# HCM Newsletter

# $\Psi_k$ Network

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

Number 21 June 1997

Editor: Z. (Dzidka) Szotek
Proposal: ERB4050PL930589
Contract: ERBCHRXCT930369
Coordinator: Walter Temmerman
E-mail: psik-coord@daresbury.ac.uk

# Contents

# 1 Editorial

In this *Newsletter* we would like to turn readers' attention to the report on the first Annual Meeting of the TMR-Network on '**Interface Magnetism**', including the programme and abstracts of all contributions. After the **Abstracts Section**, we publish the CECAM Scientific Programme. In the **Highlight of The Month Section** we have an article by *Paolo Ruggerone, Alex Kley and Matthias Scheffler* entitled "**Bridging the length and time scales: from *ab initio* electronic structure calculations to macroscopic proportions**".

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

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

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

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

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

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

# 2 News from the Network

As mentioned in the previous Newsletter we still have finances for organizing workshops and making short or longer term collaborative visits within the Network. As customary, to get hold of the funds one needs to apply by email to **psik-management@dl.ac.uk** providing a short write-up on the project of interest and the nodes to be involved in a prospective collaboration, including a sufficiently detailed cost statement of the planned visit. Visits of one month or over are strongly encouraged and are expected to lead to well established collaborations between nodes of the Network and to common publications acknowledging the support of the Network. If you are interested and belong to one of the associated member nodes of the $\Psi_k-$Network, please do contact us concerning your application as soon as possible.

# 3 News from the Working Groups

## 3.1 Reports on Workshops

## Report on the Annual Meeting of the TMR-Network

## "Interface Magnetism"

## Bristol, April 18-20, 1997

About eight months after the start of the TMR-Network, the first Annual Meeting took place in Bristol, in the Rodney Lodge of the University of Bristol in Clifton. Beginning on Friday afternoon and ending on Sunday noon, the meeting was attended by about 60 participants, a large part of which were Ph. D. students or young postdocs. The different sections of the meeting were organised according to the flagship projects of the Network, e.g. KKR, Interlayer Exchange Coupling etc. There were about 30 oral presentations of 20 or 30 minutes duration, and a lot of time was left for discussions. The meeting gave an up-to-date report of the activities of the different nodes and established the basis for future collaborations.

A special session was devoted to a discussion of the Network activities. It was good news to hear, that by summer of 1997 all postdoc positions of the Network would have been taken up. There have been also several exchange visits and some collaborations have already led to common publications. Except for the annual meeting the most important Network activities in the first two years are the topical workshops organized by different groups. This series started with two workshops on:

"Interlayer Exchange Coupling", Jülich, Nov. 25-26, 1996
organizer: Peter H. Dederichs, Jülich

"KKR-like Methods", Vienna, Febr. 15-17, 1997
organizer: Peter Weinberger, Vienna

and will be continued by three up-coming workshops in fall:

"Giant Magneto-Resistance", Dresden, Sept. 12-14(?), 1997
organizer: Ingrid Mertig, Dresden

"Spectroscopy", Munich, Nov. 21-23, 1997
organizer: Hubert Ebert, Munich

"TB-LMTO-Methods", Strasbourg, fall 1997
organizer: Hugues Dreyssé

In total the Annual Meeting was very successful and exciting. In particular it was gratifying to see many participating young students from all nodes of the Network. The meeting also benefited from the pleasant atmosphere and accommodations at the Rodney Lodge.

Peter H. Dederichs
Chairman TMR-Network

## Programme

Friday, April 18 :

## KKR session

**Chair-person: Peter H. Dederichs**

| | | |
|---|---|---|
| 15:00-15:30 | The TB-KKR method: some theoretical aspects and numerical calculations | **R. Zeller** |
| 15:30-15:50 | Real space multiple scattering method for magnetic anisotropy of Ni, Fe and Co | **W. Temmerman** |
| 15:50-16:10 | Lattice relaxations and phonons in bcc Iron | **T. Korhonen** |
| 16:10-16:30 | Energetics of impurities on the Fe(001) surface | **B. Nonas** |
| 16:30-17:00 | Tea | |
| 17:00-17:20 | Spin-orbit induced magnetic properties of impurities on and in the (001)-surface of Fe | **H. Ebert** |

## TB-LMTO session

**Chair-person: Hugues Dreysse**

| | | |
|---|---|---|
| 17:20-17:50 | Non-collinear magnetism in a real–space TB–LMTO scheme for surfaces | **R. Lorenz** |
| 17:50-18:20 | Full-potential tight-binding linear muffin-tin orbital method | **M. Alouani** |
| 18:45-20:30 | Dinner | |
| 20:30-21:00 | Calculation of magnetic properties of large systems: $O(N)$ LSGF method | **I. Abrikosov** |
| 21:00-21:10 | Magnetic anisotropy of thin Ni films on Cu(001) | **M. Freyss** |
| 21:10-23:00 | Bar | |

Saterday, April 19 :

## Surface Magnetism and Magneto Anisotropy Session

**Chair-person: Börje Johansson**

| | | |
|---|---|---|
| 9:00-9:20 | The Surface of Alloys – A new Magnetic Material | **I. Turek** |
| 9:20-9:40 | Magnetic anisotropy of Fe/Cu(100) over- and interlayers | **B. Ujfalussy** |
| 9:40-10:00 | Magnetic Anisotropy of Strained Transition Metals | **L. Nordström** |
| 10:00-10:20 | Electronic Structure of One Mn Monolayer on Fe(001) | **O. Elmouhssine** |
| 10:20-10:40 | Density Functional Theory of Crystal Field Quasiparticle Excitations and the *ab initio* Calculation of Spin Hamiltonian Parameters | **M.S.S. Brooks** |
| 10:40-11:00 | Tea | |

## Interlayer Exchange Coupling session

**Chair-person: Balazs Györffy**

| | | |
|---|---|---|
| 11:00-11:30 | Interface Reflectivities of Fe, Co and Ni(001) Layers in Cu | **K. Wildberger** |
| 11:30-12:00 | Oscillatory Magnetic Coupling in Metallic Multilayers with Random Alloy Spacers | **B. Györffy** |
| 12:00-12:30 | Interlayer exchange coupling: effect of cap-layer | **J. Kudrnovský** |
| 12:30-13.00 | Quantum-Well Induced Ferromagnetism in Thin Films | **A.M.N. Niklasson** |
| 13:00-15:00 | Lunch | |

## Gigant Magnetoresistance Session

**Chair-person: Paul J. Kelly**

| | | |
|---|---|---|
| 15:00-15:20 | Quantum well states and GMR in magnetic multilayers | **Mertig** |
| 15:20-15:40 | Ab-initio magnetoresistance in magnetic domain walls | **van Hoof** |
| 15:40-16:00 | Theory of interface resistances | **Schep** |
| 16:00-16:30 | Discussion | |
| 16:30-17:00 | Tea | |

## Spectroscopies and Magnetooptics session

**Chair-person: Paul Durham**

| | | |
|---|---|---|
| 17:00-17:30 | Magnetic linear dichroism in valence-Band photoemission from Fe(110) | **J. Henk** |
| 17:30-18:00 | A theoretical description of spin-resolved Appearance Potential Spectroscopy | **H. Ebert** |
| 18:00-18:30 | Scaling of the $L_{2,3}$ Circular Magnetic X-ray Dichroism of Fe nitrides | **M. Alouani** |
| 18:45-20:30 | Dinner | |

Sunday, April 20:

## Alloy session

**Chair-person: Walter Temmerman**

| | | |
|---|---|---|
| 9:00-9:30 | Full-potential magneto-optical calculations | **A. Delin** |
| 9:30-10:00 | Theory of Magnetic X-Ray Scattering | **P. Strange** |
| 10:00-10:20 | Magnetism and structural stability of Fe, Co, Ni and Cu alloys | **P. James** |
| 10:20-10:40 | Applications of the O(N) LSGF method | **S. Simak** |
| 10:40-11:00 | Topological disorder as an origin of a magnetic moment on Mn in Al-Mn alloys | **A. Pasturel** |
| 11:00-11:30 | Tea | |

## Discussion of Network Activities

| | |
|---|---|
| 11:30-13:00 | (a) Status Reports of the Spokespersons (5 min each) (post-doc position, exchange visits, progress of work, finances)<br>(b) Future collaborations and exchange visits<br>(c) Annual Report 1996/1997 |
| 13:00 | Lunch |

## The TB-KKR method:
## some theoretical aspects and numerical calculations

R. Zeller, K. Wildberger and P.H. Dederichs
Institut für Festkörperforschung, Forschungszentrum Jülich,
D-52425 Jülich, Germany

### Abstract

For density-functional electronic-structure calculations the traditional KKR method can exactly be transformed into a TB form if the concept of a suitably chosen repulsive reference system is used. The TB parameters (i.e. the screened KKR structure constants) can easily be obtained in real space which is a considerable advantage compared to the complicated determination of the standard KKR structure constants. The fast exponential decay of the TB parameters can be exploited to calculate the parameters in real space by using rather small clusters of repulsive muffin-tin potentials. As a consequence the main computational work consists in the inversion of rather sparse matrices. Algorithms for banded matrices can directly be applied and lead to favorable scalings of the computational effort with systems size, e.g. to linear scaling with the number of layers in systems with two-dimensional periodicity. The high accuracy of the transformation is demonstrated by density-functional calculations for fcc and bcc metals and the computational efficiency of the TB-KKR method for large systems is discussed.

# Real space mulltiple scattering method for magnetic anisotropy of Ni, Fe and Co

S.V. Beiden[a], Z. Szotek[b], W.M. Temmerman[b], G.A. Gehring[a],
Yang Wang[c], G.M. Stocks[c], D.M.C. Nicholson[c], W.A. Shelton[c]
and H. Ebert[d]

[a] Department of Physics, University of Sheffield, Sheffield S3 7RH, UK
[b] Daresbury Laboratory, Daresbury, Warrington, WA4 4AD , UK
[c] Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
[d] Institute for Physical Chemistry, University of München, Theresienstr. 37, D-80333
München, Germany

### Abstract

A fully relativistic and spin–polarized extension of the O(N) real space locally self–consistent multiple scattering formalism has been implemented and applied to the study of magnetic properties of Fe, Co and Ni. Here we report on the calculation of the magneto–crystalline anisotropy energy of these systems. We discuss the convergence of the latter, and of the spin– and orbital–moments, as a function of the number of shells included for self–consistency. The calculated values are in good quantitive agreement with the experimental results in case of Fe and Co, which indicates that the origin of the magneto-crystalline anisotropy is relatively local in real space. The result for Ni is in qood agreement with other first-principles calulations. For Co it appears to be possible to describe the change in sign of the magneto-crystalline anisotropy between fcc and hcp structures, in good agreement with experimental findings.

---

# Lattice Relaxations and Phonons in bcc Iron

T. Korhonen, N. Papanikolaou, R. Zeller, and P.H. Dederichs
*Institut für Festkörperforschung, Forschungszentrum Jülich,*
*D-52425 Jülich, Germany*

### Abstract

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

# Energetics of Impurities in the Iron (001) surface

B. Nonas, K. Wildberger, R. Zeller, and P.H. Dederichs
*Institut für Festkörperforschung, Forschungszentrum Jülich,*
*D-52425 Jülich, Germany*

### Abstract

Ab-initio calculations can shed light on impurity-surface and impurity-impurity interactions on metallic surfaces which are important for the understanding of surface alloy properties. We use a KKR-Green's Function method in the local density approximation to study the energetics of 3d-transition impurities in the (001) surface of Iron. We calculate interaction and segregation energies and discuss the stability of adatoms against an atomic exchange process with substrate atoms. In particular we compare these results with recent STM experiments by the NIST-group for Cr on Fe(001).

# Spin-orbit induced magnetic properties of impurities on and in the (001)-surface of Fe

H. Ebert and V. Popescu
*Institute for Physical Chemistry,*
*University of Munich, Theresienstr. 37,*
*D-80333 München, Germany*

B. Nonas, R. Zeller, P. H. Dederichs
*Forschungszentrum Jülich,*
*Inst. für Festkörperforschung*

### Abstract

We present a cluster method for calculating the electronic properties of magnetic solids that is based on multiple scattering theory and properly accounts for spin-orbit induced effects by using the Dirac-formalism in the framework of spin-density functional theory. The scheme allows to deal with ground state as well as spectroscopic properties without requiring the presence of translational symmetry. These properties are exploited to investigate the electronic structure of 3d- and 4d-transition metal impurities on top and within, respectively, the (001)-oriented surface of Fe. Results for the spin and orbital magnetic moments will be given and discussed. Connected with the existence of the magnetic moments of the impurity atoms, there is a magnetic dichroism in their X-ray absorption spectra. Corresponding theoretical spectra will be shown for the K- and $L_{2,3}$-edges in the XANES- and EXAFS-regions.

# Non-collinear magnetism in a real–space TB–LMTO scheme for surfaces

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

**Abstract**

We present an approach to the calculation of anisotropy energies of magnetic surfaces and the non-collinear magnetic structure in rough ultrathin $\gamma$–Fe films. Our technique is based on self–consistent real–space recursion calculations using a tight–binding–linear–muffin–tin–orbital (TB–LMTO) method including spin–orbit coupling and allowing for arbitrary orientations of the local spin–quantization axes. The method also presents important advantages in determining the magnetic groundstate in the presence of competing ferro– and antiferromagnetic interactions. Applications are presented for ultrathin Fe films and a 4–5 Fe step on Cu–substrate.

## Full-potential tight-binding linear muffin-tin orbital method

M. Alouani and J. M. Wills[a]
*IPCMS-GEMME, 23, rue du Loess, 67037 Strasbourg, France*
[a] [2]*Los Alamos National Laboratory, New Mexico 87545*

Abstract

We are developing a full-potential version of the real-space tight-binding linear muffin-tin orbital method to achieve O(N) CPU scaling of systems of many atoms per unit cell. The localization of the basis-set permits the use of finite difference methods to calculate the Hamiltonian and overlap matrix elements on each grid point. For the determination of the charge density we are considering the use of Goedecker contour integration using an integral representation of the Fermi distribution.

## Calculation of magnetic properties of large systems: $O(N)$ LSGF method

I.A.Abrikosov and B.Johansson
*Condensed Matter Theory Group, Physics Department,*
*Uppsala University, S-75121 Uppsala, Sweden*

**Abstract**

The locally self-consistent Green's function (LSGF) method is an order-$N$, $O(N)$, method for calculation of the electronic structure of systems with an arbitrary distribution of atoms of different kinds on an underlying crystal lattice. We discuss an extension of this method to the case of large magnetic systems with arbitrary orientations of local spin moments. In particular, a way of constructing a CPA-like effective medium for an alloy with non-collinear spins is described. Numerical examples are given for bcc and fcc Fe and fcc Fe-Ni alloy.

# Magnetic anisotropy of thin Ni films on Cu(001)

M. Freyss and H. Dreysse,
*IPCMS, Strasbourg, France,*
R. Lorentz anf J. Hafner,
*Tu Wien, Inst. fuer Theor. Physik, Wien, Austria*

### Abstract

Unusual magnetic behavior of Ni films on Cu(001) has been reported by various experimental groups. In a first step in the study of these systems, we report results of TB-LMTO calculations of the magnetic order of Ni films on Cu(001) substrate. Calculations are performed in the real space allowing non-collinear magnetic order. As the number of Ni layers increases, we discuss the stability of the system with a magnetization in-plane or perpendicular to the surface.

# The Surface of Alloys - A New Magnetic Material

I. Turek
*Institute of Physics of Materials AS CR, Žižkova 22, CZ-616 62 Brno and*
*Center for Computational Mater. Science, Getreidemarkt 9, A-1060 Vienna*
S. Blügel
*Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich*
J. Kudrnovský
*Institute of Physics AS CR, Na Slovance 2, CZ-180 40 Praha and*
*Center for Computational Mater. Science, Getreidemarkt 9, A-1060 Vienna*

### Abstract

Based on *ab initio* calculations we predict that the (100) surfaces of the substitutionally disordered RuV, RhV, and PdV binary alloys in the bcc structure are magnetic over a broad concentration range although they are nonmagnetic in the bulk and the metals V, Ru, Rh, and Pd are nonmagnetic in the bulk and at the surface. The LSDA calculations are performed using Green function techniques within the tight-binding linear muffin-tin orbital method in the atomic sphere approximation. We find that the magnetic moment is basically located at the V site in the surface plane of the alloys and the V moment can be as large as about $1\mu_B$ for an alloy with 75% V concentration. The origin of the surface magnetism is traced back to a surface state of V(100), which becomes occupied due to alloying and induces a magnetic instability according to the Stoner model. The results are compared to the magnetism of low-index surfaces of the disordered FeV alloy in the V-rich range. Additional nonmagnetic alloys with magnetic surfaces are suggested.

# Magnetic anisotropy of Fe/Cu(100) over- and interlayers

B. Ujfalussy, L. Szunyogh and P. Weinberger
*Institute for Technical Electrochemistry, Getreidemarkt 9, A-1060 Vienna*

### Abstract

The perpendicular magnetic anisotropy in Fe/Cu thin film over– and interlayers is investigated in terms of the fully relativistic spin–polarized band theory. The formation of the ground state is addressed and a layer–resolved analysis of the magnetic anisotropy energies for the Fe/Cu(100) and the Cu/Fe/Cu(100) system is presented both for ferromagnetic and anti-ferromagnetic cases.

## Magnetic Anisotropy of Strained Transition Metals

L.Nordström, O.Hjortstam, P.James, B.Johansson
and O.Eriksson
*Condensed Matter Theory Group, Physics Department,*
*Uppsala University, S-751 21 Uppsala, Sweden*

### Abstract

The magneto-crystalline anisotropic energy, MAE, for distorted 3d metals are calculated by means of a full-potential LMTO method. These strained bulk structures are of large interest since they are sometimes related to the crystal structure of thin epitaxially grown films. The MAE is calculated self consistently and defined as the total energy difference between two different magnetization directions[1]. Starting from a cubic lattice (fcc or bcc) we have studied the MAE as a function of tetragonal as well as orthorombic distortions. In the case of Ni and Co it is found that the MAE approximately follows predictions from phenomenological magneto elastic theory. However, for Fe the relation between MAE and different distortions turns out to be very complex. It is shown that the MAE can in some cases increases by two orders of magnitudes when breaking the cubic symmetry by performing a distortion. This can be understood as an effect of the lowered symmetry. A reasonable agreement between our calculated MAE for tetragonal Ni and measured MAE for thin Ni films on Cu(001) is found[2].

References
[1] J. Trygg, B. Johansson, O. Eriksson, and J.M. Wills, Phys. Rev. Lett. **75**, 2871, (1995).
[2] O. Hjortstam, K.Baberschke, J.M. Wills, B. Johansson, and O. Eriksson, (Accepted for Phys. Rev. B)

## Electronic structure of one Mn monolayer on Fe(001)

O. Elmouhssine, G. Moraitis, J. C. Parlebas, C. Demangeat
*IPCMS-GEMME, 23, rue du Loess, 67037 Strasbourg, France*

From XMCD experiments on one Mn monolayer on Fe(001) performed by Hillebrecht et al., Andrieu et al. and O'Brien et al., different magnetic configurations have been deduced ranging from ferromagnetic Mn monolayer with its direction of polarization either parallel or antiparallel to the magnetization of the substrate, or in-plane antiferromagnetic. In order to shed some light on this complex system we have performed TB-LMTO calculations of one Mn monolayer on Fe(001). We have studied five collinear magnetic configurations for the Mn monolayer and found that the two lowest in energy, namely c(2x2) and p(2x2)↑ (↑ indicates that the mean magnetization of the Mn monolayer points in the same direction than the Fe substrate) are nearly degenerate. The c(2x2) configuration is in agreement with Hillebrecht's results whereas Andrieu's results are compatible with p(2x2)↑ configuration. O'Brien's results are well represented by the p(2x2)↓ configuration; however, this solution is 100meV above the ground state. One may conclude that: i) either thegrowth process is different or, ii) the sum rule is not well obeyed. Theoretically one should go beyond LDA. Also one should consider possible noncollinear magnetic configurations. Similar calculations are under way for Mn/Co(001) (with J.A.C. Bland and A. Mokrani), for Fe/Co(001) (with A. Mokrani) and for 2ML-thick $Mn_{0.5}Ag_{0.5}$ alloy on Ag(001)(with P. Schieffer and G. Gewinner).

## Density Functional Theory of Crystal Field Quasi-particle Excitations and the *ab initio* Calculation of Spin Hamiltonian Parameters

M.S.S.Brooks[1], O.Eriksson,[2,3] J.M.Wills[3], and B.Johansson[2]

[1] *European Commission, Joint Research Centre, Institute for Transuranium Elements,*
*Postfach 2340, D-76125 Karlsruhe, Federal Republic of Germany*
[2] *Condensed Matter Theory Group, Institute of Physics, University of Uppsala,*
*BOX 530, S-75121, Uppsala, Sweden*
[3] *Center for Materials Science and Theoretical Division, Los Alamos National Laboratory,*
*Los Alamos, NM, 87545 USA*

We show, by carefully examining the change of total energy in constrained variational calculations using the local spin density approximation, that crystal field excitations in rare earths are quasi-particles composed of a $4f$ excitation plus it's associated cloud of shielding conduction electrons. Total energy calculations, which properly exclude the self-interaction of non-spherical $4f$ densities, are then used to calculate crystal field energies and the corresponding spin Hamiltonian parameters of TmSb and PrSb, accurately from first principles. The applicability of the Hellman-Feynman force theorem is examined and it is shown that the crystal field energies may also be obtained from a variant of the transition state theory rather than traditional crystal field theory which neglects conduction electron shielding.

## Interface Reflectivities of Fe, Co and Ni(001) Layers in Cu

Karsten Wildberger, Rudolf Zeller, and Peter H. Dederichs
*Institut für Festkörperforschung, Forschungszentrum Jülich,*
*D-52425 Jülich, Germany*

## Abstract

The reflectivity at the interface between a nonmagnetic and a magnetic layer represents the key quantity for the understanding of interlayer coupling and quantum well states (QWS) in magnetic multilayers. For this reason we calculate the reflection coefficient of a Cu Bloch electron at the (001)-interface of fcc Fe, Co and Ni layers and discuss the connection with interlayer coupling and QWS. For the calculation of the reflectivity we make use of a "one-dimensional" representation of the Cu-Green's function. The reflection coefficient shows size oscillations arizing from the interference of the waves scattered at the front and back interfaces of the magnetic layer. Compared with a semi-infinite magnetic layer this leads to anomalies in the coupling and an additional temperature dependence. Finally we demonstrate that the reflectivity and the coupling can be strongly influenced by a magnetic adlayer, e.g. a Fe monolayer on top of the Co or Ni layer.

# Oscillatory Magnetic Coupling in Metallic Multilayers with Random Alloy Spacers

Györffy($^a$),B.L., Lathiotakis($^a$), N., Staunton($^b$),J.B., Ujfalussy($^c$), B. *($^a$)H. H. Wills Physics Laboratory, University of Bristol, Tyndall Ave., Bristol BS8 1TL, UK ($^b$)Department of Physics, University of Warwick, CV4 7AL Coventry, UK ($^c$)Technical University, Vienna, Getreidemarkt 9/158, 1060 Vienna, Au*

## Abstract

In many multilayer systems displaying oscillatory magnetic coupling the nonmagnetic spacer layer is a binary, metallic solid solution[1,2] with concentration $c$. As $c$ changes the amplitude, frequency and the phase of coupling changes smoothly. We shall argue that studying these changes is a usefull way of probing the physical mechanism responsible for the magnetic interaction across the spacers. We shall show that in addition to the evolution of the Fermi Surface with the concentration $c$ the smearing of the electronic states by disorder scattering also influence the coupling. In particular the strength of the coupling is cut off by an exponential factor $\exp(-2L/l)$ where $L$ is the separation of the magnetic layers and $l$ is a mean-free path. We shall present experimental and theoretical evidence that the mean free path $l$ in the above formula is given by $l = v(\mathbf{k}^\star) \cdot \tau(\mathbf{k}^\star)$ where $v(\mathbf{k}^\star)$ is the velocity and $\tau(\mathbf{k}^\star)$ is the lifetime of the states, specified by $\mathbf{k}^\star$, connected by the caliper vector $\mathbf{Q}$, of the Fermi Surface, whose inverse is the period of the oscillations in the coupling.

References

[1] Bobo,F-J., Hennet,L., Piecuch,M., and Hubsch, J., J.Phys.: Condens. Matter **6** (1994) 2689

[2] Parkin, S.S.P., Chappert. C., Herman, F. (1993) Europhys. Lett. **24**, p 71.

# Interlayer exchange coupling: effect of cap-layer

J. Kudrnovský and V. Drchal
*Institute of Physics AS CR, Na Slovance 2, CZ-180 40 Praha and*
*Institute for Technical Electrochemistry, Getreidemarkt 9, A-1060 Vienna*
P. Bruno
*Institut d'Électronique Fondamentale, Université Paris-Sud, F-91405 Orsay*
I. Turek
*Institute of Physics of Materials AS CR, Žižkova 22, CZ-616 62 Brno*
R. Coehoorn
*Philips Research Laboratories, Prof. Holstlaan 4, NL-5656 AA Eindhoven*
P. Weinberger
*Institute for Technical Electrochemistry, Getreidemarkt 9, A-1060 Vienna*

### Abstract

The effect of non-magnetic cap-layer on periods, amplitudes, and phases of oscillations of interlayer exchange coupling (IEC) is studied theoretically on *ab initio* level. We employ the spin-polarized surface Green function technique within the tight-binding linear muffin-tin orbital method and the Lloyd formulation of the IEC. Application is made to Co/Cu/Co(001) trilayers with Cu-cap layers interfacing the vacuum through the dipole barrier. We have found a pronounced oscillatory behavior of both the amplitudes and phases of the IEC oscillations as a function of the cap-layer thickness. The case of cap-layers different from the Cu-spacer layer and thus with a different Fermi-surface topology was also studied. The extensive numerical calculations are performed for large two-dimensional sets of spacer and cap layer thicknesses and analyzed in terms of discrete Fourier transformation as well as in the real space. The results are interpreted in the framework of the electron confinement model and its predictions are verified by *ab initio* calculations.

## Quantum-Well Induced Ferromagnetism in Thin Films.

A.M.N. Niklasson, S. Mirbt, H.L. Skriver† and
and Börje Johansson
*Condensed Matter Theory Group, Physics Department,*
*Uppsala University, S-751 21 Uppsala, Sweden*
†*Center for Atomic-scale Materials*
*Physics and Department of Physics,*
*Technical University of Denmark 5,*
*DK-2800 Lyngby, Denmark*

### Abstract

We have used a first-principles Green's function technique to investigate the magnetic properties of thin films of Rh, Pd, and Pt deposited on a Ag fcc (001) substrate. We find a novel behavior where the magnetic moment of the film is periodically suppressed and enhanced as a function of film thickness. The phenomenon is explained in terms of quantum well states moving through the Fermi level with increasing film thickness.

# Quantum Well States and Giant Magnetoresistance in Magnetic Multilayers

I. Mertig, P. Zahn, und J. Binder
*TU Dresden, Institut für Theoretische Physik, 01062 Dresden*

### Abstract

Ab initio calculations of transport properties in magnetic multilayers allow a highly transparent insight to the microscopic processes of transport. In particular, a screened KKR Greens function method was applied to obtain the electronic structure of the magnetic multilayers. The conductivity of the multilayers is calculated by solving the Boltzmann equation in relaxation time approximation.

It will be shown that the conductivity profile over the multilayer is mainly determined by the local density of states. The differences of the conductivity in plane (CIP) and perpendicular to the plane (CPP) are explained in terms of probability amplitudes of the Bloch waves. It can be shown that quantum well states contribute mainly to CIP conductivity whereas extended Bloch states are responsible for CPP conductivity.

# Ab-initio magnetoresistance in magnetic domain walls

J.B.A.N. van Hoof[1,2], K.M. Schep[1,2], P.J. Kelly[2], and G.E.W. Bauer[1]
[1] *Delft University of Technology, 2628 CJ Delft, The Netherlands*
[2] *Philips Research Laboratories, 5656 AA Eindhoven, The Netherlands*

### Abstract

In this contribution we present the results of a study of transmission through Bloch walls of varying thickness for a number of different ferromagnetic materials (Fe, Ni and Co). The building blocks for these calculations are the scattering properties of a single layer of the bulk material, calculated fully quantum mechanically using electronic structure calculations in the local-spin-density approximation. The rotation of the magnetization direction in the domain wall is assumed to be linear. Using Landauer's transport formalism the conductance through the wall is calculated as a function of the domain wall thickness and the angle between the magnetization in the bounding domains. We find that the magnetoresistance found in our calculations for the thick walls is indeed small, as indicated by experiment.

# Theory of interface resistances

K.M. Schep[1,3], J.B.A.N. van Hoof[2], P.J. Kelly[3], G.E.W. Bauer[1], and J.E. Inglesfield[4]
[1] *Delft University of Technology, 2628 CJ Delft, The Netherlands*
[2] *University of Nijmegen, 6525 ED Nijmegen, The Netherlands*
[3] *Philips Research Laboratories, 5656 AA Eindhoven, The Netherlands*
[4] *University of Wales, P.O. Box 913, Cardiff CF2 3YB, United Kingdom*

### Abstract

The two-current resistor model of perpendicular transport in magnetic multilayers describes the observed dependence of the multilayer resistance on the layer thicknesses very successfully. The parameters of the model are spin-dependent bulk resistivities and interface resistances whose microscopic origin is still unclear. The values of the interface resistances extracted from experiment for (111) oriented Co/Cu multilayers are 0.26 f$\Omega$m$^2$ and 1.84 f$\Omega$m$^2$ for the majority and minority spins, respectively [W P Pratt, Jr *et al.*, J. Appl. Phys. **79**, 5811 (1996)]. In this contribution parameter-free calculations are presented for the spin dependent interface resistances of (100) and (111) oriented Co/Cu multilayers. The scattering properties of a single ideal Co/Cu interface are first calculated fully quantum mechanically using electronic structure calculations in the local-spin-density approximation. Using the "specular" transmission and reflection probabilities of the single interface as boundary conditions, a Boltzmann transport equation is then solved for the two limiting cases of ballistic and diffuse transmission through the bulk. For (111) oriented Co/Cu multilayers with diffuse bulk transport, values of 0.27 f$\Omega$m$^2$ and 1.67 f$\Omega$m$^2$ are calculated for the majority- and minority-spin interface resistances, respectively. The good agreement with the measured values shows that this microscopic mechanism is consistent with the experimental observations.

## Magnetic linear dichroism in valence-Band photoemission from Fe(110)

J. Henk[a], T. Scheunemann[b], R. Feder[b],
A. Rampe[c], D. Hartmann[c], G. Güntherodt[c]
[a] Condensed Matter Theory Group, Uppsala, Sweden
[b] Theoretische Festkörperphysik, Duisburg, Germany
[c] 2. Physikalisches Institut, Aachen, Germany

### Abstract

Symmetry considerations and analytical calculations reveal the microscopic origin of magnetic linear dichroism (MLD) from Fe(110). Numerical relativistic calculations within the one-step model and experiments serve as quantitative checks. MLD from Fe(110) depends significantly on photon energy. Thus, within the direct-transition picture, spin-orbit induced hybridization zones in the band structure can be determined. Further, the strong effect of metal optics on the asymmetry is demonstrated.

## A theoretical description of spin-resolved Appearance Potential Spectroscopy

H. Ebert and V. Popescu
*Institute for Physical Chemistry,*
*University of Munich, Theresienstr. 37,*
*D-80333 München, Germany*

### Abstract

A theoretical description of spin-resolved Appearance Potential Spectroscopy (APS) is presented on the basis of a single-particle description of the underlying electronic structure. The final expression for the signal intensity turns out to be essentially a cross section-weighted self-convolution of the density of states above the Fermi energy – in close analogy to the result for core-valence-valence – Auger electron spectroscopy (CVV-AES). Application of the formalism presented to bcc-Fe and fcc-Ni leads to results in very satisfying agreement with corresponding experimental data. Because this is achieved only by treating the involved transition matrix elements in a proper way, their properties are discussed in some detail.

## Scaling of the $L_{2,3}$ Circular Magnetic X-ray Dichroism of Fe nitrides

M. Alouani and J. M. Wills[a]
*IPCMS-GEMME, 23, rue du Loess, 67037 Strasbourg, France* [a] [2]*Los Alamos National Laboratory, New Mexico 87545* Abstract

We have implemented the calculation of the x-ray absorption cross section for left and right circularly polarized x-ray beams within the local-density approximation by means of our all-electron full-relativistic and spin-polarized full-potential linear muffin-tin orbital method. We show that the $L_{2,3}$ circular magnetic x-ray dichroism of Fe, $Fe_3N$, and $Fe_4N$ compounds scales to a single curve when divided by the local magnetic moment. We used the orbital and spin moment sum-rules to determine the spin and orbital magnetic moment of iron atoms in these ordered iron nitrides.

## Full-potential magneto-optical calculations

Anna Delin, S. Auluck, R, Ahuja, O. Eriksson,
J. M. Wills,[†] and Börje Johansson
*Condensed Matter Theory Group, Physics Department,*
*Uppsala University, S-751 21 Uppsala, Sweden*
[†]*Theoretical Division,*
*Los Alamos National Laboratory, Los Alamos, NM 87545*

### Abstract

We report on magneto-optical calculations performed with a full-potential method, i.e. no shape approximation of the potential, wave functions or charge density is inherent in the method. As far as we are aware, all calculations of magneto-optical properties published until now has utilized the ASA-approximation, sometimes together with combined corrections. It is expected that our method and the ASA-approximation should give very similar results for close-packed systems. We have tested our method on what has become the benchmark-systems for MOKE-calculations, i.e. bcc Fe, hcp and fcc Co, and fcc Ni. For these close-packed systems, our MOKE-spectra agree very well with previously published calculations,

as expected. Also, we have calculated how the MOKE-signal in fcc Co is changed due to tetragonal distortion. In this case we predict a new peak to appear below 1 eV.

## Theory of Magnetic X-Ray Scattering

P. Strange[1], E. Arola[1], B.L. Gyorffy[2], C. Hague[3] and N. Kulikov[4]

[1]Physics Department, Keele University, Keele, Staffordshire, ST5 5BG, UK
[2]Physics Department, Bristol University, Tyndall Avenue, Bristol, BS8 1TL, UK
[3]Laboratoire de Chimie Physique-Matiere et Rayonement,
Universite Pierre et Marie Curie, 11 Rue Pierre et Marie Curie, 75231, Paris.
[4]IPC des Materiaux de Strasbourg, Strasbourg, France

### Abstract

We present a first principles theory of magnetic x-ray scattering. The theory is constructed within the framework of relativistic spin-polarised multiple scattering theory, and the scattering amplitudes are calculated using second order time-dependent perturbation theory. The present work has several advantages over earlier theories. Being fully relativistic, it treats spin-orbit coupling and magnetism on an equal footing and so dichroic effects may be calculated easily. Furthermore, the Green's function expansion in terms of the scattering path operators in the multiple scattering theory allows us to include the contribution of the crystalline environment to the scattering amplitudes. Applications to pure Fe, $\mathrm{Fe}_c\mathrm{Cr}_{1-c}$ and Cu will be used to illustrate the theory.

## Magnetism and structural stability of Fe, Co, Ni and Cu alloys

P.James, O.Eriksson, B.Johansson and I.A.Abrikosov
*Condensed Matter Theory Group, Physics Department,*
*Uppsala University, S-75121 Uppsala, Sweden*

### Abstract

We present a detailed theoretical investigation of the magnetic properties as well as other ground state properties of all the binary 3d alloys including the elements Fe, Co, Ni, Cu, using the coherent potential approximation (CPA) in combination with linear muffin-tin orbitals (LMTO). Theory is shown to successfully reproduce the magnetic and other groundstate properties of these alloys. The prominent results of our study are the presence of a high spin - low spin transition for all Fe-based fcc and hcp alloys, and the finding that the equilibrium volumes are dominated by band-filling effects in combination with magnetovolume effects.

## Applications of the O(N) LSGF method

Sergei I. Simak, Igor A. Abrikosov, and Börje Johansson
*Condensed Matter Theory Group, Physics Department,*
*Uppsala University, S-75121 Uppsala, Sweden*

### Abstract

We discuss a possiblity to apply the recently developed LSGF method [1-2] to the investigation of phase stability of metallic alloys in the bulk as well as, in principle, at the surface and interface. The LSGF method is an efficient order-N technique which allows one to study the influence of the local environment on different physical properties of metallic alloys. As an example we consider ordering effects in the ternary system $Zn_{25}Ni_{25}Cu_{50}$.

[1]. I. A. Abrikosov, A. M. N. Niklasson, S. I. Simak, B. Johansson, A. V. Ruban, and H. L. Skriver, "Local environment effects in random alloys: an order N approach", Phys. Rev. Lett. **76**, 4203 (1996);

[2]. I. A. Abrikosov, S. I. Simak, B. Johansson, A. V. Ruban, and H. L. Skriver, "Locally self-consistent Green's function approach to the electronic structure problem", (to be published).

## Topological disorder as an origin of a magnetic moment on Mn in Al-Mn alloys

A. Pasturel,
*LEPES, Grenoble, France*

### Abstract

We predict that a topological disorder is the main driving force for the formation of a big magnetic moment on Mn in Al86Mn14, Al80Mn20, amd Al60Mn40 liquids. This conclusion is further supported by comparing the results for liquid Al86Mn14 with its crystalline counterpart Al6Mn which is paramagnetic due to the Van Hove singularity in the density of states. We compare the Anderson and Stoner scenarios for the moment onset in relation to the present results.

# 4 Conference Announcements

## 4.1 Third Workshop Wien97

### THIRD WORKSHOP

# WIEN97

### Full-Potential LAPW calculations with the new WIEN97 code

July 1-5, 1997
Vienna University of Technology, Austria
Chairman: K.Schwarz (TU-Vienna)
Email: kschwarz@email.tuwien.ac.at

### Final Announcement

This third workshop (within the Psik network) is concerned with recent progress in density functional calculations using the full-potential Linearized Augmented Plane Wave (FP-LAPW) method as embodied in the new WIEN97 code (or related topics).

The workshop will be organized as follows:

- A short introduction to the LAPW method and the underlying density functional theory
- The new features of the WIEN97 program package
- Introduction to the new graphical user interface
- Hands-on experience with WIEN97
- Results obtained with LAPW (WIEN95 / WIEN97) and related topics
- Poster session

**Conference site:**
The conference will take place at the TU Wien (Vienna University of Technology, A-1040 Vienna, Wiedner Hauptstr. 8-10, second floor (yellow tower, lecture hall 8)

**Contact:**
For further information look at our WWW-homepage
http://www.tuwien.ac.at/theochem/wien97/ws97/
or send an email to kschwarz@email.tuwien.ac.at.

## 4.2 Fourth Bogoliubov-de Gennes Workshop

# WORKSHOP ON THE BOGOLIUBOV-DE GENNES EQUATIONS FOR SUPERCONDUCTORS

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

*Organised by*: **B.L. Györffy** (blg@siva.bris.ac.uk)

**Bristol, July 12-13, 1997**

This workshop is the fourth in the Bogoliubov–de Gennes series of workshops. This year the following topics are planned. Further details are available from Professor B.L. Györffy at the above e-mail address or Walter Temmerman (w.m.temmerman@dl.ac.uk).

### Topics include:

| | |
|---|---|
| Dzidka Szotek (*Daresbury*) | **Quasi-particle Spectra of High Temperature Superconductors** |
| I. Dasgupta/O. Jepsen(*Stuttgart*) | **Low Energy Hamiltonians for High** $T_c$ **Superconductors** |
| Klaus Capelle (*Würzburg*) | **Relativistic Bogoliubov-de Gennes Equation and its Consequences** |
| Kevin Duncan (*Bristol*) | **de Haas-van Alphen Oscillations in the Superconducting State** |
| Martin Lüders (*Würzburg*) | **On the Electronic Correlations in the Superconducting State** |
| Colin Lambert (*Lancaster*) | **Superconducting Nano Structures** |
| A. Volkov (*Lancaster*) | **Quasi-classical and Full Solutions of the Bogoliubov-de Gennes Equations** |
| Andrew Martin (*Bristol*) | **Interfaces of s- and d-wave Superconductors** |
| James Annett (*Bristol*) | **Photoemission from the High** $T_c$ **Superconductors** |
| A.S. Alexandrov (*Loughborough*) | **Evidence for the Charged Bose Gas in the Cuprates** |
| J. Kaye (*Cambridge*) | **Angle Resolved Photoemission from the Cuprates** |
| H. Jensen (*London*) | **Simulation of Vortex Lattices (to be confirmed)** |

## 4.3 Adriatico Research Conference

# "SIMPLE SYSTEMS AT HIGH PRESSURES AND TEMPERATURES: THEORY AND EXPERIMENT"

### Miramare - Trieste, Italy

### Miramare - Trieste, Italy, 1 - 4 July, 1997

(*Organizers*: P. Loubeyre, J. Kohanoff and E. Tosatti)

The Conference will consist of keynote and invited talks. In addition, there will be a permanent Poster Session. A detailed (tentative) programme of the Conference, together with additional informations, can be found at the WEB site:

http://www.ictp.trieste.it/ kohanoff/

**The topics to be treated will include:**

Introductory general topics
Metals under pressure
Semiconductors under pressure
Hydrogen
Solid phases
Fluid phases
Astrophysics
Experimental advances
Minerals and Geophysics
High pressure chemistry
Hydrogen-bonded systems
Synthesis of new materials

**The list of invited speakers includes**:

Russell Hemley, David A. Young, Jean-Michel Besson, Guido L. Chiarotti, Friederich Hensel, Kenichi Takemura, Vadim Brazhkin, Stefano Baroni, Malcom McMahon, Pier Luigi Silvestrelli, Neil W. Ashcroft, Isaac Silvera, William B. Hubbard, Neil Holmes, Marvin Ross, Paul Loubeyre, Francesco Ancilotto, Jorge Kohanoff, Detlef Hohl, Carlo Pierleoni, Ali Alavi, Daniel Haeusermann, Mikhail Eremets, Francesco Sette, Ho-Kwang Mao, Kiichi Amaya, Reinhard Boehler, Raymond Jeanloz, Michael Haiber, Dennis Klug, Philippe Gillet, Sandro Scandolo, Renata Wentzcovitch, Katsutoshi Aoki, Michele Parrinello, Paul McMillan, John Badding, Werner Kuhs, Philippe Pruzan, Marco Bernasconi, Frederic Datchi, Maddury Somayazulu, Stephane Bernard.

## Call for Contributed Posters

Abstracts must be submitted directly via e-mail to the local organizer, Dr. Jorge Kohanoff (kohanoff@ictp.trieste.it), with a subject line "submit poster smr999 author-name". Abstracts should include title, authors and institutions, and should be written in plain text format.

**Deadline for contributed posters is**: 1 June 1997

## Participation and Registration

There is no registration fee. As a rule, travel and subsistence expenses of the participants should be covered by their home institutions.

All applicants are kindly asked to return the Registration Form (to be downloaded from `http://www.ictp.trieste.it/~kohanoff/`, or asked to `smr999@ictp.trieste.it`).

**Deadline for registration is**: 1 June 1997

## 4.4 CECAM Workshop on Reactivity at Surfaces

### Lyon, 28-30 August 1997

*Organizers:* A. Selloni and M. Scheffler

The workshop will consist of a series of invited talks and a poster session. A detailed (tentative) program can be found at the WEB site: `http://sc2a.unige.ch/~selloni/cecam.html`. Registration can be sent to A. Selloni (email: **selloni@sc2a.unige.ch**) or M. Scheffler (email: **scheffler@fhi-berlin.mpg.de**).
There is no registration fee. Financial support to participants cannot be provided.

### Motivation and objectives

The objective of this workshop is to bring together scientists with different backgrounds (chemistry, condensed matter physics, materials science, computational physics, etc.) in order to discuss current issues and perspectives in the theoretical modeling of chemisorption and reaction of adsorbates on metal and insulator (e.g. semiconductor and oxide) surfaces. Topics of interest include:

- First principles electronic structure calculations. Accuracy of various gradient-corrected functionals in the evaluation of reaction profiles.
- Models used to represent the surface: clusters vs slabs; embedding methods.
- Methods for finding saddle points on the potential energy surface.
- Dynamical effects. Analysis of the importance of the high dimensionality of configuration space. Quantum mechanical effects in the motion of the nuclei.
- Systems of very large size: semi-empirical methods; O(N) techniques.
- Calculations of electronic spectra: status and perspectives.

**List of speakers**

E.J. Baerends - *VU, Amsterdam, NL*
D.M. Bird - *University of Bath, UK*
P. Blöchl - *IBM-Zürich, CH*
F. Buda - *SNS, Pisa, Italy*
E.A. Carter - *UCLA, USA*
R. Del Sole - *Università di Roma II, Italy*
A. De Vita - *IRRMA, Lausanne, CH*
M. Gillan - *University of Keele, UK*
A. Goursot - *NSC, Montpellier, France*
A. Gross - *FHI, Berlin, Germany*
S. Holloway - *University of Liverpool, UK*
K. Jordan - *University of Pittsburgh, USA*
P. Kratzer - *Munich, Germany*
G. Pacchioni - *University of Milano, Italy*
M.C. Payne - *Cavendish Laboratory, UK*
L.G.M. Pettersson - *Stockholm, Sweden*
D.R. Salahub - *University of Montreal, Canada*
K. Stokbro - *DTU, Lyngby, Denmark*
V. Termath - *Humboldt, Berlin, Germany*
V. Stämmler - *Bochum, Germany*
C.J. Umrigar - *Cornell University, USA*
A. Vittadini - *CNR, Padova, Italy*
W. Yang - *Duke University, USA*
J.L. Whitten - *NCSU, USA*
S. Wilke - *Exxon, New Jersey, USA*

## 4.5 CECAM Workshop on Ab Initio Calculation

## in Relation to Modelling Constitutive Relations and Fracture Toughness of Metals

---

Lyon, France, 20-22 October 1997.
Organisers: M.W.Finnis and A.E.Carlsson.
Further Details: http://titus.phy.qub.ac.uk/group/Mike/CECAM/information.html

---

### Financial support from the PSIK Network

The Psik network is making available a number of bursaries to fund participants *from network nodes*, especially at post doctoral level. Applications should be made to Mike Finnis, including the abstract of a poster and the names of two referees. Applicants should include an explanation of why they wish to attend the workshop. It may not be possible for Psik to meet the full costs of travel and living expenses in all cases, so it will also be halpful to know if you would require this in order to attend. **The deadline for applications is 30 June**.

### Scientific background

*Ab initio* calculation of *materials* properties has developed over recent years to such an extent that many basic properties relevant to *mechanical properties* can be calculated. Typical examples are elastic constants of metals and alloys, surface energies and vacancy formation energies. Indeed, some quantities, such as ideal cleavage energies of solids at low temperature, can probably be more accurately calculated than measured. The most successful theoretical framework for *ab initio* is the density functional theory in the local density (or spin density) approximation. This has been implemented in a variety of ways, such as pseudopotential methods and the linear augmented plane wave or muffin tin orbital methods. While the twin demands of accuracy and faster computation time are driving major developments in *ab initio* calculation, our concerns here are rather different.

There is no doubt that *ab initio* calculations have made an impact in materials science. Nevertheless it can happen at conferences that *ab initio* results are presented and experimentalists hoping for something useful are disappointed. We see a need to focus the attention of the *ab initio* community on questions of real interest to experimentalists measuring mechanical properties and modellers trying to simulate these properties.

Mechanical properties of metals such as fracture toughness, yield stress and creep rates, present peculiar difficulties, due to the simultaneous importance of two different length and energy scales. These are on the one hand the atomic scale of interatomic bonding, dislocation cores, and defect activation energies, and on the other hand the mesoscopic scale of grain boundaries, and dislocations regarded as geometrical defects interacting elastically with each other and with other defects. But there is a way forward. *Ab initio* calculations can establish atomistic energies, e.g. a gamma surface (the sliding energy of ideal semiinfinite blocks), or the activation barrier for kink migration on a dislocation; they can also document atomistic processes, such as during grain boundary sliding, and establish data bases of energies for calibrating more empirical models of interatomic interactions. Such atomistic results can thus feed into the mesoscopic simulations at larger length scales. These simulations, in turn, are expected to yield directly observable mechanical properties such as constitutive relations and fracture toughness of metals, over the next few years.

### Motivation and objectives

The aim is to discover how to bridge the gap we perceive between *ab initio* calculations and real constitutive relations and fracture toughness of metals. The key types of ab-initio calculations include: dislocation core energies and mobilities, dislocation interactions with defects, elastic constants, response of (ideal) cracks to applied stresses, surface energies, interface energies (including sliding), and others which we expect to emerge at the workshop. Progress to this end will require good collaboration between the *ab initio* calculators, mesoscopic modellers and experimentalists. The workshop will bring these communities together and identify a wish list of *relevant* calculations, which should focus future *ab initio* effort into useful directions.

### Format

There will about 40 participants. We plan about 15 talks of 40 minutes plus 20 minutes discussion, and three focussed general discussions, which should result in some written conclusions. Posters will be welcome, and would be a requirement for funding from Psik.

### Confirmed participants

E. Aifantis, Michigan Technological University
L. M. Brown, MP Group, Cavendish Laboratory
A. Carlsson, Washington University
B.R. Cooper, West Virginia University
M. Daw, Clemson University
B. Devincre, ONERA

F. Ducastelle, ONERA
C. Elsaesser, Max-Planck-Institut für Metallforschung, Stuttgart
M. Faehnle, MPI fuer Metallforshung, Stuttgart
M.W. Finnis, Queen's University Belfast
S.M. Foiles, SMTS Sandia Livermore Laboratories
P. Gumbsch, Max-Planck-Institut für Metallforschung, Stuttgart
J. Harris, MSI/Biosym
K.-M. Ho, Ames
R.G. Hoagland, Washington State University
E.A. Holm, Sandia National Laboratories
E. Kaxiras, Harvard University
R. LeSar, Los Alamos National Laboratory
J.L. Martins, INESC, Lisbon
R. Phillips, Brown University
S. Roberts, University of Oxford
K. Schwarz, IBM
D. Siegel, University of Illinois
H.L. Skriver, Technical University of Denmark
A. P. Sutton, University of Oxford
R.M. Thomson, NIST
V. Vitek, University of Pennsylvania

# 5 Job Announcements

## Postdoctoral Position in Theory of Light Metal Alloys

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

The Solid State Theory Group at the National Renewable Energy Laboratory invites applications for a new postdoctoral research position beginning immediately. The position is for two years, renewable upon mutual agreement to a third year. The postdoctoral position is the result of a new project beginning at NREL to study the theory of energetics, thermodynamics, and phase stability in light-metal alloys (e.g., aluminum-based alloys). The Solid State Theory Group currently consists of ten Ph.D.'s in condensed matter theory and interacts with a broad range of experimentalists at NREL. Interested candidates should *immediately* send a curriculum vitae, list of publications (including preprints of unpublished papers, if possible) and list of three references to:

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

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

# *New* Postdoctoral Position in Electronic Structure Theory of Semiconductor Nanostructures

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

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

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

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

# Postdoctoral Positions

## University of Tokyo
## Strong Correlation Problem

In my group, we are going to start from this fiscal year a new project on numerical approaches for the strong correlation problem. Several postdoctoral positions are open in my group for this activity. This position is for developing and applying advanced algorithm of electronic structure calculations in strongly correlated systems. We put some special emphasis on developing and combining the first principles method with improved LDA etc. and techniques for lattice fermion models such as the Hubbard models. The scope is rather general and any acivities for understanding correlated metals by numerical tools are encouraged. It includes to clarify various properties of high-Tc cuprates, manganites, titanates, vanadiats, and all the other transition metal compounds. We are also strongly interested in developing new efficient algorithms in treating theoretical models and real materials. We put equal emphases on the algorithmic progress and applications to interesting physical phenomena.

The positions available from this year will start in this autumn, although it has some flexibility. Because the time is rather short for the process of determining this year's position, I would appreciate if you could let appropriate candidates know this information. The applications should be made to my address below with curriculum vitae, list of publication, summary of achievements in research, brief future research plan and letters of recommendation. Any questions are welcome to my email address below.

Masatoshi Imada
Institute for Solid State Physics,
University of Tokyo,
Roppongi 7-22-1, Minato-ku,
Tokyo 106, Japan

Tel: +81-3-3478-6811 ext. 5831 or 5883
Fax: +81-3-3402-8174
email address: imada@issp.u-tokyo.ac.jp

# Postdoctoral Positions

## Cavendish Laboratory, University of Cambridge, UK

This autumn I shall move to the Theory of Condensed Matter group at the Cavendish Laboratory, University of Cambridge, England.

I recently received funding to support two theory postdoctoral positions (beginning October 1987), one in each of the following areas.

- Properties of highly excited semiconductors, e.g. non-linear optics, exciton Bose condensation, excitons in disordered systems, coupled quantum wells, electron-hole liquids,....
- Strongly correlated electronic materials, e.g. high-temperature superconductivity, magnetoresistive oxides, organic conductors,...

As it is quite late in the season, I am contacting you directly to ask if you are aware of any suitable candidates for this position (which has actually been advertised for some time, see the Theory of Condensed Matter Group web page: http://www.tcm.phy.cam.ac.uk/ ).

If you know someone who might be interested, please ask them to contact me at pbl@bell-labs.com.

Peter Littlewood
Theoretical Physics Department,
Room 1D-426, Bell Laboratories, Lucent Technologies,
Murray Hill, NJ 07974, USA
Tel: 908-582-4674
Fax: 908-582-4702
email: pbl@bell-labs.com

# Postdoctoral Positions

## University of Cambridge, UK and Tamkung University, Taiwan

I am looking for two postdoctoral associates for a project sponsored by the National Centre for High Performance Computing, Taiwan. The project is funded for one year in the first instance but may be renewed for a further two years. The postdocs are expected to spend at least nine months a year in Taiwan, working in Tamkung University under the direction of Drs. M.-H. Lee and J.-S. Lin and the remainder of the year working in Cambridge. The aim of the project is to develop expertise in total energy pseudopotential calculations in Taiwan. The successful applicants would be expected to interact with experimentalists and other theoreticians to identify potential applications of the total energy methodology and to help new users to master the CASTEP codes.

I shall be happy to discuss these positions with anyone interested.

Mike Payne
TCM Group, Cavendish Laboratory,
Madingley Road, Cambridge, CB3 0HE, UK
E-mail: mcp1@phy.cam.ac.uk
Phone: 44-1223-337381

# Göteborg University

## Postdoctoral Fellow

## Electronic Structure of Complex Materials

The position is in the Materials- and Surface-Physics Group (http://fy...chalmers.se /ap/msp/) of the Department of Applied Pysics within the School of Pysics, a collaborative activity of the Matematical-Natural-Science Faculty, Göteborg University, and Chalmers University of Technology.

To be eligible for a position as research assistant you have to have passed your Ph. D. exam. Applicants that have passed their Ph. D. exams less than five years before the deadline for the application are given priority.

In the appointment special weight will be tied to scientific skills shown by the applicants's own research within the subject, which in the group primarily concerns materials theory and theory for processes at surfaces, normally with computational support. The holder of the position also has to take part in education and administration, primarily within courses preparing for research and researcher training.

The position has a duration limited to two years with possibilities for prolongation with additional four years.

The Swedish Natural-Science Research Council finances this position.

Information about the position can be obtained from Professor Bengt Lundqvist, tel.: +46-31-772 3198, email: lundqvist@fy.chalmers.se.

APPLICATION

The application should be addressed to the Dean of the Faculty of Science and should be appended with an authenticated list of qualifications, certified grades for passed exams, service certificates, scientific works and other documents that the applicant wants to refer to. If scientific work has been made in collaboration with another person this should be specified. In addition, applicants should write short accounts in English of their scientific and pedagogical activities. List of merits, accounts of scientific and pedagogical activities should be delivered in duplicate. The material of the application should be separated into two just alike packages, of which one without repacking should be possible to give to the assigned expert.

The application, together with the document of merits, should be sent to the university with the following address: Registrator, Gteborgs universitet, Vasaparken, S-411 24 Göteborg, Sweden. It should have arrived on June 4, 1997, at latest. Mark the application with ref nr E 36 180/97.

THE DEAN

There are also Ph. D. and post-doc openings in the Materials- and Surface- Physics Group.

# Postdoctoral Position

## Physics Department, Keele University, UK

## The First-Principles Simulation of Liquid Chalcogens

An EPSRC funded post-doctoral position is available immediately to work with Professor M J Gillan in the Computational Physics group at Keele University. The project associated with the position is entitled 'The first principles investigation of the liquid chalcogens'.

The project builds on research done at Keele in the last three years on liquid semiconductors and their alloys. Examples of our recent work have included the first ab initio simulations of collective dynamics in a liquid metal, investigations of the transition from metallic to semiconducting behaviour in alloys of gallium and selenium, and an extensive investigation of silver-selenium alloys, involving detailed comparisons with recent neutron diffraction results by the group of Enderby and Barnes. We have also recently reported the first ab initio m.d. simulations on highly compressed liquid iron under the conditions of the Earth's deep interior.

The aim of the present project is to use Car-Parrinello simulation in combination with other techniques, including the GW approximation for quasiparticle energies, to elucidate the structure, dynamics and electronic properties of the liquid chalcogens, primarily selenium and tellurium. The simulations will be based on the DFT-pseudopotential method. The quantities of interest will be the time-average structure, the electronic density of states, the electrical conductivity, the magnetic susceptibility, the viscosity, the self diffusion coefficient, and the bond lifetime, and the aim will be to elucidate the relations between them. Study of quasiparticle energies will be important, because we know from our own previous work that the Kohn-Sham energies will not give an adequate treatment of the density of states and conductivity. The work will represent the first application of the GW technique to liquid systems. It is also planned that the work will employ spin-DFT to probe the effect of spin fluctuations on the properties of the liquid. These fluctuations are expected to play an important role, because of the chain-like structure of liquid selenium - it is widely believed that free chain ends are associated with dangling bonds and unpaired spins. The recent work of the Keele group has made extensive use of the 512 node Cray T3D at Edinburgh Parallel Computer Centre, and it is planned that the present project will make use of this machine and of a new massively parallel machine to be installed in 1998.

The theoretical and computational physics group at Keele was founded in 1988, and has a strong track record of recent research achievements in first principles dynamics, classical molecular dynamics simulation, and the theory of novel relativistic effects in solids. The group currently has two permanent staff (Professor M J Gillan and Dr P Strange), and a number of postdoctoral positions. The group is well provided with local computational facilities, and has recently received EPSRC funding for the enhancement of these facilities for the present project. The group also benefits from allocations of time on national supercomputing facilities.

Further information about the research group can be found on the WWW at URL:

$http : //www.keele.ac.uk/depts/ph/tc/cph_h me.html$

Appointment to the post will be made initially for one year, with a possibility of extension for a further year after that. The salary is on the RA1A scale, depending on age and experience.

Applicants should have a strong academic record, including a PhD in a relevant research area. Experience in advanced computational methods and in theoretical chemistry or physics is essential. Because of the nature of the project, a strong background in both electronic structure methods and statistical mechanics is indispensable. A preference will be given to applicants having experience of coding for massively parallel machines.

Keele University occupies a large and pleasantly wooded campus about 5 km from Newcastle-under-Lyme, and is near the M6 motorway, about an hour by road from Birmingham, Manchester and Liverpool.

Enquiries should be made in the first instance by contacting Professor M J Gillan, Physics Department, Keele University, Keele, Staffordshire ST5 5BG, UK, (Email:PHA71@KEELE.AC.UK, Telephone: 01782-583339, Fax: 01782-711093). Formal applications should be made on an application form which can be obtained by writing to the Personnel Office, Keele University, Keele, Staffordshire ST5 5BG, UK. Applications for the position will be accepted until 4th July 1997 or until the position is filled.

# Postdoctoral Position
# Physics Department, Keele University, UK
# The Ab Initio Study of Liquid and Solid Iron

An NERC-funded post-doctoral position is available immediately to work with Professor M. J. Gillan in the Computational Physics Group at Keele University. The project is being carried out in collaboration with the group of Professor G. D. Price (Geological Sciences Dept., University College London) and is entitled: 'Ab initio study of the high pressure and temperature behaviour and stability of liquid and solid iron'.

The aim of the work that will be done at Keele is to use ab initio molecular dynamics (Car-Parrinello simulation) to investigate the properties of liquid iron under the conditions of the Earth's deep interior. The Earth's core consists mainly of iron with an admixture of lighter elements, the outer core being liquid and the inner core crystalline. The nature of the lighter elements is not known for certain, but they may perhaps be oxygen, silicon or sulphur. Other quantities are also extremely uncertain. Estimates of the viscosity of the outer core obtained by different methods span a range of no less than 12 orders of magnitude, and the effect of lighter alloying elements on the viscosity is very poorly understood. The temperature distribution in the Earth's core is uncertain, and the melting point of iron at the relevant pressures is known only roughly. Recent progress in the ab initio simulation of liquid metals offers the prospect of removing many of the uncertainties by doing accurate calculations. Two of the main aims of the projects are:

(i) to use ab initio free-energy calculations to determine the melting point of iron (both pure and alloyed with light elements) as a function of pressure;

(ii) to investigate how the viscosity of liquid iron depends on the presence of light elements - initially, this will be done indirectly by studying the diffusion coefficient.

The project builds on research done at Keele and in other research groups during the last three years on liquid metals and their alloys. Examples of our recent work have included the first ab initio simulations of collective dynamics in a liquid metal, investigations of the transition from metallic to semiconducting behaviour in alloys of gallium and selenium, and an extensive investigation of silver-selenium alloys, involving detailed comparisons with recent neutron diffraction results by the group of Enderby and Barnes. We have also done exploratory simulations of pure liquid iron under Earth's core conditions, and have reported results on the static structure and self-diffusion coefficient at thermodynamic states corresponding roughly to the core-mantle boundary and the inner-core boundary.

The theoretical and computational physics group at Keele was founded in 1988, and has a strong track record of recent research achievements in first principles dynamics, classical molecular dynamics simulation, and the theory of novel relativistic effects in solids. The group currently has two permanent staff (Professor M J Gillan and Dr P Strange), and a number of postdoctoral positions. The group is well provided with local computational facilities. The group also benefits from allocations of time on national supercomputing facilities.

Further information about the research group can be found on the WWW at URL:

$http : //www.keele.ac.uk/depts/ph/tc/cph_h me.html$

Appointment to the post will be made initially for one year. The salary is on the RA1A scale, depending on age and experience.

Applicants should have a strong academic record, including a PhD in a relevant research area. Experience in advanced computational methods and in theoretical chemistry or physics is essential. Because of the nature of the project, a strong background in both electronic structure methods and statistical mechanics is indispensable. A preference will be given to applicants having experience of working with massively parallel machines.

Keele University occupies a large and pleasantly wooded campus about 5 km from Newcastle-under-Lyme, and is near the M6 motorway, about an hour by road from Birmingham, Manchester and Liverpool.

Enquiries should be made in the first instance by contacting Professor M J Gillan, Physics Department, Keele University, Keele, Staffordshire ST5 5BG, UK, (Email:PHA71@KEELE.AC.UK, Telephone: 01782-583339, Fax: 01782-711093). Formal applications should be made on an application form which can be obtained by writing to the Personnel Office, Keele University, Keele, Staffordshire ST5 5BG, UK. Applications for the position will be accepted until 4th July 1997 or until the position is filled.

# Ph.D. Position

## Institut für Physikalische Chemie der Ludwig-Maximilians-Universität München

There is a vacant Ph. D. position in the Group of Professor Hubert Ebert, that is funded by the Ludwig-Maximilians University. If someone who has already got his Ph.D. is interested in the position, despite low salary given below, he would also be welcome to apply.

The succesful applicant is expected to work with Professor Hubert Ebert primarily on the relativistic effects in the spectroscopy of magnetic solids: AES, VB-XPS, core level-XPS, XAS, etc. All work will be based on the spin-polarized relativistic version of the KKR-method (multiple scattering theory), combined (where necessary) with the CPA.

- **Starting date:** More or less anytime starting from 1st June
- **Salary:** About 1600 - 1700 DM (after tax) (BAT IIA/2) depending on age and family situation.
- **More information available from:**  
  Hubert Ebert, Prof. Dr.  
  Inst. für Physikalische Chemie der  
  Ludwig-Maximilians-Universität München  
  Theresienstr. 37-41  
  D-80333 München  
  Tel.: 089-2394 4642  
  Fax: 089-2805 248  
  Email: he@gaia.phys.chemie.uni-muenchen.de

# 6 Abstracts

## Electronic and optical properties of H and OH terminated silicon quantum wires

Stefano Ossicini
*Istituto Nazionale per la Fisica della Materia*
*and Dipartimento di Fisica, Universitá di Modena,*
*41100 Modena, Italy*
O.Bisi
*Istituto Nazionale per la Fisica della Materia*
*and Dipartimento di Fisica, Universitá di Trento,*
*I-38050 Povo, Italy*

### Abstract

We report ab-initio calculations of the electronic and optical properties of Si quantum wires with different surface terminations. The results show that the substituion of H atoms with O-H group to saturate dangling bonds originates a lowering of the band gap and the appearence of new features in the low energy side of the dielectric function. A comparison is made between the theoretical outcomes and the available experimental results.

(To appear in DEFECT AND DIFFUSION FORUM (1997))
Manuscripts available from: ossicini@imoax1.unimo.it

# Optimised Pseudopotentials with Kinetic Energy Filter Tuning

M-H Lee, J-S Lin, MC Payne, V Heine, V Milman and S Crampin
*Cavendish Laboratory, University of Cambridge,*
*Madingley Road, CB3 0HE, UK*

## Abstract

We have developed an improved scheme for generating Optimised Pseudopotentials which is more systematic and leads to a better insight. The control parameter Qc connected with the kinetic energy of the pseudo wavefunction pi1(r) is used in a new way to tune the pseudopotential. The scheme uses only three constraints and three spherical Bessel functions in the expansion of pi1(r) inside the pseudising radius rc, compared with four or more previously. The combined effect is that the fidelity of the pseudopotential as seen in the logrithmic derivative, can be improved in a simple and systematic way by tuning Qc. The softness of the pseudopotential is also improved somewhat. The scheme opens the way to tailor-making pseudopotentials for specific requirements which will be particularly useful for large scael ab initio calculations.

Paper copies (sorry: not electronic) available by sending a request with your mailing address to Mrs T. Ingham at: tracey@phy.cam.ac.uk
Scientific correspondence should be sent to Dr M.-H. Lee at: mhslee@hpap.tku.edu.tw

## Self-Interaction Free Relativistic Local Spin Density Approximation: Equivalent of Hund's Rules in $\gamma$-Ce

S.V. Beiden[†], W.M. Temmerman[‡], Z. Szotek[‡], and G.A. Gehring[†]
[†]*Physics Department, University of Sheffield, Sheffield, UK*
[‡]*Daresbury Laboratory, Warrington, WA4 4AD, Cheshire, UK*

### Abstract

In this letter we present an ab initio, Density Functional Theory, justification for the validity of Hund's type of rules in the solid state with localized electrons. We demonstrate that an orbital dependent functional, such as the Self–Interaction–Corrected Local Spin Density, is capable of fully describing the localized nature of the $f$ state, so that all three Hund's Rules are fulfilled. We argue this on the basis of Linear–Muffin–Tin–Orbital calculations in the Atomic–Sphere–Approximation for the $\gamma$ phase of Ce.

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

---

## Hubbard model with orbital degeneracy and integer or noninteger filling

O. Gunnarsson
*Max-Planck-Institut für Festkörperforschung, D-70506 Stuttgart, Germany*

### Abstract

The photoemission spectrum and the specific heat are studied in the Hubbard model of small clusters including orbital degeneracy. We focus on the degeneracy and valence dependence in the limit of a large Coulomb interaction. For integer valence, it is found that the degeneracy increases the width of the photoemission spectrum and it reduces the contribution from the charge degrees of freedom to the specific heat. A deviation from integer valence reduces the width of the photoemission spectrum.

(Accepted for publication in Z. Physik B)
Manuscripts available from: gunnar@and.mpi.stuttgart.mpg.de

# The N2 and N4 optical transitions in diamond: a breakdown of the vacancy model

R. Jones, J. P. Goss
*University of Exeter, Exeter, EX4 4QL, United Kingdom*
P. R. Briddon
*Department of Physics, University of Newcastle upon Tyne,*
*Newcastle, NE1 7RU, United Kingdom*
S. Öberg
*Department of Mathematics, University ofLuleå, Luleå, S97 187, Sweden*

**Abstract**

The vacancy model for impurity vacancy defects in semiconductors assumes that the ground and low energy excited states are derivable from the four $sp^3$ hybrid orbitals on atoms bordering the vacancy. There are many cases where this model works but we describe here a counter-example concerning the lowest excited state of the V-$N_3$ defect in diamond. It is shown that a shallow electron trap, localized outside the vacancy, is involved in the first excited state and responsible for the N2 and N4 optical bands associated with the defect.

(To be published, Rapid Commumications in Physical Review)
Manuscripts available from: jones@excc.ex.ac.uk

# Dynamic Properties of Interstitial Carbon and Carbon-Carbon Pair Defects in Silicon

P. Leary, R. Jones
*University of Exeter, Exeter, EX4 4QL, United Kingdom*
S. Öberg
*Department of Mathematics, University ofLuleå, Luleå, S97 187, Sweden*
V. J. B. Torres
*Departamento de Física, Universidade de Aveiro, 3810 Aveiro, Portugal*

## Abstract

Interstitial carbon, $C_i$, defects in Si exhibit a number of unexplained features. The $C_i$ defect in the neutral charge state of gives rise to two almost degenerate vibrational modes at 920 and 931 $cm^{-1}$ whose 2:1 absorption intensity ratio naturally suggests a trigonal defect in conflict with uniaxial stress measurements. The di-carbon, $C_s$-$C_i$, defect is bi-stable, and the energy difference between its A and B forms is surprisingly small even though the bonding is very different. In the B-form appropriate to the neutral charge state, a silicon interstitial is believed to be located near a bond centered site between two $C_s$ atoms. This must give rise to vibrational modes which involve the motion of both C atoms in apparent conflict with the results of photoluminescence experiments. We use an *ab initio* LDF cluster method, AIMPRO, to calculate the structure and vibrational modes of these defects and find that the ratio of the absorption intensities of the local modes of $C_i$ is in reasonable agreement with experiment even though the structure of the defect is not trigonal. We also show that modes in the vicinity of those detected by PL for the B-form of the di-carbon center involve independent movements of the two C atoms. Finally, the trends in the relative energies of the A and B-forms in three charge states are investigated.

(Phys. Rev. B **55**, 2188-94, (1997))
Papers available from: jones@excc.ex.ac.uk

# Density Functional Study of Ferrocene

A. Resende[a], R. Jones[a], S. Öberg[b], P. R. Briddon[c] and B. R. Eggen[d]
[a]*Department of Physics, University of Exeter,*
*Stocker Road, Exeter, EX4 4QL, UK*
[b]*Department of Mathematics, University of Luleå, Luleå, S-95187, Sweden*
[c]*Department of Physics, University of Newcastle upon Tyne,*
*Newcastle upon Tyne, NE1 7RU, UK*
[d]*School of Chemistry, Physics and Environmental Science,*
*University of Sussex, Falmer, Brighton BN1 9QJ, UK*

## Abstract

The molecular structure of ferrocene is analysed using a first principles self-consistent local density pseudopotential method. The cyclopentadienyl rings are found to be almost planar and the vertical metal–ligand distance of 1.55 Å in fair agreement with the experimental value of 1.66 Å. The reorientational barrier between the $D_{5h}$ and $D_{5d}$ symmetric structures is found to be 1.15 kcal/mole.

(Submitted as a letter to the Journal of Physical Chemistry)
Manuscripts available from: resende@excc.ex.ac.uk

# The Reconstruction of the Si (110) Surface and its Interaction with Si adatoms

Madhu Menon[a,b], Nectarios N. Lathiotakis[c,d] and Antonis N. Andriotis[d]
[a] *Department of Physics and Astronomy, University of Kentucky, Lexington, KY 40506-0055*
[b] *Center for Computational Sciences, University of Kentucky, Lexington, KY 40506-0045*
[c] *Physics Department, University of Crete, P.O. Box 1470, Heraklio, Crete, Greece 71409*
[d] *Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, P.O. Box 1527, Heraklio, Crete, Greece 71110*

### Abstract

The reconstruction of the Si(110) surface and the chemisorption of Si atom on this surface are investigated using a tight-binding molecular dynamics (TBMD) scheme incorporating Green's function methods. The present method belongs to a more general class of the embedding methods which have the advantage of allowing an efficient embedding of a finite subspace in an infinite or a semi-infinite substrate. Our results support the rotational model for surface reconstruction of the n×1 (n $\geq$1) type. The reconstruction of the Si(110) surface was found to be removed, in general, upon chemisorption with Si adatoms and selectively in the presence of surface vacancies.

(Accepted for publication in Phys. Rev. B.)
Manuscripts available from: andriot@iesl.forth.gr

# Band structure theory of magnetism in 3d-4f compounds

Manuel Richter
*Max-Planck-Arbeitsgruppe "Elektronensysteme",*
*U Dresden, D-01062 Dresden, Germany*

### Abstract

The band structure theory of magnetism in 3d-4f compounds is reviewed. Among the open-shell electrons, a hierarchy of interactions is present which governs the intrinsic magnetic properties of these materials. Density functional theory (DFT) is an appropriate tool to describe and quantitatively investigate both ground state properties and model interaction parameters, which are necessary to calculate the temperature dependent behavior. The cornerstones of DFT are explicitly sketched, as well as recent developments needed to cope with the treatment of localized 4f and itinerant 3d magnetism in one and the same framework. This includes the open core scheme, self-interaction corrected DFT, relativistic DFT, and orbital polarization. On this basis, the exchange coupling among itinerant and localized states can be understood, together with the size of Curie temperature and ground state spin- and orbital magnetic moments. Finally, the problem of magnetocrystalline anisotropy is addressed, concerning both the band and the 4f crystal field contribution.

(submitted to J. Phys. D: Applied Physics)

Manuscripts available from: manuel@TMPS09.mpg.tu-dresden.de

# Correlation effects in doped $C_{60}$ compounds

O. Gunnarsson
*Max-Planck-Institut für Festkörperforschung, D-70506 Stuttgart, Germany*
E. Koch, R.M. Martin
*Department of Physics, University of Illinois, Urbana, Illinois 61801*
F. Aryasetiawan
*Department of Theoretical Physics, University of Lund,*
*S-223 62 Lund, Sweden*

## Abstract

We study the condition for a Mott-Hubbard metal-insulator transition in a Hubbard model with the orbital degeneracy $N$. We find an increase by roughly a factor of $\sqrt{N}$ in the critical value of the Coulomb interaction $U$ for which the transition takes place, explaining why $A_3C_{60}$ (A=K, Rb) are metals. We further calculate the many-body enhancement of the Pauli susceptibility. Taking this enhancement into account, we derive an estimate of the electron density of states.

(to appear in the Proceedings of the XIth Winter School on Electronic Properties of Novel Materials, Kirchberg, Austria, 1-8 March, 1997)
Manuscripts available from: gunnar@and.mpi.stuttgart.mpg.de

# Quantum Monte-Carlo calculations for integer-doped fullerides

E. Koch
*Department of Physics, University of Illinois, Urbana, Illinois 61801*
O. Gunnarsson
*Max-Planck-Institut für Festkörperforschung, D-70506 Stuttgart, Germany*
R.M. Martin
*Department of Physics, University of Illinois, Urbana, Illinois 61801*

### Abstract

The doped Fullerides can be well described by a Hubbard model, which comprises the partly filled, three-fold degenerate $t_{1u}$ orbital and the on-site Coulomb interaction $U$. The orbital degeneracy is known to shift the critical ratio $U_c/W$ for the Mott-Hubbard transition towards larger values. This puts the half-filled alkali-doped Fullerides $A_3C_{60}$ on the metallic side of the transition. Prompted by recent synthesis of isostructural families of integer-doped Fullerides with different fillings, we investigate how the orbital degeneracy affects the Mott transition at integer fillings $n \neq 3$. The calculations are done by fixed-node Diffusion Monte-Carlo, using a trial function, which permits us to systematically vary the magnetic character of the system.

(to appear in the Proceedings of the XIth Winter School on Electronic Properties of Novel Materials, Kirchberg, Austria, 1-8 March, 1997)
Manuscripts available from: gunnar@and.mpi.stuttgart.mpg.de

# Electronic structure and transport properties of decagonal Al-Cu-Co alloys

M. Krajčí and J. Hafner
*Institut für Theoretische Physik, Technische Universität Wien,*
*Wiedner Hauptstraße 8-10/136, A-1040 Wien, Austria*
M. Mihalkovič
*Institute of Physics, Slovak Academy of Sciences, Dúbravská cesta 9,*
*SK 84228 Bratislava, Slovakia*

### Abstract

The electronic structure of the decagonal phase AlCuCo and of related crystalline phases has been calculated using the self-consistent tight-binding linear-muffin-tin-orbital (TB-LMTO) technique. The description of the atomic structure is based on different variants of the model proposed by Burkov (Phys. Rev. Lett. **67**, 614 (1991); Phys. Rev. B **47**, 1235 (1993)). The chemical decoration of these models is optimized on the basis of the electronic structure calculations. This is shown to be important for describing correctly the positions of the d-bands of Co and Cu. The observed shift of the Co-d band to relatively high binding energies is related to a particular type of order. We also show that the Cu- and Co-d-band shifts play a more important role for the stabilization of the decagonal phase than the formation of a pseudogap in the Al-s,p band. Satisfactory agreement with photoemission and X-ray emission and adsorbtion spectra is obtained for a special chemical oder with preferred Co-Co coordination. The low-temperature conductivity is investigated within the Boltzmann formalism. A strong anisotropy ($\sigma_p/\sigma_q \approx 50$) of the conductivity in the model with idealized coordinates results from a pronounced anisotropy of the band structure. It is shown that thermal disorder breaks the coherence of the electronic eigenstates in the quasiperiodic plane and leads to an enhancement of the conductivity and reduction of the anisotropy ratio.

(Physical Review B, in print)
Reprint requests to: jhafner@tph.tuwien.ac.at

# Highly anisotropic electronic transport properties in decagonal quasicrystals and approximants

M. Krajčí and J. Hafner
*Institut für Theoretische Physik, Technische Universität Wien,*
*Wiedner Hauptstraße 8-10/136, A-1040 Wien, Austria*

## Abstract

We present detailed ab initio calculations of the electronic structure and transport properties in decagonal quasicrystals and approximants and in crystalline compounds in the Al-Cu-Co and Al-Mn systems. Our results explain the appearence of large transport anisotropies in the quasicrystalline and approximant phases, but not the crystalline compounds. The effect of disorder on the conductivity has been investigated.

(Submitted to J.Phys.: Condens. Matter)
Preprint request to: jhafner@tph.tuwien.ac.at

---

# Effect of the orthorhombic distortion on the magneto-optical properties of $SrRuO_3$

I. V. Solovyev
*Joint Research Center for Atom Technology, Angstrom Technology Partnership,*
*1-1-4 Higashi, Tsukuba, Ibaraki 305, Japan*

## Abstract

It is argued that the non-collinear orbital magnetism accompanying the orthorhombic distortion is an important ingredient which should be taken into consideration for making promising materials with the best magneto-optical characteristics on the basis of $SrRuO_3$.

(To be published in J. Magn. Magn. Matter., Proceedings of International Conference on Magnetism 1997)
Manuscripts available from: igor@jrcat.or.jp

# Magnetic structure and anisotropy of thin Fe films on Cu(001) substrates

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

## 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.

(Phys.Rev. B**54** (1996) 15937-50)
Reprint requests to: jhafner@tph.tuwien.ac.at

# Noncollinear magnetism in rough ultrathin $\gamma$-Fe films

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

### Abstract

In ultrathin face-centered cubic Fe films on Cu(100) substrates only the surface- and subsurface layers are ferromagnetically coupled, while the interior of the films shows various antiferromagnetic configurations, depending on the thickness of the films. We show using ab-initio local-spin-density calculations that for films with more than four monolayers this leads to a frustration of the magnetic interactions in the vicinity of a step and hence to a noncollinear magnetic structure. As a consequence rough ultrathin $\gamma$-Fe films cannot be characterized by a simple uniaxial magnetic anisotropy.

(Submitted to Physical Review Letters)
Preprint request to: jhafner@tph.tuwien.ac.at

# Ab-initio calculations of the 6D potential energy surfaces for dissociative adsorption of $H_2$ on the (100) surfaces of Rh, Pd and Ag

A. Eichler, G. Kresse, and J. Hafner
*Institut für Theoretische Physik and Center for Computational Materials Science,*
*Technische Universität Wien, Wiedner Hauptstr. 8-10,*
*A-1040 Wien, Austria*

## Abstract

Detailed investigations of the six-dimensional potential energy surface (PES) for the dissociative adsorption of a hydrogen molecule on the (100) surfaces of Rh, Pd, and Ag are presented. The calculations are based on local-density-functional theory with generalized gradient corrections to the exchange correlation functional and have been performed using the Vienna ab-initio simulation package VASP. VASP works in a plane-wave basis and uses ultrasoft pseudo potentials. We show that adsorption on Rh(100) and Pd(100) is in general non-activated, but barriers exist along certain reaction channels. The "adiabatic" minimum-energy channel has been determined by a five-dimensional minimization of the total energy at fixed height of the molecule. The variation of the covalent hydrogen-metal bond along this channel is studied using crystal-orbital-overlap-populations and the electron localization function. On Ag(100), $H_2$ adsorption is strongly activated, with a pronounced variation of the barrier over the surface cell. The results of the ab-initio calculations have been analyzed in terms of crystal-orbital overlap populations, electron localization functions and local reactivity functions. The combined results of these studies demonstrate that the local chemical reactivity of a metal surface is determined by the covalent nature of the $H_2 - \sigma$–metal-d interactions whereas the minimization of the Pauli-repulsions according to the Harris-Anderson model is less important.

(Submitted to Physical Review B)
Preprint request to: jhafner@tph.tuwien.ac.at

# Frustrated exchange interactions at the interface of antiferromagnetic films with ferromagnetic substrates

D. Spišák and J. Hafner
*Institut für Theoretische Physik and Center for Computational Materials Science,*
*Technische Universität Wien, Wiedner Hauptstr. 8-10,*
*A-1040 Wien, Austria*

### Abstract

Detailed investigations of the frustration of the magnetic exchange interactions at the interface between an antiferromagnetic monolayer of Mn and a body–centered–cubic Fe(100) substrate have been performed via selfconsistent spinpolarized tight–binding linear muffin–tin orbital calculations and the calculation of the exchange pair–interactions via a real–space Greens–function technique. We find that while the Mn–moments in the monolayer are strongly enhanced compared to those in bulk Mn. The moments in the top layer of the substrate are reduced by as much as forty percent due to the competition between the antiferromagnetic nearest-neighbour Mn-Fe and ferromagnetic Fe-Fe interactions. The strongest frustration effects arise from the strong ferromagnetic coupling between the Mn atoms in the overlayer and the Fe–atoms in the second layer of the substrate which tends to induce an antiferromagnetic component in the magnetic polarization of the top layers of the substrate. The possibility to reduce the frustration by the formation of a non–collinear magnetic structure has been investigated.

(Physical Review B (in print))
Preprint request to: jhafner@tph.tuwien.ac.at

# Surface- and interface phase transitions in thin magnetic films with frustrated exchange interactions

D. Spišák and J. Hafner
*Institut für Theoretische Physik and Center for Computational Materials Science,*
*Technische Universität Wien, Wiedner Hauptstr. 8-10,*
*A-1040 Wien, Austria*

### Abstract

Detailed studies of magnetic phase-transitions in thin magnetic films with frustrated exchange-interactions on nonmagnetic surfaces are presented. In the first part of the work we use a selfconsistent real-space tight-binding linear-muffin-tin orbital approach to determine the magnetic structure of face-centered cubic Fe films on Cu(100) substrates and a Green's function technique to calculate the exchange pair interactions. The result demonstrate a ferromagnetic coupling at the free surface and antiferromagnetic coupling in the interior of the films. The competition between ferro- and antiferromagnetism leads to a pronounced enhancement of the exchange coupling at the surface and at the interface with the nonmagnetic substrate and a strong reduction (frustration) in the inner layers. In the second part we use these results to formulate an Ising model for magnetic films with frustrated exchange interactions and to perform extended Monte Carlo simulations of magnetic phase-transitions. The result demonstrate a rich scenario of twodimensional surface- and interface-phase-transitions, coupled through weak magnetic fluctuations in the interior of the film. In addition, spin-reorientation transitions (reversible and irreversible) between high- and low-moment states are observed.

(Physical Review B (in print))
Preprint request to: jhafner@tph.tuwien.ac.at

# Ab-initio calculations of the atomic and electronic structure of clean and hydrogenated diamond (110) surfaces

G. Kern and J. Hafner
*Institut für Theoretische Physik and Center for Computational Materials Science,*
*Technische Universität Wien, Wiedner Hauptstr. 8-10,*
*A-1040 Wien, Austria*

## Abstract

We present *ab-initio* local-density functional calculations of the electronic structure of clean and hydrogenated diamond (110) surfaces. The clean surface relaxes to a structure where the chains in the first two planes are straightened so that the interatomic distances are shortened and the bond angles are increased. Upon relaxation the surface remains flat and no dimerization occurs. The dangling bonds lead to surface states within the bulk gap. The surface is metallic, but with a very low density of states at the Fermi-level. After the deposition of a monolayer of hydrogen which saturates all dangling bonds, the surface relaxes back to an almost bulk-terminated structure. The occupied surface states are removed from the gap and the surface becomes semiconducting. We also compare the C(110) surface with the other two low-index diamond surfaces.

(Physical Review B (in print))
Preprint request to: jhafner@tph.tuwien.ac.at

# Formation of magnetic moments in crystalline, quasicrystalline and liquid Al-Mn alloys

J. Hafner and M. Krajčí
*Institut für Theoretische Physik, Technische Universität Wien,*
*Wiedner Hauptstraße 8-10/136, A-1040 Wien, Austria*

## Abstract

We present *ab-initio* investigations of the formation of magnetic moments in crystalline, quasicrystalline, and liquid Al-Mn alloys. We find that the appearence of local moments on the Mn-sites is controlled by a local Stoner criterion. In the stable crystalline compound $Al_6Mn$ strong Al-p–Mn-d hybridization enhances the formation of the structure-induced Hume-Rothery-like pseudogap at the Fermi level so that the compound is nonmagnetic. In supersaturated fcc solid solutions of the same composition this hybridization is strongly reduced, the local Mn-density-of-states is impurity-like with a peak pinned at the Fermi level. This leads to a spin-glass-like magnetic structure with high moments on all Mn-sites. Quasicrystalline and liquid alloys lie between these two extremes: In both icosahedral and decagonal quasicrystals Al-p–Mn-d hybridization is generally strong in the ideal quasicrystalline structure, but there are certain local environments that support high magnetic moments on a small number of Mn-sites. The local order is reduced, but does only gradually disappear in melting. This leads to increase of the number of magnetic sites and explains the increase of magnetic susceptiblility on melting.

(Submitted to Physical Review B)
Preprint request to: jhafner@tph.tuwien.ac.at

# Ab-initio simulation of the metal/nonmetal transition in expanded fluid mercury

G. Kresse and J. Hafner
*Institut für Theoretische Physik and Center for Computational Materials Science,*
*Technische Universität Wien, Wiedner Hauptstr. 8-10,*
*A-1040 Wien, Austria*

## Abstract

We present an investigation of the variation of the structural and electronic properties of liquid mercury for states along the liquid-vapor coexistence line, spanning the range from the triple-point to the critical point. Our study is based on ab-initio density-functional molecular dynamics on the Born-Oppenheimer surface. Of central interest is the metal/nonmetal transition occurring at densities approximately twice the critical densities. We show that the density-functional calculations describe the atomic structure very accurately over the entire range from the triple point to the critical point. We find that a single-particle gap between the 6s and the 6p band opens at a density of about 8.8 gcm$^{-3}$, i.e. very close to the density where optical measurement locate the onset of the formation of an optical gap. The detailed investigation of the band edges and of the participation ratio of the eigenstates suggests that the metal/nonmetal transition is best described as a simple band-crossing transition and that electron localization and many-body effects may not be as important as assumed in current scenarios for the transition.

(Phys. Rev. B**55** (1997) 7539-48)
Reprint requests to: jhafner@tph.tuwien.ac.at

# Phonon dispersion relation in Rhodium: Ab-initio calculations and neutron scattering investigations

A. Eichler[1], K.-P.-Bohnen[2], W. Reichardt[2] and J. Hafner[1]
[1]*Institut für Theoretische Physik*
*and*
*Center for Computational Materials Science*
*Technische Universität Wien, Wiedner Hauptstr. 8-10,*
*A-1040 Wien, Austria*
[2]*Forschungszentrum Karlsruhe,*
*Institut für Nukleare Festkörperphysik,*
*P.O.Box 3640, D-76021 Karlsruhe, Fed.Rep. of Germany*

### Abstract

Phonon dispersion relation in face-centered cubic Rhodium have been investigated by ab-initio local-density functional (LDF) calculations and inelastic neutron-scattering measurements. The LDF calculations have been performed both using ultrasoft pseudopotentials and a plane-wave basis and norm-conserving pseudopotentials and a mixed basis-set and include also all-electron calculations at a few high-symmetry points. Theory predicts the existence of Kohn-anomalies that can be interpreted in terms of the calculated Fermi surfaces. The neutron-scattering experiments confirm that the ab-initio calculations are accurate to within 3 percent (including the position and amplitude of the anomalies).

(Submitted to Physical Review B)
Preprint requests to: jhafner@tph.tuwien.ac.at

This paper acknowledges financial support of the Human Capital and Mobility Programme of the European Union under contract ERBCHRXCT930369.

# Orbital magnetism in FeO

I. V. Solovyev[1], A. I. Liechtenstein[2] and K. Terakura[3]
[1] *Joint Research Center for Atom Technology, Angstrom Technology Partnership,*
*1-1-4 Higashi, Tsukuba, Ibaraki 305, Japan*
[2] *Forschungszentrum Jülich, D-52425 Jülich, Germany*
[3] *Joint Research Center for Atom Technology,*
*National Institute for Advanced Interdisciplinary Research,*
*1-1-4 Higashi, Tsukuba, Ibaraki 305, Japan*

## Abstract

Using the rotationally invariant LDA+$U$ approach we investigate the effect of the rhombohedral distortion on the orbital magnetism of FeO. The latter plays a very important role both for stretching and compressive deformations. In the first case a large orbital magnetic moment is stabilized along the [111] direction and causes similar reorientation for the spin counterpart. Opposite distortion (compression) turns the magnetic moments to the plane (111) where the orbital component is least quenched.

(To be published in J. Magn. Magn. Matter., Proceedings of International Conference on Magnetism 1997)

Manuscripts available from: igor@jrcat.or.jp

# *Ab initio* Quantum and *ab initio* Molecular Dynamics of the Dissociative Adsorption of Hydrogen on Pd(100)

Axel Gross and Matthias Scheffler
*Fritz-Haber-Institut der Max-Planck-Gesellschaft,*
*Faradayweg 4-6, D-14 195 Berlin-Dahlem, Germany*

### Abstract

The dissociative adsorption of hydrogen on Pd(100) has been studied by *ab initio* quantum dynamics and *ab initio* molecular dynamics calculations. Treating all hydrogen degrees of freedom as dynamical coordinates implies a high dimensionality and requires statistical averages over thousands of trajectories. An efficient and accurate treatment of such extensive statistics is achieved in two steps: In a first step we evaluate the *ab initio* potential energy surface (PES) and determine an analytical representation. Then, in an independent second step dynamical calculations are performed on the analytical representation of the PES. Thus the dissociation dynamics is investigated without any crucial assumption except for the Born-Oppenheimer approximation which is anyhow employed when density-functional theory calculations are performed. The *ab initio* molecular dynamics is compared to detailed quantum dynamical calculations on exactly the same *ab initio* PES. The occurence of quantum oscillations in the sticking probability as a function of kinetic energy is addressed. They turn out to be very sensitive to the symmetry of the initial conditions. At low kinetic energies sticking is dominated by the steering effect which is illustrated using classical trajectories. The steering effects depends on the kinetic energy, but not on the mass of the molecules. Zero-point effects lead to strong differences between quantum and classical calculations of the sticking probability. The dependence of the sticking probability on the angle of incidence is analysed; it is found to be in good agreement with experimental data. The results show that the determination of the potential energy surface combined with high-dimensional dynamical calculations, in which all relevant degrees of freedon are taken into account, leads to a detailed understanding of the dissociation dynamics of hydrogen at a transition metal surface.

(submitted to Phys. Rev. B)
Paper available from: http://www.fhi-berlin.mpg.de/th/paper.html
Contact person: axel@theo22.RZ-Berlin.MPG.DE

# Zincblende GaN (001) surfaces: Ga-stabilized structures and metallic bonding

Jörg Neugebauer[1], Matthias Scheffler[1], John E. Northrup[2],
and Chris G. Van de Walle[2]
[1] *Fritz-Haber-Institut der Max-Planck-Gesellschaft,*
*Faradayweg 4-6, D-14 195 Berlin-Dahlem, Germany*
*Xerox Palo Alto Research Center,*
*3333 Coyote Hill Road, Palo Alto, California 94304*

## Abstract

We have investigated energetics, atomic geometry, and electronic states of zincblende GaN (001) surfaces employing first-principles total-energy calculations. Our results reveal features not observed for other semiconductors: the surfaces are Ga-stabilized (with up to two Ga layers on the surface), and even under N-rich conditions a Ga-terminated surface is energetically most stable. Despite GaN being a wide-bandgap semiconductor the surface exhibits metallic bonding under Ga-rich conditions. Further, unusual surface structures are predicted which have never been observed for semiconductor surfaces but which closely resemble structures found at metal surfaces. Analyzing formation energies and band structure we identify the mechanisms which govern these unusual structures and discuss how they might affect growth properties.

(submitted to Phys. Rev. Lett.)
Paper available from: http://www.fhi-berlin.mpg.de/th/paper.html
Contact person: neugebau@theo23.RZ-Berlin.MPG.DE

# Density-functional theory calculations for poly-atomic systems: Electronic structure, static and elastic properties and *ab initio* molecular dynamics

Michel Bockstedte, Alexander Kley, Jörg Neugebauer
and Matthias Scheffler
*Fritz-Haber-Institut der Max-Planck-Gesellschaft,*
*Faradayweg 4-6, D-14 195 Berlin-Dahlem, Germany*

### Abstract

The package `fhi96md` is an efficient code to perform density-functional theory total-energy calculations for materials ranging from insulators to transition metals. The package employs first-principles pseudopotentials, and a plane-wave basis-set. For exchange and correlation both the local density and generalized gradient approximations are implemented. The code has a low storage demand and performs efficiently on low budget personal computers as well as high performance computers.

(submitted to Comp. Phys. Comm.)
Paper available from: http://www.fhi-berlin.mpg.de/th/paper.html
Contact person: neugebau@theo23.RZ-Berlin.MPG.DE

# Theoretical investigations on the magneto-optical properties of transition metal multilayer and surface systems

H. Ebert
*Institut für Phys. Chemie, Univ. München,*
*Theresienstr. 37, D-80333 München, Germany*
A. Perlov, A. N. Yaresko and V. N. Antonov
*Inst. of Metal Physics, Ukrainian National Academy of Sciences,*
*Vernadsky Str. 36, 252142 Kiev 142, Ukraine*
S. Uba
*Institute of Physics, Warsaw University Branch in Bialystok,*
*Lipowa 41, PL-15-424 Bialystok, Poland*

## Abstract

Results of theoretical investigations on the magneto-optical Kerr-effect in layered systems are presented that are based on a fully relativistic description of the underlying electronic structure. To investigate the importance of the various sources of the Kerr effect model calculations have been performed. Applications to multilayer systems have been done for systems with non-magnetic spacers having a relatively high (Co/Pd, Co/Pt) as well as a small induced magnetic moment (Co/Cu) and comparison with experiment is made. To investigate surface layer systems the use of auxiliary model multilayer systems is explored.

(Submitted to Proceedings of the MRS-Spring Meeting, San Francisco, April 1997)
Manuscript available as ps-file on request
from H. Ebert (he@gaia.phys.chemie.uni-muenchen.de))

# Manipulation of the spin-orbit coupling using the Dirac equation for spin-dependent potentials. II

H. Ebert, H. Freyer, and M. Deng
*Institut für Phys. Chemie, Univ. München,*
*Theresienstr. 37, D-80333 München, Germany*

### Abstract

A scheme is presented that allows to decompose the spin-orbit coupling operator into two parts within calculations based on the Dirac equation for spin-dependent potentials. The first term lifts energetic degeneracies but leaves spin as a good quantum number, while the second term causes hybridization of states with different spin character. To investigate the importance of these terms and of the mechanism connected to them a number of model calculations for the dispersion relation, the spin-orbit induced orbital magnetic moment and the magneto-optical Kerr effect in several transition metal systems have been performed by retaining just one of them. In all cases studied it was found that the first term is by far the most important source for spin-orbit induced phenomena.

(Submitted to Phys. Rev.)
Manuscripts available as ps-file on request
from H. Ebert (he@gaia.phys.chemie.uni-muenchen.de)

# Magnetic properties of 4d-Impurities on the (001) surfaces of Nickel and Iron

B. Nonas, K. Wildberger, R. Zeller, and P.H. Dederichs
*Institut für Festkörperforschung, Forschungszentrum Jülich GmbH,*
*D-52425 Jülich, Germany*

### Abstract

We present ab-initio calculations on the magnetic properties, in particular the surface enhancement, of single 4d transition metal impurities on the (001) surfaces of the ferromagnets Fe and Ni. The calculations are based on local density functional theory and apply a KKR-Green's function method for defects on surfaces. We calculate the local moments of impurities in the adatom and in-surface positions and compare with the results obtained for bulk impurities. Contrary to the large local moments found for 4d-impurities on the surfaces of the noble metals our calculations predict only a moderate enhancement of the local moments at the surfaces of the ferromagnets.

(To be submitted)
Manuscripts available from: B.Nonas@kfa-juelich.de

---

# Ab-Initio Calculation of the Optical Properties of Silicon Quantum Wires

S. Ossicini, M. Biagini, C.M. Bertoni, G. Roma
*INFM and Dipartimento di Fisica, Università di Modena,*
*Via Campi 213/A, I-41100, Modena, Italy*
O. Bisi
*INFM and Dipartimento di Fisica, Università di Trento,*
*I-38050 Povo, Italy*

### Abstract

We have studied the effect of hydrogen, oxygen passivation and inter-wire interaction on the optical properties of nanoscale Si wires. We find that wires with diameters as small as 10-25 Å are actives in the visible range. Inter-wire interaction leads to the presence of localized interface states which lower the band gap energy. The presence of dangling bonds originates broad features in the infrared region. These results are important for the discussion about absorption and luminescence in porous Si.

(MAT. RES. SOC. SYMP. PROC. VOL. 452 pp. 63-68 (1997))
Manuscripts available from: ossicini@imoax1.unimo.it

# Electron localization in the series of actinide metals. The cases of $\delta$-Pu and Es

M. Pénicaud
*Commissariat à l'Energie Atomique, Centre d'Etudes de*
*Limeil-Valenton, 94195 Villeneuve St Georges Cedex, France*

### Abstract

Ground state properties of the whole series of actinide metals available to make bulk measurements, i.e. from Ra to Es, are investigated by means of total energy calculations in the local density approximation (LDA) using a fully relativistic muffin-tin orbital band structure method. With experimental equilibrium volumes, quite good agreement is obtained, from Ra to $\alpha$-Pu, with the usual LDA scheme and, from Am to Cf, with unhybridized *5f* electron-states calculations, an excellent agreement is found, for Es, with unhybridized *5f* and *6d* electron-states calculations and, for the $\delta$-Pu phase, with unhybridized *5f7/2* electron-states calculations. Therefore it is possible to take account rather correctly of the partial localization of electronic states through their unhybridization.

(Accepted for publication in J. Phys.: Condens. Matter)
Manuscripts available from: penicaud@limeil.cea.fr

# Electronic and magnetic properties of UPdSn: itinerant 5f electrons approach

L.M. Sandratskii and J. Kübler
*Institut für Festkörperphysik, Technische Hochschule,*
*D-64289 Darmstadt, Germany*

### Abstract

Density functional theory, modified to include spin-orbit coupling and an effective orbital field to simulate Hund's second rule, is applied to investigate the magnetic structure and electronic properties of the compound UPdSn. Our theoretical results are in overall good agreement with experiment. Thus both theory and experiment find the magnetic structure of UPdSn to be noncollinear, the calculated magnetic U-moments being in very good agreement with the measurements. Also, the calculated density of states is found to simulate closely the photoemission spectrum and the very low experimental value of 5 mJ mol$^{-1}$ K$^{-2}$ for the specific heat $\gamma$ is reproduced reasonably well by the calculated value of 7.5 mJ mol$^{-1}$ K$^{-2}$. Furthermore, the interconnection of the magnetic structure with the crystal structure is investigated. Here theory and experiment agree concerning the planar noncollinear antiferromagnetic configuration in the orthorhombic crystal structure and for the monoclinically distorted lattice we obtain deviations of the magnetic moments from the plane which, although qualitatively in agreement with the experimentally observed deviations, are smaller than the latter. We carry out a symmetry analysis and show that UPdSn belongs to the class of systems possessing a magnetic structure the noncollinearity of which is predetermined by symmetry. Conclusions are drawn about the itinerant character of the U 5f electrons.

(submitted to J. Phys.: Cond. Matt)
Latex version can be obtained from: dg5m@mad1.fkp.physik.th-darmstadt.de (L. Sandratskii)

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

- B. Hammer, O.H. Nielsen, and J.K. Nørskov: *Structure sensitivity in adsorption: CO interaction with stepped and reconstructed Pt surfaces*, Catal.Lett., in print.
- T.R. Mattsson, G. Wahnström, L. Bengtsson, and B. Hammer: *Quantum mechanical calculation of H on Ni(001) using a model potential based on first-principles calculations*, Phys.Rev.B, accepted.
- A. Christensen, A.V. Ruban, P. Stoltze, K.W. Jacobsen. H.L. Skriver, J.K. Nørskov, and F. Besenbacher: *Phase diagrams for surface alloys*, submitted.
- I. Alstrup, I. Chorkendorff, and S. Ullmann: *The interaction of nitrogen with the (111) surface of iron at low and elevated pressure*, submitted.
- C. Ovesen, B.S. Clausen, J. Schiøtz, P. Stoltze, H. Topsøe, and J.K. Nørskov: *Kinetic implications of dynamic changes in catalyst morphology during methanol synthesis over Cu/ZnO catalysts*, J.Catal., accepted.
- L. Vitos, J. Kollár, and H.L. Skriver: *Atomic volumes of* $\alpha$*-phase Th, Pa, U, Np, and Pu*, Phys.Rev.B, accepted.
- S. Mirbt, I.A. Abrikosov, B. Johansson, and H.L. Skriver: *Magnetic properties of Fe embedded in V and Cr: Thin films and dilute alloys*, Phys.Rev., accepted.
- S. Mirbt, A.M.N. Niklasson, B. Johansson, and H.L. Skriver: *Calculated oscillation periods of the interlayer coupling in Fe/Cr/Fe and Fe/Mo/Fe sandwiches*, submitted.
- J. Kollár, L. Vitos, and H.L. Skriver: *The anomalous atomic volume of* $\alpha$*-Pu*, Phys.Rev., accepted.
- L. Vitos, J. Kollár, and H.L. Skriver: *Full charge density scheme with a kinetic energy correction: Application to ground state properties of the 4d metals*, Phys.Rev., accepted.
- A.V. Ruban and H.L. Skriver: *"Ab initio" calculations of partial molar properties in the single-site approximation*, Phys.Rev.B, accepted.
- Y. Yourdshahyan, U. Engberg, L. Bengtsson, B.I. Lundqvist, and B. Hammer: *A theoretical investigation of the structure of* $\kappa$-$Al_2O_3$, Phys.Rev.B, accepted.
- J. Strömquist, L. Bengtsson, M. Persson, and B. Hammer: *The dynamics of H absorption in and adsorption on Cu(111)*, submitted.
- A. Christensen, A.V. Ruban, and H.L. Skriver: *Surface segregation profile for* $Ni_{50}Pd_{50}$*(100)*, Surf.Sci. accepted.

- M.Ø. Pedersen, P.W. Murray, E. Lægsgaard, I. Stensgaard, and F. Besenbacher: *Carbon-60 induced structures on the clean and oxygen covered Cu(110) surface: Competitive adsorption*, submitted.
- L.S. Byskov, B. Hammer, J.K. Nørskov, B.S. Clausen, and H. Topsøe: *Sulfur bonding in* $MoS_2$ *and Co-Mo-S structures*, Catal.Lett., accepted.
- B. Hammer and J.K. Nørskov: *Adsorbate reorganization at steps: NO on Pd(211)*, submitted.
- T.R. Linderoth, S. Horch, E. Lægsgaard, I. Stensgaard, and F. Besenbacher: *Surface diffusion of Pt on Pt(110): Arrhenius behavior of long jumps*, submitted.
- K. Morgenstern, G. Rosenfeld, E. Lægsgaard, F. Besenbacher, and G. Comsa: *Measurement of energies controlling ripening and annealing on metal surfaces*, submitted.
- N. Takehiro, F. Besenbacher, E. Lægsgaard, K. Tanaka, and I. Stensgaard: *Formation of Cu(110)-p(2×3)N islands following dissociative adsorption of NO*, submitted.
- A.M.N. Niklasson, L. Nordström, S. Mirbt, B. Johansson, and H.L. Skriver: *Magnetic interlayer coupling and interaction between interface states in a quantum-well system*, submitted.
- B. Johansson and H.L. Skriver: *Itinerant f-electron systems*, submitted.
- I.A. Abrikosov, S.I. Simak, B. Johansson, A.V. Ruban, and H.L. Skriver: *Locally self-consistent Green's function approach to the electronic structure problem*, submitted.

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

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

# 7 CECAM Scientific Programme

## CECAM

Centre Européen de Calcul Atomique et Moléculaire, Lyon, France
tel: +33-4-7272 8637; fax: +33-4-7272 8636; e-mail: `cecam@cecam.fr`; www: `http://www.cecam.fr/`
1997 Scientific Programme

- *Methods and algorithms for mesoscopic simulation of colloidal particle systems*, June 9-12, Joost H.J. van Opheusden, and John R. Melrose.
- Enrico Fermi summer school on *Computer simulation of rare events and the dynamics of classical and quantum condensed-phase systems*, B.J. Berne, G. Ciccotti, and D. Coker, sponsored by the Italian Physical Society.
- *How can ab initio calculations be an effective tool for the study of mineral properties?*, June 26-28, Bjoern Winkler and Volker Heine.
- *First-principle theory of ferroelectric materials*, July 3-5, Raffaele Resta, Xavier Gonze, and David Vanderbilt.
- *Quantum ab-initio simulation of finite temperature electronic systems*, July 16-18, Gilles Zerah, Ali Alavi, and Bernard Bernu.
- *Theoretical and experimental approaches to nucleic acid structure and activity*, July 21-23, Lennart Nilsson, B. Montgomery Pettit, and Richard Lavery.
- *Atoms in strong magnetic fields*, August 25-27, Philippe Arnault and François Perrot.
- *Reactivity at surfaces*, August 28-30, Annabella Selloni and Matthias Scheffler.
- *Excited electrons in atoms, molecules, and solids*, September 8-10, Rex Godby and Barry Pickup.
- *Simulation of silicas: from classical pair potentials to density functional theory*, September 15-17, Xavier Gonze, Douglas C. Allan, and Jean-Christophe Charlier.
- *Surfaces and interfaces near equilibrium*, September 22-24, David P. Landau.
- *The interaction of ultra-intense short pulse laser with plasmas*, September 29-October 3, M.G. Haines, G. Bonnaud, and A.R. Bell.
- *Rheological behavior and structure of confined films. Theoretical approaches and experiments employing the Surface Force Apparatus (SFA)*, October 14-17, Alain Fuchs and Martin Schoen.

- *Ab-initio calculations in relation to modelling mechanical properties of materials*, October 20-22, M.W. Finnis and A.E. Carlsson, also sponsored by the $\Psi_k$ HCM network.
- *Multi-scale modeling and grand challenge problems in materials research*, October 23-25, Efthimios Kaxiras, Sidney Yip, Ulrich W. Suter, and Ladislas Kubin.

Scientists wishing to have more information or to participate in one of the above activities are invited to consult our WWW server or to contact the CECAM secretary, Ms. Crespeau, by phone, FAX, or e-mail.

# CECAM

## Call for Proposals 1998

### Proposals for the 1998 scientific programme are solicited from the international scientific community

CECAM meetings typically last from 3 days to 2 weeks. The choice of the format is left to the organizers, but it usually such as to favour individual interactions and an informal atmosphere. Ideally, a CECAM workshop should give rise to one or more new collaborations among the participants.

The scientific programme is decided every year by the CECAM Scientific Council, which usually gathers in November, upon peer review of proposals. The typical budget allotted to each meeting spans in the 50-100,000 French Francs range, depending on duration and foreseen attendance. Cosponsorships from other agencies are strongly encouraged.

Scientists wishing to submit a proposal should do so preferably by e-mail to the address reported above, or else contact the Director, Stefano Baroni, by e-mail, phone, or FAX. A standard TEX ttemplate for proposals is available from the CECAM WWW server.

**The deadline for submitting a proposal is August 31, 1997**

CECAM is a consortium of several European national research institutions, aimed at promoting the international cooperation in the fields of Computational Physics and Chemistry. CECAM is presently supported by Belgian FNRS and NFWO, British EPSRC, Dutch NWO, French CEA, CNRS and ENS-Lyon, Greek FORTH, Italian CNR and INFM, and Swiss FNR.

# 8 HIGHLIGHT OF THE MONTH

## Bridging the length and time scales: from *ab initio* electronic structure calculations to macroscopic proportions

Paolo Ruggerone, Alex Kley, and Matthias Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft,
Faradayweg 4-6, D-14 195 Berlin-Dahlem, Germany

**Abstract**

Density functional theory (DFT) primarily provides a good description of the electronic structure. Thus, DFT *primarily* deals with length scales as those of a chemical bond, i.e. $10^{-10}$ meter, and with time scales of the order of atomic vibrations, i.e. $10^{-13}$ seconds. However, many, maybe most, interesting phenomena happen and/or become observable on different scales, namely meso- or macroscopic lengths and on time scales of seconds or even minutes. To bridge the gap between $10^{-13}$ seconds and a second or between $10^{-10}$ meter and 10 and more nano meters is one of the important challenges we are facing today. In this paper we show how we are overcoming these time and size problems for the example of crystal growth and the evolution of nano-scale structures. The key is a kinetic Monte Carlo approach with detailed input from DFT calculations of the relevant atomistic processes.

### 8.1 Introduction

Many, maybe most, interesting physical phenomena take place with meso- or macroscopic length scales and over times of seconds or even minutes. For example, surface reconstructions sometimes evolve over a time period of seconds or even minutes, and the self-organization of nano-scale structures, such as for example quantum dots, also occurs over macroscopic times. *Ab initio* calculations (electronic structure, total energy calculations as well as molecular dynamics (MD) simulations) are concerned with length scales of a chemical bond and with times determined by interatomic force constants and the corresponding atomic vibrations. To bridge the gap *from the atomistic processes to macroscopic dimensions* is an important challenge. In this paper we show how we are coping with this issue for the example of crystal growth by means of a kinetic Monte Carlo (KMC) approach based on detailed input from density functional theory (DFT) calculations. This approach is able to describe the evolution of meso- and macroscopic kinetic growth shapes which may (see below) differ significantly from equilibrium shapes as determined by the minimum of the free energy.

The growth conditions, namely substrate temperature and deposition rate, and the presence or absence of surface defects and impurities play the relevant roles for crystal growth far from thermal equilibrium. For example, according to STM studies Pt islands on Pt (111) [1] show fractal-like structures, triangular and hexagonal shapes at different substrate temperatures. Moreover, different densities of Pt islands coexist on reconstructed and unreconstructed terraces on Pt (111) [2]. Furthermore, a small increase in the temperature produces also a transition in the shape of Ag islands on Pt (111) [3] from fractal to dendritic. It is clear that a thorough knowledge of the atomistic processes occurring at surfaces during growth is a fundamental requirement for understanding these assembling phenomena.

We note in passing two other recent methods which were developed for an *ab initio* description of different but related problems where also a meso- or macroscopic scale was relevant. Although the calculations of the equilibrium shape of (mesoscopic) quantum dots could be done using the same method as that described in this paper, equilibrium structures are more efficiently treated by energy minimization. The method by Pehlke *et al.* [4] therefore considers the (reconstructed) surfaces (i.e. facets of the quantum dot) and elastic strain relief in a hybrid approach. Yet another strategy is appropriate for describing chemical reactions. For this problem it is typically necessary (although often ignored) to consider an elaborate statistics over e.g. 10,000 and more trajectories. A recently developed *ab initio* MD on high dimensional potential energy enables such studies [5].

In this contribution we will describe and explain the microscopic processes which are relevant for understanding crystal growth, and we will illustrate how we bridge the gap from the *ab initio* characterization of the atomistic processes to a description of macroscopic phenomena. The approach is called the "*ab initio* kinetic Monte Carlo method" and proceeds in three steps:

1) Analysis of all possibly relevant atomistic processes using DFT.
2) Selection of the relevant atomistic processes and evaluation of their energy barriers and prefactors.
3) A KMC study using the parameters determined in the second step.

The main risk of this approach lies in step 1), namely that an important process is overlooked. However, as step 1) may be combined with an *ab initio* molecular dynamics study, this risk is rather low. Altogether the *ab initio* KMC approach is able to describe the evolution of structures of 10, or 100, or more nano meters in dimensions, and to cover time scales of seconds. This is done without introducing any additional significant approximation than that of the exchange-correlation functional contained in the DFT step. Typically, although often hidden, the technical approximations, as for example supercell size and/or **k**-point summation, will be relevant as well, but these could (and should) be checked by performing the necessary tests.

The paper is organized as follows. In the next Section we will give a brief picture of processes involving an adatom that has landed on a substrate. In Section 8.3 we describe the main features of the "*ab initio* kinetic Monte Carlo method" (more details are contained in Ref. [6]).

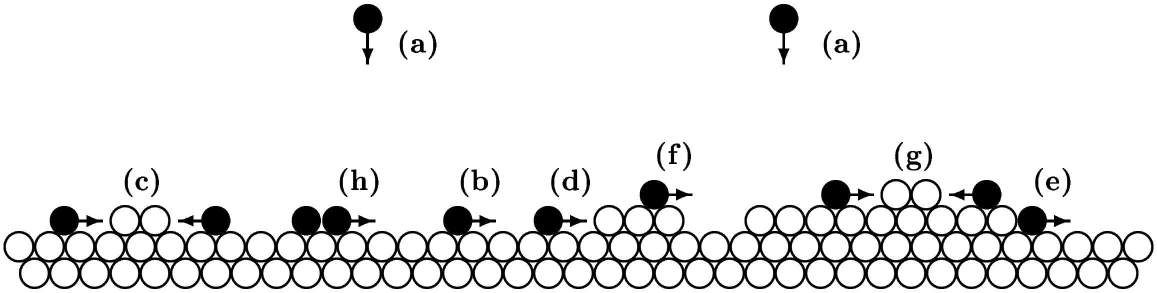

Figure 1: The different atomistic processes for adatoms on a surface: $(a)$ deposition, $(b)$ diffusion at flat regions, $(c)$ nucleation of an island, $(d)$ diffusion towards and capture by a step edge, $(e)$ detachment from an island, $(f)$ diffusion down from an upper to a lower terrace, $(g)$ nucleation of an island on top of an already existing island, and $(h)$ diffusion of a dimer (or a bigger island). For the processes $(a), (c), (f)$ and $(g)$ also the reverse direction is possible, but typically less likely.

Section 8.4 contains our results for Al on Al (111) and, particularly, a discussion of the shapes of islands and their evolution with time.

## 8.2 Atomistic Processes

During growth an atom that reaches the surface, may either stay on the surface and wander around, form an island with other wanderers, or evaporate back into the gas phase. Under typical growth conditions the latter is a very rare process and can be neglected. Thus, we focus our attention on the wandering adatom that can be involved in several processes. These are schematically illustrated in Fig. 1. After deposition $(a)$ atoms can diffuse across the surface $(b)$ and will eventually form a small nucleus when they meet another adatom $(c)$, or adatoms get captured by an already existing island or a step edge $(d)$. Once an adatom has been captured by an island, it may either leave the island and return to the flat surface (*reversible aggregation*) $(e)$ or remain bonded to the island (*irreversible aggregation*). An atom that is bonded to an island may diffuse along its edge until it finds a favorable site (this process is not shown in Fig. 1). At low coverage of adsorbed material (say $\Theta \leq 10$ %), deposition on top of islands is insignificant and nucleation of islands on top of existing islands practically does not take place. However, if the step down motion $(f)$ is hindered by an additional energy barrier (often called Schwoebel-Ehrlich barrier [7]), nucleation of island on top of islands becomes likely $(g)$, giving rise to rough surfaces. A negligible step-edge barrier favors an easy motion of an adatom from the upper to the lower terrace with a consequent growth of smooth films.

In the case of surface diffusion we have assumed that an adatom hops from one binding site to another (*hopping*), but this is not the only way: An adatom may diffuse by atomic exchange where it changes place with a substrate atom and the ejected substrate atom moves further (*exchange*). This mechanism (first discussed by Bassett and Webber [8] and Wrigley and Ehrlich [9]) is actuated by the desire of the system to keep the number of cut bonds low along the diffusion pathway. On fcc (100) surfaces diffusion by atomic exchange was observed and analyzed for

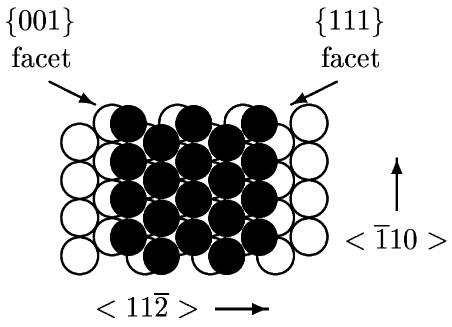

Figure 2: Top view of the two types of close-packed steps on the (111) surface of an fcc crystal. The left step has a {100} facet (square geometry) and the right one has a {111} facet (triangular geometry).

Pt [10] and Ir [11], and predicted for Al [12], Au, and strained Ag [13].

Diffusion along a step edge may also occur via the exchange mechanism as on the Al(111) surface. Since this system will be the object of our study, we add here a few more words. As illustrated in Fig. 2 on the (111) surface of an fcc crystal there are two different types of close-packed steps. They are labeled according to their {100} and {111} facets, referring to the plane passing through the adatom of the step and the neighbor atom of the substrate (often these two steps are labeled A and B, respectively). On Al(111) DFT calculations [14] show that an adatom at the {111} faceted step experiences a rather high diffusion barrier, if the mechanism would be hopping: Either it has to move over an ontop site of the substrate or to leave the step edge to finally reach an adjacent step edge position. Because this is energetically unfavorable, the system chooses an alternative: an *in-step* atom moves out of the step and the adatom fills the opened site. Thus, the coordination of all the particles does not decrease appreciably during the whole process, and the corresponding energy barrier is lower than that of the hopping process. Yet, the final geometry is indistinguishable from that of a simple hop. Along the {100} facet the Al adatom prefers to jump since the associated path goes through a bridge position with a consequent lower activation energy than for an exchange. We will see that this difference will play an important role for understanding the shapes of the islands during growth.

The exchange process may also be energetically favored for the diffusion of an adatom from the upper to the lower terrace. As already mentioned, this diffusion through a normal jump may be hindered by an additional energy barrier at the step edge. Its origin can be understood in terms of a bond counting argument. From Fig. 3($a$) it is clear that the atom moving to the right toward the step edge (black atom in the figure) breaks the bond with the terrace atom on its left before jumping down the step, but there is no terrace atom on its right to help the diffusion process in that direction. The absence of this bond generates a further increase in the energy barrier compared to this of an atom that wanders to the left. However, for the exchange mechanism the diffusion path is not affected by such a reduction of the bond number [cf. Fig. 3($b$)], and the activation barrier for the process may be lower than for the normal jump. For some metallic systems [for example, Al on Al(111) and Ag on Ag(100)] calculations [14, 15] have shown that the exchange mechanism is the favored situation for a step-down motion.

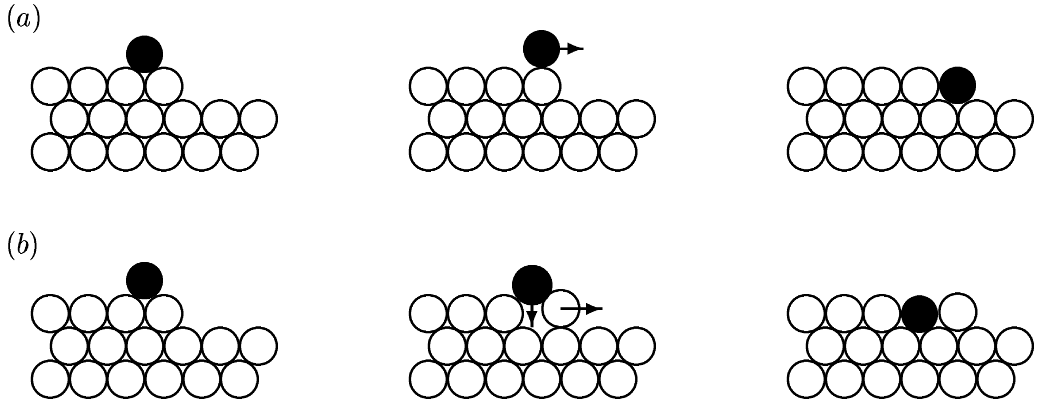

Figure 3: The motion of an atom from the upper terrace to the lower terrace down by (*a*) jump and (*b*) exchange mechanism.

## 8.3 *Ab initio* Kinetic Monte Carlo

A severe problem in describing crystal growth is the time scale. For example, it is too long for MD simulations. MD runs can provide important insight into elementary microscopic mechanisms but typically they can cover at most times of picoseconds, possibly some nanoseconds. Since growth patterns usually develop on a time scale of seconds, the inadequacy of MD is evident. Moreover, the growth structures involve large numbers of particles (from $\sim 10^2$ to $\sim 10^4$) far beyond the reach of MD (simulations with $\sim 10^2$ atoms are hardly feasible, and only for very short times). Instead, the method of choice for studying the spatial and temporal development of growth is KMC (for more details see Ref. [6], and references therein). The key idea behind KMC is to describe stochastic processes (such as deposition, diffusion, desorption, etc.) on the microscopic scales by rates usually given by:

$$\Gamma^{(j)} = \Gamma_0^{(j)} \exp(-E_\mathrm{d}^{(j)}/k_\mathrm{B}T) \quad . \tag{1}$$

Here, $\Gamma_0^{(j)}$ is an effective attempt frequency, $T$ the temperature, $k_\mathrm{B}$ the Boltzmann constant, and $E_\mathrm{d}^{(j)}$ is the energy barrier that needs to be overcome for the event $j$ to take place. In this way one avoids the explicit calculation of unsuccessful attempts, and KMC simulations therefore can describe phenomena with time scales of seconds. Furthermore, large systems can be treated without great difficulties. The basic procedure of a KMC simulation can be sketched as follows:

1) Determination of all processes $j$ that possibly could take place with the actual configuration of the system.

2) Calculation of the total rate $R = \sum_j \Gamma^{(j)}$, where the sum runs over the possible processes [see step 1)]. Deposition is accounted for in this description by the deposition rate $F$ .

3) Choose a random number $\rho$ in the range $(0,1]$.

4) Find the integer number $l$ for which

$$\sum_{j=1}^{l-1} \Gamma^{(j)} \leq \rho R < \sum_{j=1}^{l} \Gamma^{(j)} \quad . \tag{2}$$

5) Let process $l$ to take place.

6) Update the simulation time $t := t + \Delta t$ with $\Delta t = -ln(\rho)/R$ .

7) Go back to step 1).

KMC simulations have been used to study crystal growth of semiconductors (e.g. [16]) and metals (e.g. [17]). However, most of these studies have been based on restrictive approximations. For example, the input parameters, such as activation barriers, have been treated as effective parameters determined rather indirectly, e.g. from the fitting of experimental quantities. Thus, the connection between these parameters and the microscopic nature of the processes may be somewhat uncertain. Often even the surface structure was treated incorrectly, i.e. the simulation was done on a simple quadratic lattice while the system of interest had an fcc or bcc structure. Despite these approximations such studies have provided significant qualitative quantitative insight into growth phenomena. The next better approach is to use semi-empirical calculations such as the embedded atom method or effective medium theory to evaluate the input parameters for KMC simulations of growth [18]. The best, but also most elaborate procedure to obtain these input parameters is to exploit the accuracy of DFT, and this is our *approach.*

At first, a few words about the important atomistic processes. In view of our results for Al on Al (111), reviewed in Section 8.4, we consider the deposition of monoatomic species with sticking coefficient equal to one, and the process is quantitatively characterized by the deposition rate $F$.

Concerning adatom diffusion Eq. (1) reflects the idea that an adatom experiences many stable and metastable sites at the surface, and that the diffusive motion brings it from one minimum to an adjacent one on the free energy surface in the configuration space spanned by the substrate and adatom coordinates. According to Eq. (1) the two ingredients we need are the effective attempt frequency $\Gamma_0^{(j)}$ and the activation energy barrier $E_{\mathrm{d}}^{(j)}$. Both can be obtained by DFT calculations. The key quantity for the evaluation of $E_{\mathrm{d}}^{(j)}$ is the potential energy surface (PES) which is the potential energy surface seen by the diffusing adatom. The PES is defined as:

$$E^{\mathrm{PES}}(X_{\mathrm{ad}}, Y_{\mathrm{ad}}) = \min_{Z_{\mathrm{ad}}, \{\mathbf{R}_I\}} E^{\mathrm{tot}}(X_{\mathrm{ad}}, Y_{\mathrm{ad}}, Z_{\mathrm{ad}}, \{\mathbf{R}_I\}) \quad , \tag{3}$$

where $E^{\mathrm{tot}}(X_{\mathrm{ad}}, Y_{\mathrm{ad}}, Z_{\mathrm{ad}}, \{\mathbf{R}_I\})$ is the ground-state energy of the many-electron system (also referred as the total energy) at the atomic configuration $(X_{\mathrm{ad}}, Y_{\mathrm{ad}}, Z_{\mathrm{ad}}, \{\mathbf{R}_I\})$. Here, $(X_{\mathrm{ad}}, Y_{\mathrm{ad}}, Z_{\mathrm{ad}})$ are the coordinates of the adatom and $\{\mathbf{R}_I\}$ represent the set of positions of the substrate atoms. According to Eq. (3) the PES is the minimum of the total energy with respect to the $z$-coordinate of the adatom $Z_{\mathrm{ad}}$ and all coordinates of the substrate atoms $\{\mathbf{R}_I\}$. Under the assumption of negligible vibrational effects, the minima of the PES represent stable and metastable sites of the adatom. Moreover, we consider the dynamics of the electrons and of the nuclei decoupled (Born-Oppenheimer approximation) that is usually well justified for not too high temperatures. We note that the results of a KMC study of growth will be the same as that of a MD simulation, provided that the underlying PES is the same; however, as pointed out above, KMC can handle significantly longer times.

Now consider all possible paths $l$ to get from one stable or metastable adsorption site, $\mathbf{R}_{\mathrm{ad}}$, to an adjacent one, $\mathbf{R}_{\mathrm{ad}}'$. The energy difference $E_{\mathrm{d}l}$ between the energy at the saddle point along

$l$ and the energy of the initial geometry is the barrier for this particular path. If the vibrational energy is small compared to $E_{\mathrm{d}l}$, the diffusion barrier then is the minimum value of all $E_{\mathrm{d}l}$ of the possible paths that connect $\mathbf{R}_{\mathrm{ad}}$ and $\mathbf{R}_{\mathrm{ad}}{}'$, and the lowest energy saddle point is called the *transition state*. Although often only the path with the most favorable energy barrier is important, it may happen that several paths exist with comparable barriers or that the PES consists of more than one sheet (e.g. Ref. [19]). Then the *effective* barrier measured in an experiment or a molecular dynamics (MD) simulation represents a thermodynamic average over all possible pathways.

For calculating the second basic quantity, $\Gamma_0^{(j)}$, Transition State Theory (TST) [20] provides a good framework. Within the harmonic approximation $\Gamma_0^{(j)}$ is proportional to the ratio between the products of the normal mode frequencies of the system with the adatom at the equilibrium site and at the saddle point. The normal mode frequencies are obtained by diagonalization of the force constant matrix for the system with the adatom at the equilibrium site and at the transition point. The force constant matrix reflects the interactions of the adatom with the substrate and can be derived from DFT calculations [19]. TST is only valid when $E_{\mathrm{d}}^{(j)}$ is larger than $k_{\mathrm{B}}T$. When this requirement is not fulfilled, the appropriate tool is Molecular Dynamics (MD). In several works the attempt frequency has the same value for all the processes, and this value lies in the range of the highest phonon vibration or the Debye frequency. However, this assumption may not be correct. First, processes with larger activation barriers may be characterized by a larger attempt frequency than processes with smaller energy barriers [21]. Moreover, processes that involve a different number of particles and different bonding configurations may also be characterized by different attempt frequencies. For examples, experimental analyses have given $\Gamma_0^{(j)}$ for exchange diffusion larger by up to two orders of magnitude than for hopping [22].

An important step in the description of growth is *nucleation*. This is the process by which two or more mobile adatoms meet and form a stable cluster. A cluster that is formed can suffer two main fates, provided that other mobile species are available. Either the cluster dissolves again into smaller constituents or it survives and ultimately grows, as more adatoms add to its periphery. In the second case the cluster acts as the initial nucleus for the growth of islands. If agglomerates of $i^* + 1$ and more adatoms are stable against break-up, $i^*$ is called the size of the "critical nucleus" [23].

## 8.4 Results: Al/Al (111)

Having discussed the basic concepts (see Fig. 1) we describe the results obtained by combining the DFT results for Al on Al (111) obtained by Stumpf and Scheffler [14] with a realistic KMC simulation that takes into account the correct structure of the system. As already mentioned, the (111) surface of an fcc crystal is characterized by the presence of the two types of close-packed steps, shown in Fig. 2. Experimentally it has been shown that for Pt (111) [1] and Ir (111) [24] these two steps behave quite differently with respect to surface diffusion and growth. For Al (111) the DFT calculations [14] predict that the formation energies of the two steps are different with a lower energy cost for the formation of the {111} faceted step than of the {100} faceted step: 0.232 eV per atom vs. 0.248 eV per atom. Thus, the two steps have not the same equilibrium properties. What happens during growth far from equilibrium?

Stumpf and Scheffler [14] analyzed microscopic diffusion processes and in particular determined the activation energies $E_{\mathrm{d}}$ for:

(*i*) diffusion of a single adatom on the flat surface: $E_{\mathrm{d}} = 0.04$ eV;

(*ii*) diffusion from upper to lower terraces which was found to proceed by an exchange with a step-edge atom: $E_{\mathrm{d}} = 0.06$ eV for the $\{100\}$ step and $E_{\mathrm{d}} = 0.08$ eV for the $\{111\}$ step;

(*iii*) diffusion parallel to the $\{100\}$ step via hopping: $E_{\mathrm{d}} = 0.32$ eV (0.44 eV for exchange);

(*iv*) diffusion parallel to the $\{111\}$ step via exchange: $E_{\mathrm{d}} = 0.42$ eV (0.48 eV for hopping).

The DFT calculations give that the binding energy of two adatoms in a dimer is 0.58 eV [14], and we therefore assume that dimers, once they are formed, are stable, i.e., they will not dissociate and $i^* = 1$. Moreover, we assume that dimers are immobile. We note that the reported value for the self-diffusion energy barrier is rather low (0.04 eV) [14] and comparable to the energy of optical phonons of Al (111) ($\approx 0.03$ eV). Since these phonon levels are highly populated at room temperature, simulations for $T > 300$ K may not be reliable because the concept of uncorrelated jumps between nearest neighbor sites is no more valid: In the reached site the adatom cannot cancel the correlation with the previous jumps since it stays there too shortly in order to be thermally equilibrated through the interaction with the substrate. We therefore limited our study to substrate temperatures $T \leq 250$ K.

We adopt periodic boundary conditions, and our rectangular simulation area is compatible with the geometry of an fcc (111) surface. The dimensions of the simulation area are $1718 \times 2976$ Å$^2$. These dimensions are a critical parameter and it is important to ensure that the simulation area is large enough that artificial correlations of neighboring cells do not affect the formation of growth patterns. The mean free path $\lambda$ of a diffusing adatom before it meets another adatom with possible formation of a nucleation center or is captured by existing islands is proportional to $(D/F)$ [26] where $D$ and $F$ are the diffusion constant on the flat surface and the deposition rate, respectively, and should be smaller than the linear dimension of the simulation array. Because of the fast diffusion of a single adatom Al on the flat (111) surface our cell is large enough (for the imposed deposition rate of 0.08 ML/s) for $T < 150$ K, whereas for $T \geq 150$ K the dimensions of the cell are too small, and the island density is determined by the simulation array rather than the physics. Nevertheless, the island shape is determined by local processes (edge diffusions) and is still meaningful.

In the KMC program two additional insights extracted from the DFT calculations are included: (*i*) the attractive interaction between steps and single adatoms, and (*ii*) the fact that diffusion processes take place via different mechanisms (hopping or exchange). Particularly the second point plays an important role in our investigation, as already mentioned in the Section 8.3: Processes as hopping and exchange may be characterized by different attempt frequencies. For Al surfaces calculations with the embedded atom method [27] showed a difference of prefactors (and therefore, attempt frequencies) of one order of magnitude.

Some results of the *ab initio* KMC simulations are approximately drawn in Fig. 4 for a coverage of $\Theta = 0.04$ ML and $T = 150$, 200, and 250 K [25]. We discuss briefly the results for $T = 50$ K that are contained in Ref. [6]. With the substrate at this temperature during growth the shape of the islands is highly irregular and indeed fractal. Adatoms which reach a step cannot break away from it and they even cannot diffuse along the steps. Thus, at this temperature ramification occurs into random directions, and island formation can be understood in terms of the so-called *hit and stick* model (see also Ref. [28]). From Fig. 4 it appears that at a growth temperature $T = 150$ K the islands assumes a triangular shape with their sides being $\{100\}$ steps. Increasing the temperature to $T = 200$ K a transition from triangular to hexagonal form occurs and for $T = 250$ K the islands become triangular again. However, at this temperature they are mainly bounded by $\{111\}$ steps. Another interesting aspect of the simulations is the appearance of a rough ordered arrangement of the islands obtained at low temperatures ($T =$ 50 K and 150 K, cf. Ref. [25]). This arrangement is a kinetic effect and reflects the fact that the average distance between neighboring islands is proportional to $(D/F)^{\chi}$ where $\chi$ depends on the size of the critical nucleus $i^{*}$.

To understand the island shapes in the temperature regime between 150 and 250 K we consider the mobility of the adatoms along the steps (at such temperatures the adatoms at the step edges cannot leave the steps): The lower the migration probability along a given step edge, the higher is the step roughness and the faster is the growth normal to this step edge, that is, the faster is its speed of advancement. Thus, this step edge shortens as a result of the growth kinetics and eventually it may even disappear. Since diffusion along the densely packed steps on the (111) surface (the $\{100\}$ and $\{111\}$ facets) is faster than along steps with any other orientation this criterion explains the presence of islands which are mainly bounded by $\{100\}$ or $\{111\}$ steps. The same argument can be extended to the diffusion along the two close-packed steps and applied to the triangular islands at $T = 150$ K, where the energy barrier for the diffusion along the $\{111\}$ facet is larger and thus the $\{100\}$ steps survive so that triangular islands with $\{100\}$ sides are obtained. By considering the energy barriers we would expect only these islands, until the temperature regime for the thermal equilibrium is reached. However, the diffusion of adatoms is not only governed by the energy barrier but also by the attempt frequency, i.e., the prefactor $\Gamma_0$ [cf. Eq. (1)]. For Al/Al(111) the effective attempt frequencies have not been calculated, but the analysis of Ref. [14] proposes that the exchange process should have a larger attempt frequency than the hopping process. The results displayed in Fig. 4 are obtained with $\Gamma_0 = 1.0 \times 10^{12}$ s$^{-1}$ for the diffusion on the flat surface, $\Gamma_0 = 2.5 \times 10^{12}$ s$^{-1}$ for the jump along

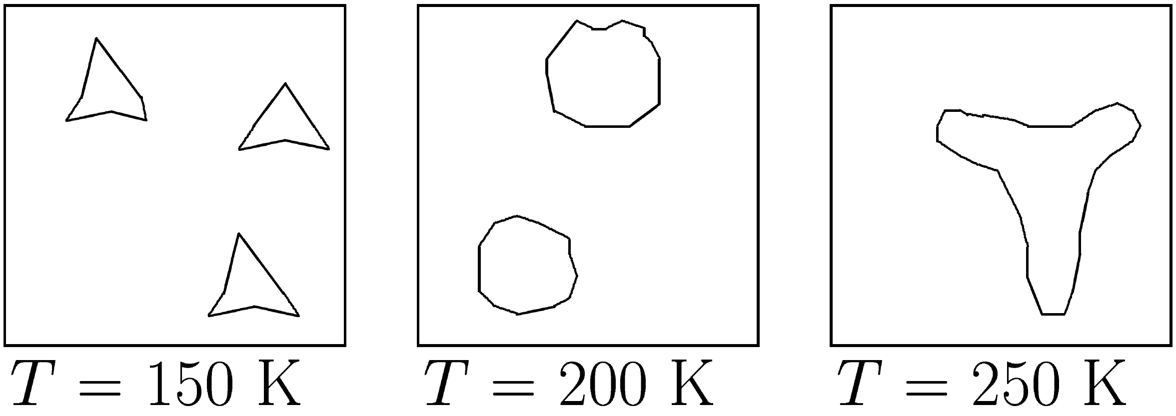

Figure 4: Hand-drawing of islands assembled at three different substrate temperatures. For good figures see Ref. [25]. The surface area of (1718 × 1488) Å$^2$ (half of the simulation array), the deposition rate was 0.08 ML/s, and the coverage in each picture is $\Theta = 0.04$ ML.

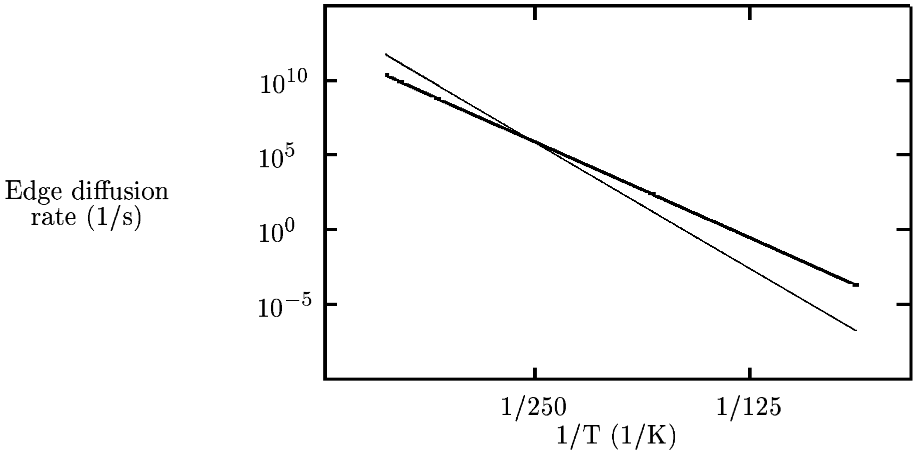

Figure 5: Temperature dependence of the edge diffusion rates (in $s^{-1}$) for atom diffusion along the {100} step by hopping with $\Gamma_0 = 2.5 \times 10^{12}$ $s^{-1}$ (thick solid line), and along the {111} step by exchange with $\Gamma_0 = 2.5 \times 10^{14}$ $s^{-1}$ (thin solid line).

the {100} step, and $\Gamma_0 = 2.5 \times 10^{14}$ $s^{-1}$ for the exchange along the {111} step. These effective attempt frequencies are the only input of the KMC not calculated explicitly by DFT, but were estimated from the theoretical PES as well as from experimental data for other systems. In Fig. 5 the edge diffusion rates along the two steps are plotted as a function of the reciprocal temperature. At lower temperatures the energy barrier dominates the diffusion rate but at $T =$ 250 K the attempt frequencies start to play a role and lead to faster diffusion along the {111} facet than along the {100} one. Thus, the latter steps disappear and only triangles with {111} sides are present. The roughly hexagonally shaped islands at $T = 200$ K are a consequence of the equal advancement speed for the two steps at that temperature. Obviously, the importance of the attempt frequencies should receive a better assessment through accurate calculations, and work in this direction is in progress. While no experimental data for Al/Al (111) are presently available we note that a similar sequence of islands as obtained above has been observed for Pt on Pt (111) by Michely *et al.* [1].

An interesting point is the evolution of the island shapes with time. This aspect is related also with a peculiarity of the triangular islands at $T = 250$ K (cf. Fig. 4): They exhibit concave sides. In order to understand this behavior we have checked the island shape at different times for the deposition at $T = 250$ K. The results are collected in Fig. 6 [25]. After 0.07 s the islands are roughly hexagonal and upon successive deposition they evolve into a nearly triangular shape. The longer sides are formed by straight {111}-faceted step edges but short {100}-faceted edges can still be identified, at least for $t \leq 0.1$ s. The latter edges become rougher and progressively disappear. Note that the development of a triangular island requires $t \sim 0.2$ s. This time is remarkably long, provided that diffusion of adatoms on the flat surface is fast at $T = 250$ K, and it confirms the need of a KMC approach for investigating in a reliable way the evolution of growth patterns. The shape of the island is the result of several processes with different time scales that are accounted for in the KMC scheme. A further confirmation of this collective action is given by the value of the temperature at which the advancement speeds for the two steps are practically equal. This corresponds at the crossing point of the two diffusion rates in Fig. 5 at

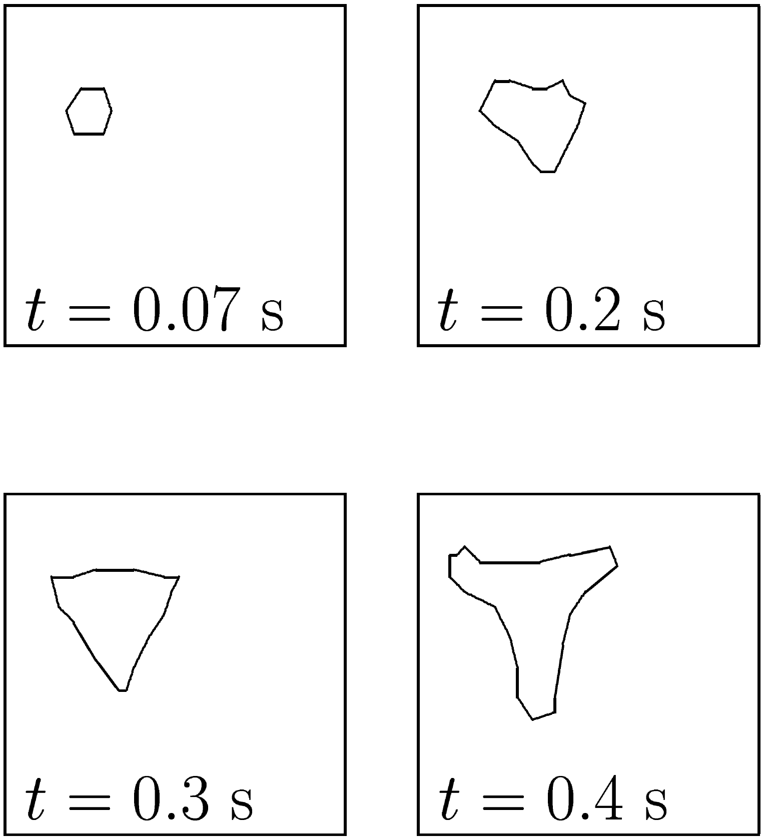

Figure 6: Hand-drawing of islands of islands at $T = 250$ K as they develop in time $t$. For good figures see Ref. [25]. The section of the simulation cell that is shown is $1718 \times 1488$ Å$^2$ and the deposition rate is 0.08 ML/s.

$T = 250$ K. From simulations this temperature is lower ($T = 200$ K). Going back to the time evolution, at $t = 0.3$ s the sides are still nearly straight, but at $t = 0.4$ s the concavities appear. The corners of the triangles seem to increase their rate of advancement during deposition. The effect can be understood on the basis of competition between adatom supply from the flat surface and mass transport along the sides. The adatom concentration field around an island exhibits the steepest gradient close to the corners, and the corners of the islands receive an increased flux of adatoms. When the sides of the islands are not too long, this additional supply of adatoms is compensated by the mass transport along the steps, i.e., the adatoms have a high probability to leave the region around the corners before the arrival of the successive adatom. For $t = 0.3$ s this scenario still seems to be true, while at $t = 0.4$ s the island edges are longer and the mass transport along the sides is not able to compensate the additional supply of particles at the corners. This means that the probability for a particle to leave the corner region and to move along the island edge before being reached by another particle decreases considerably, and the corners start to grow faster than the sides of the triangles so that the concave shape develops.

In summary, we have shown how detailed microscopic information can be combined with KMC simulations in order to gain insight in the *time* evolution of the structures assembled during growth. As we have shown for Al on Al (111), islands modify their shapes when the substrate temperature is changed, and the origin of these transitions lies in the microscopic nature of the diffusion processes occurring onto the surface. Moreover, growth patterns may develop on a time scale of seconds that cannot be reached with MD simulations, and the *ab initio* KMC approach seems to be a very powerful tool to overcome size and time limitations without loosing the microscopic description or accuracy.

## 8.5 Acknowledgments

We thank Christian Ratsch (Berlin) for many valuable discussions. One of the authors (P.R.) thanks D.E. Wolf (Duisburg) for the kind hospitality and the financial support during his stay at the HLRZ in Jülich.

# References

[1] T. Michely, M. Hohage, M. Bott, and G. Comsa, Phys. Rev. Lett. **70**, 3943 (1993).

[2] M. Hohage, T. Michely, and G. Comsa, Surf. Sci. **337**, 294 (1995).

[3] H. Brune, C. Romalnczyk, H. Röder, and K. Kern, Nature **369**, 469 (1994).

[4] E. Pehlke, N. Moll, and M. Scheffler, in *Advances in Computational Material Science*, eds. V. Fiorentini and F. Meloni (Editrice Compositori, Bologna, 1997), p. 23.

[5] A. Gross and M. Scheffler, J. Vac. Sci. Technol., in press; submitted to Phys. Rev. B.

[6] P. Ruggerone, C. Ratsch, and M. Scheffler, in *The Chemical Physics of Solid Surfaces*, vol. 8, Eds. D.A. King and D.P. Woodruff (Elsevier Science, Amsterdam, 1997), in press.

[7] G. Ehrlich and F.G. Hudda, J. Chem. Phys. **44**, 1039 (1966); R.L. Schwoebel and E.J. Shipsey, J. Appl. Phys. **37**, 3682 (1966).

[8] D.W. Bassett and P.R. Webber, Surf. Sci. **70**, 520 (1978).

[9] J.D. Wrigley and G. Ehrlich, Phys. Rev. Lett. **44**, 661 (1978).

[10] G.L. Kellog and P.J. Feibelman, Phys. Rev. Lett. **64**, 3143 (1990).

[11] C. Chen and T.T. Tsong, Phys. Rev. Lett. **64**, 3147 (1990).

[12] P.J. Feibelman, Phys. Rev. Lett. **65**, 729 (1990).

[13] B.D. Yu and M. Scheffler, submitted to Phys. Rev. Lett.

[14] R. Stumpf and M. Scheffler, Phys. Rev. Lett. **72**, 254 (1994); *ibid.* **73**, 508 (1995)(E); Phys. Rev. B **53**, 4958 (1996).

[15] B.D. Yu and M. Scheffler, Phys. Rev. Lett. **77**, 1095 (1996); Phys. Rev. B **55**, 13916 (1997).

[16] A. Madhukar, Surf. Sci. **132**, 344 (1983); S. Clarke and D.D. Vvedensky, Phys. Rev. Lett. **58**, 2235 (1987); H. Metiu, Y.-T. Lu, and Z. Zhang, Science **255**, 1088 (1992).

[17] M.C. Bartelt and J.W. Evans, Phys. Rev. Lett. **75**, 4250 (1995); Z. Zhang, X. Chen, and M. Lagally, Phys. Rev. Lett. **73**, 1829 (1994); J.G. Amar and F. Family, Phys. Rev. Lett. **74**, 2066 (1995); S.V. Khare, N.C. Bartelt, and T.L. Einstein, Phys. Rev. Lett. **75**, 2148 (1995).

[18] S. Liu, Z. Zhang, G. Comsa, and H. Metiu, Phys. Rev. Lett. **71**, 2967 (1993); J. Jacobsen, K.W. Jacobsen, P. Stolze, and J.K. Nørskov, Phys. Rev. Lett. **74**, 2295 (1995); Z.-P. Shi, Z. Zhang, A.K. Swan, and J.F. Wendelken, Phys. Rev. Lett. **76**, 4927 (1996); S. Liu, L. Bönig, J. Detch, and H. Metiu, Phys. Rev. Lett. **74**, 4495 (1995).

[19] A. Kley and M. Scheffler, in *The Physics of Semiconductors*, Eds. M. Scheffler and R. Zimmermann (World Scientific, Singapore, 1996), 1031.

[20] G.H. Vineyard, J. Phys. Chem. Solids **3**, 121 (1957); G. Wahnström, in *Interaction of Atoms and Molecules with Solid Surfaces*, eds. V. Bortolani, N.H. March, and M.P. Tosi (Plenum Press, New York and London, 1990), p. 529.

[21] G. Boisvert, L.J. Lewis, and A. Yelon, Phys. Rev. Lett. **75**, 469 (1995).

[22] G. Ayrault and G. Ehrlich, J. Chem. Phys. **60**, 281 (1974); S.C. Wang and G. Ehrlich, Phys. Rev. Lett. **62**, 2297 (1989); G.L. Kellog, Surf. Sci. **246**, 31 (1991).

[23] C. Ratsch, A. Zangwill, P. Šmilauer, and D.D. Vvedensky, Phys. Rev. Lett. **72**, 3194 (1994); C. Ratsch, P. Šmilauer, A. Zangwill, and D.D. Vvedensky, Surf. Sci. **329**, L599 (1995).

[24] S.C. Wang and G. Ehrlich, Phys. Rev. Lett. **67**, 2509 (1991)

[25] The figures with the true results are contained in the paper quoted under Ref. [6]. This article can be obtained on WWW at **http://www.fhi-berlin.mpg.de/th/paper.html**.

[26] S. Stoyanov and D. Kashchiev, in *Current Topics in Material Science*, ed. E. Kaldis (North-Holland, Amsterdam, 1981), vol. 7, pp. 69 - 141.

[27] C.L. Liu, J.M. Cohen, J.B. Adams, and A.F. Voter, Surf. Sci. **253**, 334 (1991).

[28] T.A. Witten and L.M. Sander, Phys. Rev. Lett. **47**, 1400 (1981); Phys. Rev. B **27**, 5686 (1983).