HCM Newsletter

# $\Psi_k$ Network

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

Number 15 June 1996

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# Editorial

The **Editorial** is followed by the section **News from the Network** where we report on some current issues of the Network, including the **Network conference**.

In the section **News from the Working Groups** readers will find reports on recent collaborative visits and workshops. Straight after there are announcements of available positions and forthcoming workshops and meetings. These are followed by the usual **Abstracts** section, and the **Highlight of the Month** section.The latter contains an article by Stefan Blügel (Jülich) on '*Magnetically Stabilized Surface Alloys*'.

The *Network* has a home page on **World Wide Web**. 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)* whichalso includes information on the **Network Conference**, *P. Blöchl (IBM, Zürich*, *M. Gillan (Keele)*, *E.K.U. Gross (Univ. Wurzburg)*, *B.L. Györffy (Bristol)*,*V. Heine (Univ. Cambridge)*, *J. Kübler (TH, Darmstadt)*, *R. Nieminen (TU, Helsinki)*, *J. Nørskov (TU, Lyngby)* with information on CAMP, *M. Scheffler (FHI Berlin)*, *K.-H. Schwarz (TU, Vienna)* and *A. Walker (UEA Norwich).* If you maintain a home page on your activities we will be happy to include a pointer from the *Network's* home page to your home page.

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

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

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

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

# News from the Network

Good news is that Brussels has approved an extention of the time duration of our Network until the end of 1997, however, only within the currently available funds. Since the intention of the Network is to apply for funding to the TMR Programme in February 1997, this extention, with a bit of luck, would secure a continuation of our activity. Currently, the Network's **Management Board** is preparing a renewal proposal application to the TMR Programme, based on about eight projects accompanied by eight postdoctoral positions. Therefore, the activity of the Network would be much more focused on the project, however it is envisaged that the current activity of the Network would be continued in parallel. The newsletter and other general information services are to be continued, as are the small meetings, workshops and support of short collaborative visits, subject to a succesful outcome of the TMR application.

A lot of you would have seen the WWW pages of the Network. We think that they now need a major revamp to include the scientific accomplishments of our Network. We welcome contributions and suggestions for this. In particular, colourful pictures are needed which capture the essence of our collaborations. This is to be addressed urgently since we need now to convince funding agencies that we are worthwhile renewing.

# News from the Network Conference

Currently, our effort is concentrated on the Network's Conference in Schwäbisch Gmünd (17–21 September, 1996). We hope that the conference will be well attended by all our members and sympathisers to represent all ongoing electronic structure work in Europe and other parts of the world. So far over 270 abstracts have been received. If you have not submitted your abstract, please note that we will consider all post–deadline contributions. In particular, the following symposia are under–represented: the order (N), carbon structures, organic materials and chemical reactions. Please remember that even Network members counting on financial support from the Network need to fill in the application form. The latest information on the Conference can be obtained on WWW at **http://radix2.mpi-stuttgart.mpg.de/hcm.html** and correspondance should be e-mailed to **psik@radix2.mpi-stuttgart.mpg.de**.

**See you all in Schwäbisch Gmünd!**

# News from the Working Groups

## Report on the four months secondment of R. Pérez ( Madrid node) to M. C. Payne (Cambridge node)

January 1st – April 30th 1996

## Understanding Atomic Resolution in Non–contact Atomic Force Microscopy on Reactive Surfaces

Ruben Perez* and Michael C. Payne
Theory of Condensed Matter, Cavendish Laboratory
University of Cambridge
Madingley Road, Cambridge CB3 0HE, U.K.

### Introduction

R. Pérez (Universidad Autónoma, Madrid) and M. C. Payne (University of Cambridge) have been working on the detailed study of different regimes in the tip–surface interaction using first–principles techniques. A brief account of this work was included in the October'95 issue of the Network's Newsletter.

Support from the network has enabled R. Pérez to stay for four months (starting January 1st, 1996) in Cambridge and to benefit from the expertise of Dr. Payne's group in the application of total–energy pseudopotential methods to large systems. This collaboration has also involved a group in Japan (Ivan Štich and Kiyoyuki Terakura, JRCAT, Tsukuba), which is very active in the field of first–principles simulations of real materials.

This stay has allowed us to undertake a very ambitious task: The understanding of some of the recent experimental attempts to investigate the structure of surfaces with atomic resolution using an Atomic Force Microscope (AFM) under well–controlled, ultra–high vaccuum conditions. Our numerical simulations have shown that chemical interactions between dangling bonds on reactive surfaces and the apex atom in the tip provide a mechanism for atomic resolution imaging of these surfaces. These interactions also account for some of the more surprising experimental facts, concerning instabilities in the operation of the microscope, and the changes in resolution observed in the experiments.

This work has been discussed in the following papers:

- *First Principles Simulations of Nanoindentation and Atomic Force Microscopy on Silicon Surfaces.*
  R. Perez, M. C. Payne, I. Stich and K. Terakura, in *Materials Theory, Simulations and Parallel Algorithms*, Editors: E. Kaxiras, J. Joannopoulos, P. Vashishta and R. K. Kalia, MRS Symposia Proceedings, Vol. **409** (MRS, Pittsburgh, 1996). (ISBN: 1-55899-311-8)

- *Role of Tip–Surface Covalent Interactions in Non-Contact Atomic Force Microscopy on Reactive Surfaces*

R. Perez, M. C. Payne, I. Stich and K. Terakura, submitted to Physical Review Letters (1996).

- *First Principles Simulations of Non–contact Atomic Force Microscopy on Reactive Surfaces* R. Perez, M. C. Payne, I. Stich and K. Terakura, invited paper submitted to Scanning Microscopy (1996).

and has been presented in the following conferences:

- March Meeting of the American Physical Society. (Saint Louis, Missouri, USA), March 18th–22nd 1996.
- Scanning Microscopy: Fundamental Physics and Applications. (Bethesda, Maryland, USA). May 12th–16th 1996. (invited talk)

Non–contact AFM is an active, emerging field, with an increasing number of experimental groups involved in the development of the technique. Recent experimental results on the InP(110) surface, where the AFM fails to resolve the atoms on the characteristic zig–zag chains on the surface pose a new challenge to the capabilities of the technique. A theoretical analysis of the lateral resolution of the AFM on this system will be the next step of this collaboration between the Madrid and Cambridge groups.

## Scientific Results

The motivation of our work comes from the long–standing debate in the literature about the resolution capabilities of the AFM. Progress towards true atomic resolution in atomic force microscopy in ultrahigh vacuum has been slower than in Scanning Tunneling Microscopy (STM). Operation in the contact regime, where tip and sample are in close mechanical contact, is affected by friction and local deformations of the surface which distort the images in an uncontrolled way. On the other hand, the measurement of the weak forces required for atomic resolution in the non–contact attractive regime is a challenging experimental problem.

Only recently have Giessibl (F. Giessibl, Science **267**, 68–71, 1995) and Kitamura and Iwatsuki (S. Kitamura and M Iwatsuki, Jpn. J. Appl. Phys. **34**, L145, (1995)) shown atomic resolution in the non–contact [UHV] regime using a Si tip scanning a reactive surface, the reconstructed Si(111) 7×7 surface. These experiments use a novel frequency modulation detection scheme that senses the force gradient, instead of the force itself.

A quick comparison of the AFM images in the previous references with the STM images of the same surface shows that we are still far from an equivalent performance. Giessibl's experiment shows a low-quality image of the surface, similar to Kitamura and Iwatsuki's result, except for a small area where suddenly, for the width of a unit cell, the characteristic protrusions associated with the 12 adatoms on the top layer of the reconstruction can be clearly seen. After this, the resolution deteriorates again, and no image is obtained for the rest of the scan.

Understanding the resolution capabilities of a scanning probe involves a detailed knowledge of the signal that is used to obtain the image. In the case of the AFM, this implies to establish the interactions that contribute to the total force acting between the tip and the surface. The theoretical analysis of the non–contact regime, is particularly complicated because of the need to describe the interaction in a region where the crossover between chemical bonding and long–range Van der Waals (VdW) interactions should be taking place. Our work shows that the new gradient approximations for the exchange correlation functional (GGA) are necessary for an accurate description of the chemical interactions.

Figure 1 shows our results for the binding energy and the normal force between different tips and a Si(111)-5×5 surface in a scan at a constant height of 5 Å (the closest approach) along the main diagonal of the surface. Those tips have the same geometrical structure at the apex, but different electronic charge distributions. The results clearly show that the tips with a dangling bond in the apex atom directed towards the surface provide a much stronger interaction, which is completely dominated by this feature of its charge distribution and almost independent of any other structural detail. The origin of the strong contrast between different positions in the surface is the onset of covalent bonding between the dangling bonds in the adatoms and the dangling bond on the apex atom of the tip as shown by the charge transfers and the normal displacements of the adatoms observed during our simulation of the scanning process.

The comparison of this chemical interaction with the Van der Waals interaction (see Table 1) shows that it not only has an important contribution to the total tip–surface force, but dominates the force gradients, which are used to determine the experimental image. The magnitude of the force gradients, very close to the force constant of the cantilever used in Giessibl's experiments (17 N/m), also accounts for the instabilities in the feedback operation observed.

Table 1: Comparison of the relative contribution of the covalent bonding interaction and the tip–surface Van der Waals interaction to the normal force and force gradient for a normal distance of 5 Å. The VdW values correspond to the 4 Si atoms tip we have used in our simulations (Microscopic VdW) and to a macroscopic spherical tip with the experimental curvature radius of 40 Å. The covalent bonding interactions give a very significant contribution to the normal force and dominate the force gradient.

| | Force | Gradient |
|---|---|---|
| Microscopic VdW | -0.02 nN | 0.15 N/m |
| Spherical (R=40Å) VdW | -0.50 nN | 2 N/m |
| Tip without DB | -0.07 nN | 2 N/m |
| Tip with DB | -0.39 nN | 10–12 N/m |

Our results for the different tips suggest an explanation for the sudden switch of the tip to atomic resolution observed in the experiments of Giessibl in terms of changes in the structure of the tip which affect the electronic charge density distribution at the apex. If the tip moves closer to the surface, it can pick up a Si atom from the surface, or it can lose a contaminant previously attached to it. In this case, if a dangling bond directed towards the surface is formed the contrast will be dramatically enhanced until that dangling bond is saturated again. These processes are more likely to happen in these experiments than in the ones of Kitamura and

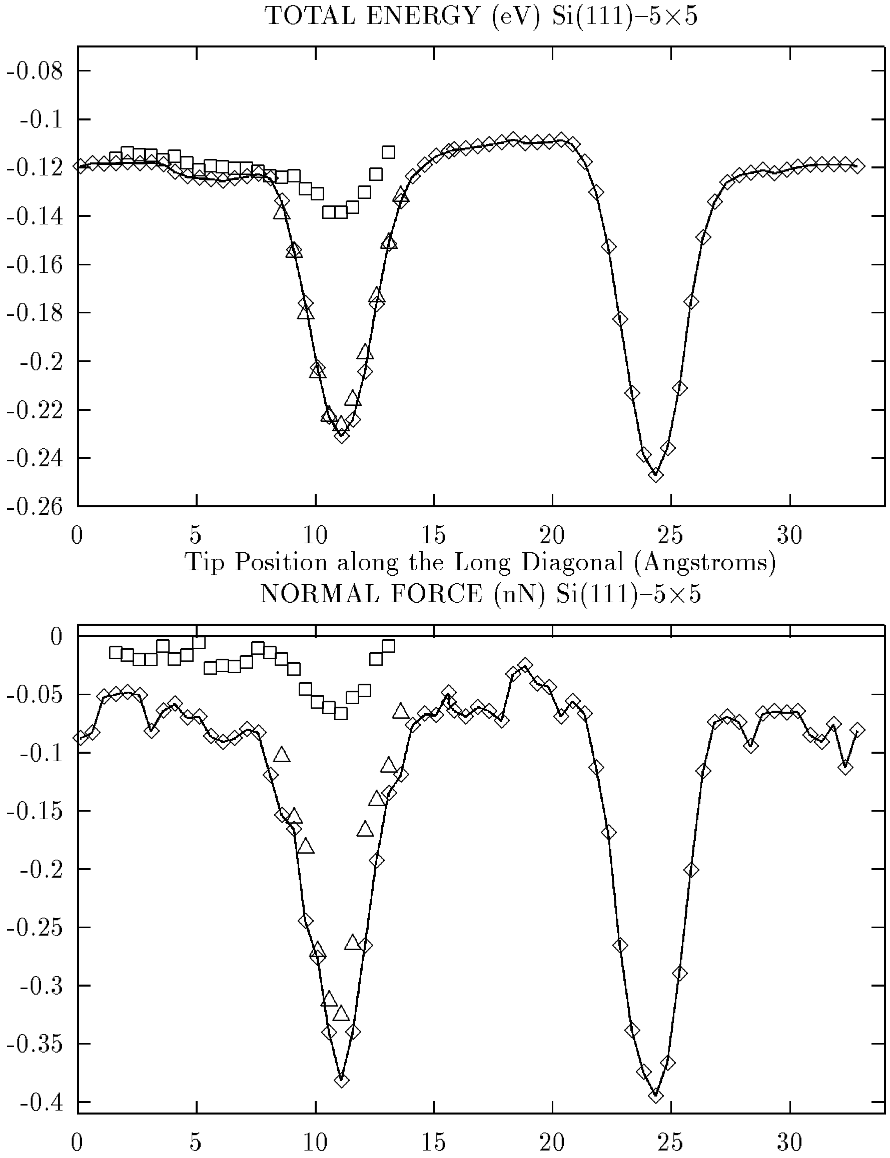

Figure 1: Total energy (in eV) and normal force (in nN) for the scan along the main diagonal of the 5×5 reconstruction at a constant height of 5 Å above the adatoms. Squares (triangles, rhombuses) correspond to the tip without (with) a dangling bond. All the tips show minima at the position of the two adatoms in the main diagonal. The corner hole is located at 17.83 Å, the unfaulted (faulted) half of the cell to the left (right).

Iwazuki, where a much stiffer piezolever (force constant of 40 N/m) is used and so fluctuations in the tip–surface distance are expected to be smaller. In fact, no noticeable increase in the quality of the images was observed in this case during the scanning process.

### Acknowledgements

R. P. acknowledges the financial support of the Human Capital and Mobility Programme of the European Union under contract ERBCHRXCT930369. Computer time was provided on the Connection Machine CM5E at JRCAT in Tsukuba and the Cray T3D at EPCC in Edinburgh. This project was partly supported by New Energy and Industrial Technology Development Organization (NEDO, Japan).

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## Report on the collaborative visit of J.M. Holender (Univ. Keele, UK) to Institut für Theoretische Physik, Technische Universität Wien, Austria

### 27Feb–5 March, 1996

This visit to Prof. Hafner's group was a continuation of a collaboration initiated by previous visit of Prof. M.J. Gillan and myself in November 1995 (Newsletter 13). There are two fields of our collaboration:

1) Scientific part - The first-principles simulation of liquid semi-metals, and specifically liquid selenium. I discussed our results with Prof. Hafner and dr. Kresse. We are preparing a joint paper on this subject.

2) Technical part - The groups use two different codes Keele group uses Cambridge code CASTEP (or CETEP on parallel machines), whereas the Vienna group use their own code VAMP (Vienna *ab-initio* molecular-dynamics package).

I spent a substantial part of my visit on discussions with dr.G.Kresse on their code (VAMP). We are testing this code now and are very pleased with its performance.

In summary, this visit was very useful and should result in even stronger collaboration between Vienna and Keele.

(J. Holender)

# Report on the collaborative visit of Uwe Schönberger (Cambridge, UK) to Queens University of Belfast, Northern Ireland

## 10–12 March, 1996

Dr. Uwe Schoenberger visited me and the Atomistic Simulation Group from 10-12 March. Our main topic of discussion was concerned with the crystal structures of $ZrO_2$ and the origin of the relative stability of the different phases monoclinic, tetragonal and cubic. Uwe has done an extensive set of FP-LMTO calcutions for cubic and tetragonal phases which he is in the process of writing up. We have discovered (Wilson et al, submitted for publication) that quadrupolar polarisability of the oxygen ions is necessary to explain the stability of the tetragonal over the cubic structure, so we discussed under what symmetries quadrupoles could appear on the oxygen ions. Uwe Schoenberger proposed to display the quadrupoles by subtracting atomic charge densities from the self-consistent ones; this worked well in alumina. A second topic was the MgO (100) surface. Tony Paxton and Tien-nga Le here have made preliminary calculations of MgO surface energies to test their LMTO procedures. It is not at all straightforward to apply FP-LMTO to oxides, so it was useful to learn from Uwe Schoenberger's experience.

Expenses:
Air fare Stanstead-Belfast + local travel: 70 GBP
Two nights subsistence: 120 ECU

(M. Finnis)

# Report on the collaborative visit of J.E. Inglesfield (Univ. Cardiff, UK) to the University of Nijmegen

### 1–6th May, 1996

This visit to Nijmegen was to continue the work of my last visit (in fact the work of my last 7 years in the Electronic Structure of Materials Group there) – the development of the embedding method with Jeroen van Hoof. The present program uses LAPW basis functions, but it is possible to replace the atomic core itself by an embedding potential (almost equivalent to APW), and we worked on this. The fact that the atomic embedding potential is energy-dependent is no problem with our new set of programs, because the Schrödinger equation is being solved at fixed (in general complex) energies. I also discussed magnetic problems with Rob de Groot, Peter de Boer (half-metallic systems), and with Peter van Gelderen (magnetic multilayers).

(J.E. Inglesfield)

# Report on the collaborative visit of Martin Lüders (Würzburg) to Vienna

9–24 April, 1996

The objective of the collaboration with the group of Prof. K. H. Schwarz in Vienna is to implement the method of the optimized effective potential (OEP) within the approximation by Krieger, Li and Iafrate (KLI) into the FLAPW code WIEN95. The main purpose of this visit to Vienna was to discuss the code, which I had written in Würzburg. The efficiency of the code was improved signifcantly during the visit and, besides that, the contribution of the core electrons was included.

(Martin Lüders)

*Report on*

# INTERNATIONAL WORKSHOP ON THE BOGOLIUBOV-de GNNES EQUATIONS FOR SUPERCONDUCTORS

*Sponsored by: CCP9 and EU–HCM $\psi_k$–Network*

*Organised by: B.L. Györffy (b.gyorffy@bristol.ac.uk)*

**H.H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol, BS8 1TL, UK**

*March 30, Saturday, 10:00am–March 31, Sunday, 2:00pm*

This workshop, with sponsorship from CCP9 and EU–HCM $\psi_k$–Network, took place at the H.H. Wills Physics Laboratory, University of Bristol, on 30 and 31 March. As the final programme, shown below, indicates it was devoted to those current problems in superconductivity which require the Bogoliubov-de Gennes version of the BCS theory for their treatment. The emerging consensus concerning $d$–wave pairing in the high $T_c$ cuprates was one of the reoccuring theorem over the two days. Very interesting new results were also reported on mesoscopic superconducting structures, dichroism in superconductors, percolating superconductivity and Bose-Einstein condensation of charged particles in a magnetic field. The power of the Bogoliubov-de Gennes equation to describe quasi-particles in superfluid $^4$He was illustrated and very well received. The general feeling was that both new physics and new techniques are emerging every day in this rapidly moving field and such workshops are very useful for the practitioners. Indeed at the end a group of us decided to form a consortium and bid for supercomputer time as a community with shared methods and aspirations.

(Balazs L. Györffy)

## Final Programme

| | |
|---|---|
| Stefan Kurth (*Antwerp*) | **Local Density Approximation for Superconductors** |
| Walter M. Temmerman (*Daresbury*) | **Quasi-particle Spectra of High Temperature Suprconductors** |
| Balazs L. Györffy (*Bristol*) | **A semi-calssical Theory for Superconductors** |
| Jonathan Robins (*Bristol*) | **Semi-classical Quatization: The Modern View** |

| | |
|---|---|
| Colin Lambert (*Lancaster*) | **Phase-coherent Transport in Mesoscopic Superconducting Structures** |
| Mark Leadbeater (*Lancaster*) | **Tunneling Calculations for Normal-Superconducting Hybrid Structures** |
| Andrew Martin (*Lancaster*) | **Self-consistent Current-Voltage Characteristics of Superconducting Nanostructures** |
| Paul Cook and Roberto Raimondi (*Lancaster*) | **A Comparison of the Mesoscopic Transport Properties of s-wave and d-wave Order Parameters** |
| Klaus Capelle (*Würzburg*) | **Dichroism in Superconductors** |
| James Annett (*Bristol*) | **The evidence for d-wave pairing in High Temperature Superconductors** |
| Martin Lüders (*Würzburg*) | **The Decoupling Scheme for the Bogolubov-de Gennes equation and Symmetry Considerations for the Gap Equation** |
| Grzegorz Litak (*Lublin*) | **Percolating Superconductivity** |
| John Matthias (*Exeter*) | **Quasiparticle Scattering in Superfluid Helium 4** |
| A.S. Alexandrov (*Loughborough*) | **Bose-Einstein Condensation of Charged Particles in a Magnetic Field** |

*Report on*

## Second HCM - WORKSHOP

# Full-Potential LAPW Calculations with the WIEN95 Code

*Technical University Vienna, Austria*

April 9-13, 1996

*Chairman:* K. Schwarz (TU Wien)

**Sponsors:**

Human Capital and Mobility Programme
Österreichische Forschungsgemeinschaft
Creditanstalt Bankverein

This second workshop was concerned with recent progress in density functional calculations using the full-potential Linearized Augmented Plane Wave (FP-LAPW) method as embodied in the WIEN95 code. The workshop was organized in two parts, namely as an introduction for novice users and applications mainly for experienced users. The HCM workshop lasted for four days and was attended by 42 researchers from eight countries. The scientific programme covered a short introduction to Density Functional Theory (DFT), band structure methods in general and the LAPW method, with corresponding algorithms and features, in particular. The outline and the handling of the program package was described in detail by P. Blaha but the participants had a chance to run WIEN95 on several workstations in five excercise sessions. This arrangement was well accepted by the new users, who could perform "hands-on" calculations with the user-friendly code and learned by practice. This part was supplemented by lectures on the use of local orbitals (by P. Dufek), DFT versions like local density approximation (LDA) or generalized gradient approximation (GGA) and the concepts of forces and their calculation (by K. Schwarz).

In the second part applications directly or indirectly related to the WIEN95 package were presented as lectures or posters illustrating many interesting band structure results such as molecular dynamics, phonons, phase stability, spin-orbit splitting, electric field gradients, crystal field parameters, photoemission or x-ray emission and absorption spectra. The solids that were investigated ranged from semiconductors, hydrides, ultrahard materials, surfaces, intermetallics to minerals. In addition to these topics a computational aspect, namely parallelizing the code, was discussed and a first experience was presented.

We have received very positive reactions from the participants who told us that they had learned a lot and they liked the balance of this workshop in terms of introduction, lectures, program handling, exercises and presentation of results. It was a very useful workshop and thus the participants clearly expressed their wish to have a similar meeting in a years time. From all the informal discussions which took place it can be expected that several interesting European collaborations will evolve from this HCM workshop and new ones will be initiated.

**The full list of participants is included below:**

Dr. Anders Alm (*Univ. Vasteras, Sweden*)
Dr. Claudia Ambrosch-Draxl (*Univ. Graz, Austria*)
Per Andersson (*Univ. Uppsala, Sweden*)
Dr. Philippe Barbarat (*CEA, Monts, France*)
Dr. Uwe Birkenheuer (*TU Munich, Germany*)
Dr. Peter Blaha (*TU Vienna, Austria*)
Dr. Philipp Dufek (*TU Vienna, Austria*)
Dr. Jörg Ehmann (*MPI Stuttgart, Germany*)
Dr. Eberhard Engel (*Univ. Frankfurt, Germany*)
Dipl. Phys. Heike Herper (*Univ. Duisburg, Germany*)
Dipl. Phys. Egbert Hoffmann (*Univ. Duisburg, Germany*)
Dr. Randi Holmestad (*NTNU-Trondheim, Norway*)
Dipl. Phys. Carsten Holtfort (*Univ. Duisburg, Germany*)
Hakan Hugosson (*Univ. Uppsala, Sweden*)
Dipl. Phys.Michael Knecht (*Univ. Munich, Germany*)
Susanne Kohlhammer (*MPI Stuttgart, Germany*)
Dipl. Phys. Thomas Luce (*FU Berlin, Germany*)
Dipl. Phys. Martin Lüders (*Univ .Würzburg, Germany*)
Joachim Luitz (*TU Vienna, Austria*)
Urban Lundin (*Univ. Uppsala, Sweden*)
Dr. Knut Marthinsen (*SINTEF, Trondheim, Norway*)
Dr. Peter Mohn (*TU Vienna, Austria*)
Dr. Vincent Natoli (*Exxon, Annandale NJ, USA*)
Renata Nogueira (*Univ. San Paolo, Brazil*)
Dr. Pavel Novak (*Praha, Czech Republic*)
Dr. Michel Penicaud (*Villeneuve St. George, France*)
Clas Persson (*Univ. Linkoping, Sweden*)
Phys. Dipl. Max Petersen (*Fritz-Haber Institut, Berlin, Germany*)
Dipl. Phys. Garcia Polanco (*Univ. Munich, Germany*)
Dipl.Phys. Alexander Quandt (*Univ. Tübingen, Germany*)
Dr. Walter Schirmacher (*TU-Munich, Germany*)
Dr. Peter Schmid-Beurmann (*Univ. Kiel, Germany*)
Wolf-Dieter Schöne (*Fritz-Haber Institut, Berlin, Germany*)
Prof. Karlheinz Schwarz (*TU Vienna, Austria*)
Dr. Bruno Siberchicot (*CEA, Villeneuve St. George, France*)
Mark Sifkovits (*Univ. Dortmund, Germany*)
Dipl. Phys. Holger Smolinski (*Univ. Dortmund, Germany*)
Torsten Soldner (*Univ. Leipzig, Germany*)
Dr. Minoru Sugihara (*Aoyama Gakuin University, Tokyo, Japan*)

Dipl. Phys. Harald Teuscher (*Univ. Tübingen, Germany*)
Frank Wagner (*Fritz-Haber Institut, Berlin, Germany*)
Dr. Björn Winkler (*Univ. Kiel, Germany*)

(Karlheinz Schwarz)

*Announcement*

# Postdoctoral Positions for Young EU Nationals

An EU-funded Training and Mobility Research (TMR) Network on Interface Magnetism has positions* for 7 young (less than 35 years) EU nationals for the following projects:

- Interlayer Exchange Coupling (Coordinator: B.L. Gyorfyy, Bristol, UK)
- Spin-polarised Spectroscopies (Coordinator: W.M. Temmerman, Daresbury, UK)
- Tight Binding KKR Green's Function Methods (Coordinator: P. Dederichs, Juelich, Germany)
- Real Space Tight Binding LMTO Methods (Coordinator: H. Dreysse, Strasbourg, France)
- Spin-polarised Spectroscopies (Coordinator: P. Weinberger, Vienna, Austria)
- Giant Magnetoresistance (Coordinator: P. Kelly, Eindhoven, Netherlands)
- Magnetic Anisotropy and Surface Structure (Coordinator: B. Johansson, Uppsala, Sweden)

The Network consists of six flagship projects, which we consider as the most important and highly challenging ones in ab–initio electronic structure calculations of magnetic properties. Four of the flagship projects include studies of the most recent discoveries of interlayer coupling, giant magnetoresistance and magnetic X–ray dichroism. The other two projects concern the implementation of new technical developments in electronic structure calculations (i.e. screened structure constants) to construct a new generation of codes able to deal with larger systems. Consequently we will be able to perform ab–initio studies of interlayer coupling, giant magnetoresistance, magnetic anisotropies and surface structures for realistic systems, larger than ever studied before. In particular we want also to study the interrelation between these properties. Moreover we want to carefully compare the details of our calculations against spectroscopic data. Each flagship project will be spearheaded by a post–doc, the only exception being the spectroscopy project which has 2 post–docs associated because of the interaction with synchrotron communities.

Additional information may be obtained from:
Peter Dederichs, e-mail: L.Gerken@kfa-juelich.de, Tel.: +49-2461-614351, Fax: +49-2461-612620

Walter Temmerman, e-mail: w.m.temmerman@dl.ac.uk, Tel.: +44-1925-603227, Fax: +44-1925-603634

* subject to the satisfactory conclusion of contract negotiations and financial procedures with the European Commission. Only nationals of EU Member States different from the country where the project is located are eligible.

*Announcement*

# Postdoctoral RA Position: University of Bristol

A postdoctoral RA position is available at the University of Bristol with Dr James Annett. The project is to investigate the electronic states in the energy gap of d-wave superconductors. In particular it is planned to determine the effects of surfaces and grain boundaries, where the density of states will be significantly modified compared to bulk superconductor. Calculating the Josephson effect between s and d-wave superconductors or between two d-wave superconductors will be the major objective. This is now a topic of considerable importance for recent experiments on high Tc superconductors. The work will involve numercal solutions of the Bogoliubov de Gennes equations in the surface/interface region. Previous experience with numerical electronic structure and/or with superconductivity would be helpful, but is not essential. Pay will be £15986 per annum initially. For more information contact: **James.Annett@bristol.ac.uk**.

# Research Associate Position

GRIFFITH UNIVERSITY
FACULTY OF SCIENCE AND TECHNOLOGY
Nathan Campus, Kessels Rd., Nathan, Queensland 4111, AUSTRALIA

## INFORMATION FOR APPLICANTS: RESEARCH FELLOW (DENSITY FUNCTIONAL THEORY)

**Position:** Griffith University Research Associate (Fixed Term)
(For 1 year initially, renewal likely for second year)

**Salary:** Research Fellow Grade 1, 33,573 Australian dollars per annum
(As at late May 1996, 1 Australian dollar = 0.80 USD, approx.)

**Location:** Nathan Campus

**Starting date:** 1 September 1996 (negotiable)

**Duties:**
The appointee will work within the research group of Associate Professor John F. Dobson on aspects of Density Functional Theory. This position is financed by an Australian Research Council Large Grant entitled
**"Fundamental improvements to density functional theory for applications in physics and chemistry"**
A principal area of concern for the appointee will be the development of suitable conserving local and gradient approximations to the dynamical response and local field functions of inhomogeneous, interacting many-electron systems. This will in turn lead to new density functionals, both of the time-dependent and the time-independent type. In the pursuit of these matters the appointee will work both with Dr. Dobson and with graduate students. All the work is of a theoretical nature, and will probably also entail some numerical computation on an IBM SP2 supercomputer.

## SELECTION CRITERIA

- Essential qualifications
  (a) PhD in theoretical physics, or possibly in a suitable area of theoretical chemistry
  (b) Some experience with theory of many-electron systems

(c) Some experience with numerical computation

(d) Good command of spoken and written English

- Desirable qualifications

  (a) Substantial grounding in electron density functional theory, including time-dependent density functional theory

  (b) A good knowledge of formal many-body theory

  (c) Experience with large computer programming tasks and/or supercomputing

Informal advice about scientific aspects of the position may be obtained by phoning Dr. Dobson on +61-7-3875-7441 or sending e-mail to: **J.Dobson@sct.gu.edu.au**.

Applications should include a curriculum vitae and list of publications, plus the names and contact details (telephone, FAX and e-mail) of two referees. Referees should be contacted in advance by applicants to ensure that each referee is prepared to comment on the strength of the application.

Applications should be airmailed to:

A/Prof. John F. Dobson
Faculty of Science and Technology,
Griffith University,
Nathan, Queensland 4111
Australia

Alternatively, applications may be e-mailed (in TEX or LATEX format, or in plain ASCII text) to **J.Dobson@sct.gu.edu.au**, or FAXED to **J.Dobson on +61-7-3875-7656**.

Closing date for receipt of applications is June 15, 1996.

*Announcement*

# Postdoctoral Position in Condensed Matter Theory

*Free University of Berlin, Germany*

Applications are invited for a postdoctoral position in Condensed Matter Theory at Free University of Berlin. The project is on "Nonlinear Optics and Nonequilibrium Dynamics in Magnetic Nanostructures".

Applicants should be highly motivated and have an excellent background
(i) either in electronic many-body theory
(ii) or in first principles electronic structure calculations.

He or she must hold a recently earned Ph. D. and be a (non-German) citizen of the European Union.

The position starts in fall, 1996, and is for up to three years. The annual salary is appr. 50000 USD (minus taxes, insurances, etc., amounting to appr. 40% depending on marital status).

Candidates should send a CV to the address below (possibly via email) and arrange for at least two letters of reference.

Dr. Wolfgang Huebner
Institute for Theoretical Physics
Freie Universitaet Berlin
Arnimallee 14
14195 Berlin, Germany
email:huebner@manuel.physik.fu-berlin.de
Tel.: +49-30/838-6124
Fax : +49-30/838-6799

*Announcement*

# Research Scientist Position at KFA Jülich

The Institut für Festkörperforschung at KFA Jülich is seeking to fill a (temporary) research scientist position in computational condensed matter theory. The initial appointment will be for 2 years, starting as early as July 1996. The appointment may be extended beyond that subject to the availability of funding. KFA Jülich is the largest German National Laboratory and harbors the German National Supercomputer Center HLRZ.

Salary will conform with German government regulations (BAT IIa, the equivalent of USD 50000-60000 before tax, depending on qualification). Funding will be provided by the Deutsche Forschungsgemeinschaft (DFG). The candidate is expected to participate in a collaborative project on molecular dynamics (MD) in organic chemical, polymer and amorphous inorganic systems. Experience with classical and first principles ("Car-Parrinello") MD, with electronic structure methods, and with parallel programming is highly desirable. We are inviting outstanding candidates with a physics, chemistry and/or computer science background to submit their resume and a list of 3 references in paper form or electronically to:

Dr. Detlef Hohl
Institut für Festkörperforschung
Forschungszentrum Jülich
D-52425 Jülich
Germany
e-mail: d.hohl@kfa-juelich.de
phone: +49-2461-61-6905
fax: +49-2461-61-2850

# *Final Circular*

## Workshop on Fe/Cr interface magnetism

Satellite Meeting of the Symposium

of the E-MRS Spring Meeting '96 on:

Magnetic Ultrathin Films, Multilayers and Surfaces

**(Strasbourg, 2-3 June 1996)**

Workshop partially supported by the EU-HCM - network:

Here is some final information on the Fe/Cr workshop in Strasbourg.

### 1. Programme

You will find in the attached programme that the workshop is organized in three sections: structural characterization, magnetic order and electronic structure, interlayer coupling and GMR. All these subjects are closely related to each other and it is the main purpose of the workshop to discuss these interrelations.

### 2. Presentations

In order to allow the most possible time for discussion oral presentations are limited to 8 min + 2 min for short questions concerning technical details of the talk. This seems reasonable taking into account that all participants are familiar with the subject and no general introductions are needed. So, please, stay within the time limit and transmit the highlight of your work to the audience as clearly as possible. There will be extra time to discuss the more general aspects after several presentations.

In addition, there will be a few extended talks as an introduction to and an overview on the different subjects. All participants are encouraged to bring additional material (e.g. transparencies from previous work) which can be introduced during the general discussions as 2-3 min presentations.

### 3. Preprints, digest

The participants are also encouraged to bring preprints and reprints of papers related to the topic of the meeting. These can be distributed or copied for interested colleagues. Those who have not sent an abstract in advance should bring a digest (1-2 pages) describing their results with relevance for the workshop.

### 4. Facilities

Overhead and slide projection is available in standard format. Anyone needing further equipment should contact the local organizers (H. Dreyssé, C. Demangeat).

### 5. Registration

Registration of the participants will start on Sunday, 2 June at half past noon (12:30) at the place of the meeting. There are no registration fees. Tickets will be sold for the dinner (banquet) on Sunday and lunch on Monday; the total cost will be around FF 250.-

### 6. Accommodation

The participants have to arrange for their own accommodation themselves. It is suggested to make use of the Hotel Reservation Form distributed with the final announcement of the E-MRS Spring Meeting. In case of difficulty you may contact the local organizers.

### 7. How to get to the meeting

Maps of the city of Strasbourg are sent with this information. To use public transportation the following is suggested:

- from the city center take tram direction "Hautepierre", exit at station "Rotonde" (one station after railway station gare in french). Then, take bus number 9 and exit at station "Haldenbourg". In principle someboby will be there on Sunday from 12:30 till 14:00.

If you arrive before (or after) follow the small map included and go to the campus named "CNRS". Ring to enter and ask for IPCMS.

### 8. Communication

During the workshop you can be reached by the following means:

Tel.: ++33 88 10 70 00

Fax: ++33 88 10 72 49

We wish you all a safe trip to Strasbourg and expect you for an exciting and stimulating meeting.

C. Demangeat, H. Dreyssé, J. A. C. Bland, G. Bayreuther

## PROGRAMME

*Sunday, 2 June*

14:00 Opening Remarks

## Structural Characterization

14:05 *B. Heinrich*
"The Role of Interfaces in the Exchange Coupling of Fe/Cr/Fe(001) Systems"
14:25 Discussion
14:35 *R. Pfandzelter*
"Growth of Cr on Fe(100) Studied by Grazing Ion-surface-scattering"
14:45 *D.E. Buergler*
"Fe/Cr/Fe Triplelayer on Ag(001)/Fe/GaAs(001):
Morphology and Chemical Properties"
14:55 *A. Davies*
"Atomic-scale Observations of Alloying in Cr/Fe(001)"
15:05 Discussion
15:25 Break
15:55 *V. Dupuis*
"From Superparamagnetic to Magnetic Ordered State in Systems
of Transition Metal Clusters Embedded in Matrices"
16:05 *R. Schad*
"The Interface Structure of GMR Superlattices"
16:15 *I.K. Schuller*
"Correlations between Structure, Magnetotransport and Magnetism
in Fe/Cr Superlattices"
16:35 Discussion

## Magnetic Order, Electronic Structure

17:00 *S.M. Dubiel*
"Application of Moessbauer Spectroscopy in the Investigation
of Charge- and Spin-density Waves"
17:10 *M. Rots, J. Meersschaut*
"Perturbed Angular Correlation Spectroscopy Study
of Thin Chromium Films and Multilayers"
17:30 Discussion
17:40 *H. Zabel*
"Spin Density Waves in Cr(001) Epitaxial Films
and Fe/Cr(001) Superlattices: Recent Results from Synchrotron
and Neutron Scattering Experiments"
18:00 Discussion
20:00 Banquet

| | |
|---|---|
| 09:00 | *F.J. Himpsel*<br>”Confinement of Empty States in Cr/Fe(100) Studied by Inverse Photoemission” |
| 09:10 | *T. Rasing*<br>”Nonlinear Magneto-optical Study of the Fe/Cr Interface” |
| 09:20 | *Y. Suzuki*<br>”Magneto-optical Properties of the Cr Wedges Grown on Fe(001)” |
| 09:25 | Discussion |
| 09:45 | *F.U. Hillebrecht, D. Knabben*<br>”Magnetic Properties of Ultrathin Cr Layers on Fe(100) and Fe(110)” |
| 09:55 | *D.L. Mills*<br>”Field Induced Spin Reorientation Transitions in Magnetic Superlattices” |
| 10:05 | Discussion |
| 10:15 | *N.I. Kulikov*<br>”Slater-Pauling curve for Fe-Cr alloys” |
| 10:25 | *Y. Kawazoe*<br>”Phase Stability of the Sigma Phase in Fe-Cr Based Alloys” |
| 10:35 | Discussion |
| 10:45 | Break |
| 11:15 | *P.H. Dederichs*<br>”Ab-initio Study of Cr and Other 3d Impurities at the Fe(001) Interface” |
| 11:25 | *S. Bluegel*<br>”Magnetism, Stability and Growth Mode of Ultrathin Cr and Mn Films on Fe(100)” |
| 11:35 | *V.M. Uzdin*<br>”Cr Overlayers on Fe. Influence of the Roughness on the Distribution of Magnetic Moments” |
| 11:45 | *G. Bayreuther*<br>”Magnetic Moments at Stepped Fe/Cr Interfaces” |
| 11:50 | *M. Freyss*<br>”Non-collinear Orders in Fe/Cr Superlattices” |
| 11:55 | Discussion |

12:15 *A. Vega*
"Magnetic and Electronic Properties of Fe/Cr Interfaces:
FeN Cluster Impurities in the Cr Matrix and Fe(Cr) Overlayers
on Cr(Fe) Substrates"
12:25 *A. Berger*
"Thermodynamic Properties of Imperfect FM/AFM-Multilayers"
12:35 Discussion
12:45 Lunch
13:45 E-MRS Awards

**Interlayer Coupling, GMR**

14:30 *P. Gruenberg*
"Bilinear and Biquadratic Interlayer Exchange in Fe/Cr
Layered Structures and its Relation to Growth and Structure"
14:50 *M.D. Stiles*
"Oscillatory Exchange Coupling in Fe/Cr/Fe"
15:00 *S. Mirbt*
"Calculated Magnetic Properties of Fe/Cr Interfaces"
15:10 Discussion
15:25 *S.N. Okuno*
"Interlayer Exchange Coupling in Fe/Cr(001) Observed
from the Fe Layer Thickness Dependence"
15:35 *J. Pflaum*
"Ferromagnetic Resonance Studies of the Influence of Cr
Interfaces on Fe Single Layers and Fe/Cr Multilayers"
15:45 *Th. Kleinefeld*
"Domain Structure and Interlayer Exchange Coupling
in Fe/Cr/Co Multilayers"
15:55 Discussion
16:10 *J. A. C. Bland*
"Biquadratic Coupling in Epitaxial Fe/Cr/Fe Structures
and the Magnetism of the Fe/Cr Interface"
16:20 *D. Stoeffler*
"Theoretical Study of Fe on Cr Monolayers Deposited on a Cr(001)
or Fe(001) Substrate: Role of Step Induced Defects"
16:30 Discussion
16:40 Break

17:10 *I. Mertig*
Ab-initio Calculations of Giant Magnetoresistance in Fe/Cr
17:20 *G. Reiss*
”Growth and Annealing Behaviour of Fe/Cr on SiOx Substrates”
17:30 *V.V. Ustinov*
”Magnetic Anisotropy and Magnetoresistance of MBE-grown Fe/Cr
Superlattices with Non-collinear Magnetic Structure”
17:40 Discussion
17:55 *F. Petroff*
”GMR”
18:05 *S.S.P. Parkin*
”Dependence of GMR and Interlayer Coupling on Fe Layer Thickness”
18:15 Discussion
18:25 Panel Discussion

*Announcement*

## VI Italian-Swiss Workshop on
## COMPUTATIONAL MATERIAL SCIENCE

*28 September - 2 October 1996*

Hotel Costa dei Fiori, S. Margherita di Pula, Sardinia, Italy

**An international workshop on issues in basic and applied material science, studied via computational approaches**

**TOPIC** - basic and practical issues in materials science treated by advanced computational techniques

**FORMAT** - about 20 invited lectures, open contributed oral session and poster session

**PROCEEDINGS** - all contributions will be published in Rendiconti della Facolta‘ di Scienze dell'Universita‘ di Cagliari. Deadline for submitting contributions is August 15, 1996: contact V. Fiorentini at fiore@ciop.unica.it. Manuscripts will be due at the Workshop

**VENUE** - Hotel Costa dei Fiori in S. Margherita di Pula (CA): an attractive sea resort on the south-western coast of Sardinia, providing comforts and an informal atmosphere

**GENERAL INFO** - see below for registration and program; for more, contact fiore@ciop.unica.it, or check out our site http://sparc10.unica.it for the forthcoming on-line info

**REGISTRATION**–

REGISTRATION and PAYMENT of conference fee are due before July 31,1996. Please send registration form (accompanied by payment receipt) by fax to:

Corsi & Congressi,
via Galassi 2, I-09131 Cagliari
tel/fax +39 70 522777

**CONFERENCE FEE** including LODGING HALF-BOARD at Hotel Costa dei Fiori from dinner on 27September to breakfast on 3 October, COFFEE BREAKS, evening REFRESHMENTS, etc., is:

double room lodging....... Italian Lire 860000 (~540 USD)
single room supplement.... Italian Lire 250000 (~540 USD)

**PAYMENT** should be effected by bank money transfer on the bank account number

11080620154 of Corsi & Congressi, at Banca Commerciale Italiana, Sede di Cagliari, Codice ABI 2002 - CAB 43950.

Name .....................................................
Institution ..............................................
e-mail address ...........................................
Arrival date:........... – Departure date:...............
Accomodation: Single room .......... Double room ...........
Would share double room with .............................
Plan to present contributed talk/poster: .................

**SCIENTIFIC PROGRAM** (NB: some of the speakers below are allotted 2 hours)

## a) MATERIALS FOR MICROELECTRONICS AND NEW STRUCTURAL MATERIALS

**L. Colombo** (Universita' di Milano)
*Extended defects and atomic diffusion in silicon*
**F. Cleri** (ENEA Casaccia Res. Center, Roma)
*Carbon nanocomposites*
**S. de Gironcoli** (SISSA, Trieste)
*Transition metal alloys ab initio*
**A. De Vita** (IRRMA-EPFL Lausanne, Switzerland)
*Carbon nanotubes ab initio*
**A. Zunger** (NREL, Golden, CO, USA)
*to be announced*
**E. Cartier** (IBM Research Center - Yorktown Heights) *
*to be announced*

## b)SEMICONDUCTORS: MICROSTRUCTURES AND MATERIALS PROPERTIES

**A. Bosin** (SISSA, Trieste)
*Acceptors and hydrogen in III-V nitrides*
**K. Maeder** (CECAM, Lyon, France)
*Disordered superlattices*
**E. Pehlke** (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin)
*Theory of the shape of quantum dots*
**M. Peressi** (Dip. Fisica Teorica, Universita' di Trieste)
*Strained interfaces*
**A. Franciosi** (INFM-TASC Laboratory, Trieste)
*Blue Lasers*

## c)EPITAXY AND OTHER SURFACES PROCESSES

**J. Tersoff** (IBM Research Center - Yorktown Heights)
*Effects of stress on epitaxy and nanofabrication*
**P. Ruggerone** (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin)
*He scattering from metals*
**F. Ercolessi** (SISSA, Trieste)
*Melting and overheating of solid surfaces*
**N. Marzari** (Rutgers University, Piscataway, NJ, USA)
*Premelting of Al surfaces by ensemble-DFT molecular dynamics*
**J. Frenken** (FOM, Amsterdam)
*The energetics of metal surfaces 'seen' by a fast STM*

Series Chairman : Prof. A. Baldereschi - EPFL Lausanne
Workshop Chairman : Prof. F. Meloni - Universita' di Cagliari
Scientific Secretary: dr. V. Fiorentini - Universita' di Cagliari

# Electronic structure of the Nowotny chimney-ladder silicide $Ru_2Si_3$

W. Wolf
*Institut für Physikalische Chemie der Universität Wien*
*Liechtensteinstraße 22a, A-1090 Wien, Austria*
G. Bihlmayer and S. Blügel,
*Institut für Festkörperforschung, Forschungszentrum*
*Jülich, D-52425 Jülich, Germany*

## Abstract

We report *ab initio* calculations for the electronic structure of the Nowotny chimney-ladder silicide $Ru_2Si_3$ in the orthorhombic low-temperature phase. We find $Ru_2Si_3$ to be a semiconductor with a direct band gap of about 0.45 eV. Since this gap is a p-d gap, the oscillator strength for a direct transition is expected to be of sizeable magnitude. Also, the calculated effective masses of hole- and electron states suggest that $Ru_2Si_3$ is a very promising material for various applications in semiconductor technology. The electronic structure is controlled by the hybridization of Si p states with Ru d states and shows similarities to the group-VI transition metal disilicides ($CrSi_2$, $MoSi_2$, $WSi_2$) and to transition metal rich silicides. The calculations are based on the density functional theory in local density approximation and are performed by means of the full-potential linearized augmented planewave method.

(submitted to Phys. Rev. B)
preprint available from: s.bluegel@kfa-juelich.de
This paper contains an acknowlegement to HCM

# The Theory of Metal-Ceramic Interfaces

M. W. Finnis
*Atomistic Simulation Group, School of Mathematics and Physics,*
*Queens University of Belfast, Belfast BT7 1NN, Northern Ireland*

### Abstract

The theory of metal ceramic interfaces is a collection of approaches which are complementary. They range from thermodynamic modelling based on empirical correlations, through the image model of adhesion, semi-empirical tight-binding calculations, to first-principles calculations based on appying the density functional theory or Hartree-Fock theory. This article reviews the present state of theoretical calculations, with particular reference to electronic structure and adhesion. A section on the thermodynamic background clarifies the concept of work of adhesion which is the goal of many calculations. Cluster models and periodic slabs have been considered, both self-consistent and non-self-consistent. The most sophisticated and complete calculations have been made for metals on MgO and alumina. There a consistent picture of the nature of the bonding has emerged, although there are still significant unexplained discrepancies in numerical values.

(A Topical Review to appear in Journal of Physics: Condensed Matter, 1996)
This paper contains an acknowlegement to HCM

# Three-particle Approximation for Transition Metal Oxides

J.Lægsgaard and A.Svane
*Institute of Physics and Astronomy, University of Aarhus,*
*DK-8000 Aarhus C, Denmark*

### Abstract

Quasiparticle spectra are calculated for NiO and CuO on the basis of band structures obtained within the *ab initio* Self-Interaction Corrected Local Spin Density (SIC-LSD) approximation. On-site Coulomb correlations are described by a multiband Hubbard model, which is treated within Igarashi's three-particle approximation. The transition-metal *d*-state spectral weight is split into a main $d^n\underline{L}$ peak and a $d^{n-1}$ satellite. We show that mean-field band structures in this way can lead to a good description of the experimental photoemission spectra of these compounds.

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

# Effect of Anisotropy on Magneto-Optical Properties of Uniaxial Crystals: Application to $CrO_2$

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*I.E. Tamm Theory Department, P.N. Lebedev Physical Institute,*
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*117924 Leninskii prosp. 53, Moscow, Russia*
†*General Physics Institute, Russian Academy of Sciences,*
*117942 Vavilov str. 38, Moscow, Russia*
‡*Max-Planck Arbeitsgruppe "Elektronensysteme",*
*Technische Universität, Abteilung Physik,*
*D-01062 Dresden, Federal Republic of Germany*

## Abstract

Effect of the magnetization direction $\mathbf{m}$ on the dielectric tensor of uniaxial crystals is described by a simple dependence of the gyration vector $\mathbf{g}(\omega)$ on $\mathbf{m}$. It is shown that the vectors $\mathbf{g}(\omega)$ and $\mathbf{m}$ as well as the orbital magnetic moment $\langle\hat{\mathbf{L}}\rangle$ and $\mathbf{m}$ are generally aligned non-collinearly in contrast to an isotropic case. Formulas describing the polar Kerr effect are derived for crystals with their principal axis $\mathbf{c} \perp \mathbf{m}$ and for polycrystals having $\mathbf{c}$ randomly oriented in the sample plane. Using these analytical results and performing *ab initio* calculations, we correctly reproduce anisotropy in optical spectra of $CrO_2$ and the main features in magneto-optical spectra of polycrystalline films of $CrO_2$. The maximal optical anisotropy and orientation dependence of $\mathbf{g}(\omega)$ of 100 % are found in the energy interval $\hbar\omega \leq 2.1$ eV coinciding with the direct half-metallic ferromagnetic gap of $CrO_2$. The noncollinearity effects in this interval are also very large. The obtained results correlate well with strong orientation dependence of $\langle\hat{\mathbf{L}}\rangle$ found in our calculations.

(to be published in Phys. Rev. B)
Manuscripts available from: uspenski@td.lpi.ac.ru

# Spin, orbital moments and magneto–optical properties of $MPt_3$ $(M = Cr,\ Mn,\ Fe,\ Co)$ compounds

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[b]*I.E. Tamm Theory Department, P.N. Lebedev Physical Institute,*
*Russian Academy of Sciences,*
*117924 Leninskii prosp. 53, Moscow, Russia*
[c]*Max-Planck Arbeitsgruppe "Elektronensysteme",*
*Technische Universität, Abteilung Physik,*
*D-01062 Dresden, Federal Republic of Germany*

## Abstract

We studied trends in the *ab initio* electronic structure, spin moments, orbital moments and magneto-optical (MO) properties of $MPt_3$ compounds. Calculated quantities agree well with experimental data. It was found that values of local orbital moments are closely connected with the predominant spin character of electronic states near the Fermi energy ($E_F$). Features of the MO spectra of compounds are primarily defined by the absorptive off-diagonal conductivity $\sigma_{2,xy}(\omega)$. Spin decomposition of this quantity showed that at the MO resonance energy $\sigma_{2,xy}(\omega)$ is mainly formed by spin-up electronic transitions to an unoccupied part of the hybridized $\{M3d\uparrow -Pt5d\uparrow\}$– band. These transitions are intense for $CrPt_3$ and $MnPt_3$ having high MO activity. A reduction of the unoccupied part of $\{M3d\uparrow -Pt5d\uparrow\}$–band in $FePt_3$ and $CoPt_3$ results in the weak electronic transitions and in small value of calculated Kerr rotation for these compounds.

(to be published in Magnetism and Magnetic Materials)
Manuscripts available from: uspenski@td.lpi.ac.ru

# Shallow Thermal Donor Defects in Silicon

C. P. Ewels, R. Jones
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*Department of Mathematics, University of Luleå, Luleå, S95187, Sweden*
J. Miro, P. Deák
*Department of Atomic Physics, Technical University of Budapest,*
*Budafoki út 8, H-1111 Budapest, Hungary*

### Abstract

An *ab initio* local density functional cluster program, AIMPRO, is used to examine nitrogen related shallow thermal donor defects in silicon. We find the bonding of oxygen with interstitial nitrogen in $N_i$-$O_{2i}$ to be almost 'normal' but the O atoms move slightly out of their bond centered sites causing the deep donor level of $N_i$ to become shallow. The defect has properties consistent with those experimentally observed for shallow thermal donors. We also find that a $C_iH$-$O_{2i}$ defect has very similar electronic properties, and suggest that shallow thermal donors do not have a unique composition.

(submitted to Submitted to Physical Review Letters, 2nd April 1996)
Manuscripts available from: ewels@excc.ex.ac.uk

# Vacancy- and acceptor- H complexes in InP

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P. R. Briddon
*Department of Physics, University of Newcastle,*
*Newcastle, NE1 7RU, UK*

### Abstract

It has been suggested that iron in InP is compensated by a donor, related to the 2316 $\text{cm}^{-1}$ local vibrational mode and previously assigned to the fully hydrogenated indium vacancy, $V_{In}H_4$. Using AIMPRO, an *ab initio* local density functional cluster code, we find that $V_{In}H_4$ acts as a single shallow donor. It has a triplet vibrational mode at around this value, consistent with this assignment. We also analyse the other hydrogenated vacancies $V_{In}H_n, n = 1, 3$ and determine their structure, vibrational modes, and charge states. Substitutional Group II impurities also act as acceptors in InP, but can be passivated by hydrogen. We investigate the passivation of beryllium by hydrogen and find that the hydrogen sits in a bond centred site and is bonded to its phosphorus neighbour. Its calculated vibrational modes are in good agreement with experiment.

(Semiconductor Science and Technology, **11** 502-507 (1996))
Reprints available from: ewels@excc.ex.ac.uk

# Oxygen-carbon, oxygen-nitrogen and oxygen-dimer defects in silicon

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*Department of Physics, University of Exeter, Exeter, EX4 4QL, UK*
S. Öberg
*Department of Mathematics, University of Luleå, Luleå, S95187, Sweden*

### Abstract

An *ab initio* local density functional cluster method, AIMPRO, is used to examine a variety of oxygen related point defects in silicon. In particular results are given for X-$O_n$ complexes where X is interstitial C, N or O. For $n = 2$, the first defect has been assigned to a P-centre giving a PL line at 0.767 eV and seen in Cz-Si annealed around 450°C, while the second has properties consistent with a nitrogen related shallow thermal donor. We have also found that a (C-H)$O_{2i}$ defect has very similar electronic properties, and this implies that shallow thermal donors do not have a unique composition. The structure and migration energy of the oxygen dimer is considered and the dimer is found to migrate very much faster than a single oxygen atom.

*Proceedings of the NATO ARW, Oxygen '96, 'The Early Stages of Oxygen Precipitation in Silicon', Kluwers Academic Press, in press.*
Manuscripts available from: ewels@excc.ex.ac.uk

# The twelve line 1.682 eV luminescence center in diamond and the vacancy-silicon complex

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*Newcastle, NE1 7RU, UK*
S. Öberg
*Department of Mathematics, University of Luleå, Luleå, S95187, Sweden*

### Abstract

A first principles cluster method is used to show that the 1.682 eV band consisting of a set of twelve close lines and observed in a range of different diamonds is due to a vacancy-silicon complex. The defect has a highly unusual and possibly unique structure consisting of a Si atom at the center of a split-vacancy and having $D_{3d}$ symmetry. Its electronic structure consists of two orbitally twofold degenerate gap levels ~1.7 eV apart. Small splittings in these levels, together with the occurrence of three Si isotopes, explain the twelve line spectrum. The method also successfully accounts for the 1.945, 2.156 and 2.985 eV optical transitions in trigonal vacancy-nitrogen defects and assigned to $[\text{V-N}]^-$, $[\text{V-N}]^0$, and $[\text{V-N}_3]$ respectively. Estimates of their radiative lifetimes are also given.

(submitted to Physical Review Letters, April 1996)
Manuscripts available from: jones@excc.ex.ac.uk

# The nitrogen-pair oxygen defect in silicon

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R. Jones, C. Ewels, J. Goss
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*Exeter, Devon, EX4 4QL, United Kingdom*
J. Miro, P. Deák
*Department of Atomic Physics, Technical University of Budapest,*
*Budafoki út 8, H-1111 Budapest, Hungary*

### Abstract

The nitrogen-pair oxygen defect in silicon has been studied by infrared absorption spectroscopy on samples implanted with various combinations of $^{14}N$, $^{15}$N, $^{16}$O and $^{17}$O. The measurements give direct evidence for the involvement of nitrogen and oxygen in the defect and show that the impurity atoms comprising the defect are only weakly coupled. *Ab initio* cluster calculation on several models of the nitrogen-pair oxygen defect have been performed and are compared with experiments. Based on these investigations a model consisting of a bridging oxygen atom adjacent to the nitrogen pair is suggested.

(Materials Science and Engineering B, **36** 91-95 (1996))
Reprints available from: ewels@excc.ex.ac.uk

# Nitrogen-Oxygen complexes in silicon

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*Department of Physics, Stocker Road, University of Exeter,*
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### Abstract

Nitrogen-oxygen complexes are known to exist in Czochralski silicon grown in $N_2$ atmosphere or after N implantation. Recently, an NNO complex has been identified to consist of two neighbouring N split-interstitials (in form of a 4-member ring with two lattice Si atoms) and an adjoining oxygen interstitial. In this paper the possibility of an alternative structure is discussed where the ring is formed with N and O atoms, and there is a neighbouring N interstitial. Using semi-empirical PM3 cluster calculations, it is shown that this N(NO) structure is more stable in the positive charge state than the (NN)O configuration while the opposite is true for the neutral species. Thereby, the NNO system is predicted to be bistable. The possible role of the (NO) ring in shallow thermal donor formation is discussed.

(submitted to Physical Review B, March 1996)
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# Cooperative polarization in ice $I_h$ and the unusual strength of the hydrogen-bond

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### Abstract

Cooperative polarisation in ice $I_h$ is illustrated in clusters of eight molecules using local density functional calculations where the exchange-correlation functional is a modified Ceperley-Alder expression. These parameter-free total energy calculations support the four-point charge/polarisable point dipole model of Kozack and Jordan and indicate that cooperative polarisation has a profound effect, not simply increasing the cohesive energy, but also making bond breaking disproportionately difficult.

(Chem. Phys. Letters (1996) **249**, 485–490)
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# Autocatalysis during fullerene growth

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### Abstract

Total energy calculations with a local spin density functional have been applied to the Stone-Wales transformation in fullerene ($C_{60}$). In the formation of the almost exclusively observed $I_h$, isomer of $C_{60}$ with isolated pentagons, the final transformation must be from a $C_{2v}$ isomer with two pentagon pairs. It was found that the energy barrier for this rearrangement was substantially reduced in the presence of an extra carbon atom. Such atoms were found to bind loosely, preferentially to regions in which there were paired pentagons. Pentagon rearrangements, which are necessary steps in the growth of fullerenes, may therefore result from autocatalysis by carbon.

(Science (1996) **272**, 87–89)

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# Energetics of fullerene isomer transformation

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## Abstract

Stone-Wales transformations are thought to be the most likely route for fullerene isomer interconversion. Several prototype reactions are investigated using local density functional theory on $C_{60}H_m$ ($m = 0, 1, 2$) and $C_{61}$ clusters. Transition state energies and geometries are calculated. Adding hydrogen or carbon atoms to $C_{60}$ is found to catalyse the transformations.

(Synthetic Metals (1996) **77**, 165–168)

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# On the graphitization of diamond surfaces: the importance of twins

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### Abstract

*Ab initio* total energy calculations reported recently by Heggie *et al.* (*Physical Review B*, **50** (1994) 5937) revealed that the tetrahedrally bonded icosahedral $C_{100}$ molecule spontaneously decomposed into two concentric fullerenes ($C_{20}$ and $C_{80}$). This $C_{100}$ molecule belongs to a series of structures that may be viewed as the diamond analogues of fullerenes (L. Zeger and E. Kaxiras, *Physical Review Letters*, **70** (1993) 2920). Since these molecules can be seen to be effectively a heavily twinned molecular diamond their stability is important in the context of investigating the diamond {111} surface where a twin emerges. We present *ab initio* self-consistent calculations on a rather small $C_{40}H_{36}$ molecule representing the core of a twin intersecting two diamond {111} surfaces and compare the results with that obtained with a non-selfconsistent density-functional based tight-binding method. Since the latter is also capable of handling larger and periodic models in a molecular dynamics relaxation we use it to study the graphitization effect in dependence of temperature. We find nearly the same ground state for the small molecule which is clearly due to a graphitization and find strong surface graphitization for a model of 128 carbon atoms at elevated temperatures. At 2700 K the top layer of this periodic model completely delaminates.

(Diamond and Related Materials (1996) **5**, 102–107)

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# The Theory of CVD Diamond Growth

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## Abstract

The theory of CVD diamond growth has developed into a mature subject of study of the last few years. We do not try to reproduce or summarise all work to date, but rather we draw out the important conceptual differences between theoretical methods that have been used and instance their practical differences with selected results from suggested CVD diamond reaction schemes.

We conclude with two recent theoretical results which indicate that surface diffusion on {110} surfaces is likely and highly anisotropic and that on some diamond surfaces (*e.g.* {111} surfaces at ledges and where twin boundaries penetrate) a displacive transition to a graphite layer can occur.

(accepted to Diamond and Related Materials, 1996)

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# Quantum steering effects in the dissociative adsorption of $H_2$ on $Rh(100)$

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## Abstract

We show on the basis of ab-initio local-density-functional calculations (with generalized gradient corrections) that the dissociative adsorption of a $H_2$ molecule on a $Rh(100)$ surface is dominated by quantum-mechanical steering effects arising from the formation and modification of covalent metal-$H$ bonds: as the molecule is lowered towards surface, bond formation occurs first with the $s$, $p_z$ and $d_{3z^2-r^2}$ orbitals extending farthest form the surface. This attracts the molecule to the on-top position. Interaction with the $t_{2g}$ orbitals orients the axis of the molecule towards the bridge sites and drives the dissociation in a bridge-top-bridge configuration. Finally bonding with the $d_{x^2-y^2}$ orbitals attracts the dissociated atoms to the fourfold hollows.

(to appear in Phys. Rev. Lett.)
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# Magnetic structure and anisotropy of thin Fe films on Cu(001) substrates

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## Abstract

We present a novel approach to the calculation of the spin-structures and magnetic anisotropies in crystals and in thin films. Our technique is based on self-consistent real-space recursion calculations using a tight-binding-linear-muffin-tin-orbital (TB-LMTO) - Hubbard Hamiltonian including spin-orbit coupling and allowing for arbitrary orientations of the local spin-quantization axes. It allows to scan the magnetic energy continuously as a function of the direction of the magnetic moment and thus to avoid the computational problems that plague other techniques for the calculation of the magnetic anisotropy energies. The method also presents important advantages in determining the magnetic ground state in the presence of competing ferro- and antiferromagnetic interactions. Applications are presented for bulk iron, free-standing iron monolayers and for thin Fe-overlayers on Cu(001) substrates. In the monolayer regime, we predict a perpendicular direction of the magnetic moment for free-standing fcc Fe(001) monolayers and for fcc monolayers on Cu(001) (with free surfaces and covered by Cu-overlayers), with anisotropy energies of the order of 1 to 2 meV. We also present a detailed investigation of the spin-structures and of the change from perpendicular to in-plane anisotropy with increasing thickness of the Fe-films. We find that stable low-moment and metastable high-moment spin-structures coexist in films with more than four monolayers. With increasing thickness of the films the perpendicular anisotropy decreases and for an ideal fcc geometry a transition to in-plane anisotropy can be expected around 8 monolayers.

(submitted to Phys. Rev. B)
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# Noncollinear magnetism in amorphous Fe-Y alloys

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### Abstract

Iron-rich amorphous alloys with non-magnetic transition-metal (TM) or rare-earth (RE) metals show a rich variety of complex spin-structures that have been described as spin-glass-like, spero- or asperomagnetic. Amorphous Fe-Y alloys have attracted particular attention because it has been suggested that in contrast to other amorphous Fe-TM and Fe-RE alloys showing re-entrant spin-glass behaviour, in Fe-Y alloys the spin-glass transition could occur directly from the paramagnetic phase. It has also been suggested that unlike most other alloys where the spin-glass-like phase is restricted to high Fe-concentrations, amorphous Fe-Y alloys are noncollinear at all compositions. We have recently presented a technique for a selfconsistent calculation of non-collinear spin-structures in crystalline and amorphous alloys based on a tight-binding-Hubbard Hamiltonian generated via a canonical transformation of the LSD Hamiltonian. This approach has been used to analyze the magnetic properties of amorphous Fe-Y alloys. We show that unlike e.g. in amorphous Fe-Zr alloys where the net magnetization is well defined in the spin-glass and in the ferromagnetic phases and independent of the initialization of the magnetic structure, for Fe-Y energetically nearly degenerate low- and high-moment phases can be induced by different initializations. This could explain the observed strong dependence of the magnetic state on the preparation of the amorphous phase and its strong variation under applied external fields or pressures.

(submitted to JMMM)
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# Metamagnetic states of $3d$ nanostructures on the Cu(001) surface

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### Abstract

Different magnetic states for a given real structure are known for bulk metals, and alloys ultrathin films, and free clusters. Here new results are presented concerning the magnetic stability of *supported* transition metal cluster on the Cu(001) surface. The calculations are performed by means of an *ab initio* KKR Green's function method. The existence of high spin and low spin ferromagnetic states and antiferromagnetic states for *3d* transition metal clusters on Cu(001) is demonstrated. As an examplinary case trimers of adsorbate atoms are considered in detail. For practically all 3d-trimers four different magnetic configurations are found. Total energy calculations show, that the energy difference between different magnetic states can be quite small (V, Mn). The reason for the occurance of multiple magnetic states is discussed.

(submitted to Phys. Rev. Lett.)
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# The Role of Orbital Polarization in Weak Ferromagnetism

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### Abstract

A density functional theory to deal in a first-principles manner with the phenomenon of weak ferromagnetism (WF) is applied to the triangular antiferromagnet $Mn_3Sn$. It explains successfully the two different types of WF due, respectively, to magnetic anisotropy and antisymmetric exchange. We take into account, for the first time, the orbital moment contribution to WF and show that, due to the non-collinearity of the spin and orbital moments of the Mn atoms, both spin and orbital moments give a comparable contribution to the ferromagnetic component. Our results are in good agreement with experimental data.

(to appear in Phys. Rev. Letters)
Revtex version can be obtained from:
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# Magnetically Stabilized Surface Alloys

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## 1 Introduction

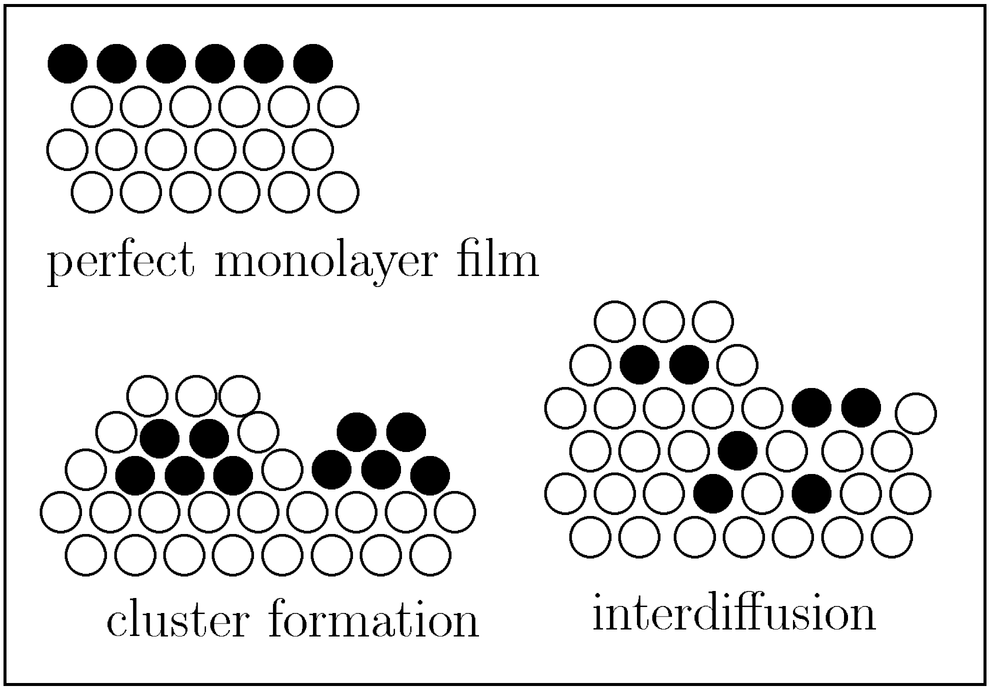
With the evolution of metallic systems from bulk through surfaces, ultrathin films, to linear chains and small atom aggregations the dimensionality, symmetry, and the coordination number, become increasingly important parameters for determining the properties of these systems. Magnetism is a feature which is particularly dependent on those parameters. The simplest low-dimensional system is the isolated atom. It is known that nearly all of the 30 transition–metal (TM) atoms have magnetic moments. In the middle of the transition-metal series the magnetic moments are as large as 5 $\mu_B$. On the other hand, one knows that among the 30 transition–metals only five of them remain magnetic in their bulk crystalline phase: Co and Ni are ferromagnetic, Cr is antiferromagnetic, and Mn and Fe are ferromagnetic or antiferromagnetic, depending on their crystal structure. Low–dimensional transition–metals should fall between these two extremes, and one may envisage a magnetic material which is nonmagnetic as a bulk metal but magnetic as an ultrathin film or as a nanostructure.

Furthermore, it is well-known that the formation of local magnetic moments plays an important role in the structure of metals and stability of alloys. Os and Ru, for example, crystallize in hcp bulk phases, but due to the magnetism, Fe crystallizes in bcc structure, although all three are isoelectronic. With the increase of local moments in low-dimensional metallic systems, the importance of magnetism for the structure and stability of these nanosystems should become increasingly more important. Recently, we have investigated this aspect for ultrathin magnetic films at one monolayer range. We have investigated the importance of the magnetism for the stability of these films and have come to an interesting conclusion that in certain cases magnetism stabilizes (ordered) two-dimensional surface alloys.

In the past, almost all *ab initio* investigations published on ultrathin magnetic films on diverse substrates described the ideal pseudomorphic ultrathin film with atoms located in the hollow sites formed by the adjacent substrate atoms. These investigations described well the electronic and magnetic properties of pseudomorphically grown films, within one surface terrace of at least 15 atoms across.

In general, however, it is experimentally very difficult to achieve pseudomorphic growth conditions. This is particularly true for transition–metal films grown on noble metal substrates. According to the conventional wisdom in this field, these types of films are thermodynamically unstable and are prepared in a metastable state. That means, they are kinetically stabilized, because the activation energy needed for diffusion is too high. Generally, the film is affected by: (i) by the surface diffusion of film atoms across the surface, which may well lead to cluster formation, and (ii) the interdiffusion of the film atoms into the substrate, which may well lead to the formation of bulk alloys or clusters of film atoms covered by substrate atoms. To illuminate both scenarios, schematically illustrated in Fig. 2, we start with a gedanken experiment of an ideal and perfect film at 0 K temperature. This film might be highly metastable and by increasing the temperature, one may finally reach the activation energy for the surface diffusion. Thus film atoms may diffuse along the surface which may then lead to the clustering of these atoms. After a further increase of the temperature one may finally reach the activation barrier for the substrate interdiffusion. Film atoms may diffuse into the substrate forming a bulk alloy or *vice versa* substrate atoms may wet the clustered film atoms.

Figure 2:



The above reasoning is supported by thermodynamic arguments where the surface free energy, $\gamma$, enters. Typically, the surface free energy of the $3d$ transition–metal film atoms,

$\gamma_{3d}$, is larger than the surface free energy of the noble metal substrate atoms, $\gamma_{Cu}$, $\gamma_{Ag}$, $\gamma_{Au}$, and a metastability of such films is anticipated. Despite the intensive study of $3d$ transition–metal monolayers on noble metal substrates, these arguments have hardly been questioned.

Experimentally, it is rather difficult to precisely determine absolute surface free energies. Usually, one measures the heat of vaporization and substitutes it into an empirical relation [1] to determine the surface free energy. It is clear, that transition–metal atoms forming ultrathin films are in a very different state than transition–metal surface atoms.

In particular, it is known from the work of the past years [2, 3, 4] that transition–metal atoms, constituting ultrathin films on noble metal substrates, show large magnetic moments, in most cases significantly larger than transition–metal surface atoms. The magnetic moments follow Hund's first rule and are largest at the center of the transition-metal series (cf. Table 2). Various magnetic phases exist, with the c($2\times2$) antiferromagnetic phase being closest in energy to the p(1×1) ferromagnetic phase. In most cases both phases exist and the local moments are of a very similar size. A general trend has emerged: V, Cr and Mn monolayer films on noble metals are c($2\times2$) antiferromagnetic, and Fe, Co, and Ni are p($1\times1$) ferromagnetic. The energy difference between these two phases is in the order of 300 meV, which is a sizable energy on the scale of the formation energy of alloys.

Table 2: Local magnetic moments in $\mu_B$/atom for $3d$ transition–metals as ferromagnetic (F) and antiferromagnetic (AF) $3d$ monolayers (ML) on Ag(001) [3], Pd(001) [5] and on Cu(001) [4]; "0" indicates that the calculated moment was smaller than the numerical accuracy estimated to be about $0.02\mu_B$/atom. "?" indicates a system, for which the calculation was not carried to self–consistency.

| | | Ti | V | Cr | Mn | Fe | Co | Ni |
|---|---|---|---|---|---|---|---|---|
| ML on Ag(001) | F | 0.34 | 2.09 | 3.78 | 4.04 | 3.01 | 2.03 | 0.65 |
| | AF | 0 | 2.08 | 3.57 | 4.11 | 3.06 | ? | 0 |
| ML on Pd(001) | F | 0 | 0.51 | 3.87 | 4.11 | 3.19 | 2.12 | 0.89 |
| | AF | 0 | 1.39 | 3.46 | 4.05 | 3.20 | 1.99 | 0.59 |
| ML on Cu(001) | F | 0 | 0 | 0 | 2.97 | 2.61 | 1.76 | 0.33 |
| | AF | 0 | 0 | 2.52 | 2.92 | 2.35 | ? | 0 |

Since the magnetic energy is proportional to the square of the local magnetic moment, we expect sizeable additional contributions to the surface free energy of transition–metal film atoms, due to large magnetic moments. It is this additional gain of magnetic energy of a $3d$ metal atom, constituting the ultrathin film, which modifies the energy balance for the structure and stability of the ultrathin films, beyond the conventional arguments of surface free energies. This argument, that the change of the magnetism provides an additional contribution to the surface free energy, has been totally neglected in the past. We shall show that indeed magnetism has a considerable impact on the stability and structure of ultrathin films, and new magnetically stabilized ultrathin systems ought to be expected.

The following simple $d$ band model (cf. Fig. 1) provides some key ideas as to what extent the formation of large magnetic moments will modify the structural stability of ultrathin films. For simplicity, we consider a transition–metal atom at half band filling (e.g. Mn). We first discuss the nonmagnetic state. The local density of majority and minority states are degenerate. All bonding states are occupied, all antibonding states are unoccupied. For atoms within the ultrathin film, due to the reduction of the coordination number, the local density of states (LDOS), $n(\varepsilon)$, is narrower than for atoms in the crystal. Since the cohesive energy (in this model the band energy $\int_0^{E_F} \varepsilon n(\varepsilon) d\varepsilon$) increases with the bandwidth, cohesive energy is gained when film atoms increase their coordination number. Therefore, the scenario of transition–metal atoms, around half band filling forming (hypothetical) nonmagnetic films, is determined by increasing their coordination number to gain maximum cohesive energy. This favors the interdiffusion of film atoms, and even more so the clustering of $3d$ metal atoms, either after interdiffusion or after diffusion along the surface. The latter $3d$ metal clusters will most likely be wetted by the substrate atoms.

In the second step we allow now the formation of local magnetic moments $M$. Magnetic energy $E_M = -\frac{1}{2} I M^2$ is gained. On the other hand, one looses kinetic energy and formerly occupied minority bonding states become unoccupied, while formerly unoccupied majority antibonding states become occupied, reducing the gain of the cohesive energy. Thus a new energy balance is found with a total energy lower than for the nonmagnetic case (otherwise no local moment could be stabilized and the system would remain nonmagnetic). For a $3d$ atom in an ultrathin film this energy balance will be different from that of a $3d$ atom in a bulk crystal. As compared to the bulk atoms, the film atoms encounter a reduction of the coordination number, which is accompanied by a narrowing of the LDOS, and a relative loss of the cohesive energy, but at the same time with an increase of the exchange splitting, and the local moment, respectively, which is accompanied by an additional gain of magnetic energy. That means, for the magnetic cases, transition–metal atoms encounter a competition between a rearrangement such as to obtain large coordination numbers to gain maximum cohesive energy, and an arrangement with a small coordination number to gain maximum magnetic energy. Consequently, magnetism tends to stabilize ultrathin films on noble metal substrates and to prevent transition–metal atoms from interdiffusion. This stabilization will be the stronger the larger the magnetic moments. However, from these qualitative arguments we are not able to give quantitative estimates for real systems.

In the following sections we present an analysis, carried out by means of *ab initio* total energy calculations, of the relationship between magnetism and structure, and stability of $3d$ transition–metal monolayers (TM) (TM = V, Cr, Mn, Fe, Co, Ni) on Cu(001). The analysis is subdivided into several steps: (i) first we show that $3d$ metal monolayers are not energetically stable against wetting by the Cu substrate atoms (cf. Sect. 3), (ii) the Cu(001)c(2×2)TM substitutional surface alloys (one–monolayer–thick alloy films of Cu and $3d$ atoms, with a checkerboard structure of $3d$ atom and Cu sites (cf. Fig. 4)) is postulated in Sect. 4, (iii) the magnetic properties are discussed in Subsect. 4.1. The energetic

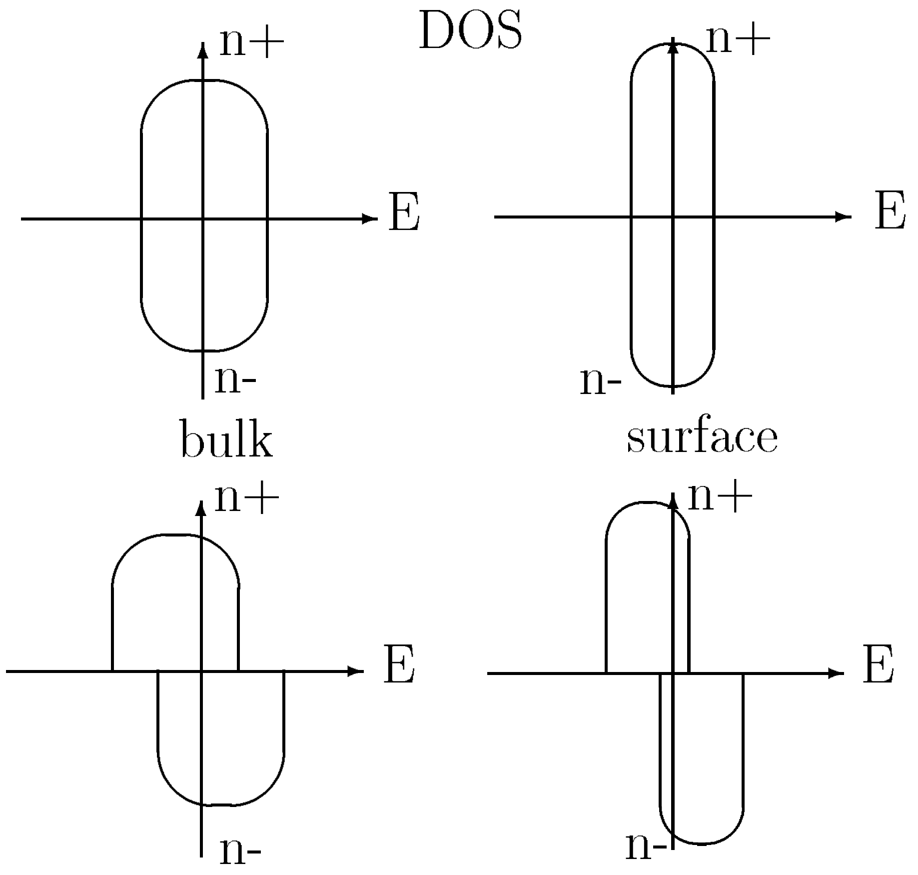


Fig. 2 Shown is a highly schematic diagram of the local density of states of d-electrons for a nonmagnetic (top) and magnetic (bottom) atom embedded in a bulk (left) and surface (right) arrangement. $E_f$ is the origin of the energy scale.

stability of the transition–metal atoms constituting the Cu(001)c(2×2)TM surface alloys, against (v) interdiffusion and (vi) clustering, is investigated in Subsects. 4.2 and 4.3, respectively, and finally we comment on the underestimation of the magnetism by the local density approximation and discuss recent results obtained by the generalized gradient approximation.

## 2 Calculational Details

All calculations were based on density functional theory in the local spin density approximation (LSDA). We used the exchange–correlation potential of von Barth and Hedin [6], but with the parameters as chosen by Moruzzi, Janak, and Williams [7]. The results for the $3d$ monolayers as overlayers and as interlayers, and the c(2×2)TM alloy film as overlayers and interlayers, were obtained with the full–potential linearized augmented–

plane–wave method (FLAPW) in film geometry [8, 9]. The unit cell contained typically 14 to 18 atoms. The lattice constant of Cu was determined by means of a total energy minimization with a bulk FLAPW code.

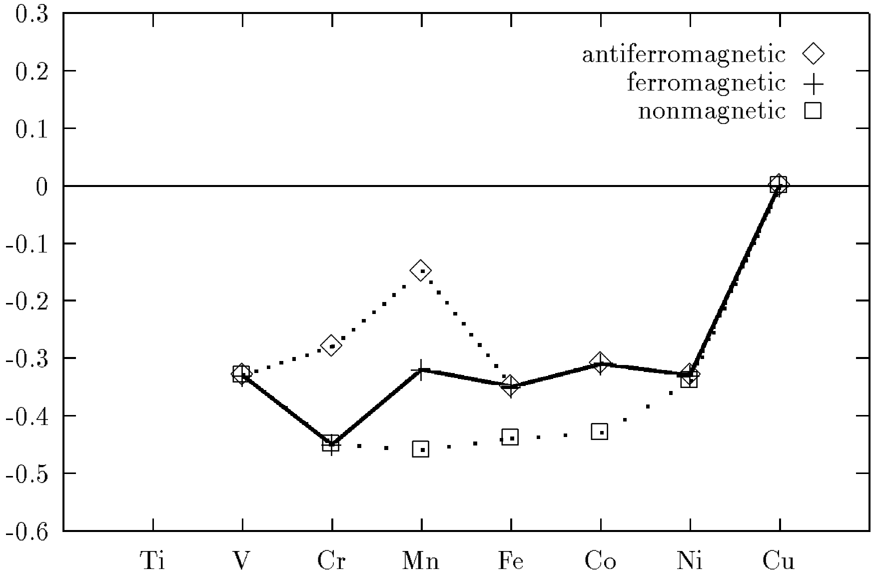
Recently, we have completed our new film and bulk FLAPW program [10], having the flexibility of calculating forces exerted on the atoms, which are used for a structural optimization of the atom positions, and which also includes the generalized gradient (GGA) approximation, in conjunction with the implementation of the appropriate fast Fourier transform (FFT)-methods, quasi-Newton methods to accelerate the convergence of the charge density. We have also explored possibilities of iterative and perturbational approaches to handle large systems. Thus the structure of some of these films have been determined by total energy [11] as well as by force calculations [12], and the calculations have been extended to include the GGA [13]. We used the versions by Perdew and Wang [14] and Perdew [15].

## 3 Energetic Stability of 3$d$ Monolayers against Wetting by the Substrate

In order to investigate the energetics of wetting, we compare the total energies of monolayers, buried as interlayers ($E_I$) in bulk Cu(001), with the total energies of monolayers deposited as overlayers ($E_S$) on the Cu(001) substrate. The role which magnetism plays in modifying the stability of the 3$d$ transition–metal films is elucidated by including calculations for p(1×1) ferromagnetic, c(2×2) antiferromagnetic, and (hypothetical) nonmagnetic monolayers.

The results of the energy differences $\Delta E_W = E_I - E_S$ – and I call this energy difference the wetting energy – are summarized in Fig. 4. We find, for all 3$d$ transition–metal monolayers, irrespective of their magnetic state, that $\Delta E_W < 0$, which means that monolayers buried as interlayers in Cu(001) constitute the energetically preferred state. Consequently, the monolayer film on Cu(001) is in a metastable state, and an additional wetting by Cu atoms is thermodynamically favorable. The wetting energy for the (hypothetical) nonmagnetic 3$d$ monolayers follows a parabola shaped curve, reflecting the $d$ band filling, with an energy gain at maximum (0.47 eV per atom) for Mn at half band filling. On the other hand, one finds, in agreement with the simple model presented in Fig. 1, that magnetism tends to stabilize the monolayer films. The reduction of the wetting energy gain due to magnetism is largest for Mn monolayers (0.32 eV per atom), for which also the largest magnetic moment was found. Besides the local moment, the magnetic structure of the monolayer plays also a crucial role for the wetting energy. For Mn one observes a big difference for the wetting energies between the ferromagnetic and the c$(2 \times 2)$ antiferromagnetic states. For the ferromagnetic state the magnetic energy gain amounts to 0.15 eV per atom, as compared to 0.32 eV for the antiferromagnetic state. For Cr the ferromagnetic state does not exist and it is degenerate with the paramagnetic one. For Fe and Co the c$(2 \times 2)$ antiferromagnetic configuration is energetically unfavorable, and has not been

Figure 4: Wetting (or interdiffusion) energy $\Delta E_W = E_I - E_S$ in eV per transition–metal atom calculated for nonmagnetic (squares connected by widely spaced dotted line), ferromagnetic (crosses connected by full line), and c$(2\times2)$ antiferromagnetic (diamonds connected by dotted line) $3d$ monolayer films on Cu(001). The solid line connects the magnetic ground state solutions. For $\Delta E_W < 0$ ($> 0$), wetting by the Cu substrate or interdiffusion into the Cu substrate, respectively, is energetically preferred (prohibited). The results are obtained from calculations neglecting any atom relaxation (all atoms are positioned at the sites of the perfect Cu lattice).



calculated. For Ni this configuration is degenerate with the nonmagnetic one. Although magnetism tends to stabilize the monolayer films, the strength of this effect is too weak.

## 4 Cu(001)c(2×2)3*d* Surface Alloys

In a further attempt to reduce the coordination number of transition–metal film atoms in order to increase their magnetic moments, with the prospect of obtaining magnetically stabilized ultrathin films, we make at this point an *ad hoc* postulation of a new class of ultrathin magnetic films: the c$(2\times2)$ substitutional surface alloys – actually more accurately of the c$(2\times2)$ substitutional surface compounds. This type of ordered phase, schematically illustrated in Fig. 4, can be thought of as a checkerboard type monolayer film consisting of $3d$ metal atoms, where every second transition–metal atom is substituted by a substrate atom, Cu in this particular example. The surface unit cell is classified by the notation c(2×2) and we call these surface alloys c(2×2)CuTM/Cu(001) or Cu(001)c(2×2)TM, respectively.

Within the surface compound layer the $3d$ transition–metal atoms are not nearest neighbour atoms, as for monolayer films, but next nearest neighbour atoms. Thus the overlap between the $3d$ wavefunctions is substantially reduced. This is the effective reduction of the coordination number mentioned above. As we shall see below, due to this reduction of the $3d$ overlap, each $3d$ transition–metal atom within the surface compound can, at least

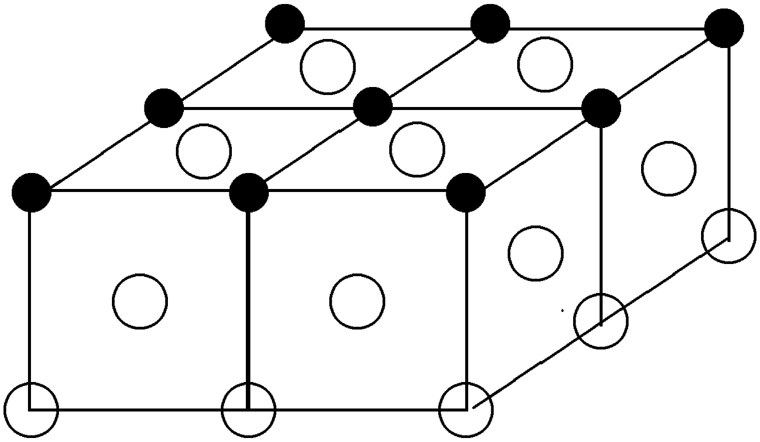


Fig. 4 Schematic representation of a substitutional (001)c(2x2) TM surface compound film of one monolayer thickness (black dots indicate the transition metal grown as overlayer on a fcc (001) substrate (open circles).

from the viewpoint of the local magnetic moments, be considered in the first approximation as a $3d$ surface impurity in the surface of Cu(001). Therefore, the interpretation of the c($2\times2$) surface compound in terms of an ordered, two–dimensional lattice of surface impurities, provides an additional aspect of this new class of films.

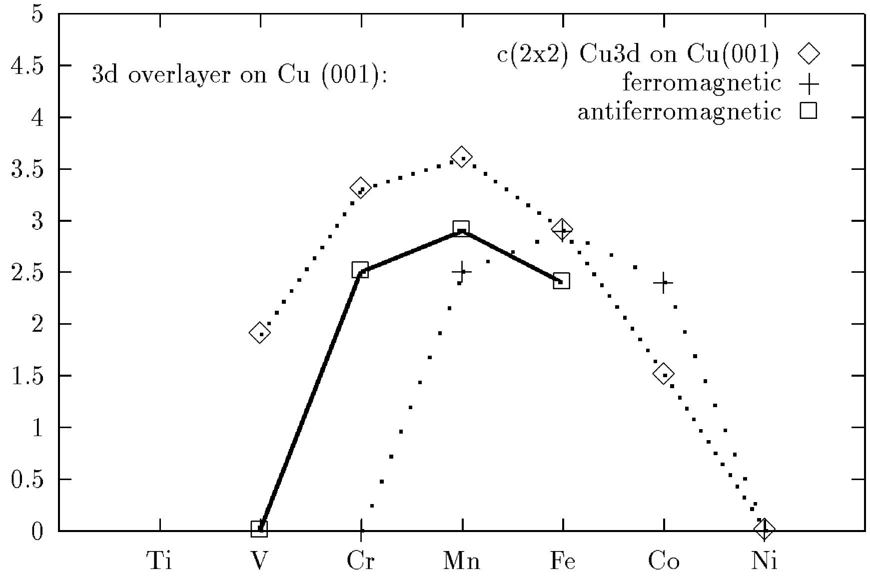
### 4.1 Local Magnetic Moments of c($2\times2$) Surface Alloys

The local magnetic moments of the $3d$ transition–metal atoms incorporated in the Cu(001)-c($2\times2$)TM surface compounds are shown in Fig. 6, together with the local magnetic moments for the p($1\times1$) ferromagnetic and c($2\times2$) antiferromagnetic phase of the $3d$ transition–metal monolayers. Indeed, we find that the reduction of the coordination number increases the magnetic moments of the transition–metal atoms within the surface alloy film. This is particularly true for the transition–metal atoms around the center of the $3d$ series: V, Cr, Mn. For V monolayers on Cu(001) no magnetism was found, while for Cu(001)c($2\times2$)V the V moment is close to $2\,\mu_B$. For Cr and Mn the magnetic moments increase by $0.8\,\mu_B$ and $0.7\,\mu_B$, respectively, in comparison to the moments of the c($2\times2$) antiferromagnetic phase of the full coverage monolayers on Cu(001).

### 4.2 Stability of c(2×2) Surface Alloys against Interdiffusion into the Substrate

After the above *ad hoc* postulation of a c($2\times2$) substitutional surface compound as a new class of thermodynamically stable, two–dimensional magnetic films on noble metal substrates, we discuss in this subsection the stability of the transition–metal atoms within the surface alloy against an interdiffusion into the substrate, by comparing total energies ($E_S$) of c($2\times2$)CuTM films deposited on Cu(001) to interlayer films buried in Cu(001)

Figure 6: Local magnetic moments in units of $\mu_B$calculated for c(2×2) ferromagnetic Cu(001)c(2×2)3$d$ surface compounds [16]. Results are compared with the local moments of p(1×1) ferromagnetic (plus signs connected by widely spaced dotted line) and of c(2×2) antiferromagnetic (empty squares connected by solid line) full coverage 3$d$ monolayers on Cu(001) [4].

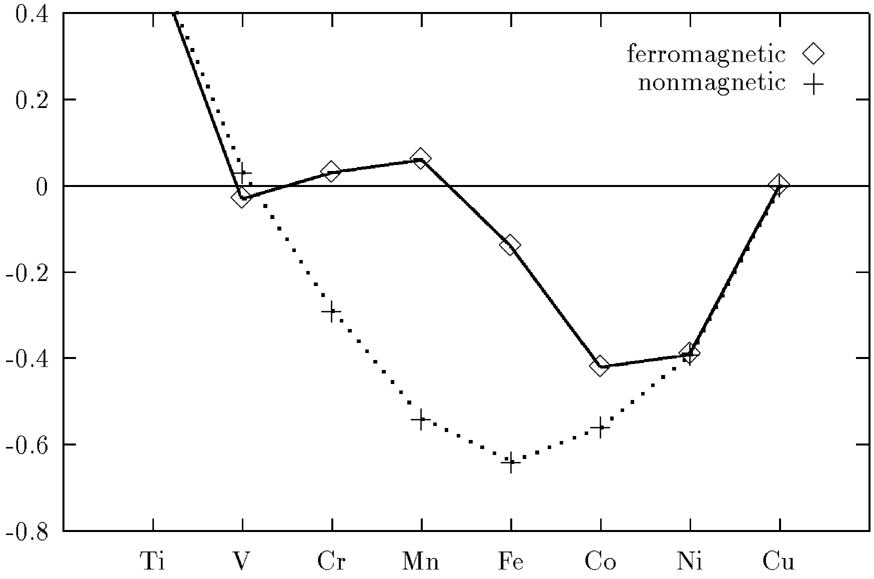


($E_I$). Since the monolayer compound film is in first approximation representative of a two–dimensional lattice of impurities, the energy difference between the surface and the bulk layer is indeed close to the energy difference between a 3$d$ impurity in the surface and in the bulk, and the energy difference may be called the interdiffusion energy or the segregation energy, depending on the sign of the energy difference. The impact of magnetism for the stability of the surface alloy films is analyzed by performing spin–polarized calculations as well as non–spin–polarized calculations of (hypothetical) nonmagnetic c(2×2)CuTM monolayer films for both structural configurations. The spin–polarized calculations have been carried out subject to the constraint, that only the ferromagnetic phase within the c(2×2) films was taken into account.

Fig. 7 shows the energy difference $\Delta E_I = E_I - E_S$. We first discuss the interdiffusion energy for the hypothetical nonmagnetic compound monolayers. Except for Cu(001)c(2×2) V and Cu(001)c(2×2) Ti, the energy difference $\Delta E_I$ is negative ($\Delta E_I < 0$), which means that the transition–metal atoms Cr, Mn, Fe, Co and Ni gain energy by interdiffusion, and for Ti and V interdiffusion in energetically prohibited. The interdiffusion energy follows a similar parabola as the wetting energy of the monolayers on Cu(001), which are in both cases a result of the $d$ band filling, just as expected from the simple model introduced above.

When we lift the constraint of nonmagnetism by carrying out spin–polarized calculations, all systems with the exception of the Ti and Ni based systems, become magnetic and we find for Cu(001)c(2×2)Cr, Mn, and Fe a remarkable change in their interdiffusion energies. For Cu(001)c(2×2)Cr and Cu(001)c(2×2)Mn, $\Delta E$ becomes even positive, which means magnetism indeed prevents Cr and Mn from diffusing into the Cu substrate. For

Figure 7: Interdiffusion energy $\Delta E_I = E_I - E_S$ in eV per transition–metal (TM) atom calculated for the Cu(001)c($2\times2$)$3d$ monolayer compound films. Crosses connected by a dotted line indicate the nonmagnetic results obtained from non–spin–polarized calculations and diamonds connected by a solid line mark the results for compound films in the c(2×2) ferromagnetic configuration. For $\Delta E_S < 0$ ($> 0$), interdiffusion is energetically preferred (prohibited). The results are obtained from calculations neglecting any atom relaxation (all atoms are positioned at the sites of the perfect Cu lattice).



Fe and Mn the reduction of the interdiffusion energy amounts to about 0.6 eV and 0.5 eV, respectively. For Fe, this is not sufficient and magnetism cannot prevent Fe from the interdiffusion into the substrate. The effect of magnetism on Cu(001)c($2\times2$)V and Co remains small ($\sim$ 0.1 eV) although for V the interdiffusion energy changes sign, but this change is marginal. For Ti and Ni the effect of magnetism is absent, because Ti and Ni remain nonmagnetic in both configurations. To summarize at this point, Cu(001)c(2×2)Cr and Mn are promising candidates for magnetically stabilized surface alloys, and Ti may be a candidate for a nonmagnetic surface alloy.

### 4.3 Stability of c($2\times2$) Surface Alloys against Cluster Formation: The Formation Energy of Surface Alloys

The second necessary condition for confirming the existence of two–dimensional surface alloys is to prevent the alloy from phase separation. Phase separation of a surface alloy is synonymous with atom rearrangement such as to obtain the clean Cu(001) substrate surface and the clustering of the former $3d$ transition–metal constituent surface alloy atoms. The clustering is modeled by the formation of monolayer films. The formation of thicker films such as double layer or triple-layer $3d$ metal films is neglected at this point. The stability of the surface alloy against the phase separation or the clustering, respectively, is investigated in terms of the formation energy

$$\Delta E_F(\{M\},\{\Delta z_M\}) \quad = \quad E_{Cu(001)c(2\times2)TM}(\,M,\Delta z_M\,)$$

$$- \frac{1}{2}\Big( E_{TM/Cu(001)}(\, M, \Delta z_M\, ) + E_{Cu(001)}(\, \Delta z\, ) \Big)\,, \qquad (1)$$

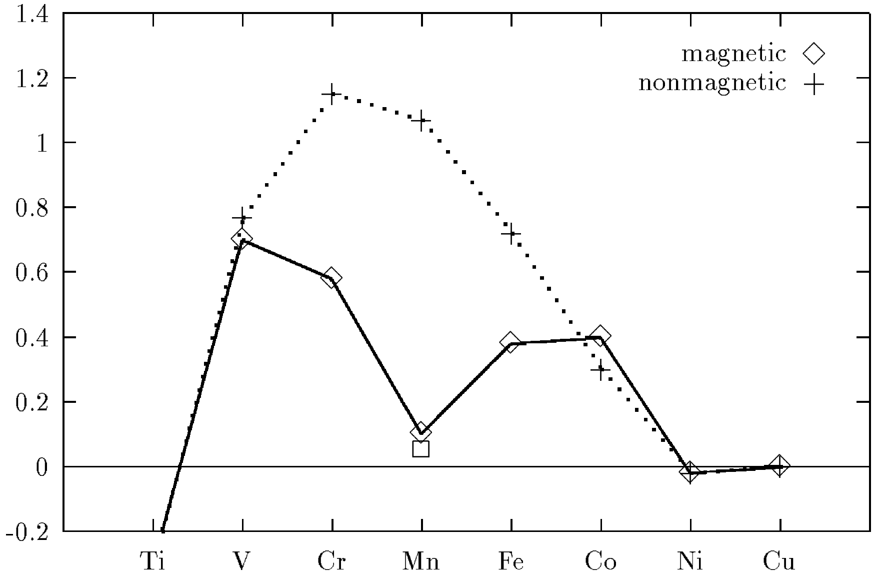
which is determined by the total energy difference between the systems containing the surface alloy ($E_{Cu(001)c(2\times2)TM}$) and the average of the total energies determined by the 3d monolayers on Cu(001) ($E_{TM/Cu(001)}$), and the clean Cu(001) surface ($E_{Cu(001)}$). The formation energy depends on the magnetism – (a) the local moments as well as (b) the magnetic ground state structure. The magnetism ($M$) enters twice, through the total energies of the surface alloys as well as of the monolayers. For each transition–metal constituent atom one has to include the minimum energy ground state magnetic configuration in order to obtain the ground state formation energy $\Delta E_F$. For the surface alloys we included calculations for the nonmagnetic (P) as well as ferromagnetic (F) configuration ($M = P, F$) (possible antiferromagnetic phases are discussed here). For the monolayers on Cu(001) we include calculations for the nonmagnetic (P), the ferromagnetic (F), and the c(2×2) antiferromagnetic state (AF) as discussed above. The formation energy depends also on the atomic positions of the atoms of each of the 3 terms entering Eq. 1. In this work we determined the minimum energy bulk lattice constant of Cu ($a_0^{Cu}$) and in order to determine the ground state formation energy $\Delta E_F$, one should at least include for each of these 3 terms the minimum energy interlayer relaxation $\Delta z_M$ of the surface layers, which depend also on the magnetic state. At present, the interlayer relaxation is neglected ($\Delta z = 0$). We shall come back to this point below.

In Fig. 8 we compare the ground state formation energy $\Delta E_F(0)$ with the formation energy resulting from non–spin–polarized calculations $\Delta E_F(P, 0)$. We find, that without the formation of local magnetic moments the $\Delta E_F(P, 0)$ is positive for all $3d$ transition–metal elements with the exception of Ti and Ni. This means, that for all these systems phase separation or clustering, respectively, is expected. Phase separation is suppressed only for Cu(001)c($2\times2$)Ti and Cu(001)c($2\times2$)Ni films. The phase separation energy ($-\Delta E_F$) is largest for Cr and Mn with about 1.1 eV/TM atom. This means, hypothetical nonmagnetic Cu(001)c($2\times2$)Cr and Cu(001)c($2\times2$)Mn surface alloy films may never be thermodynamically stable and surface alloys may only be expected for Ti and Ni systems. For Ti, since all Ti systems remain nonmagnetic, the formation energy $\Delta E_F(P, 0)$ is equal to the ground state formation energy $\Delta E_F(0)$.

For the magnetic systems, the ground state formation energy $\Delta E_F(0)$ shows a remarkably different behavior. For Cu(001) c(2×2)V, $\Delta E_F$ and $\Delta E_F(P, 0)$ are close in energy. Then for Cu(001)c($2\times2$)Cr and Cu(001)c($2\times2$)Mn the formation $\Delta E_F$ decreases continuously to a minimum for the Mn system with a formation energy of about 100 meV/Mn atom. Then, it increases again for the Cu(001)c(2×2)Fe and Cu(001)c(2×2)Co systems, and for Cu(001)c($2\times2$)Ni, $\Delta E_F(0)$ and $\Delta E_F(P, 0)$ are nearly identical. Although we again find that, with the exception of Cu(001)c(2×2)Ni and Cu(001)c(2×2)Ti, all formation energies are positive and no surface alloy should be energetically stable, due to the existence of magnetism, there exists a pronounced kink in formation energy for the Mn system, indicative that the clustering process may well be suppressed.

In general one can say, that magnetism reduces the phase separation energy and supports

Figure 8: Shown is the formation energy $\Delta E_F = E_{Cu(001)c(2\times2)TM} - \frac{1}{2}(E_{TM/Cu(001)} + E_{Cu(001)})$ in eV per transition–metal (TM) atom for the Cu(001)c(2 × 2)3$d$ surface compounds. Crosses, connected by a dotted line, indicate the nonmagnetic results yielded by non–spin–polarized calculations. The formation energies marked by diamonds, connected by a solid line, were determined by taking into account the magnetic ground state configuration for the monolayers and the c(2 × 2) ferromagnetic state for the surface compounds. For $\Delta E_F < 0$ ($> 0$), surface alloy formation (clustering) is energetically preferred. The results are obtained from calculations neglecting any atom relaxation (all atoms are positioned at the sites of the perfect Cu lattice). The square indicates the formation energy of the fully relaxed Mn system (i.e. including the relaxation for the atoms in the surface layer of the surface compound, the Mn monolayer on Cu(001) and the Cu(001) surface).



the surface alloy formation. This effect is strongest for Cr and Mn and less important for Fe. For Co it is the opposite, and for the V and Ni systems, magnetism remains unimportant. For Cr and Fe the support of magnetism is too weak and only the Mn system has a chance to become a magnetically stabilized surface alloy.

All these results have been obtained neglecting any interlayer relaxation. Since the Cu(001)c(2×2)Mn system is just at the edge of becoming a magnetically stabilized surface alloy, we have improved the investigations by including the interlayer relaxation for all 3 subsystems: ferromagnetic Cu(001)c(2 × 2) Mn, Cu(001), and the antiferromagnetic Mn monolayer on Cu(001). Including all these energies leads finally to a formation energy for Cu(001)c(2 × 2) Mn of 40 meV.

From the trend of the formation energy $\Delta E_F$, where magnetism is included, and the absolute value of $\Delta E_F$ obtained for Cu(001)c(2 × 2) Mn, there is a strong indication that magnetism may well support the formation of this surface alloy. We believe that this is the LSDA answer to this problem. As we will see below the LSDA systematically underestimates the magnetism of the Mn/Cu systems. Recently performed calculations [13] including the GGA show a formation energy of about −180meV (cf. Sect. 4.4).

To summarize the two sets of calculations, we investigated the stability of ultrathin magnetic films against alloying and interdiffusion. We found that all magnetic transition metal films on Cu(100) at one monolayer range are thermodynamically unstable. The films show a strong tendency towards clustering and wetting by the Cu substrate. This has been confirmed in numerous experiments on Co/Cu(001) and Fe/Cu(001). For Mn, we found that the Mn monolayer is (nearly) unstable against alloy formation, and the Cu(001)c(2×2) Mn surface alloy is stable against interdiffusion, suggesting the existence of a two-dimensional surface alloy. Cr shows a tendency towards clustering, but at the same time it is stable against interdiffusion, if it is incorporated into the surface layer as surface impurity, and may show interesting behaviour at step edges. A Ni film is also unstable against surface alloy formation, but the surface alloy is unstable against interdiffusion, thus Ni will diffuse into the substrate and the Ni film will disappear (depending on the temperature and activation barriers). Ti is nonmagnetic, showing a strong tendency for surface alloy formation, and at the same time, the surface alloy is stable against interdiffusion. Thus Ti/Cu(001) is a strong candidate for a nonmagnetic surface alloy.

### 4.4 Experimental Evidence

Recently, four systems of this type of surface alloys have been identified, one of which has been realized in Jona's group: Pd(001)c(2×2)Mn [17] and three of them in Wuttig's group: Cu(001)c(2×2)Mn [18], Cu(011)c(2×2)Mn [12] and Ni(001)c(2×2)Mn [19]. Due to the thermodynamic stability of these films a very precise structural characterization by I–V LEED [17, 11, 20, 12] and atomically resolved STM [21, 22] became possible. In these STM images (not shown here) one observes very perfect regular arrays of Mn atoms located at c(2×2) positions. The Cu atoms remain typically unresolved. Cu(001)c(2×2)Mn and Ni(001)c(2×2)Mn electronic structure and magnetic properties have been investigated in detail by inverse [23, 24] and spin–polarized photoemission [24], as well as by soft x–ray absorption and magnetic circular dichroism [25, 26] has been carried out. Now, they belong to the best characterized ultrathin magnetic films of all. In particular, since the structure is simple and well defined, they became model systems for the comparison between theory and experiment.

Table 3: Structural data obtained by LEED analyses for different ordered surface alloys. $\Delta z$ is the corrugation, $(z_{Atom\ 1} - z_{Atom\ 2})$ between the coordinates normal to the surface of the two structurally or chemically inequivalent atoms of a c(2×2) plane. Theoretical results (theo) are obtained by total energy or force calculations within the FLAPW-method.

| Surface Alloy | **Cu(100) c(2×2) Au** | **Cu(100) c(2×2) Pd** | **Cu(100) c(2×2) Mn** | **Ni(100) c(2×2) Mn** |
|---|---|---|---|---|
| $\Delta z$ [Å] | 0.1 | 0.02 ± 0.03 | 0.30 ± 0.02 | 0.25 ± 0.02 |
| $\Delta z$ [% ] | 5.5 | 1.1 ± 1.7 | 16.6 ± 1.1 | 13.9 ± 1.1 |
| theo [% ] | | | 14.0 | 11.5 |

In Table 3 we compile the structural results for ordered surface alloys formed on Cu(001) and Ni(001) substrates, together with earlier examples of ordered surface alloys with c($2\times2$)structure, Cu(001)c($2\times2$)Au [27, 28], and Cu(001)c($2\times2$)Pd [29, 30]. However, the latter surface alloys are nonmagnetic like the majority of surface alloys known at present [31]. A comparison of the corrugation for the surface layer shows that the two alloys containing Mn have a much larger corrugation of 0.30 Å (MnCu) and 0.25 Å (MnNi) than the CuAu and CuPd surface alloys. The earlier trend in the corrugation of the CuAu and CuPd alloys are in line with the simple argument of Wu *et al.* [29] that the corrugation of the surface alloy layer increases with increasing difference in the atomic radii of the alloy constituents. This statement is consistent with the smaller buckling of the CuPd surface alloy as compared with the CuAu surface alloy, since the atomic radius of Au is larger than the one of Pd. If this tendency would also hold for Mn, one would expect an even smaller corrugation than for the CuPd surface alloy since the atomic radius of elemental Mn is smaller than the one of Pd. On the contrary, the corrugation found for the Mn surface alloy on Cu(001) and Ni(001) is even considerably larger than the corrugation of the CuAu surface alloy. This shows that simple size arguments are insufficient to explain the buckling of surface alloys.

We have performed a structural optimization by total energy minimization [11] and force calculations [12] for ferromagnetic and nonmagnetic Mn/Cu and Mn/Ni surface alloys. In case magnetism is artificially suppressed, the corrugation is practically zero, as expected from atomic radii. However, if we include magnetism, we obtain large outwards relaxations of Mn and slight inwards compression of Cu or Ni, respectively, ending up in corrugations close to experiment (cf. Table 3). Thus this large corrugation is explained in terms of a giant magneto–volume effect, which additionally stabilizes the surface alloys.

Further, the work function change was investigated upon the formation of surface alloys [24]. This was done probing by means of inverse photoemission the binding energy shift of the image potential (surface) state, which is known to be an ideal measure for a work function change. For example, the image state shifts from 4.1 eV for clean Cu to a 0.45 eV lower energy upon alloy formation with Mn. The ferromagnetic calculations yield a lowering of the work function in the same energy range (0.31 eV) going from Cu(001) to c($2\times2$)Cu/Mn/Cu(001), while calculations for a hypothetical nonmagnetic CuMn/Cu(001) surface alloy lead to a work function change which amounts only to 0.05 eV. Thus we have identified the formation of the high magnetic moments as the basic origin for the large modifications of the electronic structure which causes the work function change.

## 5 Limit of LSDA

A closer look reveals that the local spin density approximation systematically underestimates the surface magnetism of Mn. (i) The formation energy was found too small. The alloy exists over a large temperature range, but the calculated formation energy is positive, which means the alloy should not form and entropy, not included in the analysis, should work against the alloy formation. (ii) The corrugation is systematically too small. (iii) The work function change is too small. (iv) The experimentally observed exchange splitting [24] is much larger than the theoretically determined one. Although the exchange splitting is not a ground state property and cannot be expected to be very precisely reproduced within the density functional theory, experience has shown that an agreement between theory and experiment, better than 1 eV, is not uncommon for transition–metal films.

In collaboration with T. Asada [13] we have started to extend the above calculations to the generalized gradient approximation on exchange and correlation of Perdew and Wang [15]. The results look very promising. The trends do not change, but the formation energy for the Mn/Cu surface alloy changes sign ($\sim -180$meV instead of $+100$meV). A more complete analysis will be presented in future.

## 6 Summary and Outlook

Exemplary for $3d$ transition metal monolayers on noble metal substrates, detailed calculations for 3d monolayers on Cu(100) have been performed, showing clear trends as follows: i) Magnetism acts against interdiffusion. At low coverage, where the magnetism of Cr and Mn is very large, interdiffusion is suppressed. ii) Magnetism reduces clustering and promotes alloy formation. For Mn we find a strong tendency for alloy formation. From i) and ii) we expect for the case of the Cu substrate a thermodynamically stable, two dimensional surface alloy: Cu(100)c(2×2)Mn. Although in detail, the results depend on the Cu substrate, the trends presented above have an universal character. Therefore, Cu(100)c(2×2)Mn is only an example of a much wider class of magnetic surface alloys. Recently, several of these surface alloys have been found experimentally, in agreement with the trends presented above. We found in addition a nonmagnetic surface alloy Ti/Cu(001), which is not yet confirmed experimentally. Total energy and force calculations are applied to determine the structure of the surface alloys. From the comparison between theory and experiment we conclude that the LSDA underestimates the magnetism of Mn. Recent improved calculations using the GGA look promising.

While in this article we have shown the possibility of magnetically stabilized surface alloys, many questions remain unanswered. For example, do additional magnetic surface alloys exist, that are not based on Mn, but possibly on Cr? What is their magnetic order, how large is their critical temperature $T_c$ for the magnetic transition, which surface alloys at one monolayer range will form multilayer alloy films? Do additional structural phases as a function of the coverage exist? Is there a structural order–disorder transition? What is the termination of the surface alloys at step edges. More questions can easily be asked. I hope we will answer some of these questions in future.

# 7 Acknowledgement

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