compared with those found for bulk single crystal oxide surfaces. By adsorbing and desorbing probe molecules onto those film and single crystal surfaces the defect structure of the surfaces may be studied in thermal desorption experiments.

- ### Application of Spin-polarized Photoelectron Diffraction and Auger Electron Diffraction to investigate Transition Metal Oxides

  P. Rennert, L. Niebergall, and A. Chassé, Martin-Luther-Universität Halle-Wittenberg, Halle

  The theory of photoelectron diffraction has been extended to include spin polarization and dichroism. Relations between spin-up and spin-down intensities are discussed, which follow from the symmetry properties of surfaces. The spin polarization is caused due to the spin-orbit interaction and the interference of the different final state channels.[1]

  Calculated spin-polarized photoelectron spectra are shown for the iron oxide magnetite grown on Pd. A straightforward way to investigate the magnetic properties from these spectra is derived.

  Multiplet splittings of core-level binding energies may be used to produce photoelectron peaks with high spin polarization.[2] In this case we have an internal source of highly-polarized photoelectrons whose spin orientation is known with respect to the magnetic moment of the emitting atom. No external spin detector is required and meaningful measurements might be carried out above the Curie or Néel temperatures of ferromagnets and anti-ferromagnets, respectively. Theoretical results are discussed for manganese and cobalt oxide. It is shown that this method may be used to probe short-range magnetic order over a range of a few bond distances.

  If it is possible to separate Auger spectra for a singulett and a triplett hole pair, respectively, we have an internal spin-polarized electron source and we may investigate the magnetic structure of the sample. Results are discussed for Cr and its oxide.

  1 P.Rennert, W.Mück and A.Chassé, Phys. Rev. B53 (1996) 14262.

  2 B.Sinković, D.J. Friedman and C.S. Fadley, J. Magn. Magn. Mat. 92 (1991) 301, and references therein.

- **Nonlinear-nonreciprocal Spectroscopy in Antiferromagnets**

  D. Fröhlich, Universität Dortmund, Dortmund

  Magnetic ordering leads to time-noninvariant susceptibility tensors (c-tensors) in addition to the time-invariant tensors (i-tensors) in the paramagnetic phase. By the nonlinear optical method of second-harmonic generation c- and i-tensor contributions and their interference are studied with different experimental methods. We will present new results of nonlinear phase spectroscopy and domain topography on Cr_2O_3, $YMnO_3$, and $LiNiPO_4$.

- **Investigations of the magnetic properties of thin film oxides**

  H.P. Oepen and C. Teichert, Max-Planck-Insitut für Mikrostrukturphysik, Halle

  The potential of the Scanning Electron Microscope with Polarization Analysis (SEMPA) and the magneto- optic Kerr effect (MOKE) to investigate magnetic properties of thin film oxides will be discussed and first results presented. The contrast mechanism of the SEM PA technique and the correlation to the electronic structure of the sample will be worked out. Preliminary results of the analysis of domain structures in natural magnetite will be shown. Strong magnetic contrast could be achieved only after covering the sample with a Co layer. The influence of the ferromagnetic layer on the magnetic microstructure is critically reviewed.First MOKE results have been obtained for spinel films in a thickness range of around 100 nm. By reactive growth epitaxial Fe-Mg-O spinel films on (100) MgO have been created [1]. Strong dependencies of the magnetization curves on composition have been found. Due to different optical response a decrease of the Kerr ellipticity is found with increase of $MgFe_2O_4$ content. Besides that a strong change of the magnetic behavior becomes obvious from the magnetization curves. The sensitivity of the MOKE set up and fields of applications will be discussed.

  [1] S. Senz, A. Graff, C. Teichert, M. Zimnol, H. Sieber, S.K. De, H.P. Oepen, D. Hesse, J. Kirschner, U.M. Gösele, Mat. Res. Soc. Symp. Proc. 474 (1997), in press

- **The Surface Geometry of α-Fe_2O_3 (Hematite) (0001)**

  Xiao-Gang Wang, Matthias Scheffler, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

  The chemical reactivity of solids is well known to be largely determined by the surface electronic structure, where the latter is closely correlated with the atomic geometry. Therefore (in particular for semiconductors and metals) the identification of surface geometries has been (and still is) an important subject of surface science.

  Despite the importance of metal oxides for several profitable industrial processes, good quality studies of surface geometries of these systems are scarce. Experiments are very complicated, and in theoretical studies substantial difficulties arise because the interesting metal oxides involve $3d$ transition metals as well as oxygen which implies significant charge transfer, a highly corrugated electron density, strong electrostatic fields, and even magnetism. The strong electrostatic fields suggest that relaxations and reconstructions could be significant, and thus large super-cells are required for good quality calculations. In fact, such studies only became possible by recent improvements of the computational methods [1].

Motivated by the previous work [2] we decided to study a corundum-type oxide surface Fe_2O_3 (0001). The structure of Fe_2O_3 (0001) can be described in terms of a stacking of layers: O_3-Fe-Fe-O_3-Fe-Fe- $\cdots$. The surface geometry of the flat surface was unclear and even the surface stoichiometry (be it e.g. O_3, or Fe or Fe-Fe) was not known.

Using density-functional theory (DFT-GGA) and employing the FP-LAPW method [1] we have calculated the surface energies and structural relaxations of all (1×1) α-Fe_2O_3 (0001) surfaces. These results are analyzed with respect to the atomic chemical potential, which might be tuned in experiments by the O_2-gas pressure.

The results clearly show that normally the Fe terminated surface, Fe-O_3-Fe-Fe-O_3- $\cdots$, is energetically favorable. Under strongly oxygen-rich conditions, an oxygen terminated surface, O_3-Fe-Fe-O_3- $\cdots$, becomes possible.

For the Fe terminated surface, we find that the first Fe layer encounters a large inwards relaxation ($\approx$ 55%). For the subsurface O_3 layers, we find a reconstruction which has not been reported so far for corundum-type metal oxides: a small in-plane rotation.

[1] B. Kohler, S. Wilke, M. Scheffler, R. Kouba, and C. Ambrosch-Draxl, Comput. Phys. Commun. **94**, 31 (1996); M. Petersen, F. Wagner, and M. Scheffler, in preparation.

[2] M. Ritter, H. Over, and W. Weiss, Surf. Sci. **371**, 245 (1997);
Th. Schedel-Niedrig, W. Weiss, and R. Schlögl, Phys. Rev. B **52**, 17449 (1995).

• Electronic and structural properties of thin layers of CoO on Au(111) and Ag(100)

M. Heiler, I. Sebastian, K.-M. Schindler, H. Neddermeyer, Martin-Luther-Universität Halle-Wittenberg, Halle

Ordered thin films of transition metal oxides have become an interesting subject in surface science since their properties are widely unknown and they may be used as model substrates. Following our experimental work on NiO on Au(111) and Ag(100) [1] we have studied the growth of CoO layers on the same substrates. Due to the slightly larger lattice mismatch of ideal CoO on these substrates in comparison with NiO and due to the differences in the number of valence electrons of both oxides, differences in their structural properties and electronic states might be expected. As experimental methods we used angle-resolved UV photoelectron spectroscopy (ARUPS), Auger electron spectroscopy, low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM). Thin layers of CoO were prepared by deposition of Co from an effusion cell in an O2 atmosphere onto Au(111) and Ag(100). The substrate temperatures during deposition were varied between room temperature and 600 K. According to LEED at 300 K epitaxial CoO(111) is formed on Au(111). UV photoemission (hn=3D21.2 eV) then shows 4 peaks which are assigned to emission from O- and Ni-related states, respectively. For CoO/Ag(100) we obtained epitaxial CoO(100) layers by deposition at 500 K. In ARUPS the O-related transitions show distinct dispersion with the polar angle of emission in contrast to the Co-related peaks. In general, photoemission from a thick (monolayers of Co) CoO(100) film is in agreement with previous results from bulk CoO(100) [2] indicating that indeed stoichiometric CoO has been formed by this kind of preparation. Surprisingly, at low coverages (below 2 monolayers of deposited Co) the films are not yet fully oxidized as can be concluded from ARUPS which still shows emission at the Fermi level from Co metal. STM essentially confirms the growth of CoO(111) layers on Au(111) (CoO/Ag(100) has not yet been studied by STM). In contrast to NiO(111), thin films of CoO(111) grow with the bulk lattice parameter in registry with the substrate as can be conluded from the Moir=E9 pattern on the CoO islands. In case of NiO(111) we observed the formation of a 2x2 reconstruction (previously assigned to an octopolar reconstruction) due to the polar nature of the (111) surface of the oxide. Absence of such a reconstruction for CoO(111) could in principle be explained by OH-termination of the surface.

[1] Th. Bertrams et al., Appl. Surf. Sci. 75, 125 (1994). [2] Z.-X. Shen et al., Phys. Rev. B 42, 1817 (1990).

- **Simulations of growth processes on surfaces with methods of QMD**

  G. Seifert, Technische Universität, Institut für Theoretische Physik, D–01062 Dresden, Germany

  For the *ab initio* or nearly ab initio description and prediction of growth processes on an atomistic level the methods of Quantum Molecular Dynamics (QMD) based on the Density-Functional-Theory (DFT) are very powerful tools. Within the framework of a very efficient local orbital DFT-QMD treatment - the DFT based "Tight-binding" scheme - one can simulate for example the elementary steps of homo- and heteroepitaxial growth processes. The parallelization of the computer allows now the consideration of more than 1000 atoms in QMD simulations. The method has been proofed to give reliable results for systems containing a series of elements, as among others boron, carbon, nitrogen, oxygen, silicon and mixtures of them.
  Applications to diamond growth and Si-C heteroepitaxial growth will be shown.

- **Structure and Properties of Oxide and Supported Clusters**

  S. Nayak , P. Jena*, V.S. Stepanyuk†, W. Hergert†*
  ** Virginia Commonwealth University, Richmond, Virginia, U.S.A.,*
  † FB Physik, Martin-Luther-Universität Halle-Wittenberg, Halle

  Despite considerable work on clusters in the past two decades, little emphasis has been placed on the understanding of clusters interacting with reagent molecules such as O_2 or with substrates. Yet, these problems are important not only because they can provide a molecular level understanding of the evolution of atomic and electronic properties in systems which are either covalently or ionically bonded. Similarly for clusters to be used as materials they need to be deposited on surfaces or isolated in matrices. Understanding the interaction of the clusters with substrate atoms is, therefore, of fundamental importance since both the electronic and structural properties of clusters might be substantially influenced. This talk will focus on our recent work that addresses these issues. We will demonstrate that clusters of Sb_xO_y and Si_xO_y ($x \leq 8, y \leq 16$) bear the signature of bulk behaviour at very small sizes, while clusters of MnO are very different from bulk MnO - the former are ferromagnetic while crystals of MnO are anti-ferromagnetic. Mn clusters supported on noble metal surfaces also exhibit magnetic bistability. Unlike any other element in the periodic table, the clusters of Mn, whether they are free or interacting with

O_2 and/or surface, retain their atomic like magnetic moment. Possibilities of using these small clusters in the design of novel electronic, magnetic and optical properties will be discussed.

- **Non-stoichiometry-induced metallicity in oxides: an ab initio study**

F. Finocchi and C. Noguera, Laboratoire de Physique des Solides, associé au CNRS Bât. 510, Université Paris-Sud, 91405 Orsay (FRANCE), and J. Goniakowski CRMC2, associé au CNRS Campus de Luminy, 13288 MARSEILLE Cedex 9 (FRANCE)

Non-stoichiometry in oxides or oxidation of metals are important processes often related with profound modifications of the electronic properties, potentially useful for technological applications. By means of a combination of ab-initio Molecular Dynamics simulations and band-structure total-energy techniques, we have studied the modifications of an oxide electronic structure with its stoichiometry. We will illustrate them by two examples: unsupported lithium oxide clusters $Li_{4+p}O_2$, bearing an increasing number p of excess lithium atoms, and MgO(100) surfaces with an increasing density of oxygen vacancies in the surface layer. We will focus on the degree of localization of the excess electrons and on the coexistence between ionic and covalent bonds in these systems, and on their consequences on physical properties.

- **Lattice Distortion, Orbital Ordering and Magnetism in Perovskite Transition-Metal Oxides**

K. Terakura[*], *I. Solovyev*[†] *and H. Sawada*[†]
[*]*JRCAT, National Institute for Advanced Interdisciplinary Research, 1-1-4 Higashi, Tsukuba, Ibaraki 305, Japan,* [†]*JRCAT, Angstrom Technology Partnership, 1-1-4 Higashi, Tsukuba, Ibaraki 305, Japan*

The transition-metal oxides (TMO) with the perovskite structure exhibit a variety of interesting phenomena with regard to dielectric properties, magnetic properties and transport properties. Among them, the colossal magnetoresistance (CMR) is one of the most actively studied phenomena in recent years. There are basically two important aspects in the theoretical studies of the related materials. First, it is generally believed that the electron correlation effects will be crucial in these oxides and therefore it is an important task for us to check the adaptability of our theoretical tools, LSDA, GGA and their modifications. Second, one of the unique features of the related materials is the important role of the orbital degree of freedom. In the materials which exhibit CMR, we have often not only the magnetic ordering but also the orbital ordering and charge ordering.

We have studied these two aspects with a new version of the LDA+U method based on the LMTO-ASA and also with the first-principles molecular dynamics method using the plane-wave basis [1-6].

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1995), p.95.

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3. H. Sawada, N. Hamada, K. Terakura and T. Asada, Phys. Rev. B **53**, 12742 (1996).
4. I. Solovyev, N. Hamada and K. Terakura, Phys. Rev. Lett. **76**, 4825 (1996).
5. H. Sawada, Y. Morikawa, K. Terakura and N. Hamada, to appear in Phys. Rev. B.
6. H. Sawada and K. Terakura, to be submitted to Phys. Rev. B.

• Epitaxial ferroelectric thin films of Bi-layered Perovskites deposited by large area pulsed laser deposition

A. Pignolet, C. Curran, S. Welke, M. Alexe, S. Senz, D. Hesse, U . Gösele, Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle/Saale, Germany

The last decade has seen a surge of interest in ferroelectric thin films, due to the wide range of their potential applications in microelectronics. In particular, thin films of bismuth-layered perovskites are very promising candidates for the integration in microelectronics, especially for non-volatile film memories. Pulsed laser deposition (PLD) has quickly emerged as a unique deposition technique particularly suited to produce good quality thin films of complex superconductor and ferroelectric oxides. Epitaxial thin films of the layered perovskites $Bi_4Ti_3O_{12}$ and $SrBi_2Ta_2O_9$ have been deposited by Pulsed Laser Deposition onto (100)-oriented single crystalline silicon coated with a stack of epitaxially grown buffer and oxide electrode layers of LSCO/CeO_2/YSZ deposited by PLD. This multilayer serves as a template to promote the epitaxial growth of the Bi-layered ferroelectric films. For electrical measurements, epitaxial conductive oxide electrodes such as LSCO were finally deposited on top of the multilayered structure. The thickness and composition uniformity as well as the structural and electrical properties of the epitaxial ferroelectric Bi-layered films will be presented and discussed.

• First-principles study of lattice instabilities and vibrations in perovskite-type oxides

A. V. Postnikov, R. I. Eglitis, G. Borstel, Universität Osnabrück – Fachbereich Physik, 49069 Osnabrück

Oxides of cubic perovskite structure are famous for the variety of structure distortions and phase transitions they undergo with lowering temperature, in no clear correlation with the chemical composition of the material. We study in more detail pure $KNbO_3$ that undergoes a sequence of ferroelectric transitions and $KNbO_3$ which remains cubic for all temperatures but exhibits a strong tendency towards ferroelectric transition and becomes ferroelectric on slight doping with e.g. lithium. Lattice instabilities and zone-center phonons are studied based on high-precision total-energy calculations with the use of first-principles (FP-LMTO) and semiempirical tight-binding (INDO) calculation schemes. The effect of impurities is analyzed with the use of large supercells.

The ferroelectric instability can be reproduced quantitatively with sufficient accuracy with the use of first-principles calculation schemes based on the density functional theory, but it is a hard test on the accuracy of the calculation scheme in question. Relevant technical problems of calculations done for perovskite-type oxides are discussed.

Apart from the softening of zone-center TO phonons that results in the onset of a ferroelectric state in $KNbO_3$, the spatial extent and the anisotropy of ferroelectric correlations are discussed based on the results of frozen-phonon supercell calculations, elucidating the nature (displacive vs. order-disorder) of the ferroelectric phase transition.

For Li-doped $KTaO_3$, in addition to off-center displacements and relevant energy barriers as calculated for single impurities, the interaction effects between impurities at diferent separation in crystal are discussed.

- **Determination of Orbital Symmetry and Spin Polarization by Linear Polarization Effects in X-ray Spectra**

  G. Dräger, Martin-Luther-Universität Halle-Wittenberg, Halle

A selective survey is given on polarization and direction effects in X-ray spectra which can be observed by working with single-crystal samples and taking advantage of linearly polarized synchrotron radiation. The first item deals with polarization effects in the X-ray absorption near edge structure (XANES) arising from linear dichroism and from the angular dependence of the 1s-3d quadrupole transitions. Recently obtained Ni K and Fe K spectra of Ni0 and Fe0, respectively, are reported, where we can differentiate between eg and t2g components of the empty states. In the second part the angular dependence of resonantly excited X-ray emission spectra (RXES) is considered. Analyzing the polarization and beam direction effects in the Mn $K\beta_{1,3}, \beta'$ emission of Mn0 the orbital symmetry and spin polarization of the empty Mn 3d states can be determined experimentally in a good agreement with the theoretical predictions.

- **Oxidation of Magnetic Ni(110) probed by Magnetic Second Harmonic Generation**

  K.J. Veenstra, P.E. Hansen, A. Kirilyuk and Th. Rasing, University of Nijmegen, Nijmegen, The Netherlands

Magnetization induced optical Second Harmonic Generation (MSHG) is a suitable technique for studying magnetic surfaces and interfaces due to its sensitivity for changes in the spin-dependent electronic structure at magnetic surfaces. Our measurements on Ni(110) show very strong changes of the MSHG signal upon oxidation of only 1% of a clean surface. At higher coverages the MSHG-response oscillates till the saturation coverage (1 ML NiO) is reached. The maxima and minima in the signal correspond to the oxygen induced superstuctures as observed with LEED. During exposure also the magnetic contrast is measured showing changes in the surface spin-polarized bandstructure and magnetic anisotropy for Oxygen coverages smaller than 0.1 ML.

- **Electronic structure, Magnetism and Surface States of TM-oxides**

  A.I. Lichtenstein, Forschungszentrum Jülich, I.V. Solovyev, JRCAT-ATP, Tsukuba, S.L. Dudarev, University of Oxford

Electronic structure, spin and orbital ordering of transition-metal (TM) oxides are investigated in framework of rotationally invariant LDA+U method. Strong Coulomb correlations in such antiferromagnetic Mott insulators made local density approximation inappropriate for the electronic band structure calculations. We analyzed the magnetic interactions in MnO and NiO and made comparison with the LDA results. Mechanism of orbital enhancement is also related to the screened Coulomb interactions in 3d-shell. Numerical calculations successfully explain spin and orbital magnetic ordering in FeO and CoO. The LSDA+U method has been applied to identify the origin of surface electronic states on the (100) surface of NiO. The energy of one of the surface states corresponds to the top of the valence band and the wave function of this state is predominantly localized on the oxygen surface sites. The other state is situated at the bottom of the conduction band and its wave function is localized on the nickel sites. The presence of these surface states closely related with the results of STM-experiments.

- **On-site correlation in narrow band materials**

F. Manghi, Istituto Nazionale per la Fisica della Materia and Dipartimento di Fisica, Universita' di Modena, Via Campi 213/a, I-41100 Modena, Italy

It is well established that the description of electronic states in narrow band materials - transition metals, transition metal oxides, cuprates, etc. .. - requires improvements over the single particle approximation, with a proper inclusion of many body effects associated to the on-site Coulomb interaction of localized electrons. In many of these systems the itinerant character of valence electrons which is clearly shown by the energy k-dispersion observed in photoemission spectroscopy coexists with strong local electronic correlation responsible of other observed features such as satellite structures, band-narrowing effects and opening, in some cases, of a Mott-Hubbard gap. It seems therefore necessary to combine a realistic band structure description with an accurate treatment of many body effects.

Results of a recently developed method [1] designed to treat highly correlated and highly hybridized systems will be presented: the single-particle band states are determined in a localized basis - either ab-initio LMTO or semi empirical Tight Binding - and used as input mean-field eigenstates for the calculation of self-energy corrections according to a 3-body scattering solution of a multi-orbital Hubbard Hamiltonian. Self-energy corrections, spectral functions and quasiparticle spectra for nickel, NiO and $CuGeO_3$ will be reported. The calculated quasi-particle spectra show a remarkable agreement with photoemission data in terms of band width, k-dispersion, exchange splitting and satellite energy position. The correct insulating behavior of NiO and $CuGeO_3$ is also reproduced.

[1] Manghi F. Calandra C., Ossicini S., Phys. Rev. Lett. 73, 3129 (1994); Manghi F. Bellini V., Arcangeli C., to appear on Phys. Rev. B (1997)

- **Applications of Self–Interaction Corrections to Localized States in Solids**

W.M. Temmerman[(a)], *Z. Szotek*[(a)], *A. Svane*[(b)], *H. Winter*[(c)], *S.V. Beiden*[(d)] *and G.A. Gehring*[(d)]

[(a)] *Daresbury Laboratory, Warrington, WA4 4AD, UK;* [(b)] *Institute of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus C, Denmark;* [(c)] *Forschungszentrum Karlsruhe, INFP, Postfach 3640, Karlsruhe, Germany;* [(d)] *Physics Department, University of Sheffield, Sheffield, UK*

The local–spin–density (LSD) approximation to density functional theory provides a simple and rather successful scheme for describing many interacting electrons in a solid. There exist, however, important cases where electron correlations are too strong to be properly treated within the LSD. Prominent examples are the high–temperature superconductors, the 3d transition metal oxides and the rare earths such as Ce and Ce compounds. In this contribution we will argue that the self–interaction corrected local spin density (SIC–LSD) approximation is a physical transparent and accurate scheme to improve the LSD for Coulomb correlated systems. For NiO, we will make a comparison of this scheme with the LDA+U method. We will demonstrate that the relativistic generalisation of the SIC-LSD provides a bridge between the atomic and band pictures by showing that all three Hund's rule are fulfilled in elemental Ce. The use of parallel platforms is essential to study the more complex systems which give rise to Hamiltonian matrices with dimensions higher than 50: parallellization over k-points in the Brillouin zone integration is the most efficient strategy.

- **Theory of femtomagnetism in metals**

W. Hübner[1,2] *and G. P. Zhang*[2]
[1] *Institut de Physique et Chimie des Materiaux de Strasbourg, Unite Mixte 380046 CNRS-ULP-EHICS, 23, rue du Loess, 67037 Strasbourg Cedex, France,* [2] *Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany*

The spin dynamics in Ni is studied by an exact diagonalization method on the ultrafast time scale. It is shown that the femtosecond relaxation of the magneto-optical response results from exchange and spin-orbit interaction. Each of the two mechanisms affects the relaxation process differently. We find that the intrinsic spin dynamics occurs during about 10 fs while extrinsic effects such as laser-pulse duration and spectral width can slow down the observed dynamics considerably. Thus, our theory indicates that there is still room to accelerate the spin dynamics in experiments.

- **Study of structural phase transitions and characterization of ferroelectric materials by methods of nonlinear dynamics**

M. Diestelhorst and H. Beige, Martin-Luther-Universität Halle-Wittenberg, Fachbereich Physik, Friedemann-Bach-Platz 6, 06108 Halle/Saale, Federal Republic of Germany

It is well known that the structural phase transitions in ferroelectric materials are connected with strong nonlinear properties. So we should expect all features of nonlinear dynamical systems such as period-doubling cascades and chaotic behaviour in a dynamical system that contains a ferroelectric material.

The experimentally investigated nonlinear dynamical system is a series resonance circuit, consisting of a linear inductance and a nonlinear capacitance. Different ferroelectric materials (crystals, liquid crystals, and thin films) have been used as a nonlinear capacitance.

Analysis methods of the nonlinear dynamics for dissipative chaotic systems (e. g. phase portrait, Fourier spectra, correlation dimension, and Lyapunov exponent) are used for the study of structural phase transitions and for the characterization of the large-signal behaviour of ferroelectric materials. In particular, the comparison of calculated and experimentally recorded phase portraits gives information about the nature of the nonlinear dielectric properties and the active physical mechanisms.

Furthermore, it is shown that by a small perturbation of an external control parameter the chaotic behavior of the ferroelectric system can be switched over to a regular motion by stabilizing one of the many regular states of the system.

- **Spin Dynamics in CoPt3 alloy films**

  J.-Y. Bigot, E. Beaurepaire, V. Halte, J.-C. Merle, IPCMS Strasbourg

Recently it has been shown that it is possible to optically induce a demagnetization in ferromagnetic systems in the subpicosecond timescale (1,2). So far only partial demagnetization of about 50 percent could be obtained. During this workshop we will report on recent measurements in CoPt3 alloy films with perpendicular anisotropy that show a complete demagnetization during the laser pulse excitation (100 fs). The switching behavior of the sample will be discussed in detail.

(1) Beaurepaire, Merle, Daunois, Bigot Phys. Rev. Lett. 76, 4250 (1996)

(2) Holfeld, Matthias, Knorren, Bennemann Phys. Rev. Lett. 78, 4861 (1997)

- **Elemental steps in the growth of thin, crystalline β-Ga_2O_3 films on the CoGa(001) surface - studied by EELS and STM**

  G. Schmitz, M. Eumann, and R. Franchy, Institut für Grenzflächenforschung und Vakuumphysik, Forschungszentrum Jülich GmbH, D-52425 Juelich, Germany

With a new UHV-apparatus in which EELS, STM, LEED, and AES are in-situ combined, we have studied the elemental steps of the oxidation of the CoGa(001) surface in the temperature region between 300 and 700 K. At 300 K and low O_2 exposure, oxygen atoms are chemisorbed on defects and on steps of the clean surface terraces. For higher exposure up to saturation, the nucleation of an amorphous Ga-oxide film is observed. The EEL spectrum of the amorphous film exhibits two losses at 380 and 675 cm-1. After annealing the amorphous Ga-oxide films at 700 K or by oxidation directly at 700 K, thin and well-ordered β-Ga_2O_3 films are formed. EEL spectra of the β-Ga_2O_3 films show intense Fuchs-Kliewer (FK) modes at 306, 455, 645 and 785 cm-1 in good agreement with calculated spectra using the IR parameters of Ga_2O_3. The band gap of the β-Ga_2O_3 films was determined to be 4.5 +/- 0.2 eV. In addition, a gap state at 3.3 eV was found. The observed LEED pattern of β-Ga_2O_3/CoGa(001) can be explained by a (2x1) structure in two perpendicularly oriented domains. STM images with atomic resolution confirm the two domains structure and allow the determination of the two dimensional lattice parameters of β-Ga_2O_3. At 700 K and low oxygen exposure, the oxide grows in long, perfectly ordered islands of rectangular shape with a width of only a few lattice constants depending on exposure. The islands start to grow at step edges of the clean surface and are oriented along the [100] and [010] directions, respectively, corresponding to two domains. EEL spectra of these islands already exhibit the characteristic losses of β-Ga_2O_3.

Participants of the Workshop (coming from outside of Halle)

I. Batyrev	Queen's University of Belfast, Belfast (Northern Ireland)
E. Beaurepaire	IPCM, CNRS, Strasbourg, Strasbourg (France)
O. Bengone	IPCM, CNRS, Strasbourg, Strasbourg (France)
J.-Y. Bigot	IPCM, CNRS, Strasbourg, Strasbourg (France)
P.H. Dederichs	IFF, Forschungszentrum Jülich, Jülich (Germany)
H.-J. Freund	FHI der Max-Planck-Gesellschaft, Berlin (Germany)
D. Fröhlich	Universität Dortmund , Dortmund (Germany)
P. Jena	Virginia Commonwealth University , Richmond (U.S.A.)
A.A. Katsnelson	State University Moscow, Moscow (Russia)
K. Kokko	University of Turku , Turku (Finland)
A.I. Lichtenstein	IFF, Forschungszentrum Jülich, Jülich (Germany)
F. Manghi	Universita di Modena , Modena (Italy)
S. Nayak	Virginia Commonwealth University, Richmond (U.S.A.)
C. Noguera	Universite Paris-Sud, Orsay (France)
V.V. Pavlov	Universität Dortmund, Dortmund (Germany)
A. Postnikov	Universität Osnabrück, Osnabrück (Germany)
M. Scheffler	FHI der Max-Planck-Gesellschaft, Berlin (Germany)
G. Schmitz	IGF, Forschungszentrum Jülich, Jülich (Germany)
G. Seifert	Technische Universität Dresden, Dresden (Germany)
W. Temmerman	Daresbury Laboratory, Warrington (U.K.)
K. Terakura	Nat. Inst. for Adv. Interdisciplinary Res., Tsukuba (Japan)
Xiao-Gang Wang	Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin (Germany)
A. Vega	University of Valladolid , Valladolid (Spain)
K.J. Veenstra	University of Nijmegen, Nijmegen (The Netherlands)

3.3 Final Report on the HCM Network Activity

Final Report
1 January 1994 - 31 December 1997

HCM Ψ_k-Network on
Ab initio (from electronic structure) calculation of complex processes in materials

Contract Number: CHRXCT930369

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

Preamble

This Network has been 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 aim of the Network was 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. The main objective of the Network was to jointly develop, share and disseminate electronic structure techniques, including the writing of shared computer codes.

Such was the succes of the Network's bimonthly newsletter that nearly 600 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 the Network's activity was the conference that took place in Schwäbisch Gmünd on 17–21 September, 1996. It was attended by 319 scientists active in the field of *ab initio* electronic structure calculations.

Wider benefits and perspectives

This Network has resulted in a remarkable achievement. Our subject has been growing in scientific maturity and extent very rapidly over the last 15 years, and particularly the last 4 years covered by the Network. The achievement is that this development in Europe has been on a European basis rather than a national one, which has contributed greatly to the quality of the work and to its growth in many new small groups across Europe.

There have been plenty of activities and results obtained in the Network as the following pages will show. But in addition the Network has also sown very many seeds which we can see growing but whose fruits lie in the future. Two of these are the TMR Networks: on **'Interface Magnetism'**, in operation for over a year, and on **'Electronic structure calculations of materials properties and processes for industry and basic sciences'**, to start presumably on March 1, 1998. It takes a lot of trust and harmonisation for groups to devote substantial time, money and precious computing resources to close collaborations, but several of the major groups have reached that stage as a result of working together in the HCM Network. The two TMR Networks are therefore a direct result of the groundwork laid by the HCM Network.

The same remarks apply to the proposal for a 'Programme' submitted to and now approved by the European Science Foundation to expand geographically to the whole of Europe the kind of work done by the HCM Network. The HCM Network was set up as an unusually wide one, with 40 original nodes and many more associated groups and individual researchers. That has turned out to have been the right decision, in order to build a cohesive European scientific community in our field as mentioned above. We are very hopeful that the ESF Programme will foster further the European cohesiveness and maintain the benefits that derive from it for both large and small groups.

Due to many workshops and regular management board meetings close interactions and very good personal relations between the group leaders of the major European groups developed. As a consequence many cooperations across borders have started. Even more important was that the Network Management Board members started to feel and act like members of one European family, as such taking over the responsibility for the electronic structure community in Europe. An outcome of this was the organisation of the first International Conference devoted entirely to Electronic Structure Calculations which took place in Schwäbisch Gmünd on 17-21 September, 1996.

Another outstanding success that will long outlive the present Network is the Ψ_k-Newsletter. This now goes out electronically to nearly 600 email addresses some of which represent whole groups. When the Network started, there was not even an address list of researchers in our field. Now the Ψ_k-Newsletter is the medium for advertising jobs, publicising one's latest results, announcing workshops and conferences in our subject not only in the Network, describing scientific highlights obtained in Europe, as well as containing all the activities of the Network. This Newsletter perhaps more than anything else has created a cohesive European community of researchers in our field where previously there had been many rather isolated individuals and some largely national connections.

But research in our field ultimately comes down to individuals, and by 'the seeds that have been sown' we also mean the very many personal contacts that have been established through people meeting at the Network workshops and training weeks. Across Europe we see people now consulting one another about technical questions, trying one anothers codes, and sending their students and postdocs for further experience, in the way that is common across USA.

People simply do not do that sort of thing unless there has been some personal contact and trust established. That is why the importance of the workshops, training sessions, Network Board meetings and the big conference in Schwäbisch Gmuend far transcends the immediate results achieved. Such collaborations do not figure in our report if they then did not involve further Network money, and in any case most of the results will be harvested in the future.

In the same vein we can point to the benefit of many individual discussions and swapping of experience and ideas below the level of actual collaborations, that have come out of the above contacts. These also have not involved any specific additional Network funds and so are not reported here.

It is important to appreciate one technical aspect of our science to understand the importance of the European dimension. Our subject is like a web, with many cross connections in all directions. There is a unifying framework but not a single computer code or bag of tricks. For example one researcher working on magnetism may need to consult another group doing calculations about chemical catalysis on surfaces, because they both encounter a particular problem relating to metals (as distinct from insulators and semiconductors). Thus one nation is too small a unit for having available all the necessary experience.

A brief summary of the type of science in the Network and what has been achieved

Much of the important behaviour of materials involves processes at the atomic level, where the atomic structure or movement of atoms is crucial. This includes all of chemistry, including catalysis at surfaces and in zeolites, all of magnetism and much else of materials science. The computer simulation of such processes is not new. What is new is a proper account of the bonding between atoms and magnetic, etc., state in the atoms. This is achieved through solving the quantum mechanical Schrödinger equation for the whole system being simulated in the computer at every step of the process. This daunting task has become possible to a useful accuracy through the growth of computer power coupled to very sophisticated theoretical and computational developments.

The subject has seen a very rapid expansion during the period covered by the Network, both in the development of the techniques and in their ever widening range of applications. These now include even some in biochemistry and in mineralogy, as well as the physics, chemistry and materials science (including surface science) mentioned above. The Network has particularly fostered such developments and sharing the experience of what works and what does not around Europe. We have also seen a growth in the number of calculations directed at technological problems, not many yet but a noticeable growth in number and variety. The new TMR Network on **'Electronic structure calculations of materials properties and processes for industry and basic sciences'** is directed specifically at expanding those.

To cater both for the speed of development and the speed of expansion, the training courses or training workshops have been an outstanding success of the Network, and have met a real need.

In total 24 of these have been held during the course of the Network, usually lasting a few days each. Because of the sophistication and variety of the techniques, these have been especially important for spreading best practice around Europe and disseminating the most up-to-date computer codes with training in their use. Otherwise, as with so much of computing, it is a case of 'garbage in, garbage out'. With a proper sharing of expertise it is possible for researchers to do first class work even in small groups and isolated places, and it has been a particular emphasis of the Network to help achieve that.

To cover all the types of material and process requires a variety of computer codes and special tricks. There is an overall uniting methodology, namely the Density Functional Theory formulation of quantum correlation with or without a variety of Generalised Gradient Corrections. However beyond that different types of code or approximation are appropriate for particular types of material, e.g. random alloys, semiconductors, magnetic multilayers, systems with hydrogen bonds, etc., and for particular processes e.g. nuclear magnetic resonance as a diagnostic tool depending on electric field gradients. The list of special tricks is endless, and they often cut across other divisions, e.g. the use of supersoft pseudopotentials or methods to speed convergence of recalcitrant metallic systems.

It is this diversity of very sophisticated codes and tricks that makes it so important to have a European-wide cohesive scientific community in order for us to achieve first class science.

Some scientific highlights are included at the end of this Newsletter, but the scope of the work can be gauged from the outstandingly successful Network conference held during September 17-21, 1996, in Schwäbish Gmuend, attended by 319 participants. The programme required up to three parallel sessions to cover 37 subject topics, and there were 53 invited speakers, plus 235 oral and poster contributed papers.

Management of the Network

Doubts had originally been expressed by the EU Commission about how such a large Network of 40 nodes and more associated groups could be effectively managed and how one could collaborate in such a large unit.

As already indicated above, the large Network turned out to be the right vehicle for stimulating the development of the subject across Europe and to cater for the diverse cross connections in our subject.

But tight management was needed and was maintained in the following way.

1. The scientific field was divided into 11 major areas of collaboration called Working Groups, each with a group leader. Six of these were devoted to technical developments, five were concentrated on leading edge projects, and the remaining one on the large systems.

2. The Network Management Board of 22 members has been quite large, to include the leaders of the ten Working Groups and representatives of all major countries. Most Board members wore two or more hats, including acting as chairman, deputy chairman, coordinator,

treasurer and Newsletter editor.

3. Only two Board meetings per year were needed because there was continuous email contact within the Board as well as within the Network as a whole (e.g. to share interests and initiate collaborations).
4. Small decisions were reached very fast with a time limit set at 2 weeks, particularly regarding requests for money for individual collaborations. This was achieved through the use of email and the special responsibility of the relevant Working Group leader and the national representative to vet the quality of the proposed science and control the Working Group delegated budget. We are really rather proud of how quickly, effectively and non-burocratically this functioned.
5. A large fraction of each Board meeting was devoted to scientific discussion of the latest issues and ideas, which helped to achieve a high attendance of Board members and to keep in focus that our raison-d'etre was high quality science.
6. The circulation of the Newsletter every two months achieved excellence communication with the Network members, and could be supplemented by extra messages in between through the same email list.

Statistical Summary

Here we briefly summarize the outcome of the Network activity.

- **24** newsletters with average 60-70 pages each of scientific and informational content
- **6** hands-on computer codes training courses [5 days each]
- **18** workshops organized or co-organized [2-6 days]
- **253** participants supported to attend workshops/meetings
- **8** secondments (one month or more)
- **14** collaborative visits (two weeks or more, but less than a month)
- **57** collaborative visits (less than two weeks)
- **133** publications acknowledging the network, but many more were published in collaboration, however, without use of the Network money
- **8** Network Management Board meetings with scientific discussions
- **3** major computer codes widely shared within the Network, and many more less widely used, but also developed or disseminated in collaboration within the Network
- **1** large network conference with 319 participants and 288 contributions, 158 participants receiving financial support
- **7** supported visiting scientists/consultants (from outside the Network) to workshops and meetings.

4 News from the TMR1 Network

Report of TMR-Network: "Interface Magnetism"

This Network is concerned with ab initio calculations of magnetic properties of surfaces, interfaces and multilayers. The Network is structured around 6 projects with 6 partners in the UK, Germany, France, Austria, the Netherlands and Sweden contributing. While initially it was difficult to find a sufficient number of good post-docs, at the end of the first year all positions were filled and we have at present 8 young researchers funded by the network. Thus at the TMR-postdoc level the network is fully operational.

The status of the different projects is as follows:

Interlayer Coupling

This Project has a post–doc based with the UK team (N. Lathiotakis from GR, since January 1997). His research sofar involved the study of alloying effect in interlayer coupling of CuNi multilayers.

The Austrian and French team started a strong collaboration on interlayer coupling, which partly involved also the Dutch and German teams. Particularly interesting results have been obtained for the effect of interface diffusion, of alloying the spacer and magnetic layers and the effects of cap layers (see the highlight further down).

The Magnetic Anisotropy and Surface Structure

This Project has a post–doc based with the Swedish team (J. Henk from DE, since April 1997). The magnetic anisotropy of ultrathin films and its dependence on film thickness and relaxation is studied by means of relativistic self-consistent total-energy calculations for the prototypical systems Ni/Cu(001) and Co/Cu(001). A second post-doc of the German team is located in Juelich (R. Abt from AT, since May 1997). He studies the energetics of magnetically stabilized surface alloys, like Mn c(2x2)/Ni(001).

Another strong effort comes form the Austrian group together with FR-participants; here the oscillatory behaviour of the magnetic anisotropy with magnetic layer thickness and thickness of the cap layer is of central interest.

Giant Magneto Resistance (GMR)

The project has a post-doc based with the Dutch team (A. Brataas from NO, starting August 1997). The work of the Dutch team consists of phenomenological models, studying the transport through magnetic/nonmagnetic interfaces in different regimes and different levels of approximation. It is accompanied by ab-initio treatments of GMR in the ballistic regimes. The milestone of the first year ("open systems") could be reached in time with calculations for non-periodic multilayers.

In parallel to these effort, calculations based on a Boltzmann approach are performed by the German team, and the Austrian groups have started an ambitious program development based on the Kubo-Greenwood formula and the coherent potential approximation.

Spin–Polarised Spectroscopies Project

The Vienna based post-doc (U. Pustogowa from DE, since September 1996) has developed the AES, XPS, XES codes (milestone after 12 months). Interestingly, one finds that the intensity spectrum in the XES is sensitive to the relative angle between the direction of the emitted photon and that of the magnetization of the specific site, thus it can, in principle, be used for the determination of the latter.

The Daresbury based post-doc (A. Ernst from DE, since January 1997) has developed a real space version of the k-resolved photoemission code. In collaboration with the Keele group a relativistic version is being developed. Furthermore, the Keele group has developed and programmed up a theory of magnetic x-ray scattering. Being a fully relativistic and first principles theory, this allows us to investigate dichroic effects and is sensitive to the local environment.

The Swedish based post-doc (J. Henk) has given strong support to experimental spectroscopy groups in Europe: (i) Prof. Güntherodt in Aachen on magnetic linear dichroism from Fe(110) (ii) Prof. Kaindl in Berlin in the study of the spin-filter effect at the Fe/W(110) interface (iii) Prof. Bauer in Clausthal-Zellerfeld by spin-polarized LEED from ultrathin Co-films on W(110)

Tight–Binding KKR-Green's Function Methods

The KKR-post-doc is located with the German team in Juelich (N. Papanikolaou from GR, December 1996 - February 1997; T. Korhonen from FI, since January 1997). The project concerned the development of a full-potential KKR method to calculate forces and lattice relaxations and resulted in three publications. Thus the "full potential" milestone of the first year has been met in time.

In parallel to this the work on developing tight-binding methods is proceeding well. Codes for the slab-, surface- and multilayer geometry are being developed and in addition the Munich-Juelich collaboration is extending the KKR-programs into fully relativistic Dirac Codes.

Real Space Tight-Binding LMTO-Method

The postdoc position of the project is based with the French team. Since no first rank candidate could be found, the position is temporarily frozen. Instead a PhD student has been taken (I. Galanakis from GR, starting June '97). A strong collaboration has been established between the Austrian and French teams on the determination of the electronic structure of complex materials by using the ab-initio TB-LMTO approach. The general scheme of the real space calculation has been developed. Particular efforts have been devoted to the inclusion of the spin-orbit interaction.

Another large effort has been brought by two PhD students, one in Strasbourg and another in Vienna, to implement a parallel computer code. Thin films of Ni on Cu(001) have been studied in order to understand surprising experimental results.

In parallel to these activities the Austrian node is permanently improving its TB-LMTO codes.

The **scientific highlight** of this Network was the discovery of the importance of the 'cap' in the oscillatory magnetic behaviour of magnetic multilayers. Suppose a particular surface of a non-magnetic metal such as Cu is covered in turn by n layers of a magnetic material (metal, such as e.g. Co), m layers of a non-magnetic metal (*spacer*), p layers of another magnetic material (metal), and finally is capped by r layers of a non-magnetic metal. Assuming that the orientations of the magnetic field in the two magnetic slabs is either parallel (ferromagnetic) or antiparallel (antiferromagnetic), the energy difference between these two types of arrangements of the magnetic fields, usually refered to as *Interface Exchange coupling*, oscillates characteristically with respect to n, m, p and r, i.e., with respect to all different types slab thicknesses. In particular the oscillations with respect to the so-called non-magnetic spacer – the metallic system, sandwiched by the two magnetic slabs, became subject of a – at the beginning controversial – heated scientific discussion. Not incorporated in the initial description was the effect of the *cap*, namely oscillations caused by a variation of the *cap thickness.* This kind of oscillations was discovered by members of the TMR network on *Interface Magnetism* and resulted in a series of three joint publications, combining in particular the Austrian, German and French nodes. Two of these publications were contributions to important Materials Science Meetings (MRS and E-MRS), the remaining one is to appear in the Oct. 1-st issue of Physical Review B.

The Network had its inauguration with a management board meeting at the Ψ_K-Network Conference in Schwaebisch Gmuend, Sept. 17-21, 1996. Part of this conference was a special symposium on Interface Magnetism which was well attended. During the reporting period two topical workshops on Network projects were organised by the participants. The **workshop** on **"Interlayer Exchange Coupling"** in Juelich, November 25-26, 1996, as well as the **workshop** on **"KKR-like Methods"** in Vienna, Febr. 15-17,1997, were very encouraging and attending by 20 and 30 network members, respectively. The first **Annual Network Meeting** took place in Bristol, April 18-20, 1997 and was accompanied by a management board meeting. This annual meeting was highly successful and was attended by **60 participants**, mostly young postdocs and PhD students of the network. A third workshop on **"Giant Magneto Resistance"** took place at Dresden, Sept. 13-14, 1997. In addition two miniworkshops on special network projects were attended by several participants ("Miniworkshop on Sparse Matrices", KKR-Project, Manchester, April 23, 1997; "Miniworkshop on Tunneling", GMR-Project, Orsay, July 9-11, 1997). More detailed information on these events was published in the past Ψ_k–**Newsletters**.

The Network has launched a home page on WWW

(http://www.dl.ac.uk/TCSC/projects/TMR/main.html),

where also all the Newsletters can be found

(http://www.dl.ac.uk/TCSC/HCM/PSIK/newsletters.html).

The interaction with the **industrial partner Philips** concerns the projects Interlayer Coupling and Giant Magneto Resistance. Two common publications with participants from AT, DE, Fr and the Philips group exist on the interlayer coupling project and the cooperation on the GMR project is just starting. The coworkers of Philips have actively participated at the workshop on Interlayer Coupling, the Annual Meeting as well as the recent GMR workshop. Thus the interaction between the network and Philips is proceeding smoothly and encouragingly.

Peter H. Dederichs
Chairman

Walter M. Temmerman
Coordinator

5 News from the TMR2 Network

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

This TMR Network is expected to start on 1st March 1998 with a duration of 4 years. Among its first activities is the **'Industry Workshop'** to initiate a new phase of the Ψ_k−Network. Its preliminary announcement follows below. Other activities of this Network include the appointment of 8 post-docs associated with each of the Network sub-projects (see below), other workshops (e.g. 'hands-on computer code' workshops on various electronic structure methods), another big conference a la Schwäbisch Gmünd (in collaboration with other networks) and of course the continuation of this Newsletter.

The 8 post-doc positions to be filled are dedicated to the following tasks (researcher in charge is also quoted with email address):

1. **Molecular processes on oxide surfaces**.
   Paris, France. Dr. E. Wimmer; ewimmer@msi.fr
2. **Self-Interaction Correction calculations on f-electron systems**.
   Aarhus, Denmark. Dr. A. Svane; svane@dfi.aau.dk
3. **Oxide interfaces and surfaces**.
   Belfast, UK. Prof. M. Finnis; m.finnis@qub.ac.uk
4. **Oxide interfaces and surfaces**.
   Keele, UK. Prof. M. Gillan; pha71@cc.keele.ac.uk
5. **Non-collinear magnetism**.
   Vienna, Austria. Prof. J. Hafner; jhafner@tph.tuwien.ac.at
6. **Molecular dynamics with LAPW**.
   Jülich, Germany. Dr. S. Blügel; s-bluegel@kfa-juelich.de
7. **Electron excitations and optical properties**.
   Helsinki, Finland. Prof. R. Nieminen; rniemine@csc.fi
8. **Superconductivity**.
   Würzburg, Germany. Prof. E.K.U. Gross; gross@physik.uni-wuerzburg.de

If you are interested in more details, please contact the researcher listed (or the Network Coordinator) for further information.

Network Coordinator
Axel Svane
svane@dfi.aau.dk

5.1 INDUSTRY WORKSHOP

on 3-4 June, 1998, in Vienna

TO INITIATE THE NEW PHASE OF Ψ_k–NETWORK

The new phase of the Ψ_k–Network is characterised by a close interaction with industry. To this end, a workshop will be held on 3-4 June, 1998, in Vienna, which will bring together leading industrial researchers with the scientists from our Network. This workshop is intended to be a forum for industrial researchers to present the current challenges involved in the development of novel materials and processes, and for the scientists of the Network to update the industrial reseachers on the most recent developments of methodologies and applications.

After the successful first phase of the Ψ_k–Network, which has culminated in the large conference in Schwäbisch-Gmünd, we are now in the remarkable position of having funding from the European Commission for a ”Training and Mobility of Researchers” (TMR) Network as well as funding from the European Science Foundation. Strictly speaking, the contract with Brussels for the TMR-2 has not been sigend yet, but it is most reasonable to assume that it will be finalised soon.

One of the underlying themes, especially of the TMR-2 project, is the interaction between the research groups of the Network with the European industry. During the past five years, we have witnessed a growing impact of electronic structure methodology in industrial research. This includes areas such as heterogeneous catalysis, the development of materials and processes in microelectronics, and materials for display and information technologies (including magnetic media). In the domain of structural materials, the control of corrosion, fatigue, and aging continues to be an extremely important technological objective. While it is clear that computational methods cannot solve these daunting problems alone, simulations on the atomistic and electronic levels are making important contributions. In fact, advanced theoretical and computational approaches - many of which are being pioneered by European research teams - together with the remarkable progress in computer technology offer unprecedented opportunities. In this context, we hope that the upcoming workshop will reflect this exciting situation and will provide a stimulating forum for the interaction between industry and fundamental research. We are looking forward to seeing you at the workshop. For the moment, keep the dates open in your calendar. Details of the registration and further information are in preparation.

For further details please contact Walter Temmerman at: w.m.temmerman@dl.ac.uk

6 News from the ESF Programme

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

Towards the end of 1996 the Ψ_k-community led by Volker Heine submitted to the European Science Foundation (ESF) a proposal for the creation of a wide open-ended ESF Programme on *Electronic Structure Calculations for Elucidating the Complex Atomistic Behaviour of Solids and Surfaces* (the text of the proposal was published as a special issue of the HCM Newsletter in November 1996). In February 1997 the Physical and Engineering Scientific Committee (PESC) of the ESF accepted our proposal and decided to create the Programme *Electronic Structure* with top priority. As the financing of the ESF activities depends on contributions from the national member organizations, the Secretariat of the ESF sent in June 1997 invitations to its members to subscribe to the new ESF Programmes and to guarantee by their contributions the budget of the Programmes. At this stage some lobbying was absolutely necessary and we are very grateful to those colleagues who undertook the steps necessary to persuade their national organization that participation in the Programme *Electronic Structure* was in their own interest. End 1997 the ESF had received sufficient support for our Programme so that the PESC could decide to launch the Programme for a period of five years starting in 1998. *Electronic Structure* even received the strongest support out of all Programmes the ESF ever proposed.

To-date Austria, Belgium, Denmark, Finland, Germany, Hungary, Ireland, Italy, Poland, Portugal, Slovenia, Sweden, Switzerland and the UK have confirmed their financial support to the Programme, assuring an annual budget of 770 kFF that even exceeds the budget of about 585 kFF p.a. we had originally proposed. France and Spain had originally announced that they would join the Programme, but at the date at which the PESC decided to launch the Programme, participation had not yet been confirmed. However, at least for France I have been informed by Hugues Dreyssé that the CNRS decided to support the Programme "at a reasonable level". Hence our French colleagues will be part of the club.

Now we must go to work. The proposed activities of the ESF Programme consist of the electronic information services through the Ψ_k-Newsletter (which will be partially supported), Research Workshops and Major Collaborations, Small Collaborations and Individual Consultations, Hands-on Code-Sharing Workshops, and Secondment Visits. The activities with the ESF-Programme will be directed by a Coordinating Committee consisting of Volker Heine, Jürgen Hafner (Co-chairmen), Walter Temmerman (Secretary), Stephan Blügel, Hugues Dreyssé, Mike Finnis, Erhard Gross, Jose-Luis Martins, Risto Nieminen, Rafaele Resta and Erich Wimmer, supported by a larger Programme Board (see the published proposal for a complete list). Requests for support should be directed to the Secretary who will consult the members of the Coordinating Committee by email to ensure quick decisions. In the moment applications from Pablo Ordejon, Giulia Galli, David Pettifor and Luis Seijo for supporting a CECAM Workshop on "Local Orbitals for Large Scale Atomistic Simulations" and from Andrew Fisher for supporting an ESF-Conference on Surface Physics are pending. Details about the administrative procedures will be announced once we have received the necessary instructions from the ESF.

A start-up meeting for the ESF-Programme will be held together with our new TMR-Network *Electronic Structure Calculations of Materials Properties and Processes for Industry and Basic Sciences* (TMR2-Network). The joint start-up TMR/ESF workshop will concentrate on the interaction between academia and industry. It is planned to hold the meeting on 3-4 June, in Vienna. Details will be announced soon. I think we should all make an effort to make this meeting a success and a signal to industry.

Jürgen Hafner

Wien
28 January 1998

7 Workshop/Conference Announcements

7.1 Workshop in Aspen

Physics of Insulators: Aspen, June 15-July 3 (Application deadline Feb 1)

The workshop “Physics of Insulators” is scheduled at the Aspen Center for Physics, in Aspen, Colorado from Monday, June 15 to Friday, July 3, 1998. This workshop will combine the relevant aspects of many-body physics and computational materials theory to explore recent progress in the theoretical foundations, computational methodology, and current and future applications to key problems in the physics of individual insulating materials. Topics of discussion will include:

(1) the development of new density functionals for insulators;
(2) quantitative approaches to strongly correlated insulating systems;
(3) the theory of macroscopic electric fields in insulators; and
(4) realistic calculations of excited state properties.

Workshops at Aspen have a very special character, which bears little or no resemblance to conferences or “workshops” held elsewhere. They are intended to bring researchers with common interests together for an extended period of time (for our workshop, three weeks) to work together exploring issues of current interest in depth and developing new collaborations and lines of investigation. Participants should be at the postdoctoral level or above, with some exceptional cases, and are selected by the Aspen Center for Physics admissions committee based on on a brief application. The application form is available elecronically on the Aspen Center for Physics web page, and must be submitted before **February 1, 1998**.

We hope that you will consider participating in this workshop, and encourage you to pass this information on to colleagues interested in this area. For more information on the workshop ”Physics of Insulators,” please consult
http://pantheon.yale.edu/ rabe/aspen98.html.

More information about the Aspen Center for Physics, including the full program of summer 1998 workshops, is available at **http://andy.bu.edu/aspen**.

For further questions and discussion, you may also contact one of the workshop organizers, listed below.

Hoping to see you in Aspen next summer,

Jim Chelikowsky, jrc@msi.umn.edu
Don Hamann, drh@bell-labs.com
Karin Rabe, rabe@critical.eng.yale.edu

7.2 NATO Advanced Study Institute

Quantum Monte Carlo Methods

A NATO Advanced Study Institute on Quantum Monte Carlo methods in physics and chemistry will be held at Cornell University from the 13th to the 24/25th of July 1998. For those participants who qualify, all housing, most food costs and part of the travel costs will be covered by the institute, funded by NATO, CECAM and the Cornell Theory Center. For further information please consult the web page:

http://www.tc.cornell.edu/Edu/QMC-NATO.

We would appreciate your bringing this announcement to the attention of any of your associates who may be interested in attending.

Cyrus Umrigar and Peter Nightingale,
Directors

7.3 First Crete Euroconference

on

”ANOMALOUS COMPLEX SUPERCONDUCTORS (ACS-I)”

HERAKLION, 25 September – 02 October 1998

We are happy to inform you that the European Union will finance a series of Euroconferences in Crete on the **’Physics of Anomalous Complex Superconductors’**.

Our first event is planned for the week 25 September – 2 October 1998.

The members of the PROGRAM COMMITTEE of the first event are:

J. Fink (Dresden)
P.B. Littlewood (Cambridge)
D. van der Marel (Groningen)
H.R. Ott (Zurich)
D. Schweitzer (Stuttgart)
G. Varelogiannis (Heraklion)
D. Vollhardt (Augsburg)

International ADVISORY COMMITTEE:

A. Abrikosov (*Argonne*)
P.B. Allen (*SUNY*)
H. Alloul (*Orsay*)
B. Batlogg (*Bell Labs*)
A. Bianconi (*Roma*)
R.J. Birgeneau (*MIT*)
M. Cardona (*Stuttgart*)
G. Crabtree (*Argonne*)
G. Deutscher (*Tel Aviv*)
R. Dynes (*San Diego*)
E.N. Economou (*Heraklion*)
D. Edwards (*London*)
P. Fulde (*Dresden*)
T. Geballe (*Stanford*)
V.L. Ginzburg (*Moscow*)
D.C. Johnston (*Ames*)
K. Kitazawa (*Tokyo*)
G. Kotliar (*Rutgers*)
P. Lederer (*Orsay*)
A.J. Leggett (*Urbana*)
E. Liarokapis (*Athens*)
K. Levin (*Chicago*)
S. Maekawa (*Nagoya*)
K. Maki (*USC*)
M. Onellion (*Wisconsin*)
M. Peter (*Geneva*)
N. Plakida (*Dubna*)
H. Rietschel (*Karlsruhe*)
J.R. Schrieffer (*Tallahassee*)
F. Steglich (*Darmstadt-Dresden*)
C.C. Tsuei (*IBM-Y.H.*)
J. Wilson (*Bristol*)
P. Wyder (*Grenoble*)
J. Zaanen (*Leiden*)

LOCAL ORGANISING COMMITTEE:

Chairman: G. Varelogiannis

Members: E.N. Economou
J. Giapintzakis
N. Papanicolaou

Very preliminary list of CONFIRMED INVITED SPEAKERS:

G. Aeppli (NEC-Princeton)
H. Alloul (Orsay)
L. Greene (Urbana)
W. Hanke (Wurzburg)
P. Kes (Leiden)
K. Kitazawa (Tokyo)
P.A. Lee (MIT)
S. Maekawa (Sendai)
K. Maki (USC)
J. Mannhart (Augsburg)
J. Sauls (Northwestern)
Z.-X. Shen (Stanford)
J. Zaanen (Leiden)

PRELIMINARY INFORMATION ON THE PROGRAM:

Confirmation is pending from 12 speakers (Invitations just sent). We expect to have after dinner panel discussions on hot subjects each one directed and coordinated by a member of the program committee. During the panels drinking of wine or ouzo or beer is possible ! We expect 60 to 70 talks of which the contributed talks will have a duration of 20 or 30 minutes, the invited talks a duration of 30 minutes or 45 minutes if they have the character of a review. Some of the poster contributions will benefit a 5 minutes oral presentation.

In Euroconferences is encouraged the participation of young European researchers (under 35) who may apply to receive financial aid (see below).

HOW TO RECEIVE MORE INFORMATION

Circulars with more information will be mailed soon. If you are interested and need more information you can be included in our list and receive such information by surface mail. It is sufficient to send an e-mail to the following address:

varelogi@sisifos.iesl.forth.gr

with subject: ACS1-yourname

It is sufficient to include in your message your full coordinates (full address, fax, telephone, e-mail) and state in the first line of your message if you are: "Interested to participate only" or "Interested to participate and submit an abstract" (please use the above mentioned e-mail address administrated by sisifos).

Of course, by submitting an abstract and/or an application for financial aid as described below you will automatically receive the above mentioned information by surface mail.

Analogous e-mails to the present with updated information will follow soon. We are also preparing a WEB site for our conference where all updated information will be available. The address of this WEB site will be provided in a future e-mail when ready.

IMPORTANT DATES:

Deadline for abstract submission: **MARCH 30, 1998**.

Deadline for applications for financial aid to young European reasearchers: **MARCH 30, 1998**.

The program committee will communicate its decisions to potential participants before **APRIL 30, 1998**.

Participants must definitely confirm their participation before **MAY 15, 1998**.

Make a deposit for accomodation before **JUNE 1, 1998**.

HOW TO SUBMIT AN ABSTRACT:

Send by surface mail an A4 page with, first line the title, next line addresses of the authors and if possible e-mail of one or more of the authors, next the abstract. This page will appear in a booklet. The corresponding author must be underlined. Please type this page as clearly as possible using for example Latex or Word. The title must be in bigger and bold letters, family names of the authors in capital letters. Try to be brief.

Make a cover letter where your full coordinates including fax, phone, e-mail, etc., clearly appear.

Send the cover letter with the abstract page in the address:

Dr. G. Varelogiannis
ACS-I (Abstract Submission)
IESL-FORTH
P.O. Box 1527
71110 Heraklion Crete, GREECE

We must receive your abstract before **MARCH 30, 1998** (the earlier we receive it the more time we have to think on it).

If you also wish to apply for financial support, see NEXT paragraph, send your abstract and your application for support TOGETHER.

HOW TO APPLY FOR FINANCIAL SUPPORT:

In a first page declare your intention to apply for financial aid to attend the first euroconference on 'Anomalous Complex Superconductors' taking place on September 25-October 2, 1998, in Crete. Your full coordinates must appear in this cover letter.

Next page, give a brief curriculum vitae which should contain the following information:
- Name, Firstname, Age, Nationality, Professional Status,
- Address of activity (University/company, Postcode, City, Country Tel, Fax, E-MAIL),
- Intsitution of graduation,
- Brief curriculum vitae since graduation (maximum 16 lines),
- Current or projected research activities and motives for wishing to attend the euroconferences (max 6 lines),
- Declare if you or your research group hold a grant from which participation in the event could be funded,
- Indicate your FIVE best or most recent publications (Give title of paper, journal, volume and page numbers, names of all authors)
- Describe the estimated costs of travel using the most economical fares (indicating the trajects)

At the end of the application make the following statement:

"I declare the above truthful and sincere. If awarded support from the organisers of the event, I will not cover any of the expenses covered by the organisers by another source "

Date and signature

Mail it including your eventual abstract to the following address:

Dr G. Varelogiannis
ACS-1 (Application for Financial Support)
IESL-FORTH
P.O. Box 1527
71110, Heraklion Crete, GREECE

SCIENTIFIC OBJECTIVES:

We propose a simultaneous comparative study of characteristic anomalies of high-T_c superconductors and analogous anomalies in other "complex" superconductors like heavy fermions, organics, fullerides, borocarbides, ruthinates etc. All these materials have in common the complexity of the dimensional, magnetic, phonon and structural phenomena. The answer to the high-T_c puzzle is somewhere in the interplay of all these complex effects. An in depth simultaneous comparative analysis of all manifestations of this complex behavior in the various materials is necessary in order to distinguish relevant from irrelevant aspects for high-T_c and try to obtain some systematic theoretical understanding of the mechanisms through which this complex behavior influences T_c. Such a study has not been done so far because the intense controversies on fundamental physical aspects of the oxides focused the interest on them and made a useful comparative analysis with the already controversial physics of other complex superconductors not of first priority. After the first excitement, the study of high-T_c reached actually a maturity level. It is time now to start our systematic comparative study and this will be the task of our events.

Such a comparative study in a series of Euroconferences is necessary because in numerous institutes activity on superconductivity is rather new and basically motivated by the oxides. To the researchers working in these institutes access to the physics of the other complex superconductors through critical discussions with colleagues is impossible and our events are expected to accommodate this handicap. The young generation of researchers in the field had to handle an enormous amount of information on the oxides and the exciting physics of the other anomalous superconductors is basically unknown to them. Since young researchers will have to discover in the future novel classes of high-T_c superconductors, provide them with a complete, beyond the oxides, pedagogic picture of the influence of complex material and physical aspects on superconductivity will be a strategic advantage for the future European research in the field. In this proposal the training objectives will be particularly emphasized in the design of our events.

We intend to organize a series of events, that will have very high scientific quality and will provide at the end a complete pedagogically valid picture. The quality of each event will be guaranteed by a program committee constituted by more than five researchers active in the field from different European countries, and its composition is expected to evolve from event to event. Therefore, a large number of European specialists will participate very actively in the organization of our events.

A circular with more details (more about the confirmed speakers, the costs, the venue etc.) will follow soon.

For information or suggestions do not hesitate to send e-mail to:

Georgios Varelogiannis
IESL-FORTH & Univ. of Crete
P.O. Box 1527
71110 Heraklion Crete, Greece
Fax: + 30 81 391569
Tel: + 30 81 391544
E-mails: varelogi@iesl.forth.gr
varelogi@sisifos.iesl.forth.gr

8 Job Announcements

Announcement

Post-doctoral Position

Large-scale Simulation and Visualization of Interfacial Materials

Argonne National Laboratory

The Interface Materials group in the Materials Science Division has a post-doctoral opening in the area of large-scale atomic-level simulation and graphic visualization of interfacial materials. The successful applicant will perform molecular dynamics simulations on massively parallel computers (IBM-SP and Cray T3E) to investigate the role of grain boundaries in various properties of metallic, covalent and/or predominantly ionic ceramic polycrystalline microstructures. A PhD in a theoretical discipline obtained within the last three years is required. US citizenship is not required. Please send resume and names of three references to **Dr. Dieter Wolf or Dr. Simon Phillpot, Materials Science Division, Bldg. 212, Argonne National Laboratory, Argonne, IL 60439; e-mail: dieter_wolf@qmgate.anl.gov; simon_phillpot@qmgate.anl.gov**.

Announcement

SCIENTIST on "Nonlinear spectroscopy of atoms and molecules"

LENS-European Laboratory for non Linear Spectroscopy - Florence (Italy)

INFM - the Italian Institute for the Physics of the Matter - has a job opening for a SCIENTIST on "Nonlinear spectroscopy of atoms and molecules"

A Scientist position is available to perform "Nonlinear spectroscopy of atoms and molecules" at the LENS-European Laboratory for non Linear Spectroscopy - Florence (Italy)- http://www.lens.unifi.it/. Candidates should have a PhD in Physics or related subject; a two years experience in the field of spectroscopy of atoms and molecules is required, some knowledge of Italian is desirable.

The position is initially for a first period of 1 year which can be further extended up to a maximum of 5 years, starting from February 1998. The gross salary will be around 3,5 million Italian Liras per month. Candidates should submit their application, with detailed CV, updated list of publications and a copy of PhD certificate - by January 31st 1998- to: INFM - Rif. 129- Corso Perrone 24, I-16152 Genova, Italy The application form is available at http://www.infm.it.

For any further information please contact INFM, phone nnumber: +39-10-65987 12/48, fax: 6506302, e-mail: bolla@infm.it or pernati@infm.it.

Matilde Bolla
INFM - Ufficio lavoro
http://www.infm.it/
tel. +39-10-6598712
fax: +39-10-6506302

Post-Doctoral Postions in Solid State/Materials Theory

The Department of Materials Science & Engineering, The University of Illinois

The Department of Materials Science & Engineering at The University of Illinois has an immediate opening for up to two Post-Doctoral Research Associates. Persons skilled in the use and development of electronic-structure (ES) methods, with a background in KKR ideal but not required, are sought. On-going research interests include coupling of ES and thermodynamic approaches to calculate structural and magnetic phase stability in multicomponent alloys systems (bulk and at interfaces/surfaces); studying the origin of easy-forming, metallic glasses using classical density-functional methods; and developing a tight-binding-like KKR (with a wavelet basis set) to study the kinetics of growth of multilayers by via ab-initio molecular dynamics, or embedding such a method into finite-element/continuum code to study fracture or crack propogation.

While e-mail is acceptable for inquiry, candidates should send a curriculum vitae, names of references, copies of up to three selected publications, and statement of research interests to:

Prof. Duane D. Johnson
202 Metallurgy and Mining Bldg.
Dept. of Materials Science & Engineering
1304 West green Street, C-246
University of Illinois, Urbana, IL 61801, USA
Ph: 217-265-0319
Fax: 217-333-2736
e-mail: duanej@uiuc.edu
web: www.mse.uiuc.edu

The University of Illinois is an Equal Opportunity/Affirmative Action Employer.

Ph. D. Position

Condensed Matter Theory

Munich, Germany

Applications are invited for the above position funded by the German Ministry of Education and Research. The position is available at least for 3 years starting 1st of April 1998 or later and is meant for a Ph.D. student (i.e. someone who would like to get his degree from the University of Munich). Nevertheless, the applicant should have already some experience in computational Condensed Matter Theory. She/he is expected to contribute to the current projects of our group in Munich within a German network that primarily consists of experimentalists using polarized radiation for electron spectroscopy of solids.

More detailed information concerning the project can be obtained upon request.

Some information on Munich can be found on:

`http://www.leo.org/leo_e.html \\`
`http://www.munich-online.de/enmunich_online.html \\`

Finally and most important: the salary will be around DM 1700- after tax but can be higher depending on the age and family status of the applicant.

All applications should be sent to:

Prof. Dr. H. Ebert
Institut für Physikalische Chemie
Universität München
Theresienstr. 37-41
D-80333 München
Tel.: (089) 23 94 - 46 42 / - 42 18
Fax.: (089) 28 05 - 248 and (089) 23 94 - 4158
Email: he@gaia.phys.chemie.uni-muenchen.de

Announcement

Ph. D. Position

Max-Planck-Institut fuer Metallforschung in Stuttgart, Germany

There is a PhD position (A13/2) available in the department "Microstructure and Properties of Ferromagnets and Superconductors" (Prof. Kronmueller) at the Max-Planck-Institut fuer Metallforschung in Stuttgart, Germany. It is planned to calculate crystal field parameters and magnetostriction in rare-earth - transition-metal intermetallics and at interfaces and surfaces of these materials by the full-potential linear-muffin-tin-orbital method and/or the full-potential linearized-augmented-plane-wave method. Applicants should have experience with ab-initio computer codes. Please contact: **Prof. Dr. M. Faehnle, Max-Planck-Institut fuer Metallforschung, Heisenbergstr. 1, D-70569 Stuttgart, Germany. FAX: ++49 711 689 1932, e-mail: FAEHN@physix.mpi-stuttgart.mpg.de**.

Announcement

Postdoc and Ph. D. Positions in Stuttgart

At the Max-Planck-Institut für Metallforschung in Stuttgart, Germany, in the department "Microstructures and Interfaces" (Prof. Dr. M. Rühle) a **postdoctoral position** (BAT 2a salary in the German public system) and **two PhD positions** (A 13/2 salary) in Condensed Matter Theory are available.

The postdoctoral candidate will investigate microscopic mechanisms of adhesion, wetting and reaction of transition-metal films on ceramic perovskite substrates by means of density-functional calculations with an ab-initio mixed-basis pseudopotential method. The applicant should have experience in first-principles techniques for electronic-structure calculations.

Topic of the one PhD work will be a theoretical study of atomic and electronic structures and properties of grain boundaries in α-Al_2O_3 by means of empirical atomistic simulations (ionic shell models) and ab-initio density-functional calculations (pseudopotentials, mixed basis). Topic of the other PhD project will be a theoretical investigation of electronic structures at interfaces in ceramics (e.g. electron energy loss spectra of pure and Y-doped α-Al_2O_3) and their relations to segregation and atomic structures. Applicants for the PhD positions should have a degree equivalent to a German university diploma in physics, chemistry or materials science, and good knowledges in condensed matter theory.

All three theoretical projects are in close connection to experimental investigations in the department by atomic-resolution and analytical electron microscopy.

Please send your application to:
Dr. C. Elsässer, Max-Planck-Institut für Metallforschung, Seestr. 92, D-70174 Stuttgart.
Fax: ++49 711 2095 320, email: `elsae@marvin.mpi-stuttgart.mpg.de`.

Announcement

Position in Theory of Electronic Properties of Substituted Polymers

Department of Chemistry, University of Konstanz, Germany

At the Department of Chemistry, University of Konstanz, Germany, is a position in **theory of electronic properties of substituted conjugated polymers** available. The candidate will apply density-functional calculations in studying the effects of various substituents to different conjugated polymers in order to *i*) study the effects of the substituents on the frontier orbitals, *ii*) compare singly substituted materials with periodically substituted ones, and *iii*) calculate hyperpolarizabilities of the materials. The project is supported by the German Research Council (DFG) and the position is available at the earliest possible time for approximately 14 months with extensions possible. The salery follows BAT IIa/2 according to the German salery scale.

Candidates are requested to contact:

Michael Springborg
Department of Chemistry
University of Konstanz
D – 78457 Konstanz
Germany

Tel. +49 7531 88 2024
Fax: +49 7531 88 3898

e-mail: mcs@chclu.chemie.uni-konstanz.de

Announcement

Postdoctoral Position in Solid State Theory Group

National Renewable Energy Laboratory

http://www.sst.nrel.gov

The Solid State Theory Group at the National Renewable Energy Laboratory invites applications for a new postdoctoral research position. The position is for two years, renewable upon mutual agreement to a third year. The postdoctoral position is the result of a project at NREL to study the **theory and phase stability of light-metal alloys**. The Solid State Theory Group currently consists of ten Ph.D.'s in condensed matter theory (including Drs. Alex Zunger, Su-Huai Wei, and Chris Wolverton) and interacts with a broad range of experimentalists at NREL. For more information about group research activities, see http://www.sst.nrel.gov. The theory group is a renowned research group with an outstanding record of publication and innovation. Furthermore, the group has outstanding computational facilities, an excellent basic-research atmosphere, and is located in the beautiful Rocky Mountains (less than one hour from hiking and ski resorts). Interested candidates should immediately send in writing a curriculum vitae, list of publications (including preprints of unpublished papers, if possible) and list of three references to:

Dr. Chris Wolverton
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 cmw@sst.nrel.gov.

9 Abstracts

Electronic structure of FeS_2: The crucial role of electron-lattice interaction

V. Eyert
Hahn-Meitner-Institut, Theory Department,
Glienicker Straße 100, D-14109 Berlin, Germany
K.-H. Höck
Institut für Physik, Universität Augsburg,
Memminger Straße 6, D-86135 Augsburg, Germany
S. Fiechter, H. Tributsch
Hahn-Meitner-Institut, Department of Solar Energetics,
Glienicker Straße 100, D-14109 Berlin, Germany

Abstract

Using the results of fully self-consistent all electron first-principles calculations for semiconducting iron pyrite we discuss the major factors governing the semiconducting properties as well as the chemical bonding of this material. The calculations are based on density functional theory within the local density approximation and employ the ASW method in its scalar-relativistic implementation. The electronic properties are dominated by strongly hybridized Fe $3d$ and S $3p$ states. The chemical bonding is analyzed using an *ab initio* implementation of the crystal orbital overlap population (COOP). Chemical stability is shown to result mainly from the Fe-S bonding. While the upper part of the valence band is formed mainly from Fe $3d$ t_{2g} derived states the conduction band comprises the e_g derived levels. The conduction band minimum, in contrast, is exclusively due to S $3p$ states this fact explaining the observed high optical absorption. For the same reason the optical properties are strongly influenced by the short sulfur-sulfur bonds. We demonstrate that only small deviations in the sulfur pair bond lengths involve rather drastic changes of the near-gap electronic states which might even turn the indirect bandgap into a direct one. These findings allow to understand the rather high sensitivity of the optical bandgap to the incorporation of defects. Finally, our results open new perspectives for photovoltaics applications of FeS_2.

(Phys. Rev. **B57**, (15 March 1998))
Manuscripts available from: eyert@physik.uni-augsburg.de

The electronic structure of V_2O_5: Role of octahedral deformations

V. Eyert
Hahn-Meitner-Institut, Theory Department,
Glienicker Straße 100, D-14109 Berlin, Germany
K.-H. Höck
Institut für Physik, Universität Augsburg,
Memminger Straße 6, D-86135 Augsburg, Germany

Abstract

We present the results of all-electron electronic structure calculations for semiconducting vanadium pentoxide. The calculations are based on density functional theory within the local density approximation and employ the ASW method in its scalar-relativistic implementation. The electronic properties are modified significantly by strong hybridization between O $2p$ and crystal field split V $3d$ states. Strong deviations of the VO_6 octahedra from cubic coordination give rise to the narrow split-off conduction band as a characteristic feature of V_2O_5. Furthermore, we demonstrate that distortions of the octahedra along the crystallographic c axis drastically increase the bonding-antibonding splitting of the V $3d_{xz}/3d_{yz}$ derived bands whereas distortions perpendicular to the c axis reduce the bandwidth of the split-off V $3d_{xy}$ bands. Both effects contribute to the stability of V_2O_5 and enhance the optical bandgap.

(submitted to Phys. Rev. **B**)
Manuscripts available from: eyert@physik.uni-augsburg.de

Ab-initio Study of Iron and Iron Hydride: I. Cohesion, Magnetism and Electronic Structure of Cubic Fe and FeH

C. Elsässer[1),2)], J. Zhu[1)], S. G. Louie[1)], M. Fähnle[2)] and C. T. Chan[3)]
[1)] *Department of Physics, University of California,*
Berkeley, CA94720, USA
[2)] *Max-Planck-Institut für Metallforschung,*
Heisenbergstr. 1, D-70569 Stuttgart, Germany
[3)] *Ames Laboratory and Department of Physics, Iowa State University,*
Ames, IA 50011, USA

Abstract

The ab-initio mixed-basis pseudopotential method based on the density functional theory is applied to study the cohesion, ferromagnetism and electronic structure of iron and iron monohydride with cubic crystal structures. Spin-unpolarized and spin-polarized calculations are used to assess the transferability of normconserving ionic pseudopotentials for iron, and the level of accuracy obtainable for structural equations of states with reasonable effort. The influence of generalized gradient corrections on the cohesive properties is investigated. The results are put in direct comparison to corresponding all-electron results obtained by using both FLAPW and LMTO-ASA methods.

(Submitted to J. Phys.: Condens. Matter, January 1998)

Contact person for manuscripts: C. Elsässer, `elsae@marvin.mpi-stuttgart.mpg.de`

Ab-initio Study of Iron and Iron Hydride: II. Structural and Magnetic Properties of Close-Packed Fe and FeH

C. Elsässer[1),2)], Jing Zhu[1)], S. G. Louie[1)],
B. Meyer[2)], M. Fähnle[2)] and C. T. Chan[3)] [1)] *Department of Physics, University of California, Berkeley, CA94720, USA*
[2)] *Max-Planck-Institut für Metallforschung, Heisenbergstr. 1, D-70569 Stuttgart, Germany*
[3)] *Ames Laboratory and Department of Physics, Iowa State University, Ames, IA 50011, USA*

Abstract

The energetical ordering and magnetic states of hexagonal and double-hexagonal close-packed (hcp, dhcp) as well as face-centered cubic (fcc) Fe and FeH crystals are studied via spin-polarized ab-initio total-energy calculations in the local spin density approximation and with generalized gradient corrections by means of the mixed-basis pseudopotential and the all-electron LMTO-ASA methods. In all three structures, the magnetic spin moments go to zero under volume compression. For pure Fe in the compressed nonmagnetic state, the hcp structure is found to have the lowest energy, fcc the highest, and dhcp lies in between. The two hexagonal structures have significantly smaller than ideal c/a ratios. For compressed nonmagnetic FeH the energetical ordering of the structures is reversed, compared to pure Fe, with fcc ground-state structure and almost ideal c/a ratios for both hexagonal structures. In the ferromagnetic states at expanded volumes, the energetical orderings are again opposite to those of the nonmagnetic states both for Fe and FeH. In ferromagnetic FeH these energy differences are particularly small, yielding almost an energetical degeneracy of all three close-packed structures.

(Submitted to J. Phys.: Condens. Matter, January 1998)

Contact person for manuscripts: C. Elsässer, `elsae@marvin.mpi-stuttgart.mpg.de`

Ab-initio Study of Iron and Iron Hydride: III. Vibrational States of H Isotopes in Fe, Cr and Ni

C. Elsässer[1),2)], H. Krimmel[1)], M. Fähnle[1)],
S. G. Louie[2)], and C. T. Chan[3)]
[1)] *Max-Planck-Institut für Metallforschung,*
Heisenbergstr. 1, D-70569 Stuttgart, Germany
[2)] *Department of Physics, University of California,*
Berkeley, CA94720, USA
[3)] *Ames Laboratory and Department of Physics, Iowa State University,*
Ames, IA 50011, USA

Abstract

Adiabatic potentials, energy levels and wavefunctions for collective vibrational states of hydrogen isotopes in monohydrides of transition metals with face-centered cubic lattices, γ-FeH and NiH, and with body-centered cubic lattices, α-FeH and CrH, are investigated by means of ab-initio total-energy calculations in the local-density and local-spin-density approximations (LDA, LSDA). The study for the different transition-metal monohydrides, including PdH and NbH studied earlier, yields a general insight into the microscopic vibrational potential wells: The topology of their spatial shapes is specific to the metal lattice, but their depths and curvatures change quantitatively in a systematic manner along the transition-metal series. The calculated excitation energies agree very well with results of inelastic-neutron-scattering (INS) experiments both for nonmagnetic NiH, treated in LDA, and ferromagnetic γ-FeH, treated in LSDA. The theoretical data for the two considered hydrides with bcc structure, which do not exist experimentally, provide an ab-initio database for the construction of metal-hydrogen interaction models, e.g., for studies of self-trapped vibrational states of isolated H atoms in transition metals.

(Submitted to J. Phys.: Condens. Matter, January 1998)

Contact person for manuscripts: C. Elsässer, `elsae@marvin.mpi-stuttgart.mpg.de`

Glucose in aqueous solution by first principles molecular dynamics

C.Molteni and M.Parrinello
Max Planck Institut für Festkörperforshung
Heisenbergstrasse 1, D-70569 Stuttgart (Germany)

Abstract

We present the results of the first *ab initio* molecular dynamics simulations, based on the Car-Parrinello method, of glucose in water, performed to investigate structural aspects of the anomeric equilibrium in aqueous solution. The analysis of the hydrogen bonds around the crucial anomeric oxygen shows a distinct solvation behaviour for the β and α anomers. While the β anomer, which is the most abundant in water, allows the water molecules to flow in a disorderly manner around its anomeric site, the α anomer tends to bind them more tightly.

(to appear in J. Am. Chem. Soc. 1998)
Preprints available from: molteni@prr.mpi-stuttgart.mpg.de

Electronic, Magnetic and Structural Properties of Perovskite Manganites

K. Terakura[a,b], I. V. Solovyev[c] and H. Sawada[c]
[a] *JRCAT, National Institute for Advanced Interdisciplinary Research,*
1-1-4 Higashi, Tsukuba, Ibaraki 305, Japan
[b] *Institute of Industrial Science, University of Tokyo,*
Roppongi, Minato-ku, Tokyo 106, Japan
[c] *JRCAT, Angstrom Technology Partnership,*
1-1-4 Higashi, Tsukuba, Ibaraki 305, Japan

Abstract

A review work devoted to the description of the basic properties of $LaMnO_3$ and related materials within the framework of the present band-structure theory based on the density-functional method (it is shown how the band-structure theory works and also does not work for the perovskite transition-metal oxides).

General contents:

1. Introduction
2. Methodological Aspects in the Band-Structure Calculations
3. Effects of the Lattice Distortion in $LaMnO_3$
3.1 electronic structure of $LaMnO_3$
3.2 orbital ordering and stability of the A-type antiferromagnetic order in $LaMnO_3$
3.3 magnetic anisotropy
3.4 non-collinear spin magnetism
3.5 non-collinear orbital magnetism and optical non-reciprocity
4. Structural Optimization of $LaMnO_3$
5. An Alternative View for the Stability of the A-type AF ordering in $LaMnO_3$
6. Two examples of the t_{2g} Systems: $LaVO_3$ and YVO_3
7. Half-Metallic States of Ferromagnetic $La_{1-x}A_xMnO_3$ (A: divalent element)
8. Concluding Remarks

(to be published in "Colossal Magnetoresistance Oxides", ("Monographs in Condensed Matter Science by Gordon and Breach") edited by Y. Tokura)

Manuscripts available from: igor@jrcat.or.jp

Metal-insulator transition in approximants to icosahedral AlPdRe

M. Krajčí[a,b] and J. Hafner[a]
[a] *Institut für Theoretische Physik*
and Center for Computational Materials Science,
Technische Universität Wien,
Wiedner Hauptstraße 8-10/136, A-1040 Wien, Austria
[b] *Institute of Physics, Slovak Academy of Sciences,*
Dúbravská cesta 9, SK-84228 Bratislava, Slovak Republic

Abstract

The electronic structure of icosahedral Al-Pd-Re alloys has been calculated for a series of large approximants. For the 1/1 to 3/2 approximants with up to 2292 atoms/cell the electronic eigenstates have been calculated selfconsistently via diagonalization of the Hamiltonian in a tight-binding linear-muffin-tin orbital representation. For the 5/3 and 8/5 approximants only the total and partial densities of states have been calculated using the real-space recursion method. The electronic structure of Al-Pd-Re differs from that of other icosahedral phases by (i) the appearence of a semiconducting gap for certain approximants and (ii) by a scaling behaviour of the participation ratio of the states close to the Fermi level, indicating a critical character of the eigenstates. Our results for the electronic structure are discussed in connection with the outstanding physical properties of icosahedral Al-Pd-Re alloys, and in particular with the possible occurence of a metal-insulator transition in this material.

(Submitted to Phys. Rev. Lett.)

Manuscripts available from: jhafner@tph.tuwien.ac.at

Reaction channels for the catalytic oxidation of CO on Pt(111)

A. Eichler and J. Hafner
[a] *Institut für Theoretische Physik*
and Center for Computational Materials Science,
Technische Universität Wien,
Wiedner Hauptstraße 8-10/136, A-1040 Wien, Austria

Abstract

The catalytic oxidation of CO on O-precovered Pt(111) surfaces has been modelled via ab-initio local-density functional calculations. It is shown that the co-adsorption of CO stabilizes the chemisorbed molecular precursor of O_2 over the dissociated atomic oxygen. The reaction between the peroxo-like precursor and coadsorbed CO leads to the lowest reaction barrier ($E_{\mathrm{barr}} = 1.18$ eV). The reaction between adsorbed atomic O and CO has a larger barrier of 1.85 eV, but can occur as a second step of the precursor mediated reaction.

(Submitted to Phys. Rev. Lett.)
Manuscripts available from: jhafner@tph.tuwien.ac.at

Adsorption of CO on Pd(100): steering into less favored adsorption sites

A. Eichler and J. Hafner
[a] *Institut für Theoretische Physik*
and Center for Computational Materials Science,
Technische Universität Wien,
Wiedner Hauptstraße 8-10/136, A-1040 Wien, Austria

Abstract

Molecular steering effects have been shown already in a number of cases to constitute an effective mechanism to avoid barriers and enhance sticking at low incidence energies. We present a study of the adsorption process of CO on the Pd(100) surface, where a similar mechanism leads to trapping of some of the molecules in less favorable surface sites. The electronic charge transfers and redistributions connected with this process are analyzed in detail.

(Phys. Rev. B, in print)
Manuscripts available from: jhafner@tph.tuwien.ac.at

Is Hund's Second Rule Responsible for the Orbital Magnetism in Solids ?

I. V. Solovyev[1], A. I. Liechtenstein[2] and K. Terakura[3]
[1] *JRCAT-ATP, 1-1-4 Higashi, Tsukuba, Ibaraki 305, Japan*
[2] *Forschungszentrum Jülich, D-52425 Jülich, Germany*
[3] *JRCAT-NAIR, 1-1-4 Higashi, Tsukuba, Ibaraki 305, Japan*

Abstract

We analyze the physical grounds for the first principles band structure theories aiming to deal with the orbital magnetism in solids. We argue that the key parameter responsible for the exchange-correlation enhancement of the orbital magnetic moments is "Hubbard U" rather than the intra-atomic Hund's second rule coupling, being consistent with a more general concept of the orbital polarization in solids. This leads us to a unified rotationally invariant LDA+U prescription for the orbital magnetism. Validity of the present theory is demonstrated by numerical calculations, which perfectly account for the orbital magnetism as well as the canted magnetic structure in CoO.

(submitted to Phys. Rev. Letters)
Manuscripts available from: igor@jrcat.or.jp

Poisoning of Hydrogen Dissociation at Pd (100) by Adsorbed Sulfur Studied by *ab initio* Quantum Dynamics and *ab initio* Molecular Dynamics

Axel Gross[1], Ching-Ming Wei[2], and Matthias Scheffler[1]
[1] *Fritz-Haber-Institut der Max-Planck-Gesellschaft,*
Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany
[2] *Institute of Physics, Academica Sinica,*
Taipei, Taiwan 11529

Abstract

We report calculations of the dissociative adsorption of H_2 at Pd (100) covered with 1/4 monolayer of sulfur using quantum dynamics as well as molecular dynamics and taking all six degrees of freedom of the two H atoms fully into account. The *ab initio* potential-energy surface (PES) is found to be very strongly corrugated. In particular we discuss the influence of tunneling, zero-point vibrations, localization of the nuclei's wave function when narrow valleys of the PES are passed, steering of the approaching H_2 molecules towards low energy barrier configurations, and the time scales of the center of mass motion and the other degrees of freedom. Several "established" concepts, which were derived from low-dimensional dynamical studies, are shown to be not valid.

(Submitted to Phys. Rev. Lett. , Jan 1998)
Contact person: gross@fhi-berlin.mpg.de

Non-local electron-positron correlations in metals. I. Electron–positron enhancement factors and correlation potentials

A. Rubaszek
W. Trzebiatowski Institute of Low Temperature and Structure Research,
Polish Academy of Sciences, P.O.Box 937, 50-950 Wrocław 2, Poland

Z. Szotek and W.M. Temmerman
Daresbury Laboratory, Warrington, WA4 4AD, Cheshire, U.K.

Abstract

Non–local electron–positron correlation effects in solids are studied. The importance of state–selectivity of the electron–positron enhancement factors is discussed. The weighted density approximation is applied to calculations of the non–local state–selective electron–positron correlation functions and potentials. Also, differences in the electron–positron enhancement factors due to the *s*, *p*, *d* and *f* angular momentum channels of the electron density are studied. The influence of the electron–positron interaction on the positron density distribution in solids is discussed.

(Submitted to Phys. Rev. B)
Manuscripts available from: Z.Szotek@dl.ac.uk

Non-local electron-positron correlations in metals. II. Positron lifetimes

A. Rubaszek
W. Trzebiatowski Institute of Low Temperature and Structure Research,
Polish Academy of Sciences, P.O.Box 937, 50-950 Wrocław 2, Poland

Z. Szotek and W.M. Temmerman
Daresbury Laboratory, Warrington, WA4 4AD, Cheshire, U.K.

Abstract

We apply the formalism of the non–local state–selective electron–positron correlation functions, developed within the weighted density approximation in our preceding paper, to the *ab initio* calculations of positron lifetimes in a variety of metals and silicon. We discuss the influence of various approximations to the electron–positron interaction on the positron lifetimes. Moreover, we study how different angular momentum channels of the electron density contribute to the total positron annihilation rates and lifetimes. We compare the results to those calculated within the local density approximation.

(Submitted to Phys. Rev. B)

Manuscripts available from: Z.Szotek@dl.ac.uk

Preprints from
Center for Atomic-scale Materials Physics (CAMP)

- J.Schiøtz and E.A. Carlsson:
  Dislocation emission from sharp and blunt cracks in f.c.c. metals,
  submitted

- T.R. Linderoth, S. Horch, E. Lægsgaard, I. Stensgaard, and F. Besenbacher:
  Dynamics of Pt adatoms and dimers on Pt(110)-(1×2) observed directly by STM,
  Surf.Sci. accepted

- F. Besenbacher, I. Chorkendorff, B.S. Clausen, B. Hammer, A. Molenbroek, J.K. Nørskov, and I. Stensgaard:
  Catalyst design from first principles,
  submitted

- A.V. Ruban, H.L. Skriver, and J.K. Nørskov:
  Crystal-structure contribution to the solid solubility in transition metal alloys,
  Phys.Rev.Lett. accepted

- S.I. Simak, A.V. Ruban, I.A. Abrikosov, H.L. Skriver, and B. Johansson:
  Ordering in Cu_2NiZn,
  submitted

- L. Vitos, A. V. Ruban, H.L. Skriver, and J. Kollár:
  The surface energy of metals,
  submitted

- L. Vitos, H.L. Skriver, and J. Kollár:
  Kinetic energy functionals studied by surface calculations,
  submitted

- J.H. Larsen and I. Chorkendorff:
  Increased dissociation probability of CH_4 *on Co/Cu(111)*,
  submitted

- A. Bach Aaen, E. Lægsgaard, A.V. Ruban, and I. Stensgaard:
  Submonolayer growth of Pd an Cu(111) studied by Scanning Tunnelinh Microscopy,
  submitted

More information can be obtained from helle@fysik.dtu.dk

Helle Wellejus
CAMP, Department of Physics
Building 307, Technical University of Denmark
DK - 2800 Lyngby, Denmark

10 SCIENTIFIC HIGHLIGHTS

Density-Functional Molecular-Dynamics Techniques, Pseudopotential Techniques and Reduced (0-1-2) Dimensionality Working Groups

Node: **Jülich**

Re-exchange controlled Diffusion in Surfactant-mediated Epitaxial Growth: Si on As-terminated Si(111)

K. Schroeder, B. Engels, P. Richard and S. Blügel

Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany

Abstract

For a Si adatom on the Si(111) surface passivated by an As surfactant layer the adatom diffusion barrier (E_D), the exchange barrier (E_{EX}) for incorporation and the energy gain (E_B) due to incorporation into the As layer are calculated using an *ab initio* total energy and force method. We found that the activation energies for surface diffusion and exchange are similar in size and much smaller than the activation energy for the re-exchange (E_{REEX}) process ($E_D \sim E_{EX} << E_{REEX} = E_{EX} + E_B$). We propose that adatoms are rapidly incorporated into the As layer and the effective diffusion is determined by the re-exchange process.

Comment:

We have prepared the figures in this Newsletter with gnuplot in TEX-format for easy distribution. More detailed figures in postscript–format and a movie of the exchange process can be found at the following www-address:

http://www.kfa-juelich.de/iff/personen/K.Schroeder.html

Understanding, controlling and modifying the growth of nanoscale-size structures is of major importance for the design of new semiconductor quantum devices. Unfortunately, many interesting materials such as Ge/Si cannot be grown easily as multiple heterostructures with atomically flat interfaces because the strain due to lattice mismatch leads to three-dimensional (3D) islanding.

Several groups[1, 2, 3, 4] have shown that monolayer (ML) coverage of surfactants can improve the layer-by-layer growth in heteroepitaxy. For example, group-V elements (Sb, As) change the growth mode for Ge on Si(111) from 3D islands (Stranski-Krastanov growth) on clean Si(111) to 2D islands (Frank van der Merwe growth). In general, the growth of films depends on the surface free energies, kinetic effects, and the strain energy. Surfactants influence the growth in several ways: They have a low surface free energy which makes them float on the surface of the growing crystal without being incorporated. This changes the kinetics of the surface motion and of the incorporation of deposited adatoms and leads to a modification of adatom diffusion.

The kinetics of surface processes of an adatom are not yet understood in detail. But they determine the growth mode decisively[5]: If the diffusion length of adatoms (i.e. the distance the atoms move on average before they are incorporated) is large compared to the terrace width of the crystal surface, the atoms are likely to be incorporated at a step edge. Then, the crystal grows by step-flow mode. On the other hand, if the diffusion length is much smaller than the terrace width, e.g. due to trapping at surface impurities or incorporation into a surfactant layer, growth proceeds by nucleation and growth of islands.

To get some insight into the *kinetic aspects of surfactant mediated growth* without the complication of strain, Si(111) homoepitaxy was studied. Even then, the prediction of the influence of a particular surfactant species on surface kinetics, and in particular on the diffusion length, is far from being trivial. There are two opposing effects due to surfactants: Group-V elements like As passivate the Si(111) surface due to their extra electron [for As termination this leads to an unreconstructed Si(111) surface[6]]. This tends to lower the diffusion barrier of deposited atoms and to increase the diffusion length. On the other hand, adatoms have to be incorporated under the surfactant layer eventually. Intuitively, one expects a high activation barrier for this exchange process due to the required breaking of bonds. Incorporation tends to decrease the diffusion length because the adatoms are trapped. The diffusion length is determined by the relation of the kinetic coefficients, i.e. the barrier heights, for surface diffusion and exchange, respectively. Two different scenarios of the effect of surfactants (and in particular of As) on the kinetics of adatoms have been discussed:

(i) Voigtländer *et al.* [7] have performed experiments on homoepitaxy of Si on clean and As(1 ML) covered Si(111). They find a drastic increase of the island density on the As (or Sb) covered surface and a decrease of the width of the island free (denuded) zone along step edges. They interpreted these results as a decrease of the diffusion length of Si adatoms in the presence of surfactants due to a reduction of the *effective* diffusion coefficient. From the experiment one cannot decide whether this effect is due to an increase of the diffusion activation energy on the surfactant covered surface, or whether the termination of the diffusion path by incorporation of the Si adatoms under the surfactant layer plays the decisive role.

(ii) On the other hand, Kaxiras[8, 9] assumes that deposited adatoms move rapidly across the passivated surface. He argues further that surfactants not only passivate the flat surface but also the step edges, which reduces the incorporation probability of adatoms. Thus, although in this scenario the diffusion length is much larger than the terrace width, homogeneous nucleation of islands on the terraces can take place, in spite of a high activation barrier for exchange. Kaxiras *et al.* [9] have substantiated these arguments by *ab initio* calculations for the exchange of *full monolayers* of adatoms and surfactants for which they find high energy barriers.

In this letter we investigate for the first time the barriers for all kinetic processes for single Si adatoms on a surfactant (1 ML As) covered Si(111) in a large surface supercell. We determine the equilibrium configuration of the Si adatom by minimizing the total energy of the supercell with respect to all atomic coordinates and find saddle points by restricted relaxation similar to the "hyper-plane adaptive constraint (HAC)" method [10], i.e. by minimizing the energy subject to additional constraints. We calculate the activation energies E_D for surface diffusion, E_{EX} for incorporation of a Si adatom by exchange with an As surfactant atom, and E_{REEX} for re-exchange. We find a complex exchange path which avoids to a large extent the breaking of bonds. This leads to a surprisingly low E_{EX} which is comparable to E_D. As a consequence, we suggest a new scenario: the re-exchange controlled diffusion of Si adatoms on surfactant covered Si(111), in full agreement with experiments.

All calculations have been carried out by use of norm-conserving pseudopotentials [11] of the Kleinman-Bylander form [12] and the local density approximation [13] combined with iterative diagonalization schemes for the eigenvalue problem [14]. Force calculations combined with molecular statics [15] are used to determine the minimum energy configurations and the reaction pathways. The surface is simulated by a repeated slab model consisting of 6 atomic Si(111) layers in an inversion symmetric arrangement, 1 ML As on each Si surface, and 1 adatom on each As layer, separated by a vacuum equivalent to 6 atomic Si layers. We find that the p(3×3) periodic cell in the lateral directions, 4 $\mathbf{k}_{\|}$-points in the surface Brillouin-zone and a 13.69 Ry cut-off energy in the planewave basis set are necessary to obtain well converged results [16]. The symmetry-unrestricted geometry optimization includes all atoms except those of the 2 innermost atomic layers of the slab. To establish minimum energy configurations we converged the forces acting on the atoms to less than 0.1 mRy/a.u.

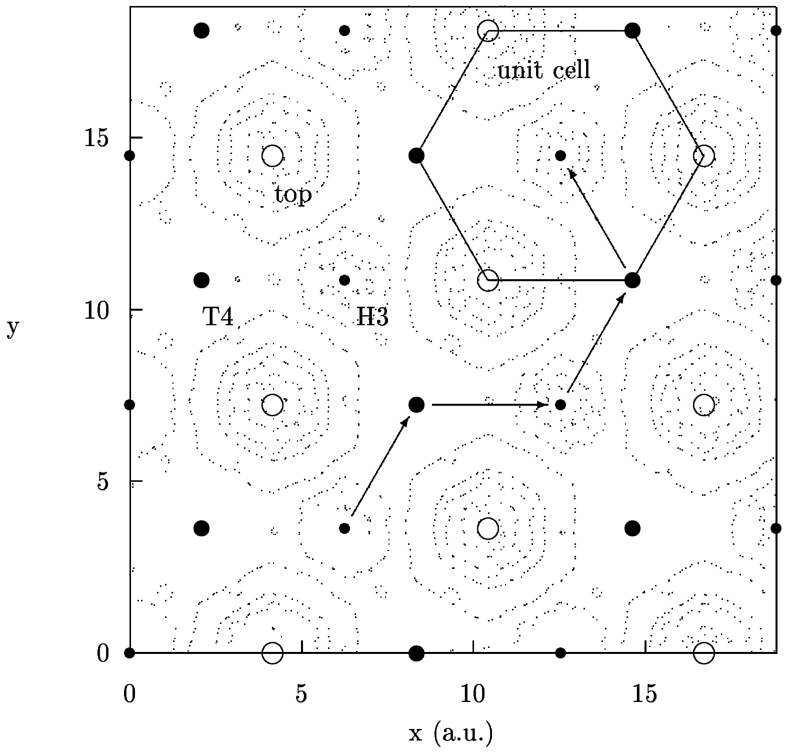

Figure 1: Energy contour for a single Si adatom above the As surfactant layer. The minima are at H3 (small full dots) and the saddle points for diffusion are at T4 (middle size full dots). The diffusion path from H3 via T4 to H3 is indicated.

Si adatom diffusion: We map out the total energy surface $E(x, y) = min_z E(x, y, z|\{\mathrm{R}\})$ by fixing the lateral position (x, y) of the Si adatom and minimizing the total energy with respect to the z-coordinate of the adatom and the coordinates of all As and Si substrate atoms $\{\mathrm{R}\}$. Results are shown as a contour map in Fig.1. We have calculated the total energy for the Si adatom at 16 lateral positions within the irreducible triangle of the (1×1) surface unit cell of the 1 ML As covered Si(111) surface[6], including the corner points "top" (lateral position of the As top layer), T4 (1st Si layer) and H3 (3rd Si layer). We find that the equilibrium position for the Si adatom is the H3-position. The saddle point for migration into a neighboring unit cell is the T4-position, for the top-position we find the highest energy. Detailed calculations show that H3 is the only minimum and that the path H3–T4 is a trough in the energy surface. The energy difference E_D= 0.25 eV between the H3 and T4 positions is the activation energy for surface diffusion of the Si adatom on the As-layer. Compared to the diffusion on the clean Si(111) (7×7) surface with an experimentally determined activation energy of 0.76 eV[7] diffusion is much faster. This supports the idea of passivation due to group-V surfactants. The diffusion path according to our calculation is $H3 \rightarrow T4 \rightarrow H3 \rightarrow \ldots$ in troughs of the energy surface.

We found that relaxations of the As-layer and the Si substrate layers are very important for surface diffusion. For a rigid surface (at equilibrium positions of As-passivated Si(111)) the energy difference between H3 and T4 is only about half the barrier height E_D quoted above. Relaxation lowers the energy of the H3 configuration, and thus it slows down the surface diffusion.

Energy gain due to exchange of a Si adatom with an As surfactant: We calculated the configuration and energy of an incorporated Si by relaxing a configuration with the Si atom on a substitutional site and the replaced As atom on a neighboring adatom position H3. The Si atom remains close to the substitutional site and the As adatom moves closer to the incorporated Si atom. The energy of the equilibrium configuration (Si_{Sub} + As_{Ad}) is lower than the Si adatom configuration by E_B= 0.8 eV, as one expects for a good surfactant which moves to the surface to reduce the surface free energy.

Exchange Process: The search for the saddle point on the exchange reaction path Si_{Ad}+$\mathrm{As}_{Sub} \rightarrow$ Si_{Sub}+As_{Ad} is exceedingly more complicated than for the diffusion saddle point. In principle one has to determine saddle points in a multi–dimensional configuration space spanned by the position vectors of all atoms in the supercell. One usually makes the assumption that only the coordinates of the atoms mainly involved in the transition, i.e. in our case the Si adatom and of the replaced As atom, have to be restricted and that the other atoms follow their motion. This leads to the following procedure in the spirit of the HAC-approach [10]: (i) we define starting configurations *along the direct exchange path* from the Si adatom (Si_{Ad}+As_{Sub}) to As adatom configurations (Si_{Sub}+As_{Ad}) at fractions of 1/32 of the total path length; (ii) the two exchanging atoms are allowed to relax perpendicular to the direct path-vector; (iii) all other atoms are allowed to relax freely. In this way it is possible to determine energies at configurations which are not extrema on the energy surface.

The application of the procedure just described is complicated by the existence of side minima (SM) along the exchange path which are to be expected in covalently bonded materials with directed bonds. Then one first has to determine the side minima and then apply the restricted minimization to all partial paths between neighboring minima. We followed a multiple–step procedure: (1) determine a (preliminary) saddle point by applying the HAC–method to the direct path, (2) relax the system from close to the determined saddle point by unrestricted minimization to a minimum configuration. If this is not one of the minima already known, use the HAC–method on the partial paths between all neighboring minima starting from step (1) again. In this way, we successively map the configuration space close to the transition path and can be pretty sure to have considered all relevant minima and paths. We are particularly interested in paths with low barriers since they dominate the transition rate of a thermally activated system.

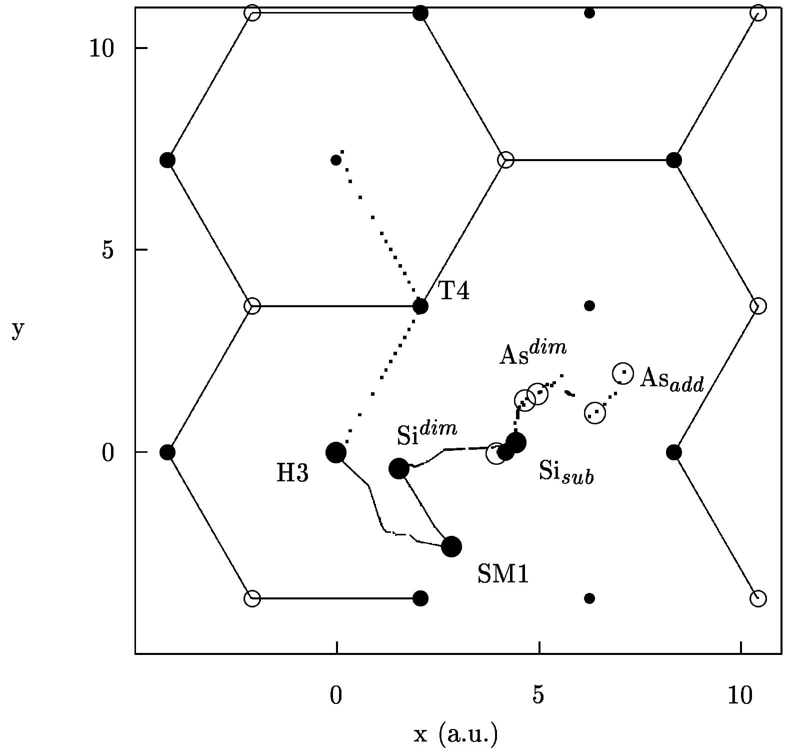

Figure 2: Positions along the exchange path projected to the surface plane. Shown are the paths of the Si atom (full line) and the As atom (dotted line) involved in the reaction. The atom positions for the local minima encountered on the path are indicated by circles (full lines for Si, dotted for As). The dashed line H3–T4–H3 is the diffusion path of the Si adatom.

The optimal path[16] is shown in Fig. 2. The coordinates along the exchange path of the two participating atoms are shown, projected to the surface of the crystal. The energy along the path is plotted in Fig. 3 vs. the path length of the Si atom. The locations of the side minima are indicated by open circles in Fig. 2 and the atomic structures of three configurations are shown in Fig. 3. One local minimum (named “dimer” configuration) is found about halfway between Si adatom and substitutional Si. It consists of a Si-As-dumbbell parallel to the surface whose center of mass is close to the top position. The energy of this dimer is approximately the same as for the Si adatom at H3. We found the barrier on the direct path from Si_{Ad} to the dimer configuration to be larger than 1 eV. Thus, the system prefers a detour via a side minimum (named SM1) with a much smaller barrier of $E_{EX} = 0.27$ eV. This is the highest barrier along the optimal exchange path. On the partial path from Si_{Ad} to SM1 the vertical height of the Si atom decreases, but only one of the 3 Si-As bonds is broken, thus leading to the moderate energy barrier. From SM1 again for energetic reasons the optimal path goes via the dimer configuration (with a low barrier of ≈ 0.15 eV) instead of directly towards the substitutional site (with a barrier > 1 eV). On the path SM1 → dimer the coordination number of the Si and As atoms stays the same but bond angles are stretched. On the final path dimer → Si_{Sub} both atoms change their bonding partners. A barrier of ≈ 0.11 eV has to be overcome. The final configuration Si_{Sub}+As_{Ad} shows a 4-coordinated Si_{Sub} atom in an almost ideal tetrahedral surrounding which leads to the appreciable energy gain with $E_B = 0.8$ eV. We find one additional minimum (named SM3) with a lower binding energy close to the end configuration Si_{Sub}+As_{Ad}, but with the As atom at a closer (projected) distance. We checked for further side minima by full relaxation of all atoms starting from the configurations close to the saddle points of the partial paths. In each case, the system found one of the previously determined minima.

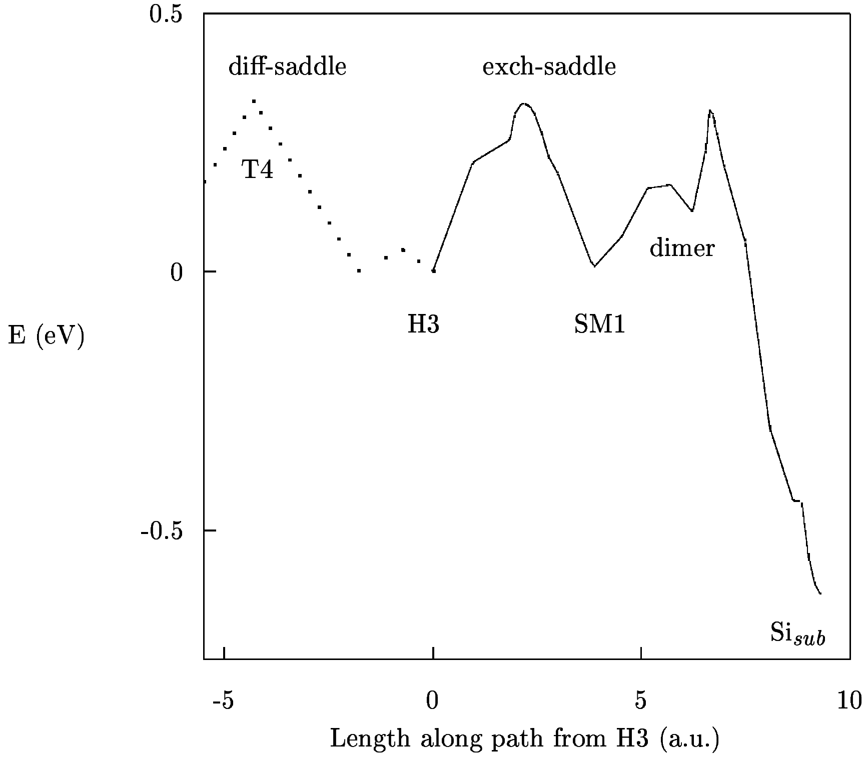

Figure 3: Energy (relative to H3 position of Si adatom) along the diffusion path (to the left of x = 0) and along the exchange path to substitutional Si (to the right). The atomic configurations for important minima are shown as insets: H3: Si_{Ad}; SM1: asymmetric dimer; Si_{Sub}: substitutional Si and As adatom (light: Si adatom; gray: As; black: Si bulk). [The insets can be found in the complete figure]

In summary, there are several local minimum configurations along the optimal exchange path. The highest barrier $E_{EX} = 0.27$ eV is found on the path from H3 to SM1 ("entrance channel", with the Si adatom above the As layer), the other barriers on the paths from SM1 to dimer and from dimer to SM3 ("exit channel", with the As atom above the top layer) are much smaller.

Scenario for diffusion of Si adatoms on As adlayer: In our calculation we find the following hierarchy of activation energies: $E_D = 0.25$ eV $\approx E_{EX} = 0.27$ eV $<< E_B = 0.8$ eV. Thus, the absolute minimum configuration (Si$_{Sub}$+As$_{Ad}$) can be reached immediately when diffusion is thermally activated. A newly deposited Si adatom can only make very few diffusion jumps before it is incorporated into the As-layer. Any further diffusion jump has to be thermally activated from this configuration. One possibility for a diffusion jump is to follow the exchange path backwards by re-exchange Si$_{Sub}$+As$_{Ad}$ $\rightarrow$ Si$_{Ad}$+As$_{Sub}$. The activation energy E_{REEX} involved in this process is $E_{REEX} = E_{EX} + E_B \approx 1.1$ eV. This is the *effective* activation energy for diffusion of the Si adatom. The jump sequence suggested by these results is Si$_{Ad}$(H3) $\rightarrow$ Si$_{Sub}$ $\rightarrow \ldots \rightarrow$ Si$_{Ad}$(H3) $\rightarrow$ Si$_{Ad}$(H3,next cell) $\rightarrow \ldots \rightarrow$ Si$_{Sub}$, where the transfer from one unit cell to a neighboring cell always goes via the T4 site.

Another possibility would be similar to the "kick-out" mechanism [17] found e.g. for Au in Si. The As adatom can de-bind and diffuse freely, if the binding and diffusion energies are lower than for Si adatoms. The Si atoms are re-activated for diffusion by re-exchanging with any of the freely diffusing As adatoms. The activation energy would again be E$_{REEX}$. No information on the binding or diffusion energy of As adatoms on the As-terminated Si(111) surface is available yet.

The calculated values for the effective diffusion energy with local re-exchange of As$_{Ad}$ and Si$_{Sub}$ and the relation of the exchange and "genuine" surface diffusion barriers are in accord with the experimental findings of Voigtländer *et al.* [7]. Compared to the experimentally determined activation energy on clean Si(111), E$_{D,clean}$ = 0.76 eV, the *effective* diffusion barrier, E_{REEX}, is increased. The diffusion length of Si adatoms is indeed reduced due to As surfactants, because the Si atoms are trapped in the As-layer. With increasing temperatures one expects the diffusivity to go up, which leads to fewer and larger islands at higher temperatures, as found in experiments.

In this contribution we have investigated the exchange reaction of an isolated Si adatom on the Si(111) surface passivated by an As surfactant. We found a very complicated continuous exchange path, which avoids to a large extend the breaking of chemical bonds. This leads to a rather low exchange barrier which is comparable to the energy barrier for adatom diffusion. This finding is in contrast to the widely accepted and rather intuitive view that the thermally activated surface diffusion should always be (much) faster than the exchange process. We believe, the fact that the relaxation slows down the surface diffusion and at the same time lowers the exchange barrier is a general feature on covalently bonded semiconductor surfaces. Taking into account that for a good surfactant the incorporation of deposited adatoms is always energetically favorable we believe that the re-exchange dominated adatom diffusion on surfactant layers is a quite general process and may not be ignored.

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Density-Functional Molecular-Dynamics Techniques Working Group

Nodes: **Antwerp and Lisbon**

Hightligths of collaboration in the framework of the Ψ_k network

Ab-initio calculations for $AsNCa_3$ at high pressure

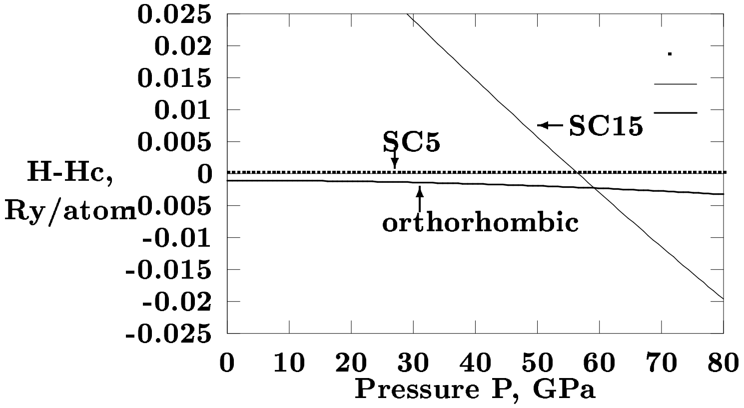
P.R. Vansant, P.E. Van Camp, V.E. Van Doren and J.L. Martins*

Department of Physics, University of Antwerpen (RUCA),
Groenenborgerlaan 171, B-2020 Antwerpen, Belgium
**INESC, Rua Alves Redol 9, P-1000 Lisboa CODEX, Portugal; Instituto*
Superior Tecnico, Avenida Rovisco Pais 1, P-1096 Lisboa, Portugal.

A structural optimization at constant pressure based on a variable-cell-shape scheme [1] is applied to $AsNCa_3$. The scheme minimizes the enthalpy also as function of the metric g_{ij} and of the positions of the atoms.

The structure of $AsNCa_3$ was found experimentally (see Ref. [2]) to be a distorted cubic perovskite structure which has a primitive orthorhombic (*Pbnm*) symmetry. Also theoretically the lattice parameters and internal structural parameters (existing due to the distortion) were determined and correspond within less than 1% to the experimental data.

The pressure dependence of the structure is determined by considering the difference in enthalpy $(H - H_c)$ between the considered structure and the cubic perovskite structure consisting of 5 atoms (SC5) as function of the pressure (see figure). When increasing the pressure the orthorhombic structure becomes more stable in comparison with the SC5 cubic structure. However, starting from a pressure of about 60 GPa another cubic phase SC15 consisting of 15 atoms is found to have a lower enthalpy. At this pressure a phase transition to this SC15 structure might occur. The nitrogen is then surrounded by *eight* calcium atoms as closest neighbours instead of *six* in the orthorhombic structure.



Such a SC15-like structure could also be a possible phase of $MgSiO_3$ in the earth's lower mantle.

For the orthorhombic structure a decrease of the bandgap is found with increasing pressure. The bandgap energies are 0.87 eV, 0.54 eV, 0.28 eV , 0.10 eV and 0.003 eV for respectively 0 GPa, 15 GPa, 30 GPa, 45 GPa and 60 GPa. Because LDA-calculations could give up to 50% smaller bandgaps in comparison with the correct one, a scissors-operator could be applied to obtain fairly good estimates of the bandgap energies at all those pressures. The $AsNCa_3$ compound in the orthorhombic phase is not yet metallic at 60 GPa. The SC15 structure, however, is already metallic at the moment this structure becomes more favourable in enthalpy.

Acknowledgement
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Structural Phase Transitions of Lithium Pnictides under Pressure

P.E. Van Camp and V.E. Van Doren

Department of Physics, University of Antwerpen (RUCA),
Groenenborgerlaan 171, B-2020 Antwerpen, Belgium

The lithium pnictides, Li_3X with X=N, P, As, or Sb, are superionic conductors that have been studied before because of their potential use as electrolytes in solid state batteries. Experimentally, Li_3N is found to have the hexagonal D^1_{6h} structure (with one molecule per cell) and to undergo a phase transition at 0.42 GPa [1] or at 0.6 GPa [2] to another hexagonal structure (D^4_{6h}) with two molecules per cell. Upon releasing the pressure the D^4_{6h}- structure remains stable at zero pressure. This means that at zero pressure both hexagonal structures coexist. No other transitions are observed to a pressure of 8 GPa [2]. Both Li_3P and Li_3As are found in the D_{6h}^4-structure and no transitions were observed as yet.

In the present work we calculate the total energy at different pressures of Li_3N, Li_3P and of Li_3As in the D_{6h}^1-, D_{6h}^4- and the T_d^1-structure. The last structure (which has four molecules per cell) is included because it is the structure of the related compound Li_3Bi. The calculations are performed in the framework of the local density approximation and using ultra-soft pseudopotentials [3] and a large plane wave basis (kinetic energy cut-off of 100 Ry). For the exchange-correlation part we use the Ceperley-Alder expression [4] as parametrized by Perdew and Zunger [5]. The optimization of the lattice parameters and of the internal parameters is performed with the Broyden-Fletcher-Goldfarb-Shanno-algorithm [6]. The calculated total energies are then fitted to the third-order Birch [7] equation of state from which the bulk modulus and its pressure derivative are determined.

The calculated and experimental lattice constants (in Å), bulk moduli (in GPa) and their pressure derivatives for Li_3N are given in the table. In all cases the calculated ground state turns out to be in the D_{6h}^4- structure. Because the atomic volume in the D_{6h}^1-structure is larger than that of the D_{6h}^4-structure the calculated transition between the two structures is at a negative pressure (for Li_3N -1.1 GPa with a volume increase of 23% and an energy difference at the transition of only 16 meV/atom). The transition from D_{6h}^4 to T_d^1 is found at 37.9 GPa, with a volume decrease of 8% and an energy difference at the transition of 109 meV/atom. For Li_3P the transition between the two hexagonal structures is at -4.1 GPa with a volume increase of 31% and an energy difference at the transition of 174 meV/atom. For Li_3As these values are respectively -3.8 GPa, 31% and 183 meV/atom.

		Present work	Hartree-Fock [8]	Exp. [9]
D_{6h}^1	a	3.508	3.61	3.648
	c	3.745	3.84	3.873
	c/a	1.0674	1.0637	1.062
	B_0	61.02	-	-
	B_0'	3.7	-	-
D_{6h}^4	a	3.418	-	-
	c	6.100	-	-
	u	0.5776	-	-
	c/a	1.7846	-	-
	B_0	78.166	-	-
	B_0'	3.77	-	-
T_d^1	a	4.824	-	-
	B_0	82.75	-	-
	B_0'	3.84	-	-

Acknowledgement

This work is supported by the Belgian NSF (FWO) under grant No. 9.0053.93 and partly by the HCM network "Ab-initio Calculations of Complex Processes in Materials" grant No. ERBCHRXCT930369.

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Density-Functional Molecular-Dynamics Techniques Working Group

Node: **Helsinki**

Scientific Highlight

A major research topic in the node's activities has been the first-principles simulation of defect-related phenomena in semiconductors, both in silicon and in II-V and II-VI compound materials. Both native and introduced defects profoundly affect the electronic and optical properties of semiconductors, both as bulk materials and in engineered structures, such as superlattices and heterostructures. As there is a strong coupling between the ionic and electronic degrees of freedom, sophisticated numerical and theoretical techniques are required for predictive calculations of the defect-related properties.

Defects play a central role in semiconductor doping, as complexes formed by the dopants and by point defects (vacancies, interstitials) govern the compensation of carriers and determine the doping limits. Large lattice relaxations transform shallow levels to deep ones in the semiconducting gap. Another typical feature are the metastabilities associated with several defect complexes, especially in compound semiconductors.

Specific projects carried out recently include

(i) metastable defects in GaAs: extension of the DX and EL2 concepts
(ii) doping of ZnSe: self-compensation and carrier limits
(iii) band offsets at GaAs/ZnSe interfaces
(iv) antisite defects in SiC
(v) defects, oxygen and broadband luminescence in GaN and AlN
(vi) amorphisation of Si by ion irradiation
(vii) oxygen clusters in Si

The node works in close collaboration with companies active in the semiconductor area, such as Okmetic Ltd (major manufacturer of Si wafers) and Semitronic Ltd (SiC growth). The results and information obtained through the Network activities have benefited also the collaboration projects with industry.

For further information and complete publication lists, please consult the node's WWW page:

http://www.fyslab.hut.fi/

Density-Functional Molecular-Dynamics Techniques and Large Systems Working Groups

Node: **Lyngby**

Scientific Highlights

The Center for Atomic-scale Materials Physics (CAMP) at the Department of Physics, The Technical University of Denmark, consists of about 25 researchers including PhD students and Postdocs. The research has been in fundamental aspects of materials physics and surface physics with a particular emphasis on:

1) Metal on metal growth – including studies of surface alloy formation, segregation and elementary diffusion process by DFT and simulations of dynamics and kinetics using molecular dynamics and kinetic Monte Carlo methods based on semi-empirical interatomic potentials of the effective medium type.

2) Nano-structures and interfaces – including studies of metallic point contacts, nano-tribology, interface structures, and the magnetic, electrical, and mechanical properties of nano-structured materials.

3) Chemical properties of surfaces – including studies of adsorption, and further reactions on transition metal and semiconductor surfaces. Models have been developed on this basis describing the electronic factors of a surface determining the reactivity.

The group has benefitted from the network mainly through the newsletter and participation in the Network Conference in Schwäbisch Gmünd. The group has a number of collaborations with members of the Network and, very importantly, with experimentalists and industry.

Pseudopotential Techniques and Density-Functional Molecular-Dynamics Techniques Working Groups

Node: **Cambridge**

Simulations related to the mechanical deformation of materials

A fundamental understanding of the mechanical properties of solids is difficult because two length scales are involved simultaneously, the atomistic scale and the mesoscopic scale of elastic strain. The jointly sponsored Network/CECAM workshop was directed at the problem of bridging the gap between these two length scales. Small ab initio calculations can determine parameters which can be fed into simulations on the larger mesoscopic scale.

The research was started in Cambridge by G. Francis with calculations of the structure of grain boundaries in germanium as an example of a strongly covalently bonded material. A tilt boundary was found to have one more or less unique structure with much lower energy than any other, while a twist boundary had many different structures of roughly equal energy.

Francis then carried out simulations in which one grain was slid over the other at the grain boundary, using the germanium twist boundary. These were then extended by Carla Molteni. The first result was that sliding proceeds by a series of stick/slip processes, i.e. the bonds across the boundary would be increasingly strained until there was a sudden topological rearrangement of the bonding. The sliding was therefore discontinuous, with the energy and stress building up to a maximum until the 'click' of the rebonding. The second finding was that the rebonding occurred over only a small region of the boundary. It is not clear that would be possible in a simple 2-dimensional model with a boundary line, but it is in 3 dimensions. In a typical case only two bonds were detached from two atoms and swapped around. The third result was that the configurational path did not reverse if after some distance one reversed the direction of slide. Also as one continued, the surface got increasingly disordered with the disordered region growing in width. Both of these are indications of irreversibility and energy dissipation. Fourthly Molteni was able to work out the displacement path of the atoms during rebonding and thus the energy barrier at various stages of the sliding before the spontaneous 'click' at zero Kelvin when the barrier has gone to zero. At non-zero temperature the rebonding would occur with a probability given by a Boltzmann factor before the 'click'. In this way the relation between stress and strain rate was calculated, based on one typical rebonding which was investigated in detail. Fifthly the behaviour of 'gap states' in the semiconductor band gap was noted. The electronic structure of semiconductors with defects is often discussed in terms of gap states, the notion being that atomic relaxations are driven or accompanied by suppressing states in the band gap and driving them into the valence or conduction band, particularly the valence band. This was indeed observed at the 'click'.

At the same time V. Deyirmenjian carried out ab initio simulations of pulling a specimen of aluminium apart, containing an array of defects in the form of lines of vacancies. These were intended to be somewhat like microcracks, the computing resources not allowing anything more realistic. The intention was to see how the break-up proceeded from the defects. Deformation started by creating what could be described as a dislocation, but the atoms flowed rather smoothly over one another in a way more reminiscent of a fluid than how one might envisage a crystal.

Another aspect of that research project was to compare the ab initio results with those obtained using traditional empirical classical potential models of the interatomic bonding, such as the pairwise Morse potential and the Sutton-Chen 'glue' model. The Morse potential gave qualitatively completely wrong behaviour, while the 'glue' model gave also a type of flow movement but not quantitatively correct even when the parameters of the 'glue' model had been tuned to the properties of our computational aluminium. There were systematic deviations particularly at large strains, and an idea of our collaborator Professor M. Finnis was able to improve that significantly. The conclusion is that if it is sufficient to have some sort of ductile behaviour, then a Sutton-Chen model as modified by Finnis can give it, but that ab initio calculations are required for more accurate results pertaining to a specific metal.

In order to compare the grain boundary sliding in a ductile metal with that in the covalently bonded germanium, Molteni carried out analogous simulations on a twist and a tilt boundary of aluminium. In the one case the sliding was completely smooth and reversible with no stick/slip 'clicks'. The atoms just flowed over each other, reminiscent of the behaviour observed by Deyirmenjian noted above. In the other boundary there were some stick/slip 'clicks' but the energy jumps were an order of magnitude smaller than in the case of germanium. In a third simulation, the smoothly flowing boundary was taken and one atom removed to form a vacancy. This was found to be an 'irritant' in the boundary and the sliding was no longer smooth, ie it had developed stick/slip jumps when configurations of atoms got hung up around the vacancy. Here one grain seemed to roll over the other, with a group of three atoms rotating as a whole like a wheel– a rather bumpy triangular wheel but the adaptable flowing could cope with that. What matters in metallic bonding of an sp-bonded element like aluminium is that the local volume around an atom is nearly constant in order to accommodate the valence electron gas; but with the ionic radius only half of the atomic radius, the spatial arrangement of the nearest neighbours is less important. The sideways migration of the boundary was also observed.

All the above results concern clean boundaries without impurities. However impurities affect grain boundaries substantially, as shown for example by measurements in the group of Professor Gust in Stuttgart on grain boundaries of aluminium containing a very small bulk concentration of order 20 ppm of gallium. It was found that such small concentrations increased the grain boundary mobility by about a factor of ten. Gallium is a notorious embrittler of aluminium, but that may be a different phenomenon because it appears to involve high concentrations of gallium being sucked into the grain boundaries. Simulations were carried out on a $\sigma = 11$ (113) tilt boundary containing from zero to two monolayers of gallium. This boundary is a particularly well fitting boundary, with the environment of each atom not differing very much from that in bulk aluminium as regards the number and distances of the near neighbour atoms. Consequently the boundary energy is rather low compared with other less well fitting boundaries such as obtained in the sliding simulations of Molteni. The only local strain in the boundary is between two atoms that straddle the boundary, whose separation is 0.15 $\AA$ smaller than the nearest neighbour distance in bulk aluminium. When gallium atoms are substituted in those sites, the structure relaxes with substantial reduction in energy and a reduction in that interatomic distance to what it is in pure gallium. However it must not be thought that gallium is just a smaller atom than aluminium; in solid solution gallium has almost exactly the same atomic volume as aluminium, and in the pure state even a 10 percent larger one. Detailed results were obtained on the energetics of boundaries with 10 different concentrations of gallium, on the relaxations in the boundaries, the looseness of the atoms as measured by restoring force constants for displacements, and the energy barrier for boundary migration. These could all be explained in terms of the 'two radii' behaviour of atoms in such systems. The 'volume radius' determines the volume per atom needed to accommodate the conduction electron gas, which energetically is the stronger force. The 'near-neighbour' radius gives then the preferred near neighbour distance at that atomic volume, which depends on the crystal structure. In aluminium the two radii are nearly equal, but in gallium the near-neighbour radius is significantly smaller, which accounts for its unusual crystal structure. In the aluminium grain boundary the gallium impurities allow the relaxation of the particularly tight contact. The observed energy lowering can be more or less completely ascribed to a reduction in local strain energy. From this picture one can predict more significant effects in less well fitting boundaries including the build up of a fraction of a monolayer in thermodynamic equilibrium at room temperature. The mobility of the boundary is enhanced because gallium atoms in the boundary can more easily slide past other atoms because of the smaller near-neighbour radius while the structure is held open by the larger volume radius.

So far computational limitations have prevented any sliding calculations with impurities, but simulations involving a dislocation interacting with a grain boundary are planned. That is a more important process in plastic deformation of materials than the grain boundary sliding.

The above calculations are obviously still a long way from answering what happens in real macroscopic deformations, but they have demonstrated some of the variety of processes occurring at the atomic level and the kind of calculations that are now possible.

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Acta Metallurgica et Materiala (submitted Aug. 1997).

Muffin tin techniques Working Group

Node: **Strasbourg**

Highlight of the results obtained with the TB-LMTO code

O. Elmouhssine, P. Krüger, G. Moraitis[1], M. A. Khan,
H. Dreyssé, J. C. Parlebas and C. Demangeat
Institut de Physique et Chimie des Matériaux (IPCMS-GEMME)
UMR 46 du CNRS-Université Louis Pasteur, 23 rue du Loess, 67037 Strasbourg Cedex, France

J. Izquierdo and A. Vega
Departamento de Fisica teorica y Nuclear, Universidad de Valladolid
47011 Valladolid, Spain

F. Amalou, H. Bouzar and M. Benakki
Département de Physique, Université de Tizi-Ouzou, Algérie

A. Mokrani
Groupe de Physique du Solide pour l'Electronique,
Université de Nantes, 2, rue de La Houssinière, 44072, Nantes, France

(December 10, 1997)

The course "Hands-on TB-LMTO computer program" was announced in the April issue (1994) of the HCM Newsletter. Two members of the theoretical group: G. Moraitis (professor) and A. Vega (post-doc from Valladolid) have registered and both of them have attended the course organized by Ove Jepsen on October 24-28, 1994, at the Max-Planck Institute in Stuttgart. Back from Stuttgart, G. Moraitis has used the code for spectroscopic and theoretical investigations of sub-stoichiometric Ti-nitrides, Ti-carbonitrides, and band structures of CoRh, CoRu, Co_3Pt alloys.

Also, calculations concerning "Spin-flop transition in Fe_nCr_m superlattices" [1] have shown the sensitivity of the Fe/Cr interface coupling with the lattice parameter. O. Elmouhssine and P. Krüger have been strongly involved in calculations concerning the adsorption of very thin films (of the monolayer range) of transition metals on metallic, or graphitic substrates. The Ph.D. thesis of Elmouhssine (April 1998) will contain the following results:

i) p(2x2) versus c(2x2) configurations for one Mn monolayer on Fe(001) [2]. This contribution shows clearly that besides the well known c(2x2) configuration, almost degenerate and more complex configurations are present and may explain the controversial XMCD results obtained by different experimental groups;

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[1] present address: Département de Physique, Université de Ouagadougou, Burkina Faso

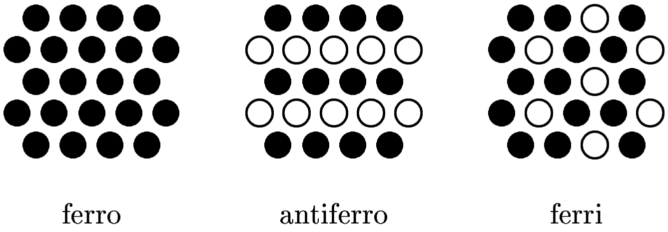

Figure 4: Magnetic configurations considered for the $3d$ transition metal monolayers on graphite (0001). Full and open circles represent up and down spins, respectively.

ii) Similar configurations are shown to be present for Mn monolayer on Co(001). These results are not in complete agreement with recent XMCD results of O'Brien and Tonner but can explain MOKE results [3];

iii) Complex magnetic configurations have been detected by O'Brien and Tonner for $Fe_n/Co(001)$. Those layered antiferromagnetic configurations [4] are shown to be present when n $\geq$ 3;

iv) Growth, structural stability, electronic structure and magnetism of MnAg(001) surface alloys [5, 6];

P. Krüger (Ph.D. thesis in January 1998) has used the TB-LMTO code for the following studies on transition metal monolayers (ML) deposited on the graphite surface:

(i) $4d$ transition metal ML [7, 8] have been investigated in an epitaxial structure, which is compatible with the experimental findings for the Ru/C(0001) system. It is found that only Ru and Rh ML can be ferromagnetic for metal-graphite interlayer distances above 2.5 Å. Due to the highly anisotropic hybridization with the C p_z orbitals, the moments depend strongly on the the adsorption site.

(ii) For the $3d$ transition metal ML [9] three magnetic configurations have been compared (see fig. 4 and table 1).

We find that the V and Cr ML are nonmagnetic, while the Fe, Co and Ni ML are ferromagnetic on graphite. For the Mn ML, the antiferromagnetic and ferrimagnetic configurations are degenerate and more stable than the ferromagnetic one. The absence of magnetic solutions for the adsorbed Cr ML can be related to the great sensitivity of Cr to frustration of the nearest neighbour coupling, which is important for the hexagonal lattice. For the unsupported Cr ML, the antiferromagnetic and a ferrimagnetic configuration exist, but they are almost degenerate with the nonmagnetic solution. By comparison with the free standing ML, we find that the graphite–metal interaction substantially reduces the magnetic moments of the adsorbed ML.

More recently, F. Amalou, a Ph.D. student registrated at the University of Tizi-Ouzou (Algeria) has started a thesis on the determination of the magnetic configurations at the surfaces of FeCr and FeRh alloys [10].

M. M. Schwickert et al (Phys. Rev. B, in press) have depicted through MOKE an oscillatory period in the interlayer exchange coupling in Fe_5V_m superlattices: within a collaboration with Valladolid we have performed calculations for both Fe_5V_m superlattices and for V_m thin films on Fe(001) and Fe(011) [11].

		Cr		Mn		Fe		Co		Ni	
		free	ads	free	ads	free	ads	free	ads	free	ads
Fo	μ	–	–	3.0	1.0	2.7	2.1	1.9	1.3	0.4	0.3
	$-E_M$	–	–	6	2	41	9	25	5	1	0.5
AF	$\lvert\mu\rvert$	1.5	–	3.1	1.9	2.5	1.2	1.4	–	–	–
	$-E_M$	0	–	33	6	29	3	7	–	–	–
Fi	μ_1	1.6	–	3.2	1.9	–	–	–	–	–	–
	μ_2	-2.2	–	-2.8	-2.0	–	–	–	–	–	–
	$-E_M$	1	–	27	6	–	–	–	–	–	–

Table 1: Magnetic moments (in units of μ_{B}) and magnetic energies (E_M, in units of mRy) of the different solutions of the $3d$ transition metal monolayers on graphite (0001). Fo, AF, Fi, free, and ads means ferromagnetic, antiferromagnetic, ferrimagnetic configuration (see fig 4), unsupported monolayer, and on graphite adsorbed monolayer, respectively. In the ferrimagnetic solutions, μ_1 (μ_2) is the moment of the majority (minority) type of atoms.

The node greatly appreciated and benefited from the HCM Ψ_k-Network. First the Network made possible the participation in various European conferences of senior scientists and French students which would have been almost impossible without Network's help. Another very important point is the financial support of the Network given to workshops organized by the French node. In 96 and 97 we organized three workshops supported by the Network. Once again clearly without this help, some eminent colleagues would have not been able to attend these meetings. Moreover, the collaboration with the Stuttgart node on TB-LMTO was very productive (more than 10 papers) and obviously the Network contributed greatly to the dissimenation of the TB-LMTO method and the results. We also appreciated very much the Ψ_k-Newsletter which has become a very useful tool. Finally, we would like to mention that various discussions during meetings were of great help to two members of our node in finishing a review paper published in Sur. Sci. Report on Surface and Interface Magnetism.

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Green's Function Techniques, Muffin Tin Techniques and Algorithms for Parallel Computers Working Groups

Node: **Messina**

Scientific Highlights

The research work of our group has been devoted to the study of multicomponents metallic systems, with the purpose to understand their physical properties on the basis of *ab initio* calculations, mainly implemented within the multiple scattering framework (KKR or KKR-CPA). The work has been developed along the following lines:

1. Electronic Topological Transitions and Fermiology
2. Phase stability of metallic alloys
3. KKR-CPA and Bloch Spectral Function codes for any lattice

which will be discussed separately.

1. Electronic Topological Transitions and Fermiology

When a metallic alloy is subjected to a thermodynamic transformation (e.g. an uniaxial strain or a change of the composition) the band structure does change. As a consequence some bands at Fermi level might move up or down producing a change in the shape and the connectivity of the Fermi Surface, when the Fermi level passes across Van Hove singularities. These, since I.M. Lifshitz's 1960 paper[1], are called Electronic Topological Transitions (ETT). Lifshitz's theory shows that whenever such phenomenon occurs there is a "singular" contribution to the density of states and to the system grand potential that can be written as:

$$n(\epsilon) = n_0(\epsilon) + n_1(\epsilon) \tag{1}$$

$$\Omega = \Omega_0 + \Omega_1 \tag{2}$$

$$n_1(\epsilon) = \alpha|\epsilon - \epsilon_1|^{\frac{1}{2}}\Theta(\epsilon - \epsilon_1) \tag{3}$$

$$\Omega_1(\mu) = -\frac{4}{15}\alpha|\mu - \epsilon_1|^{\frac{5}{2}}\Theta(\mu - \epsilon_1) \tag{4}$$

where μ is the chemical potential and ϵ_1 is the energy of the Van Hove singularity. In the above equations, α is related to the effective mass of the band (assumed parabolic in a neighbourhood of ϵ_1). Ω_1 can be positive or negative depending on the kind of the Van Hove singularity and on the fact that it falls above or below the Fermi level. Accordingly, to open or close a new bit of the Fermi surface requires or releases energy. We remark that the above equations holds in absence of impurity scattering.

On the basis of the above simple arguments, one can see that on varying the concentration of a metallic solid solutions (and therefore the valence electrons per atom, in case of non homovalent components) such "transitions" can occur, although the impurity scattering will broaden the effect of the transition. Then the transport properties will be affected, because they depend on integrals over the Fermi Surface, but also equilibrium quantities will, because of the work involved on changing the shape of the Fermi Surface.

We have studied the effects of compositional changes on the Fermi Surface topology on metallic random alloys in a review paper [2], where we also discussed the concept of Fermi surface for a disordered alloy and the technical problems connected with its numerical determination. Later, we have studied the influence of the ETT's on the equilibrium properties [3], also in presence of impurities and temperature effects, and illustrated such work for the case of Ag_cPd_{1-c} alloys [4] that present five distinct ETT's, on varying the concentration. In particular, in ref. [3] we have shown how ETT's are responsible of the deviations from Vegard's law for the atomic volume change with the concentration.

2. Phase stability of metallic alloys

The study of the phase equilibria of metallic alloys can be cast into the Density Functional theory in several ways. For instance, in order to predict the equilibrium phase of a given binary alloy, one could perform the electronic total energy calculations of many different possible phase and find out the stablest one. This procedure has several inconveniences, either due to the large amount of different possible structures for the same alloy, or to the treatment of the solid solution phase, that, unless one uses an O[N] method, as those of ref. [5, 6], requires further approximations in order to take into account the substitutional disorder.

Another inconvenience arises when one is interested in understanding the mechanisms that drive the system toward a particular phase, which is not necessarily transparent from a first principles calculation. This can be bypassed by the study of the Fermi Surface of the random phase, that often contains the seed of the ordering or phase separation occurring at low temperature [7, 8]. But, in many cases, for which the fcc Cu_cPd_{1-c} alloy is one of the most striking example, it might not be enough. In fact, in the Cu rich side of the phase diagram, such alloy orders into fcc based structures ($L1_2$), with an alternate sequence of Cu and Cu-Pd planes along the (0,0,1) direction. This ordering phenomenon, as it is well known[8], can be understood in terms of the Fermi Surface nesting mechanism, that enhances the concentration fluctuations susceptibility along the nesting direction. However, about the equiatomic composition, although the ordering occurs as an alternate sequence of Cu and Pd planes, again along the (0,0,1) direction, the equilibrium β phase has the B2 structure, i.e. geometrically a bcc rather than a fcc lattice. This implies that notwithstanding the homogeneous phase is unstable with respect to concentration waves along the (0,0,1) direction, other phenomena must occur. In the case of $Cu_{0.50}Pd_{0.50}$ an uniaxial strain of 40 percent along the (0,0,1) direction is required in order to reach the B2 phase making this problem untreatable by the perturbation theory. However, it is appealing to interpreting such Bain transition in terms of the coupling between strain and concentration fluctuations. Therefore we have chosen the route to calculate the total energy along the appropriate Bain path for alloys with superimposed concentration waves and try to get insights on the mechanisms producing the phase transformation.

Following this strategy, we have computed, by relativistic KKR and KKR-CPA methods the total energy of the equiatomic CuPd for: 1) the random alloy in the body centered tetragonal lattice; 2) the intermediate ordered alloy ($Cu_{0.75}Pd_{0.25}$)-($Cu_{0.25}Pd_{0.75}$) in the simple tetragonal lattice with two atoms per unit cell and 3) the ordered alloy again in the former lattice, varying the c/a ratio along the Bain path for all of them. In all these cases when $c/a = 1$ one gets the bcc or B2 lattices and when $c/a = \sqrt{2}$ one gets the fcc or $L1_0$ lattices.

We have found that the total energy has a function of c/a for the case 1) has two local minima corresponding to the bcc and fcc lattices separated by a relatively high energy barrier (6mRy); for the case 2) has again two local minima but the energy barrier is much lower (2mRy) and for the case 3) the $L1_0$ (fcc) lower minimum disappears and the overall lowest total energy value is taken by the B2 lattice. This suggests the following picture for the kinetics of the transformation: 1)In the random alloy phase any strain fluctuation driving toward the bcc lattice are restored by elastic forces, because the fcc local minimum is separated from the bcc minimum by the energy barrier; 2) on lowering the temperature concentration (and charge) waves occur, and the atomic diffusion in the two sublattice reduces the energy barrier; 3) the absence of the local minimum in the $L1_0$ lattice allows for a plastic deformation toward the B2 equilibrium phase.

By the analysis of the contributions to the total energy one sees that the exchange-correlation energy does not vary along the Bain path, while the equilibrium arises through a competition from the electrostatic and the band energies. The former as a minimum at the bcc-like lattices and a maximum at the fcc-like lattices, while the latter behaves exactly in the opposite way. The reason of the behaviour of the electrostatic energy is strictly related to the charge transfer, that in such systems is from Pd to Cu. The maximum charge charge transfer is in the B2 phase, a lattice quite common amongst the ionic salts, and reach the value of 0.28 electrons. We notice that in such system a concentration wave and a charge density wave are the same thing, therefore the charge transfer is directly related to the Fermi Surface nesting occurring in the random phase. But the charge transfer increases the electrostatic attraction between the Cu and Pd planes, perpendicular to the (0,0,1) direction, providing the energy to strain the lattice.

In order to complete the mechanism of this Bain transition remains to understand the reason why the band energy grows towards the B2 lattice. This is due to the applied strain that pushes the Fermi level into the Pd d-states, opening a hole pocket in the Fermi Surface. According to the ETT theory of the former section, this requires work, and this explain why the band energy favours fcc-like lattices.

The results illustrated above have been submitted recently for publication [9].

3. KKR-CPA and Bloch Spectral Function codes for any lattice

In order to perform the calculations described above, within the KKR-CPA framework, one new code had to be developed. The techincal problems related to the KKR structure constants calculations and the Brillouin Zone integration for an arbitrary Bravais lattice, the two major tasks of the extensions, have been described in ref. [10]. Here we give a very brief list of the features of a new method for the Brillouin Zone integration of KKR-type functions, that have a pole structures, but is easily extensible to any band theory.

The method sets an adaptive grid of lines in the irreducible segment of the Brillouin Zone, and perform the integrals along the lines by means of a local fit by rational functions of the integrand. The integrals in the direction grid is performed by means of and adaptive technique, based on an iterative "local" halving of the integration intervals whenever the relative difference of three points trapezoidal rule and Simpson's rule integrals is greater than an arbitrary input tolerance, ϵ. This method proves particularly efficients for KKR functions, where a precise integral can be obtained by calculating the integrand functions only in a neighbourhood of a pole, and this is precisely what the method does. In ref. [10] we compare the results of this method with others.

However, the most interesting feature of the method is that allows to get Brillouin Zone integrals correct within an error proportional to ϵ. As a consequence one could put error bars in the total energy calculations.

Benefits from the Network:

Computer Codes received:

Magnetocrystalline anisotropy energy and spin polarised relarivistic KKR-CPA codes for cubic lattices from Warwick Group (J.B. Staunton and S.S.A. Razee).

Computer Codes jointly developed(Warwick Group):

Magnetocrystalline anisotropy energy for any Bravais lattice.

Other important benefits:

We are aware that our work has been enriched by the scientific contacts offered by the Network and by the discussions with the members and their coworkers from outside the Networks (e.g. Eastern European countries).

Workshop Organization:

Our group organised Ψ_k Network International Workshop on Parallel Algorithms for Large System, held in Taormina ,26-28 November 1994 which has been supported by Ψ_k Network, Regione Siciliana and Local Funds.

Computer Codes:

Bloch Spectral Function (KKR-CPA) Code for cubic lattices passed to Warwick (J.B. Staunton) and Bristol (B.L.Gyorffy) Groups.

Code for Brillouin Zone integration using the Hybrid Method of E.Bruno and B.Ginatempo passed to Warwick Group (J.B. Staunton).

Spin-polarized relativistic Bloch Spectra Function Code for any Bravais lattices passed to Warwick Group (J.B. Staunton).

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Green's Function Techniques Working Group

Node: **Nijmegen/Cardiff**

Scientific Highlights

The Psi-k network encouraged us right at the start to organize a one-day meeting in Muenster on Green function methods, and scientists came from Germany, Greece and The Netherlands to discuss applications to surface electronic structure, photoemission, and electronic structure in general. Another, smaller meeting was organized in Nijmegen in 1994 to discuss calculations of dielectric functions, when scientists from Dublin, Twente and Nijmegen got together to discuss bond models and electron gas methods for dielectric functions. This meeting has in fact led to the participation of Twente (Wijers) in the Network, and collaboration between Twente and Dublin.

The Network facilitated several very useful trips abroad. In January 1995 Jeroen van Hoof, Martina Heinemann and John Inglesfield visited the group of Podloucky in Wien to discuss embedded LAPW calculations of surfaces versus slab LAPW calculations. We are still in discussion, so this was a useful contact. Jos Thijssen, then Nijmegen but now Cardiff, participated in the network conference on order(N) methods, and this has led to new research activities. Since Inglesfield moved to Cardiff, the network has funded visits to Cardiff of Jeroen van Hoof and Patrick Slavenburg to discuss their research, and of John Inglesfield to Nijmegen. Several papers are being written up in the fields of surfaces, interfaces and alloys as a consequence of these visits. The visits also enabled Jeroen van Hoof to mount his embedded electronic structure codes on the Cardiff machines, and this is proving invaluable for the research activities in Cardiff.

The highlight of Psi-k activities in Nijmegen was the development by Jeroen van Hoof, in collaboration with Simon Crampin (Bath) and Inglesfield, of the new embedding method, which can be used to calculate the electronic structure of surfaces, interfaces and bulk material self-consistently, taking into account the substrate on the same footing as the region being embedded. In this method, the system is divided up into layers which are embedded onto other layers to build up the surface, interface or bulk. The new code has been used to calculate surface and interface electronic structure, and the most exciting applications to date are by Van Hoof in collaboration with workers from Delft and Philips on magneto- resistance through metallic multilayer systems.

The following published papers acknowledge network support:

Embedding method for confined quantum systems,
S. Crampin, M. Nekovee and J.E. Inglesfield,
Phys. Rev. B51 7318 (1995).

Generating tight-binding Hamiltonians with finite-difference methods,
J.M. Thijssen and J.E. Inglesfield,
Phys. Rev. B51 17988 (1995).

Quantum-well states in Cu/Co overlayers and sandwiches,
P. van Gelderen, S. Crampin and J.E. Inglesfield,
Phys. Rev. B53 9115 (1996).

Effect of interface magnetic moments and quantum-well states on magnetization-induced second-harmonic generation,
P. van Gelderen, S. Crampin, Th. Rasing and J.E. Inglesfield,
Phys. Rev. B54 R2343 (1996).

$TiFe_{1-x}Co_x$ *alloys and the influence of anti-structural atoms*,
P. Slavenburg,
Phys. Rev. B **55**, 16110 (1997).

Improved Density Functionals Working Group

Nodes: **Aarhus, Daresbury and Karlsruhe**

Scientific Highlights

During the Network period and to a large extent as a consequence of the Network structure, the Aarhus node initiated a collaboration with the Daresbury node and the Karlsruhe node on the application of self-interaction corrected electronic structure calculations to rare earth materials. This has resulted in 2 publications, [1],[2], and two in preparation [3], [4].

Conventional electronic structure methods fail badly in the description of materials characterized by localized f-electrons, while the SIC-LSD method presents a scheme to describe the electrons as either localized or delocalized. In [1] the series of Cerium Pnictides was studied and the experimental trends in structures as a function of hydrostatic pressure reproduced. In particular, for CeP an isostructural rocksalt→rocksalt phase transition is observed at a pressure of 55 kbar with a $\sim 10\%$ volume kollapse. The calculations show this to occur as a consequence of the Ce f-electron changing character from being localized to being delocalized. The calculated transition pressure is 79 kbar. Similar transitions are found in CeAs, CeSb and CeBi, however accompanied by change in crystal structure (to the CsCl structure). In all cases the experimentally observed phase transitions are reproduced, and additional phase transitions are predicted at high compressions (see Table).

Table 2: Calculated and experimental transition pressures for the electronic and structural phase transitions in the cerium pnictides. The errorbars in the quoted experimental transition pressures are estimates based on the hysteresis loop observed in the experimental PV curves. Also quoted are the specific volumes on the two sides of the transition. The notation (d) and (l) refers to calculations with delocalized or localized Ce $f-$electrons, i.e. tetravalent or trivalent Ce atoms. B2* denotes the distorted B2 structure.

compound	transition	P_t (kbar)		V_h ($a_0{}^3$)		V_l ($a_0{}^3$)	
		theo.	expt.	theo.	expt.	theo	expt.
CeN	B1(d) → B2(d)	620	-	148	-	141	-
CeP	B1(l) → B1(d)	71	90,55	325	308	297	298
CeP	B1(d) → B2(d)	113	150(40)	288	285	246	247
CeAs	B1(l) → B2(d)	114	140(20)	332	315	265	274
CeSb	B1(l) → B2*(l)	70	85(25)	400	398	353	354
CeSb	B2*(l) → B2*(d)	252	-	311	-	295	-
CeBi	B1(l) → B2*(l)	88	90(40)	427	399	376	360
CeBi	B2*(l) → B2*(d)	370	-	317	-	304	-

The Ytterbium Pnictides were subsequently studied [4]. Here the heavy fermion character of these compounds were reproduced, and the gradual change from trivalent to divalent Yb behavior from YbP over YbAs and YbSb to YbBi reproduced.

1. A. Svane, Z. Szotek, W. M. Temmerman and H Winter, *Theory of the Electronic and Magnetic Structure of Cerium Pnictides under Pressure*, Solid State Commun. **102**, 473 (1997).
2. W. M. Temmerman, A. Svane, Z. Szotek and H. Winter, *Applications of Self-Interaction Corrections to Localized States in Solids*, in 'Electronic Density Functional Theory: Recent Progress and New Directions', Eds J. F. Dobson, G. Vignale and M.P. Das (Plenum, 1997.)
3. A. Svane, J. Lægsgaard, Z. Szotek, W. M. Temmerman and H Winter, *Electronic and Magnetic Structure of Cerium Pnictides under Pressure*, 1998, in preparation.
4. W. M. Temmerman, A. Svane, Z. Szotek and H. Winter, *Self-Interaction Corrected Theory of Ytterbium Pnictides*, 1998, in preparation (preliminary results presented at the Schwäbisch Gmünd Conference).
5. J. Lægsgaard and A. Svane, *Three-particle Approximation for Transition Metal Oxides*, Phys. Rev. B**55**, 4138 (1997).

Improved Density Functionals and Reduced (0-1-2) Dimensionality Working Groups

Nodes: **Modena and Trento**

Scientific Highlights

The activity of the Modena and Trento nodes has been devoted to study i) the effects of on-site correlation in narrow band materials, ii) the optoelectronic properties of confined systems, iii) electronic properties of superconductor-semiconductor superlattices.

i) On-site correlation in narrow band materials.

The physics of materials such as transition metals, transition metal oxides, cuprates, etc.. is dominated by the competition between inter-site hopping and on-site electron-electron repulsion. In these systems in fact the itinerant character of valence electrons coexists with strong local correlations responsible of spectroscopical features such as satellites , band-narrowing and opening of Mott-Hubbard gaps. In spite of the enormous amount of theoretical and experimental work which has been done on cuprates since the discovery of high T_c superconductors, an unified theoretical description of the whole valence spectrum, from the high binding energy region, dominated by satellites, up to the valence band top, including both unperturbed single particle like and strongly correlated Cu derived structures, is still missing; this is due to the difficulty to combine an accurate treatment of many body terms with a realistic description of the band structure.

We have developed a method which includes both the hybridization between Cu and the ligands (or between sp and d states in the case of transition metals) accounted for by first principle band theory, and a treatment of e-e interaction which must be non-perturbative - to deal with systems which are in the high correlation regime - and beyond mean field - to include finite lifetime excitations. This approach allows to augment conventional band theory via the inclusion of on-site correlation: the single-particle band states are determined according to the density functional theory in the local density approximation (LDA) and the localized e-e interaction is described as a 3-body scattering (3BS) solution of a multi-orbital Hubbard Hamiltonian.

The 3BS method can be seen as an extension to the solid state of the configuration-interaction scheme used for finite systems (molecules and clusters): the Hubbard Hamiltonian is projected on a set of states obtained by adding a finite number of e-h pairs to the ground state of the single-particle Hamiltonian and this expansion is truncated to include just one e-h pair. The effect of electron correlation on one electron removal energies from a partially filled band is then described as hole-hole and hole-electron interaction. The 3BS theory corresponds to the solution of a 3-body scattering problem involving two holes and one electron.

The method can be applied to the study of both valence and core states. where again the interplay between the localized and itinerant character of electron states is crucial to describe the response of an itinerant electron system to the creation of a core hole, dominated by the many-body effects associated to the on-site coupling between localized (core) and itinerant (valence) states.

ii) optoelectronic properties of confined systems

The discovery of intense visible room temperature photoluminescence from porous Si has raised a renewed interest in understanding the electronic structures of low dimensional Si nanostructures. In particular, structures microscopically well characterized are desirable for the understanding of luminescence through a comparison between theoretical and experimental results. In particular we have study how the quantum confinement effect modifies the electronic and optical properties of semiconductor systems of low dimensionality:

a) Small Silicon Clusters

We have study the electronic structure and optical activity of small hydrogen-saturated Si clusters, through an approach which can treat both small molecules and bulk crystals. Our scheme fully incorporates the correlation effects that become critical in the small-cluster limit. We find that, when correlation is properly included, even small clusters of ~ 50 Si atoms can be active in the visible range ($h\nu \sim 1.6 - 1.9$ eV). Furthermore this activity is associated with the "crystalline" silicon in the core of the cluster, thus confirming the role of quantum confinement as generating the visible emission.

b) Quantum confined semiconductor slabs

Semiconductor structures microscopically well characterized are desirable for the understanding of luminescence through a comparison between theoretical and experimental results. By performing first principle LMTO calculations of ultra-thin Si(111) layers (1-7 Si double layers (dL)) embedded in CaF_2 we were able to begin correlating the electronic properties of Si nanostructures with their structural properties in a systematic way. We have checked the quantum confinement hypotesis for the Si band opening as a function of thickness and pointed out the different nature of valence and conduction band states in the energy region around the gap. In order to better understand the role of interface states and chemical deposition on the mechanisms of light emission at Si surfaces, we have also studied the different behavior of Ca and H bonds at the Si surface. Using the same theoretical method we have studied the dependence of the electronic properties of Si(111) slabs saturated by hydrogen atoms on the two sides of the slabs. In this way we obtain results for the H-Si-H system, which are directly comparable with the corresponding results for the CaF_2-Si-CaF_2 superlattice. Moreover in order to further investigate the role of the saturating agent we have performed investigation replacing the H atoms on one side of the Si slabs by OH groups. Indeed we have study, even using the LMTO-ASA approach the electronic properties of confine rare earth arsenides in gallium arsenide, showing the possible conditions for a gap opening in the rare earth arsenides compounds.

c) Si quantum wires

The purpose of this task was to show that reliable selfconsistent density of states and energy bands for complicated Si quantum wire systems can be obtained using an electron method (LMTO), which makes possible the calculation of both valence and core states. For these systems we have also developed an extension of our calculations, which enables the computation of the optical matrix elements. This is an important application in order to indagate the nature and the properties of the light-emitting states in the quantum confined Si wires. The results show the opening of the band gap, their quasi-direct nature and the different role of quantum confinement for valence and conduction band states. Detailed comparison has been made between the theoretical results and the experimental outcomes regarding core level shift, Auger lineshape, luminescence properties. Moreover we have performed combined LMTO and Pseudopotential calculations to elucidate the role of dangling bonds, surface states and chemical deposition and modifications (e.g. formation of H-Si bonds, role of the Si-SiO_2 , Si-Ca and Si-F bonds) on the mechanisms of light emission.

iii) Electronic properties of superconductor-semiconductor superlattices.

One of the central problem in the theory of high-T_c superconductivity is to what extent the superconducting properties are bound to the two dimensionality of the CuO_2 planes, and how the extension into the third dimension is achieved by the coupling between adjacent CuO_2 planes. Charge transfer effects in $YBa_2Cu_3O_7$/ $PrBa_2Cu_3O_7$ superlattices have been proposed by many authors as the origin of the experimentally observed strong depression of the critical temperature. We performed self-consistent LMTO-ASA calculations and found that no remarkable change in the electronic structure of the superconducting CuO_2 planes occurs in the studied structures, when the PBCO layer thickness is varied. The observed depression of the critical temperature does not seem to be originated intrinsically by a severe modification of the electronic structure or by the hole-filling mechanism.

Electronic Structure in the Normal and in the Superconducting State Working Group

Nodes: **Bristol-Daresbury-Stuttgart-Würzburg**

Electronic structure in the normal and superconducting states.

Balazs L. Gyorffy (convener of the Working Group)
University of Bristol, UK

The four nodes involved in this Working Group are: Daresbury Laboratory (*Z. Szotek and W.M. Temmerman*), University of Bristol (*B.L. Gyorffy, P. Miller, and J.F. Annett*), Max-Planck-Institute in Stuttgart (*O.K. Andersen and O. Jepsen*), and University of Würzburg (*E.K.U. Gross, K. Capelle, M. Lüders, and S. Kurth*). The activities during the review period were driven by needs of close and very fruitful scientific collaboration which resulted in a number of significant papers (see below). They took the form of research visits and weekend workshops and, in addition to refereed publications, they were reported on, regularly, in the HCM Ψ_k−Network Newsletter.

The scientific aim of the Group was to adopt the computational techniques for studying the electronic structure of normal metals for the analogous task focused on superconductors. The fact that an enormous amount of expertise is available, particularly within the HCM Ψ_k−Network, about how to calculate the electronic structure of condensed matter from first principles, but none of this has been brought to bear on the description of the superconducting state, lends much impetus to this project. Indeed, we found that the very first implementations of our strategy yielded surprising new insights into the physics of quasi-particles in the superconducting state. Three of the most striking ones of these are highlighted below.

- We found [1, 2, 3] that a relatively simple 8-band model representation of the first-principles, Local Density Approximation (LDA), calculations of the electronic structure of YBCO bilayer gave a very good quantitative account of the superconducting transition temperature T_c, the quasi-particle spectra (see Figure) and the specific heat with only one adjustable parameter. Moreover, these calculations strongly suggest that the effective electron-electron attraction in this high temperature superconductor (HTS) operates between electrons, with anti-parallel spins, on nearest neighbour sites in Cu $d_{x^2-y^2}$ orbitals.
- One of the interesting, generic features of the first-principles calculations of the electronic structure of the HTS matrials, seems to be a set of bifurcated saddle points near the Fermi energy, ε_F. We discovered [4] that the evolution of the relative position of ε_F, with respect to this Van Hove singularity, with doping can give a good quantitative account of the experimentally observed rise and fall of T_c accompanying such changes. Such evidence in

support of the Van Hove scenario may turn out to be a significant step towards solving the central problem of HTS, namely identifying the mechanism of pairing.

- We formulated a relativistic version of the theory of superconductivity and found, for the first time, the complete form of the spin-orbit interaction as it enters the fundamental, Bogoliubov-de Gennes, equations of superconductivity. A surprising feature of the new theory is dichroism in the absorption of electromagnetic radiation by superconductors. Our predictions [5, 6] are currently attracting considerable experimental interest.

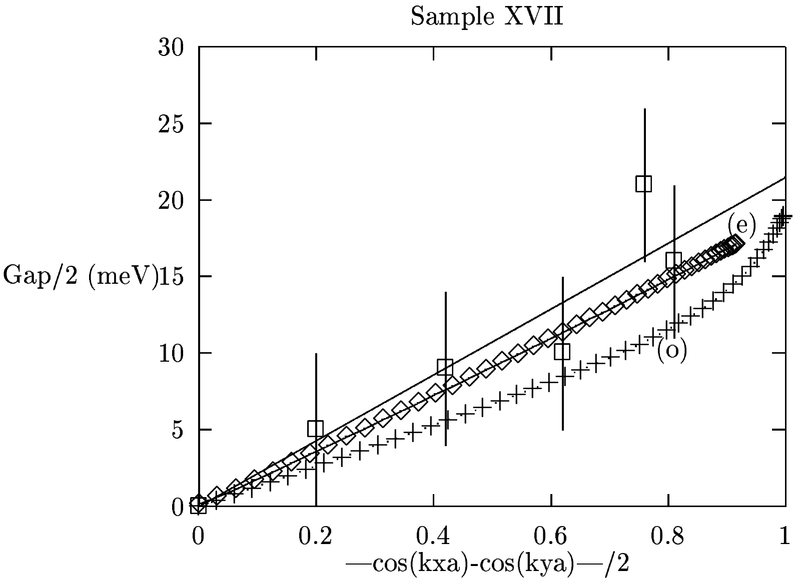

Figure 5: A comparison of the calculated gap for the intra-layer nearest neighbour Cu $d_{x^2-Y^2}$$-$Cu $d_{x^2-Y^2}$ interaction, for the even (e) and odd (o) sheets of the YBCO Fermi surface, with the experimental data deduced by Schabel et al. (Phys. Rev. B**55**, 2796 (1997)).

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Surface and Interface Magnetism Working Group

Nodes: **Athens and Jülich**

Scientific Highlights

Magnetic impurities in simple metals

The presence or absence of a magnetic moment of an impurity diluted in a nonmagnetic metal host is determined by a competition between intra-atomic exchange interaction and interatomic electron motion. Within the framework of the Anderson model, the impurities are distinguished as magnetic and nonmagnetic according to the ratio of two parameters: the mean intra-atomic Stoner exchange energy and the width of the impurity virtual bound state.

The experimental investigations of the magnetic properties of impurities diluted in simple metals were for many years restricted to $3d$ impurities in noble metals and aluminium. Recently, the variety of host materials was extended to include alkali and alkali-earth metals. The relevant experimental studies apply the time-differential perturbed γ-ray distribution method to investigate the local magnetic behaviour of impurities implanted by recoil into the host crystal. Alkali and alkali-earth metals provide a wide range of host free-electron densities ρ, and thus one can closely study the transition of the impurities from itinerant to atomic configurations.

In collaboration with the Jülich group (P. H. Dederichs and R. Zeller) we have studied extensively the magnetic behaviour of impurities in simple metals by means of first-principles local-spin-density-functional electronic-structure calculations, using both the KKR Green function method and the jellium model. We found that, in the vicinity of the transition from a spin-polarized to a non-spin-polarized impurity state the local moment varies proportionally to $\sqrt{1-\rho/\rho_c}$ for $\rho < \rho_c$. This expression is very similar to the result of the Landau theory for second-order phase transitions and, as it turns out, it also applies to free-electron densities away from the critical point ρ_c [1, 2]. We also predicted that, besides the $3d$ and $4d$ impurities, also the $5d$ and some sp impurities are magnetic in the late alkali metals [3].

This project continued also within the framework of the Ψ_k-Network. For this purpose, several visits took place: N. Stefanou and N. Papanikolaou visited Jülich and P. H. Dederichs visited Athens. We have studied the local magnetic properties of impurities at interstitial positions [4], the problem of orbital polarization within the framework of the local-spin-density $+U$ approximation [5], as well as magnetic impurities in alkali-earth metals [6].

Transport properties of aluminium-based dilute alloys

Transport properties, like the Hall coefficient, the magnetoresistance, the thermopower, etc., of dilute metallic alloys at low temperatures are valuable tools in the investigation of both the topography of the Fermi surface of the host crystal and the scattering properties of the impurity atoms.

Detailed and systematic measurements of the galvanomagnetic coefficients (the magnetoresistivity tensor) in a series of aluminium-based dilute alloys, performed at the Research Centre "Democritos" in Athens, showed important variations of these quantities with different solute atoms. These variations are due to the scattering of the electronic states of the anisotropic parts of the host Fermi surface from the impurity potential and have defied so far a consistent interpretation. Although aluminium is a simple metal with a roughly spherical Fermi surface, there are important deviations from the spherical shape with abrupt curvature variations near the Brillouin-zone boundaries. The fact that the detailed structure of these strongly anisotropic regions plays the most decisive role in the determination of the low-field galvanomagnetic coefficients makes the calculation of these quantities cumbersome.

In a series of papers we reported a systematic study of the low-temperature thermopower [7] and galvanomagnetic properties at weak fields [8, 9] of aluminium-based dilute alloys with $3d$ and $4sp$ impurities. Our theoretical method relies on the so-called on-Fermi-sphere approximation, which allows us to combine the exact topography of the host Fermi surface, described by the 4OPW model, with the scattering phase shifts, obtained from self-consistent local-density-functional impurity-in-jellium calculations. This method involves an all-electron description of the impurity, which enables us to reliably represent also the case of deep d potentials of the $3d$ impurity series for which an OPW description is not suitable. Thus, weak sp- as well as strong d-resonance scattering are treated on the same footing. The transport coefficients are calculated within the framework of Boltzmann transport theory. The appropriate linearized Boltzmann equation is solved exactly by iteration. For the calculation of the magnetoresistivity tensor, we use an efficient scheme based on a Jones-Zener-like expansion at weak magnetic fields, which leads to a hierarchy of integro-differential equations, that we solve self-consistently by an iterative procedure. Our calculations explain successfully the experimental results.

Lattice relaxations around impurities in metals

A point defect in a crystal, such as a vacancy or an impurity atom, does not only break the periodicity of the one-electron potential, but also induces a displacement of its neighbouring atoms from their ideal lattice positions. These displacements are in fact long ranged, varying with the inverse of the square of the distance from the impurity, and lead to a macroscopic volume change of the crystal. A complete information about this displacement field can be obtained by diffuse X-ray or neutron-scattering experiments but, unfortunatelly, very few systems have been measured. Detailed information about many more systems has been obtained by extended X-ray-absorption fine-structure (EXAFS) measurements, which yield reliable data for the first-nearest-neighbour shifts. In addition, lattice-parameter measurements are available for many systems, giving direct information about the volume changes induced by the impurities.

From the theoretical point of view, the treatment of structural relaxation due to defects in crystals is a difficult task. In the past this problem has been mostly dealt with on a phenomenological basis, e.g. by applying models of lattice statics or continuum theory. A reliable microscopic description of lattice-relaxation effects based on first-principles electronic-structure calculations requires very accurate total energies or forces and has mostly been attempted so far for simple metals and semiconductors on the basis of pseudopotential treatments.

In collaboration with the Jülich group (P. H. Dederichs and R. Zeller), we have extended the full-potential KKR Green function method to treat the structural distortion around impurities in crystals [10]. This is an all-electron method which can be applied also to the case of transition metals where pseudopotential treatments are not appropriate. We applied this method to predict the atomic positions in the neighbourhood of *d* and *sp* substitutional impurities in Cu [10, 11] and Al [12], by using both the total energy and the ionic Hellmann-Feynman force methods. We also studied the influence of the lattice relaxation on the magnetic properties of the impurities in these systems. The calculated atomic displacements, total volume changes and local magnetic moments are in good agreement with the experimental data. In addition, our results for the magnetic properties of the $3d$ impurities in aluminium seem to resolve the discrepancy between experiment and previous calculations. For an account of this work, which shows also the efficiency of the method to determine the phonon dispersion curves from a single self-consistent calculation of the coupling constants in real space, we refer to the highlight of the October '97 issue of the Network Newsletter.

For this project, N. Stefanou visited Jülich for one month (September 1996). Also, N. Papanikolaou visited Jülich several times as a Ph.D. student and also worked in Jülich as a postdoc from March to December 1996.

Hyperfine interactions of impurities and adatoms at surfaces

Due to modern electronic-structure calculations, most of the basic processes and properties in simple solid materials are rather well understood. However, this is clearly not true for complex systems with reduced symmetry like, e.g., point defects at surfaces, interfaces, layered structures, etc.. Such complex systems, whether they exist naturally or are artificially fabricated, exhibit a rich variety of interesting physical properties and became in the recent years a subject of considerable interest for fundamental as well as for applied research.

The aim of this project is to study the properties of single adatoms and small clusters at surfaces (and interfaces) with the help of first-principles electronic-structure calculations. Mostly due to the development of scanning tunnelling microscopy (STM), such nanostructures at surfaces have recently received a strongly increasing attention. Compared to the STM techniques, a unique and complementary microscopic information can be obtained from the hyperfine structure of these systems, which is caused by the interaction of the electronic degrees of freedom and the nuclear fields, and became available from experiment in recent years. However, a detailed understanding of the local environment that causes the observed hyperfine structure can only be achieved with the help of *ab-initio* electronic-structure calculations.

During the last decades numerous measurements of magnetic hyperfine fields at impurities and neighbouring host atoms have been performed in bulk ferromagnetic or non-magnetic materials and first-principles theoretical calculations provided a consistent interpretation of the experimental data. However, considerable deviations from the bulk properties might occur when the impurities are located close to or at the surface or an interface. To date, quite a few experiments have been performed with probe atoms positioned in atomic layers close to or at a surface or an interface. This field has been pioneered by the Kostanz group with ^{111}Cd- perturbed-angular-correlation (PAC) experiments on the surfaces of Cu and Ni [13, 14]. While in the past most experiments had been performed with ^{57}Fe or ^{111}Cd probe atoms, the availability of the ISOLDE facility at CERN makes experiments with new isotopes like Cl, Br, Se or Pd/Rh possible. For instance, Granzer *et al.* [15] from the Hahn-Meitner Institute on Berlin have recently performed interesting experiments for the hyperfine fields of Se adatoms on Ni(111) and Ni(001) surfaces which were found to deviate drastically from the known bulk values. The observed strong deviation of the surface values from the bulk field yields a significant reason for a theoretical treatment of this problem. While the theory in the past focused strongly on magnetism of surfaces and thin films, recently also the magnetic properties of single adsorbate atoms and small clusters received considerable attention [16, 17]. The study of hyperfine interactions in these systems will contribute further to the understanding of electronic structure and magnetism at complex surfaces.

The Jülich group (P. H. Dederichs and coworkers) has developed a KKR Green function program for the calculation of the electronic structure of ideal surfaces, interfaces and layered structures. Also a Green function computer code, based on the atomic-sphere approximation for the potential but using the full multipole expansion for the charge density for point defects at these interfaces is available. In collaboration with the Jülich group we have calculated the electronic structure and the hyperfine fields for all the $3d$ and $4sp$ elements considered as impurities and adatoms at Ni(001) and Fe(001) surfaces. For this purpose, Ph. Mavropoulos visited Jülich from 15 June to 31 August 1997 and worked intensively in close collaboration with the group of Prof. P. H. Dederichs on this project. We are at present analysing our results, which seem to explain successfully the observed drastic reduction of the hyperfine field on Se adatoms on Ni surfaces. As a subsequent step, we plan to implement the full-potential and lattice-relaxation treatments into the computer codes and study their influence on the results.

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Surface and Interface Magnetism Working Group

Node: **Vienna: Group of P. Weinberger**

Scientific Highlights

In the Vienna node of P. Weinberger at the Center for Computational Materials Science & Institut für Technische Elektrochemie, Technical University of Vienna essentially four rather interrelated topics were dealt with in strong collaboration with non-Austrian members[2] of the HCM network. All four topics were related to problems of semi-infinite systems (solid systems with surface or with interfaces). In particular since magnetic properties of such systems are of enormous technological interest.

Interface exchange coupling

In this particular field of research, various studies were performed such as the effect of alloying the spacer material, of changing the type of magnetic slabs and also the kind of new features to be expected when terminating the multilayer system by a non-magnetic cap. Typical examples of collaborations in this field of research are listed below:

J. Kudrnovský, V. Drchal, P. Bruno, I. Turek and P. Weinberger, *"Interlayer magnetic coupling: effect of alloying in the spacer"*, Phys. Rev. B54, R3738 (1996).

J. Kudrnovský, V. Drchal, R. Coehoorn, M. Šob and P. Weinberger, *"Calculated phases of the oscillatory exchange coupling between Fe-Co-Ni alloys across a Cu spacer"*, Phys. Rev. Lett. **78**, 358 (1997).

J. Kudrnovský, V. Drchal, P. Bruno, R. Coehoorn, J.J. De Vries, K. Wildberger, P.H. Dederichs and P. Weinberger, *"Effect of cap-layers on interlayer exchange coupling"*, MRS Symposium Proceedings (Eds.: J. Tobin et al.) Vol. **475**, 575 (1997).

J. Kudrnovský, V. Drchal, P. Bruno, I. Turek and P. Weinberger, *"Interlayer exchange coupling: effect of the cap-layers"*, Phys.Rev. B**56**, 8919 (1997).

Magnetic anisotropy of layered systems

By using a (fully)-relativistic spin-polarized approach quite a few new features of the magnetic anisotropy in magnetic multilayers were found such as oscillations in the interface exchange coupling, anomalous enhancement when considering a cap of non-magnetic material, but also

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[2] Non-Austrian coauthors from the HCM network are underlined.

oscillatory behavior of the magnetic anisotropy energy. It was even shown that for certain systems an ab-initio determination of anisotropy constants is possible. Again below are examples of such research as an outcome of collaboration with non-Austrian members of the HCM network.

L. Szunyogh, B. Úfalussy, P. Weinberger and C. Sommers, *"Fully relativistic spin-polarized description of interface exchange coupling for Fe multilayers in Au(100)"*, Phys.Rev. **B54**, 6430 (1996).

B. Úfalussy, L. Szunyogh, P. Bruno and P. Weinberger, *"First principles calculations of the anomalous perpendicular anisotropy of a Co monolayers on Au(111)"*, Phys. Rev. Lett. **77**, 1805 (1996).

P. Weinberger, C. Sommers, U. Pustogowa, L. Szunyogh and B. Újfalussy, *"Ab-initio determination of magnetic interface coupling constants"*, J. Phys. I France **7**, 1299 (1997).

L. Szunyogh, B. Úfalussy, C. Blaas, U. Pustogowa, C. Sommers and P. Weinberger, *"Oscillatory behavior of the magnetic anisotropy energy in Cu(100)/Co_n multilayer systems"*, Phys.Rev.B**56**, 14 036 (1997).

Screened KKR & transport for multilayer systems

Since it is also always necessary to improve the theoretical tools to be used in numerical applications, some research was devoted to a generalization of screening with a multiple scattering approach, but also to the use of such an approach in order to calculate transport properties:

R. Zeller, P.H. Dederichs, B. Úfalussy, L. Szunyogh and P. Weinberger, *"Theory and convergence properties of the Screened Korringa-Kohn-Rostoker method"*, Phys.Rev.**B52**, 8807 (1995).

P. Weinberger, P.M. Levy, J. Banhart, L. Szunyogh and B. Úfalussy, *"Band structure and electrical conductivity of disordered semi-infinite systems"*, J.Phys.Cond.Matt. **8**, 7677 (1996).

Alloy theory

As part of the studies devoted to non-magnetic systems order phenomena of two-dimensional alloys at the surface were investigated and in particular great attention was given to a careful discussion of an Ising-type description of surface segregation. As can be seen from the list below, also here the interaction with the HCM network proofed to be extremely useful.

R. Tetot, J. Kudrnovský, A. Pasturel, V. Drchal and P. Weinberger, *"Phase diagram of the Cu-Pd surface alloy"*, Phys. Rev. **B51**, 17 910 (1995).

V. Drchal, J. Kudrnovský, A. Pasturel, I. Turek and P. Weinberger, *"Ab-initio theory of surface segregation: selfconsistent determination of the concentration profile"*, Phys. Rev. **B54**, 8202 (1996).

Surface and Interface Magnetism and Improved Density Functionals Working Groups

Node: **Munich**

Application of current density functional theory to spontaneously magnetised solids

H. Ebert, Marco Battocletti, and T. Huhne
Institute for Physical Chemistry, University of Munich,
Theresienstr. 37, D-80333 München, Germany
and
E.K.U. Gross
Institute for Theoretical Physics, University of Würzburg,
Am Hubland, D-97074 Würzburg

Recently there has been a lot of interest in properties of magnetic solids that are caused by spin-orbit coupling. Some few examples for these are the magneto-crystalline anisotropy [1], galvano-magnetic effects [2] and various dichroic phenomena in electron spectroscopy [3]. Corresponding theoretical investigations are in general performed within the framework of local spin density functional theory (SDFT). The influence of spin-orbit coupling is accounted for either in the variational step of a conventional $\vec{k}$-space band structure method [4] or by working on the basis of the Dirac equation for a spin dependent potential.[5, 6]

The most prominent shortcoming of this approach is that it gives the spin-orbit induced orbital magnetic moment of transition metals up to 60% too small compared to experiment. The main reason for this is that local SDFT is primarily coined to account for spin polarization and therefore supplies even in its present proper relativistic form [7, 8] an insufficient theoretical basis to calculate quantities connected with the orbital electronic current [9]. To overcome this problem Brooks and coworkers [10, 11] introduced the so-called orbital polarization (OP) formalism, that was borrowed from atomic theory and is meant to account for Hund's second rule i.e. to maximize the orbital angular momentum.

In contrast to the OP-formalism, the current density functional theory (CDFT) has a firm basis, does not leave the framework of density functional formalism and should also cure or reduce the above mentioned problems. Starting from a relativistic formulation based on quantum electrodynamics such an approach has been worked out first by Rajagopal and Callaway [12]. The resulting Dirac-Kohn-Sham equation for a system without external vector potential reads as follows

$$\left[c\vec{\alpha}\cdot\left(\frac{\hbar}{i}\vec{\nabla}+\frac{e}{c}\vec{A}_{xc}\right)+\beta mc^2+V_H(\vec{r})+V_{xc}(\vec{r})\right]\Psi_i(\vec{r})=\epsilon_i\Psi_i(\vec{r})\ . \tag{5}$$

Here the exchange-correlation scalar and vector potentials V_{xc} and $\vec{A}_{xc}$, respectively, are functionals of the density n and the physical (gauge-invariant) current density $\vec{j}$. Unfortunately no parametrisation for the corresponding exchange-correlation energy is available so far. Vignale and Rasolt [13, 14, 15], on the other hand, derived a consistent non-relativistic formulation of CDFT in terms of the paramagnetic current density $\vec{j}_p$ and suggested an appropriate parametrisation for the exchange-correlation energy.

The Vignale–Rasolt CDFT-formalism can be obtained as the weakly relativistic limit of Eq. (5). This property has been exploited to set up a computational scheme that works in the framework of CDFT and accounts for the spin-orbit coupling at the same time. In practice this means that a hybrid scheme has been developed where only the kinematic part of the problem is dealt with in a fully relativistic way whereas the exchange-correlation potential terms are treated consistently to first order in $1/c$. The corresponding modified Dirac equation that automatically accounts for the spin-orbit coupling and at the same time incorporates a term that explicitely represents a coupling to the electronic orbital degree of freedom is given by:

$$\left[-i\hbar c\vec{\alpha}\cdot\vec{\nabla}+\beta mc^2+V_{eff}(\vec{r})+\beta\sigma_z\cdot B_{eff}(\vec{r})+\sum_{\sigma}\beta H_{op,\sigma}P_{\sigma}\right]\Psi_i(\vec{r})=\epsilon_i\Psi_i(\vec{r})\,. \qquad (6)$$

As within standard SDFT the scalar potential terms V_{eff} and B_{eff} stand for the average and difference, respectively, of the two spin-dependent potentials $V_H+V_{xc,\sigma}$. The additional term with

$$H_{op,\sigma}=-\frac{i\hbar e}{2mc}\left[\vec{A}_{xc,\sigma}(\vec{r}),\vec{\nabla}\right]_+ \qquad (7)$$

represents the coupling of the orbital current and the exchange-correlation vector potential $\vec{A}_{xc,\sigma}$. Since in the present formalism $\vec{A}_{xc,\sigma}$ is defined in a spin-dependent way, the spin-projection operator $P_\sigma=\frac{1\pm\beta\sigma_z}{2}$ appears, in addition to $H_{op,\sigma}$, in Eq. (6).

The scheme sketched above has been implemented by applying appropriate extensions to a spin polarized relativistic Korringa-Kohn-Rostoker-Green's function (SPR-KKR-GF) band structure program working in the atomic sphere approximation (ASA) as well as to corresponding routines for the core states. Within the Wigner-Seitz sphere the particle density n_σ was taken to be spherically symmetric. The current density $\vec{j}_{p,\sigma}$, on the other hand, was taken to be rotationally symmetric with the symmetry axis pointing along the direction of the magnetisation, which in turn was fixed parallel to the crystallographic z-axis. This means that $\vec{j}_{p,\sigma}$ is everywhere parallel to the polar unit vector $\vec{e}_\phi$ and depends only on the spherical coordinates r and θ. For that reason the resulting exchange-correlation vector potential $\vec{A}_{xc,\sigma}$ is also parallel to $\vec{e}_\phi$ and rotationally symmetric. This has the important consequence that the coupling term in Eq. (7) causes no further reduction in symmetry compared to a conventional spin polarized relativistic calculation based on SDFT. An analysis of the results for $\vec{A}_{xc}$ shows that it depends only weakly on the azimuthal angle θ. For that reason the average of $\vec{A}_{xc}$ with respect to θ has been used to simplify the solution of the radial Dirac equations.

Obviously one of the central quantities of CDFT is the paramagnetic current density $\vec{j}_{p,\sigma}$. For bcc-Fe the valence band part of $\vec{j}_{p,\sigma}$ obtained with our approach is shown in Fig. 6. When suppressing any potential term in the Dirac equation that couples to the orbital current, the spin-orbit induced current density $\vec{j}_{p,\sigma}$ scarcely depends on whether the calculations are performed in the ASA-mode or a full potential (FP) mode (FP-OP-SPR-KKR). In fact the spin-resolved results shown in Fig. 6 have been obtained from full potential SPR-KKR calculations [17]. An angular momentum decomposition of $\vec{j}_{p,\sigma}$ reveals that – as one expects – it is nearly exclusively due to the d-electrons. Accordingly, its radial distribution is closely linked to the corresponding

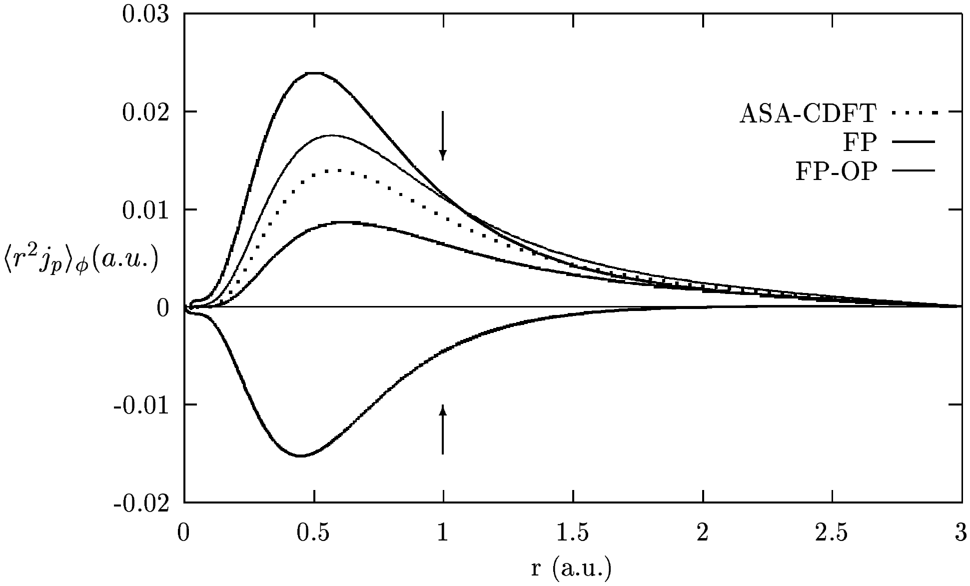

Figure 6: Magnitude of $r^2\vec{j}_p$ for bcc-Fe in the (100)-plane ($\theta = \frac{\pi}{2}$) and averaged with respect to its ϕ-dependence. The various curves show results stemming from FP-SPR-KKR (FP) calculations based on the plain SDFT-Dirac equation, calculations including the OP-term (FP-OP) and work done within CDFT using the ASA-SPR-KKR (ASA-CDFT) [16], respectively. In addition the decomposition of the FP-result into its spin-projected contributions $\vec{j}_{p,\uparrow(\downarrow)}$ is given marked with arrows ($\uparrow, \downarrow$).

radial wave functions. As can be seen both spin-parts $\vec{j}_{p,\sigma}$ are of opposite sign and differ in a pronounced way in magnitude. Connected with $\vec{j}_{p,\sigma}$ there are corresponding orbital angular momenta $\langle l_z \rangle_\sigma$ that in turn give rise to the orbital magnetic moment $\mu_{orb} \approx \mu_B \sum_\sigma \langle l_z \rangle_\sigma$ which is obviously dominated by its minority spin contribution [18]. There is a rather appreciable contribution to $\vec{j}_{p,\sigma}$ due to the core electrons. However, the contributions for different spin character nearly cancel each other and for that reason these have not been included in Fig. 6.

The valence band contribution to the exchange-correlation vector potential $\vec{A}_{xc,\sigma}$ obtained for bcc-Fe within CDFT is shown in Fig. 7 for $\theta = \pi/2$. Obviously, $\vec{A}_{xc,\sigma}$ is much larger for the minority than for the majority spin direction as it was found for the current density distribution. However, the vector potential possesses a rather complex radial variation that shows no direct and simple relationship to the corresponding current density $\vec{j}_{p,\sigma}$. Again, as for $\vec{j}_{p,\sigma}$, there are quite appreciable contributions to $\vec{A}_{xc,\sigma}$ from the core states in the region near the nucleus. However, suppression of these contributions has hardly any influence on the orbital magnetic moment μ_{orb}. For that reason one can conclude that the variation of $\vec{A}_{xc,\sigma}$ in the region between $r \approx 1$ a.u. (Bohr radius) and the Wigner-Seitz-radius is most important for μ_{orb}.

Application of the SPR-KKR method in the framework of relativistic SDFT leads to 2.27, 1.57 and 0.57 μ_B for the spin magnetic moments of bcc-Fe, fcc-Co and fcc-Ni, respectively. These values agree within a few percent with experiment and change by less than 1% when the the CDFT-formalism is adopted. As Fig. 8 shows, quite pronounced deviations from experiment occur if the orbital magnetic moment μ_{orb} is calculated using the plain SPR-KKR. This discrepancy is reduced for the CDFT-formalism which obviously has the effect of enhancing the spin-orbit induced orbital moments. However this enhancement is somewhat too small for Fe,

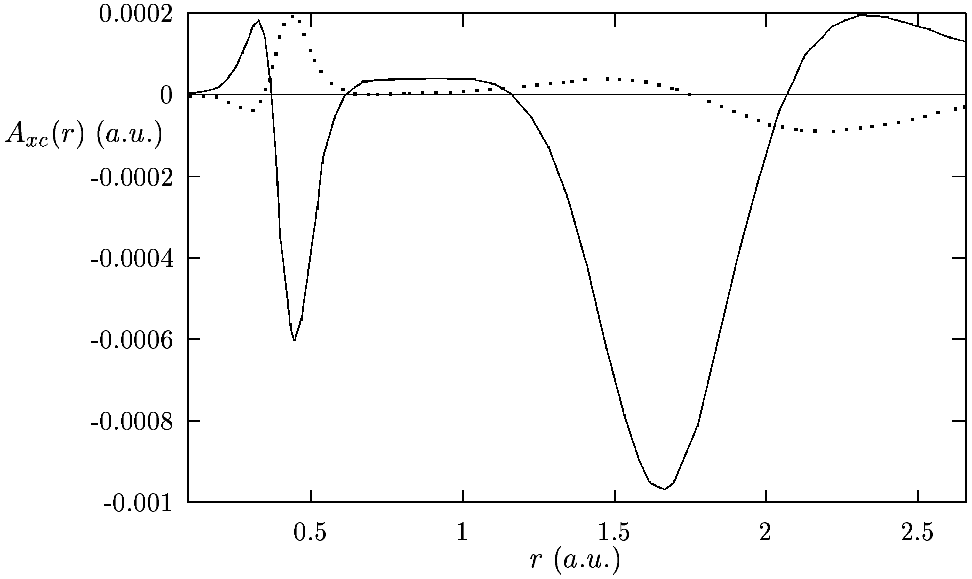

Figure 7: Valence band part of the polar component of the spin-dependent exchange-correlation vector potential $\vec{A}_{xc,\sigma}(r,\theta)$ for bcc-Fe (in atomic units). The full and dashed lines give the potential for minority and majority character, respectively, for $\theta = \pi/2$.

while it is much too small for Co. There are several possible reasons for this: First of all one has to note that the parametrisation used for the CDFT exchange-correlation energy based on linear response theory has only a certain range of applicability which is definitively left for the systems investigated here. In addition one may expect that the various technical approximations made to implement the CDFT have their influence on the final result, making a full potential treatment necessary. Nevertheless, these first results obtained for magnetic solids using the CDFT are encouraging and it can be expected that the observed deviation from the experimental values will be reduced with better parametrisations available [21].

By taking the average of $\vec{A}_{xc,\sigma}$ with respect to the angle θ, the term $-\frac{i\hbar e}{2mc}\left[\vec{A}_{xc,\sigma}(\vec{r}),\vec{\nabla}\right]_{+}$ in Eq. (7) may be replaced by $\frac{e}{2mc}\frac{\overline{A}_{xc,\sigma}}{r\sin\theta}\hat{l}_z$ where $\hat{l}_z$ denotes the z-component of the orbital angular momentum operator. This term is similar in form to the expression $B_{\sigma}^{OP}(r)\hat{l}_z$ recently obtained within the extended orbital-polarization (OP) formalism [20] that introduces a potential term instead of using just an energy shift as proposed originally by Brooks [10]. Obviously, B_{σ}^{OP} can be seen as a vector potential coupled to the orbital current represented by $\hat{l}_z$. However, one has to keep in mind that the physical picture behind the OP-formalism is quite different from the CDFT as used here. While for the former case one tries to account in an approximate way for intra-atomic correlations the vector potential occurring within CDFT is due to diamagnetic contributions to the exchange-correlation energy of the electron gas. Accordingly it is not surprising that the resulting vector potential function (see Fig. 9) for the OP-formalism is quite different from that obtained within CDFT. In spite of this fundamental difference one finds the current density $\vec{j}_{p,\sigma}$ calculated within the extended OP-formalism to be very similar to that calculated within the framework of CDFT. The corresponding curves shown in Fig. 6 differ only in their absolute magnitude (this applies for $\vec{j}_{p,\sigma}$ as well as $\vec{j}_p$) with the total current density $\vec{j}_p$ of bcc-Fe being higher compared to the CDFT-result when calculated with the OP-formalism. As a consequence the deviation from experiment for the corresponding orbital magnetic moment

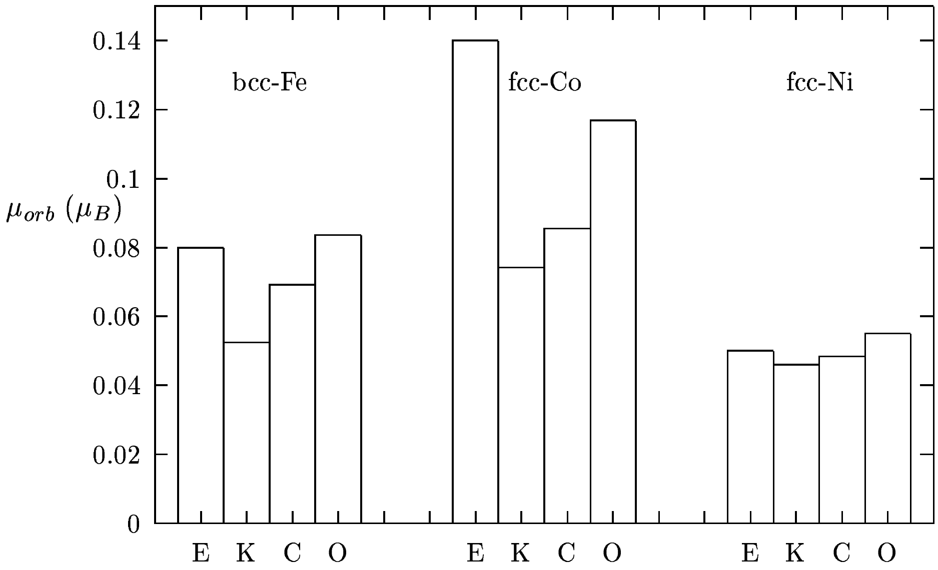

Figure 8: Orbital magnetic moments for bcc-Fe, fcc-Co and fcc-Ni. The columns denoted by E, K, C, and O represent from left to right the experimental data [19] and the theoretical data obtained by the plain SPR-KKR-, within CDFT as described in the text as well as the OP-SPR-KKR [20] including the OP-potential term.

is reduced for Fe and also for Co (see Fig. 8). From these results one may conclude that the OP-formalism, that is extremely simple to be implemented, may be used to study the influence of corrections to the exchange-correlation energy due to finite orbital currents as long as no better parametrisations for this have been derived within CDFT.

Finally, it seems worth to address a special feature of the non-relativistic CDFT Kohn-Sham equation. This equation differs from the ordinary SDFT Kohn-Sham equation by the appearance of the exchange-correlation vector potential $\vec{A}_{xc}$. This term ensures that the single-particle orbitals resulting from the CDFT equations not only reproduce the spin densities n_σ but also the current densities $\vec{j}_{p,\sigma}$ of the interacting system of interest. Since the exchange-correlation potential breaks time reversal symmetry it is conceivable that non-relativistic CDFT without additional spin-orbit coupling might lead to a finite orbital magnetic moment. To investigate this question we performed a calculation including spin-orbit coupling that led to a finite orbital magnetic moment. Then, starting with this solution, the spin-orbit coupling was switched off [22]. In the subsequent self-consistent iterations the orbital magnetic moment approached zero, demonstrating that the presence of $\vec{A}_{xc}$ alone cannot sustain a finite orbital magnetic moment.

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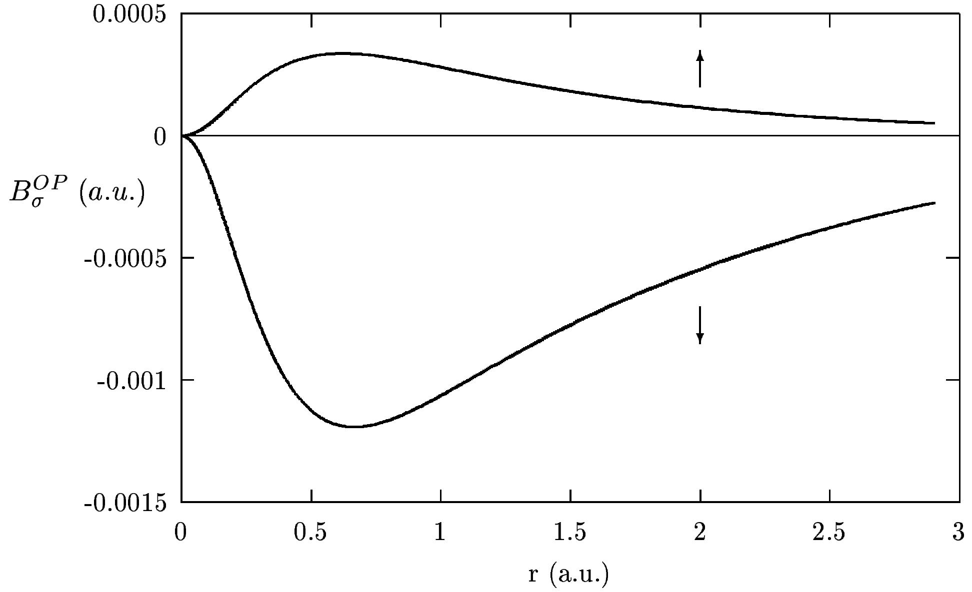

Figure 9: The OP potential term B_σ^{OP} for bcc-Fe as calculated by the self-consistent FP-OP-SPR-KKR.

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Molecules and Organic Solids Working Group

Node: **Zurich**

Scientific Highlights

This node was part of two intensive collaborations, one with the group of Prof. Schwarz (TU Wien) the other with Prof. Koenig and Dr. Katan (University Rennes I and CNRS.)

Former PhD Students from Prof. Schwarz' group, Dr. Margl and Dr. Nusterer visited the IBM Zurich Research Laboratory on a regular basis for several years, and spent the larger fraction of their work time at the Zurich Laboratory. Dr. Sarnthein from the Vienna group and Dr. Katan (Rennes) spent several extended periods in Zurich. The Swiss Office for Education and Science supported, under the umbrella of the Network, several coordinative and collaborative visits of Dr. Blöchl in Vienna, and the participation of Dr. Andreoni, Dr. Blöchl, Dr. Meijer and Prof. Petrilli from our Institution at the network conference in Schwäbisch Gmund.

The common theme of our collaborations have been applications of the Projector Augmented Wave (PAW) method, which has been developed by Dr. Blöchl at the Zurich Research Laboratory. The PAW method is a new electronic structure method, which is particularly suited to study large molecules and complex materials with high accuracy. This approach has been implemented into an ab-initio molecular dynamics approach, also called the Car-Parrinello method after its inventors, which allows to study the atomic motion in time at finite temperatures.

The collaborations have been particularly useful to gain experience in a number of different fields, ranging from materials science to chemistry, from electronic and optical properties to catalysis. The expertise of the Vienna group with the LAPW method, which is considered one of the most accurate electronic structure methods, helped to prove accuracy and reliability of the PAW method. We find, that the expertise build up in these studies is highly valuable for addressing problems of technological interest.

In the following, I will briefly summarize our main collaborative activities:

Dynamical properties of organometallic sandwich compounds [1,2,6]

Sandwich compounds are a class of synthetic materials that are presently reaching fame as polymerization catalysts. We studied two members of this class, ferrocene and beryllocene. Though they themselves do not exhibit catalytic behavior, they exhibit extreme dynamical behavior, ranging from a wheel like rotation of aromatic rings to full fluxionality between two binding modes. These substances have been widely studied, and allowed to benchmark our dynamical calculations by comparing with experiments. Furthermore, our calculations offered a new interpretation of the measured findings in the case of ferrocene. These studies have been the basis for a number of investigations of homogeneous catalytic processes, carried out at IBM Research Laboratory in collaboration with the ETH Zurich and at the University of Calgary, CA.

Diffusion in the super-ionic conductor Li_3N [5]

Li_3N exhibits large ion conductivities, which has been widely studies because of potential applications in solid state batteries. We have investigated the Li ion diffusion mechanisms at finite temperatures. We found that the rate is mostly controlled by the number of Li-vacancies, while the diffusion process itself is very rapid.

Adsorption of Methanol and Water in Zeolites [3,4,7,9,11]

Zeolites are solid state catalysts used widely in petrochemistry. One of the key problems of zeolite chemistry is how polar molecules interact with acid sites giving rise to catalytic activity. This problem has not been able to resolve unambiguously either by theory nor experiment. We brought to bear all the advantages of our methodology, treating the full crystal structure and not isolated fragments, including electron correlations through density functional theory, and by monitoring the dynamics at finite temperature and in "real" time. On the hand of a prototypical zeolite, we found that the adsorption is strongly coverage dependent: Proton transfer from the acid site to the adsorbed molecule, which is often responsible for catalytic activity, occurs only at larger coverages. These findings provide immediate explanation of puzzling observations of catalytic processes in zeolites. We verified our results by comparing with measured i.r. spectra. The findings have recently been reproduced by other groups for a number of different zeolites.

Electric field gradient calculations with the PAW method [14]

Nuclear probes such as Mössbauer spectroscopy and NMR are particularly sensitive to the electronic wave functions near the nucleus. It has been shown that it is particularly difficult to obtain accurate theoretical predictions for those quantities, because most electronic structure methods approximate the wave function in the relevant region. Dr. Blaha and Prof. Schwarz have been among the pioneers of the calculation of electric field gradients. Together with Prof. Petrilli (Universidade de Sao Paolo and visiting scientist at the IBM Zurich Research Laboratory) we made extensive numerical tests and comparisons with measured and other calculated results. Not only was the comparison with experiments matching the experimental error bars, but also the agreement between the PAW and LAPW methods exceeded the discrepancy from experiment. This opens, for the first time, the possibility to use these quantities for a test of the underlying approximations, such as the choice of the density functionals.

Phase transitions of charge transfer molecular compounds [6,10,12,13]

Charge transfer molecular compounds exhibit a rich phase diagram of electronic and structural phase transitions. For two representative crystals, we investigated the dynamical properties of the molecules and the interactions between the molecules in the low and high symmetry structures. Model parameters required for investigations of the phase transition itself have been derived from our calculations.

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5. "Ab-Initio Molecular-Dynamics study of diffusion and defects in Solid Li_3N",
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10. "Ab-initio calculations of one-dimensional band structures of mixed-stack molecular crystals",
    C. Katan, C. Koenig and P.E. Blöchl, Solid State Comm. 102, 589 (1997)

11. "First-principles molecular dynamics study of small molecules in zeolites",
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12. "Electronic structure calculations and molecular dynamics simulations of mixed-stack charge-transfer complexes",
    C. Katan, C. Koenig, P.E. Blöchl to be published in Biuletyn Instytutu Chemii Fizycznej i Teoretycznej Politechniki Wroclawskiej 4, (1997) (ISSN 1426-36-96)

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Node: **Rennes**

Highlights of Rennes-Zürich Collaboration

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*

This collaboration has been initiated 3 years ago by a Joint Project between IBM Zürich Research Laboratory and University of Rennes. It started with the training of C. Katan (young researcher) in the Projector Augmented Wave (PAW) method developped by P.E. Blöchl and was pursued with a work on the electronic and dynamical properties of molecular charge transfer compounds. C. Katan spent in total 3 months at IBM-Zürich, one of them having been supported by the Network. The publications cited below acknowledge this support.

Charge transfer salts are molecular compounds which exhibit a dazzling variety of phase transitions which can be driven by pressure, temperature, photoirradiation,... They exhibit features ranging from zero to three dimensions and are an ideal ground for fundamental studies which may be useful to understand materials of technological interest such as organic magnets, materials for light emmiting diodes, superconductors, dyes and conducting polymers.

In our quest to obtaining a detailed microscopic understanding of these materials and their transitions, we selected two salts showing a *neutral to ionic* transition: TTF-CA which is the prototypical complex for these transitions and TTF-2,5Cl_2BQ which is less cpu demanding. We first studied all three isolated molecules. The vibrational spectra depending on charge of CA allowed us to make contact with experiments that deduce the ionicity of the crystal from I.R. and Raman spectra [1]. Then we investigated the 1D properties of the crystalline high and low symmetry phases [2, 3, 4]. In particular we got a clear understanding of the tight relation between symmetry breaking and charge transfer increase. At last, we analyzed the 3D interactions combining our ab-initio calculations with a simple tight binding model. Ab-initio values for the charge transfer and the hopping integrals have been derived and their nature has been elucidated.

We derived also a set of parameters that are essential for models allowing to derive a consistent description of the phase transition from which complex nonlinear excitations can be elucidated.

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Molecules and Organic Solids Working Group

Node: **Konstanz**

Scientific Highlights

During the last few years we have continued our work on developing and applying methods for electronic-structure calculations. Our main emphasis has been on quasi-one-dimensional materials, i.e., chain compounds, where we assume that treating a single, isolated, infinite molecule is a good approximation. To this end we apply a first-principles method we have developed ourselves.

Being a relatively small group our interactions with the colleagues in the network have been somewhat limited. On the other hand, the availability of various types of expertise within the network has been very valuable for our work, as shall be demonstrated below.

During her stay in Konstanz, Catia Arcangeli worked on implementing a generalized-gradient approximation for treating exchange and correlation effects within the density-functional formalism. This should replace the local-density approximation that we so far had been using but which we found could not describe the properties of the systems of our interest correctly. Thus, in particular for hydrogen-bonded systems (that are relevant for a number of biological systems) our local-density calculations gave results that were in wild conflicts with experimental information. It is believed that this can be improved by applying the generalized-gradient approximation. Through the network it was possible for Catia Arcangeli to participate in the Ψ_k network workshop 'Quantum Theory of Solids: Improved Density Functionals' in Århus, June 1994. This was a very convenient opportunity for us to learn about the generalized-gradient approximations. At the moment this work is being continued through studies of proton transport in α-helices that is done in a collaboration with Iris Howard, University of Texas.

Sergei Simak, University of Rennes, visited us for two weeks during December 1994, also made financially possible by the network. Sergei Simak worked on organic molecular crystals, and it was valuable to interchange information and explore whether a joint project could be established. Some calculations on some molecules were done using our code, but ultimately it was decided by the group in Rennes instead to use the code by Peter Blöchl for these studies.

Finally, the network made it possible for Karla Schmidt and myself to participate in the network conference in Schwäbisch Gmünd, September 1996. This conference was very useful and gave actually the inspiration to our only paper that is the direct outcome of our participation in the network.

Our work has continuously been inspired by the input from other work, where the Ψ_k newsletter has been a very important source of information. Of basic contributions to the field of electronic-structure calculations we mention the following two that also should have impacts on the work of the other participants of the network:

We have implemented a method for calculating forces within our full-potential LMTO method for helical polymers. This method includes all terms that correct for approximate eigenfunctions and approximate potentials, and is unique in taking care of the separation of space into muffin-tin spheres and the interstitial region, also for very open systems where about 50% of the valence electrons are found in the interstitial region. Furthermore, through the scheme of our paper below we can without noteworthy additional complications treat metallic systems where the orbital occupancies no longer are constants. We are currently testing a molecular-dynamics program that subsequently will be applied to various polymeric systems, first of all the conjugated polymers.

In many cases the polymeric systems possess deviations from pure periodicity. This may be due to extra charges or to structural distortions. Since these defects may be quite delocalized it is very difficult to treat them theoretically. On the other hand, their existence is important for a number of properties of the materials, and it is therefore highly desirable to be able to obtain results also from theoretical calculations. A standard approach is to apply model Hamiltonians where the parameters may be obtained either from exact calculations on some simplified structures or from experimental information. During the last years we have shown that there is a very simple scheme that can be used to give highly accurate information on the energies of the localized orbitals as long as the defect is extended and as long as a single-particle model is applicable. When the latter not is the case, one needs to include many-body effect as, e.g., contained within the (extended) Hubbard model. Here, however, it is not obvious how to determine the parameters of the model Hamiltonian from theory. This is first of all the case for fairly delocalized electrons for which a separation into atomic components is non-trivial. We have therefore developed a method that relies on the so-called constrained-density-functional method and that can be used in calculating the values of the Hubbard parameters without being strongly dependent on the ambiguity of separating the orbitals into atomic components. The method has been tested on some simple, finite and infinite, systems, and is currently being applied on some carbon-based polymeric materials.

Publication:

M. Springborg, R. C. Albers, and K. Schmidt: Fractional occupancies and temperature in electronic-structure calculations, Phys. Rev. B, January 15th, 1998.

Node: **Stuttgart/Belfast**

Highlights of Collaborations on Large Systems

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

Introduction

The bonding at interfaces in materials is of wide ranging scientific and practical importance, and has received considerable attention from our electronic structure community. One area of research reported by the Cambridge group has been to understand the mechanism of sliding of grain boundaries, and the embrittling effect of impurities, focussing on the effect of Ga at grain boundaries in Al. Another focus of interest, reported here, has been the intrinsic adhesion of metals to oxides. 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.

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. Compared to the calculations for boundaries in Si and Al, larger basis sets are needed to describe the bonding in oxides and transition metals, which means that so far only the simplest systems have been tackled.

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.

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).

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 first results of this collaboration are set in the context of other theories and models of metal-ceramic bonding in ref. [2].

Another issue is to try to find simpler models which describe either the atomic interactions or the electronic structure of such interfaces. We have recently made developments of the tight-binding model to embrace polarisable ionic crystals (Finnis *et al* to be published) which we plan to pursue further in the Belfast group in collaboration with Dr. Polatoglou's group in Thessaloniki. 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. Classical models, which are computationally even simpler than tight-binding, such as introduced in our collaboration with Berlin [3], may also prove useful.

Advances in ab initio methods and computer hardware since the start of the PSIK project have been so great that we are able to return to the direct calculation of adhesion energies of metals on alumina, which was practically impossible at the beginning of the project. Experimental interest in adhesion of metals to sapphire remains high, as witnessed by a recent(December 97) issue of Physical Review Letters [4], so future theoretical work in the area is sure to be welcome.

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