Ψ_k Newsletter

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

Number 28   August 1998

Contents

1 Editorial

In this Newsletter we have a report on the TMR1-Network's second annual meeting which took place at the beginning of June in Vienna. It contains the programme and abstracts of all presented papers. In this issue, there is also a report on the *'Industry Workshop'* which took place in Viena on 3-4 June. Additionally to the abstract of presented papers, this report contains also the scientific highlights of the Workshop. Moreover, readers will also find abstracts in the usual section dedicated to them. There are also a few conference/workshop announcements in various sections and readers are advised to check the table of contents for details. General job announcements can be found in the usual place. The scientific highlight of this Newsletter is by B. Nonas, K. Wildberger, R. Zeller, and P.H. Dederichs on **'Energetics of 3d impurities on the (001) surface of iron'**.

The *Networks* have a home page on World Wide Web (WWW). Its *Uniform Resour ce Locator* (URL) is:

http://www.dl.ac.uk/TCSC/HCM/PSIK/main.html

The above contains pointers to several other nodes: *O.K. Andersen (Stuttgart), P. Blöchl (IBM, Zürich), M. Gillan (Keele), E.K.U. Gross (Univ. Würzburg), B.L. Györffy (Bri stol), V. Heine (Univ. Cambridge), R. Jones (Univ. Exeter), J. Kübler (TH, Darmstadt), J.L. Martins (INESC, LISBON), R. Nieminen (TU, Helsinki), J. Nørskov (TU, Lyngby)* with information on CAMP, *M. Scheffler (FHI Berlin), K.-H. Schwarz (TU, Vienn a), G.P. Srivastava (Univ. Exeter), A. Walker (UEA Norwich)*, and *A. Zupan (Department of Physical and Organic Chemistry, Jozef Stefan Institute, Ljubljana, http://www-k3.ijs.si/ales/pp.html.* There are also pointers to the WWW home page of the Solid State Theory Group at National Renewable Energy Laboratory, Golden, CO 80401 *(http://www.sst.nrel.gov)*, and to the home page of Prof. David Vanderbilt, Department of Physics and Astronomy, Rutgers University *http://www.physics.rutgers.edu/ dhv.* If you maintain a home page on your activities we will be happy to include a pointer from the *Networks'* home page to your home page.

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

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

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

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

2   General News

As you may have noticed the activities of the two TMR Networks and the ESF Programme, covered by this Newsletter, are often very strongly linked. In most cases more than one or all of them coorganize a workshop or a conference. Therefore, frequently it is not possible to uniquely assign reports or announcements to specially dedicated sections. This is why sometimes we have to join sections and in other cases place reports or announcements in a section belonging to one network only, however, providing clear statement concerning involvement of other networks. At first sight, it may appear cumbersome to the readers, although the choices are always made on the basis of credits due to a given network or programme concerning particular activity. In this Newsletter, it is the case for the report on the *Industry Workshop* and the announcement of the TB-LMTO Workshop.

The ESF Programme Board meeting took place during the *Industry Workshop* in Vienna in June. A financial support for a number of workshops and conferences was approved. Moreover, a policy of supporting individual collaborative visits was established and since then already a few have been approved. As mentioned in the preceding Newsletters, all researchers from countries participating in the ESF Programme are welcome to apply to **psik-management@dl.ac.uk** for funding of intended visits by submitting a short scientific proposal and a cost statement.

In the past Newsletters it was mentioned that in July 2000, we are intending to organize a conference, which will be a follow-up of the big Ψ_k-Conference in Schwäbisch Gmünd of September 1996. Therefore, we would appreciate very much if you shared with us your thoughts on the need for such a conference and the suitability of date.

3 News from the TMR1 Network

3.1 TB-LMTO Workshop Announcement

WORKSHOP ON THE TB-LMTO METHOD

Monastery of Mont Saint Odile - France (one hour drive from Strasbourg)
2-5 october 1998

Supported by TMR * "Interface Magnetism" and ESF**
Program STRUC (Electronic Structure Calculations for elucidating the complex atomistic
behaviour of solids and surfaces)

MOTIVATION

In recent years, computational materials science has clearly emerged as an important field in
its own right. It is now well established that methods based on a microscopic description of the
electronic structure are central points. In order to describe always larger systems, localized
orbitals approaches are very useful. The TB-LMTO (Tight-Binding Linear Muffin-Tin
Orbitals) method combines the precision of the ab-initio methods and the flexibility of the
tight-binding schemes. The always increasing facilities provided by the supercomputers has for
good shown the interest of the order N methods. For thoses reasons the TB-LMTO is widely
used to study many different problems. This workshop intends to allow a large meeting of
scientists involved in the development and the use of this method. The workshop will focus on
the magnetic properties but other field of applications will be considered

SCOPE

The workshop will have two parts. The most important one will be devoted to invited talks
where speakers will be asked to present the fundamental aspects of the problems. In a second
part applications of this method will emphasize the interest of the method.

Aspects to be covered include:

- - Full Potential approaches

- - Relativistic DFT

- - Toward an Implementation of Relativistic DFT

- - Magnetic anisotropy

- - Non-collinearity

- - Alloy: CPA-TB-LMTO

- - Magnetic Interlayer coupling

- - Surface segregation and Surface roughness

- - Spectroscopic aspects

- - Response function

- - Recursion method

- - Latest developments of order(N)

- - Large systems studies

- - Sparse matrix techniques

The confirmed **invited** speakers are (14/7/98):

I. Abrikosov (Uppsala), O. Andersen (Stuttgart), M. Alouani (Strasbourg), H. Ebert (Munich), O. Eriksson (Uppsala), J. Hafner (Vienna), J. Kudrnovsky (Praha), M. Methfessel (Frankfurt/Oder), D. Stoeffler (Strasbourg), H. Skriver (Aarhus), I. Turek (Brno), W. Temmerman (Daresbury) and J. Wills (Los Alamos).

To be confirmed: I. Duff (RAL, Daresbury)

FINANCIAL SUPPORT

A large number of PhD students or post-docs are expected to participate. Financial support of the TMR network " Interface Magnetism" and of the ESF program STRUC could be provided to elegible persons. The housing costs will be moderate and the fees modest. The total number of participants should not go beyond sixty.

PUBLICATION

We intend to publish a book about the TB-LMTO method, giving all basic aspects of this method (which now can be found only in specialised publications) and few applications.This book will consist of selected contributions to this workshop and have around 300 pages.

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PREREGISTRATION

I would like to be informed on this TB-LMTO workshop; YES - NO
I intend to participate to this TB-LMTO workshop: YES - NO
I intend to present a contribution (tentative title):
I would need a financial support: YES - NO
Name, Last name:
Address:
Tel:
Fax:
E-mail:

————————————————————————————————————

ORGANIZATION

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* Training and Mobility Research, a european network sponsored by the EC.

** European Science Fundation

Training and Mobility of Researchers (TMR) Network

"Interface Magnetism"

SECOND ANNUAL MEETING

Technische Universität Wien

June 5 – June 7, 1998

Vienna, Austria

PROGRAM AND ABSTRACTS

Center for Computational Materials Science
(CMS)

The second annual meeting of the TMR Network on Interface Magnetism took place in Vienna on June 5-7, 1998. More than 70 researchers from the Austrian, Dutch, French, German, Swedish and UK nodes attended this meeting. The following pages show the abstracts of the talks. European collaborations accounted for 30% of the contributions, which is a substantial increase on last years' annual meeting in Bristol. This reflects a growing trend, facilitated by the TMR Network, to tackle the most demanding computational projects internationally, since no country on its own has all the necessary computational expertise.

This TMR-Network combines the effort of scientists from 13 different universities, 2 research institutions and one industrial laboratory. It is structured around six flagship projects. Four of these projects include studies of the most recent discoveries of interlayer coupling, magnetic anisotropy and surface structure, giant magnetoresistance and magnetic X-ray dichroism. The remaining two projects are concerned with the implementation of new technical developments in electronic structure calculations, specifically screened structure constants, to construct a new generation of codes capable of dealing with ever larger systems. Through the TMR-Network collaborations progress has been substantially accelerated, in particular, in the development of the screened KKR method and its application to GMR.

The proceedings of this meeting are to be published in the December 1998 issue of Philosophical Magazine. It is gratifying to see that more than 50% of these papers have been presented by young researchers under 35 years of age, who include the TMR employed post-doctoral researchers.

The development and accomplishments of this TMR-Network have greatly benefited from the altruistic dedication and major scientific vision of Prof. Peter Dederichs (Forschungszentrum Juelich, Germany) and Prof. Balazs Gyorffy (University of Bristol, UK). It so happens that this year they celebrate their 60-th birthdays. Therefore, we use this opportunity to wish them continued scientific accomplishments and thank them for their indispensable involvement and contributions to the TMR-Network on *"Interface Magnetism"*. Many happy returns to both of them!

Walter M. Temmerman
(The Network Coordinator)

- **Interlayer Coupling (IEC)**

  1. J. Opitz, P. Zahn, and I. Mertig
     "Interlayer exchange coupling: A comparison of two theoretical concepts"
     Nodes: <u>G</u>

  2. S. Simak
     "Exchange coupling in $Fe/(Mo_{1-x}Re_x)_n/Fe(100)$ and (110) multilayers"
     Nodes: <u>S</u>

  3. S.S.A. Razee, J.B. Staunton, F.J. Pinski, B. Ginatempo, and E. Bruno
     "Effect of atomic short-range order on magnetic anisotropy"
     Nodes: <u>UK</u>

  4. V. Drchal, J. Kudrnovský, P. Bruno, P.H. Dederichs, and P. Weinberger
     "The combined effect of temperature and disorder on interlayer exchange coupling in magnetic multilayers"
     Nodes: <u>A</u>, F, G

  5. N.N. Lathiotakis, B.L. Gyorffy, J.B. Staunton, B. Újfalussy, B. Ginatempo, E. Bruno
     "Periods and damping of the oscillatory exchange coupling across $Cu_{(1-x)}Ni_x$, $Cr_{(1-x)}V_x$ and $Cr_{(1-x)}Mo_x$ binary alloy spacers"
     Nodes: <u>UK</u>

  6. I. Turek, P. Weinberger, M. Freyss, D. Stoeffler, and H. Dreyssé
     "Interfacial interdiffusion and magnetic properties in Fe/Cr mulitlayers"
     Nodes: <u>A</u>, F

- **Magnetic Anisotropy and Surface (Interface) Electronic Structure (MAE)**

    1. O. Eriksson and P.Ravindran
       "Giant magneto-crystalline anisotropy and magneto-optical effects in binary inter-metallics"
       Nodes: <u>S</u>

    2. P. James
       "Magnetic anisotropy in tetragonal and trigonal Fe, Co, and Ni"
       Nodes: <u>S</u>

    3. T. Korhonen, N. Papanikolaou, R. Zeller, and P.H. Dederichs
       "Ab-initio calculations of forces and lattice relaxations"
       Nodes: <u>G</u>

    4. J. Henk, A.M.N. Niklasson, B. Johansson, and H.L. Skriver
       "Magnetic structure of ultra-thin Ni films on Cu(001)"
       Nodes: <u>S</u>

    5. C. Sommers, C. Uiberacker, P. Weinberger, and L. Szunyogh
       "Electronic structure and magnetic properties of ferromagnetic FeCu "superlattices" on Cu(100)"
       Nodes: <u>F</u>, A

    6. J. Zabloudil, C. Uiberacker, U. Pustogowa, L. Szunyogh, and P. Weinberger
       "Layer-resolved anisotropy energies of free surfaces of (Fe-x-Co(1-x))n/Cu(100)"
       Nodes: <u>A</u>

    7. L. Szunyogh, J. Zabloudil, P. Weinberger, and C. Sommers
       "Concentration dependent spin-flip energies of alloyed surface magnets"
       Nodes: <u>A</u>, F

    8. L. Udvardi and L. Szunyogh
       "Ab initio calculation of Heisenberg parameters for thin magnetic films"
       Nodes: <u>A</u>

    9. R. Abt, G. Bihlmayer, T. Asada, and S. Blügel
       "Magnetic Surface Alloys: Recent progress"
       Nodes: <u>G</u>, A

    10. S. Blügel, J. Redinger, and R. Podloucky
        "Role of surface orientation on the ferromagnetism of $3d$, $4d$ and $5d$ transition-metal monolayers on Ag"
        Nodes: <u>G</u>, A

    11. R. Hafner, R. Lorenz, and J. Hafner
        "Electronic structure and magnetic properties of Fe-Cr multilayers"
        Nodes: <u>A</u>

- **Giant Magnetoresistance (GMR)**

  1. J. Binder, P. Zahn, I. Mertig, R. Zeller, and P.H. Dederichs
     "Magnetic properties of impurities and impurity pairs in magnetic multilayers"
     Nodes: G

  2. Arne Brataas, Yu. V. Nazarov, J. Inoue, and Gerrit E. W. Bauer
     "Non-equilibrium spins and Coulomb charging in ferromagnetic double barrier junctions"
     Nodes: NL

  3. C. Blaas, L. Szunyogh, P. Weinberger, I. Mertig, C. Sommers, and P.M. Levy
     "GMR of interdiffused Co/Cu layered systems"
     Nodes: A, G, F

  4. A. Pasturel, E.Yu. Tsymbal, and D. Nguyen Manh
     "Spin-polarized electron tunneling in the Co/Al_2O_3 interface"
     Nodes: F

- **Spin-polarized Spectroscopies (SPEC)**

  1. A. Delin
     "Calculated magneto-optical spectra of 3d elements and compounds"
     Nodes: S

  2. V. Popescu and H. Ebert
     "A theoretical description of spin-resolved Appearance Potential Spectroscopy of magnetic surface layer systems"
     Nodes: G

  3. T. Huhne and H. Ebert
     "A scheme to deal with the magneto-optical properties of surface layer systems"
     Nodes: G

  4. A. Ernst, W. M. Temmerman, Z. Szotek, and P. J. Durham
     "Real-space non-relativistic angle-resolved photoemission"
     Nodes: UK

  5. A. C. Jenkins, W. M. Temmerman, K. Attenkofer, V. Popescu, and H. Ebert
     "Magnetic circular dichroism in Gadolinium metal: The L edges."
     Nodes: UK, G

  6. U. Pustogowa, L. Szunyogh, and P. Weinberger
     "Spin-polarized XE spectroscopy for disordered semi-infinite systems"
     Nodes: A

- **Tight-Binding KKR-Green's Function Methods (KKR)**

  1. L. Petit, S.V. Beiden, W.M. Temmerman, Z. Szotek, G.M. Stocks, and G.A. Gehring
     "Screened Real Space Study of the Magnetic Properties of Co and Ni."
     Nodes: UK

  2. P. Zahn, I. Mertig, R. Zeller, and P.H. Dederichs
     "Screened KKR with hard core potentials"
     Nodes: G

  3. R. Zeller, T. Hoshino, M. Asato, J. Zabloudil, P. Weinberger, and P.H. Dederichs
     "Total energy calculations with the Full-Potential KKR method"
     Nodes: G, A

  4. C. Uiberacker, J. Zabloudil, A. Ernst, P. Weinberger, and P.H. Dederichs
     "Layer relaxation within the Screened KKR method"
     Nodes: A, UK, G

- **Real Space Tight-Binding LMTO Methods (LMTO)**

  1. .

  2. I. Galanakis, M. Alouani, J. M. Wills, M. Pérez Jigato, and H.Dreyssé
     "A real-space full-potential LMTO method for non-collinear magnetism"
     Nodes: F

  3. J. Izquierdo, A. Vega, O. Elmouhssine, H. Dreyssé, and C. Demangeat
     "Induced V polarization at the interface with Fe: $Fe_n V_m$ superlattices and thin V_m films on Fe substrate"
     Nodes: F

  4. C. Cornea, M. Freyss, H. Dreyssé, and D. Stoeffler
     "Non collinear magnetism of large systems studied by semi empirical tight binding method"
     Nodes: F

  5. R.Ahuja, O.Eriksson and B.Johansson
     "Electronic and Optical Properties of FeS_2 and CoS_2"
     Nodes: S

- **Other fields (O)**

1. G. M. Stocks, B. Újfalussy, Xindong Wang, D. M. C. Nicholson, W. A. Shelton, Yang Wang, and B. L. Gyorffy "Towards a constrained local moment model for first principle spin dynamics"
   Nodes: UK,A

2. V.Crişan, H.Ebert, P.Entel, and H.Akai
   "The stability of the $Cu_x Zn_y Al_{100-x-y}$ alloys"
   Nodes: G

3. Ph. Mavropoulos, S. Stefanou, R. Zeller, and P.H. Dederichs
   "Hyperfine fields of probe atoms on the Fe and Ni(001) surface"
   Nodes: G

4. A. Mavromaras, L. Nordström
   "Indirect exchange and magnetic ordering in elemental and layered heavy rare earth systems"
   Nodes: S,G

5. B. Nonas, P.H. Dederichs, L.T. Wille, and H. Dreyssé
   "Growth mode of Cr on Fe(001 described by ab-initio interactions"
   Nodes: G, F

6. I.A.Abrikosov and B.Johansson "Application of $O(N)$ LSGF method for calculation of systems with noncollinear magnetic configurations"
   Nodes: S

7. P. Andersson and B. Johansson
   "Magnetic effects in hydrogenated Fe/V superlattices"
   Nodes: S

8. A. Niklasson
   "Interface magnetism of 3d transition metals"
   Nodes: S

9. W. Hofer
   "Electronic structure of a realistic STM - tip: the role of different apex atoms"
   Nodes: A

10. M. Šob, L.G. Wang, and V. Vitek
    " Theoretical tensile strength in metals and intermetallics"
    Nodes: A

11. P. Mohn, E. Supanetz
    "Spinordering in $Fe_{3-x} Mn_x Si$ Heusler alloys"
    Nodes: A

Abstracts

IEC − 1

Interlayer exchange coupling:
A comparison of two theoretical concepts

J. Opitz, P. Zahn, and I. Mertig

TU Dresden, Institut für Theoretische Physik, D-01062 Dresden, Germany

Interlayer Exchange Coupling (IEC) is calculated for (X=Co,Ni)/Cu (100) multilayers. The calculations are based on density functional theory using two different Greens function methods. Results of a supercell formulation with periodically repeated layers are compared to results for bilayers treated as planar perturbations.

The coupling energy is obtained within a frozen potential approximation. It will be shown that the results of both methods are in exellent agreement concering the oscillation periods. Variations of the amplitude should be related to multiple scattering effects in the superlattice.

IEC − 2

Exchange coupling in $Fe/(Mo_{1-x}Re_x)_n/Fe(100)$ and (110) multilayers

N. V. Skorodumova[1], I. A. Abrikosov[1], S. Simak[1], B. Johansson[1], Yu.Kh.Vekilov[1]

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[2]*Condensed Matter Theory Group, Department of Physics,
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The exchange coupling in sandwiches of layers of pure bcc Mo and random bcc $Mo_{88}Re_{12}$ embedded in Fe matrix has been studied by the first-principles Green's function technique. We have calculated up to 20 layers of the spacer material for the planes (100) and (110) and obtained oscillation periods. The exchange coupling amlitude and periodicity are analysed with respect to the two effects: (i) the interface orientation and (ii) the electronic topological transitions resulting in essential difference between the Fermi surfaces of $Mo_{88}Re_{12}$ and pure Mo.

IEC − 3

Effect of atomic short-range order on magnetic anisotropy

S.S.A. Razee[1], J.B. Staunton[1], F.J. Pinski[2], B. Ginatempo[3] and E. Bruno[3]

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We present a theory to study the relation between compositional order and magnetocrystalline anisotropy of ferromagnetic alloys. The ordering phenomenon is represented by static concentration waves. The electronic part is described within the spin-polarised relativistic Korringa-Kohn-Rostoker coherent-potential approximation. This scheme can be used to investigate the change in the magnitude as well as the direction of magnetic anisotropy in an alloy at the onset of ordering. The same framework can also be used to study directional chemical order produced by magnetic annealing. We have calculated the magnetocrystalline anisotropy energy of ordered fcc-$Co_{0.5}Pt_{0.5}$ alloy using this method. We find that the magnetocrystalline anisotropy energy of the ordered phase is two orders of magnitude larger than that of the disordered phase. Also, that the direction of 'easy' magnetisation in the ordered phase depends on the type of ordering. These results are in good agreement with the experimental observations.

IEC − 4

The combined effect of temperature and disorder on interlayer exchange coupling in magnetic multilayers

V. Drchal [1,2]**, J. Kudrnovský** [1,2]**, P. Bruno** [3]**, P.H. Dederichs** [4]**,
and P. Weinberger** [2]

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We study the combined effect of temperature and disorder in the spacer on the interlayer exchange coupling (IEC). The temperature dependence of the IEC is treated 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. The integrals involving the Fermi-Dirac distribution are calculated using an efficient method based on the representation of integrands by a sum of complex exponentials. Application is made to $Co/Cu_{1-x}M_x/Co(001)$ trilayers (M = Zn, Au, and Ni) with varying thicknesses of the spacer.

IEC − 5

Periods and damping of the oscillatory exchange coupling across $Cu_{(1-x)}Ni_x$, $Cr_{(1-x)}V_x$ and $Cr_{(1-x)}Mo_x$ binary alloy spacers

N.N. Lathiotakis[1], B.L. Gyorffy[1], J.B. Staunton[2], B. Újfalussy[3], B. Ginatempo[4], and E. Bruno[4]

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The Fermi surface origin of the periods and damping in the oscillatory coupling across $Cu_{(1-x)}Ni_x$, $Cr_{(1-x)}V_x$ and $Cr_{(1-x)}Mo_x$ alloy spacers was studied. In the case of $Cu_{(1-x)}Ni_x$ ($0 \leq x < 0.5$) spacer, the calculated extremal vectors of the Fermi surface for both (111) and (110) directions are in remarkable agreement with the existing experimental data. The lack of observing of oscillation damping in the same systems is also consistent with the large calculated coherence lengths of the quasiparticle states at the properly defined alloy Fermi surface.

In the case of the $Cr_{(1-x)}V_x$ ($0 \leq x \leq 1$) spacer for the (110) direction, the observed decrease of the oscillation period with x strongly indicates (in agreement to our Fermi surface calculations) that the corresponding extremal vector is the small principal axis of the N-hole ellipsoidal pocket.

Finally, in the case of $Cr_{(1-x)}Mo_x$ ($0 \leq x \leq 1$) and also for the (110) direction, our calculations show that the observed decrease of the oscillation period with concentration x is not necessarily contradictory with the rigid band model (proven to be valid) and could be explained by the lattice deformation of the $Cr_{(1-x)}Mo_x$ layers in the sandwich structures with Iron.

IEC − 6

Interfacial interdiffusion and magnetic properties in Fe/Cr mulitlayers

I. Turek, P. Weinberger

Center for Computational Materials Science, Gumpendorferstr. 1a, A-1060 Wien, Austria

M. Freyss, D. Stoeffler, and H. Dreyssé

Institut de Physique et Chimie des Matériaux de Strasbourg, 23 rue du Loess, BP 20 CR, F-67037 Strasbourg, France

We present results of LSDA electronic structure calculations for epitaxial Cr overlayers on a ferromagnetic Fe(001) substrate in presence of interdiffusion at the Cr/Fe interface. The interfacial interdiffusion is simulated by two-dimensional substitutionally disordered alloy and the

corresponding selfconsistent electronic structure is obtained within the Tight-Binding Linear Muffin-Tin Orbital (TB-LMTO) method and the coherent-potential approximation (CPA). We analyse the total energies of different solutions of the LSDA-CPA problem and discuss several topics relevant to the Cr/Fe system, e.g. segregation tendencies for ultrathin Cr films and a magnetic π phase shift for thicker Cr films. A brief comparison of the *ab initio* results to a semiempirical tight-binding theory and experiment is presented as well.

MAE – 1

Giant magneto-crystalline anisotropy and magneto-optical effects in binary intermetallics

P. Ravindran and O. Eriksson

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In order to understand the origin of magneto-crystalline anisotropy in bilayer materials we have made systematic magnetocrystalline anisotropy energy (MAE) calculation for tetragonal MnX (X=Al, Hg, Ni, Pt or Rh) CoPt, NiPt and FeZ (Z=Ni,Pd or Pt) using the full-potential LMTO method which include orbital polarization correction. The role of crystal field splitting, exchange splitting and spin-orbit splitting on MAE is analysed. We have also calculated the magneto-optical (MO) polar Kerr effect and specific Faraday effect from the full potential calculation which include both intra-band as well as interband contributions. The calculated spectra are found to be in good agreement with the available experiemtal results. The possible connection between MAE and MO is discussed. We have found the MAE for MnPt greater than 5 meV and this value is larger among the binary transition metal intermetallics sofar studied. We have also obtained the record level Kerr rotation of 1.4 degree in this compound.

MAE – 2

Magnetic anisotropy in tetragonal and trigonal Fe, Co, and Ni

Peter James, O. Hjortstam[†], O. Eriksson, B. Johansson, L. Nordström

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Calculations of the magnetostriction coefficients, λ_{001} and λ_{111}, for cubic Fe, Co and Ni have been performed. According to magneto-elastic theory these can be calculated using the change in magnetocrystalline anisotropy energy, MAE, for small tetragonal and trigonal distortions. The electronic structure calculations are made with the full-potential linear muffin-tin orbital (FPLMTO) method within the local approximation to the density functional theory. The MAE is defined as the difference between two self-consistently calculated total energies for two inequiv-

alent crystal directions. In accordance with earlier reports, the MAE is exploding in magnitude when the cubic symmetry is lowered to tetragonal and trigonal symmetries.

MAE – 3

Ab-initio calculations of forces and lattice relaxations

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We present first-principles calculations of forces and lattice relaxations in bcc Fe. In particular, relaxations around 3d, 4d, and 5d transition metal impurities are calculated. 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 an ionic version of the Hellmann-Feynman theorem. Lattice statics methods are used to describe the longer ranged relaxations. The results are compared with lattice parameter measurements for the volume changes.

MAE – 4

Magnetic structure of ultra-thin Ni films on Cu(001)

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Both the electronic and ferromagnetic structure of Ni films on Cu(001) with thicknesses from 1 to 10 layers have been calculated using the relativistic layer-KKR method. The layer-resolved magnetic moments are enhanced at the surface, reduced at the Ni/Cu interface, and oscillate distinctly in magnitude in between. The magnetic anisotropy shows a transition from perpendicular to in-plane magnetisation in agreement with that observed experimentally. Further, both electronic and magnetic structure depend significantly on relaxations within the Ni films. Quantum-well states provide a clue for the interpretation of the results.

MAE − 5

Electronic structure and magnetic properties of ferromagnetic FeCu "superlattices" on Cu(100)

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With respect to the parent lattice of fcc Cu the magnetic anisotropy energy of $Cu(100)/(FeCu)_n$ with n varying between 2 and 15 is investigated using the spin-polarized relativistic Screened Korringa-Kohn-Rostoker method. It is found that the anisotropy energy per repetition rapidly converges to a constant value of about 0.46 meV, indicating that for a system of this kind, even for a much larger number of repetitions, the orientation of the magnetization remains perpendicular-to-plane (out-of-plane). For reasonably thick films discrete Fourier transformations of the layer-resolved magnetic moments and of the layer-resolved band energy with respect to atomic layers show a period of two, namely the number of atomic layers in each repeated unit.

MAE − 6

Layer-resolved anisotropy energies of free surfaces of (Fe-x-Co(1-x))n/Cu(100)

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The magnetic moments in the $(Fe_xCo_{1-x})_n/Cu(100)$ system are calculated and shown for $2 \leq n \leq 7$ and $x = 0.9$ as resolved with respect to layers and components. While, as reported previously, in the ground state antiferromagnetic interlayer coupling between buried Fe layers occur, surprisingly, also antiferromagnetic Co–Co and Fe–Co interlayer coupling is found. However, by assuming only ferromagnetic nearest–neighbor Fe–Co and Co–Co interactions on top of the dominating antiferromagnetic Fe-Fe nearest–neighbor interactions, it is revealed that a simple Ising-model is consistent with the results of the selfconsistent calculations. When analyzing also the layer- and component-like band energy contributions to the magnetic anisotropy energy, remarkably different behavior for the Fe and Co contributions can be seen.

MAE − 7

Concentration dependent spin-flip energies for alloyed surface magnets

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Single- and double spin-flip energies are calculated for n layers of homogeneously disordered Fe_cCo_{1-c} on Cu(100) with n varying between three and six. It is found that these spin-flip energies describe quite accurately the type of the most favourable magnetic coupling between the magnetic layers and also give a rather detailed picture for the occurance of certain magnetic configurations. A phasediagram of ferro- versus antiferromagnetic coupling with respect to the number of layers and Fe concentration turns out to be closely related to the phasediagram of the reorientation transition in this system.

MAE – 8

Ab initio calculation of Heisenberg parameters for thin magnetic films

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We present first principles calculations of the Heisenberg exchange parameters, J_{ij}'s in thin films on top of a Disordered Local Moment description of the paramagnetic state and also from the ferromagnetic state. The results concern Fe, Co and Ni films on a Cu(001) substrate showing that a first nearest–neighbor approximation for the coupling constants is hardly realistic. Furthermore, J_{ij}'s display significant dependence on the layer positions, giving a typical maximum for layers near the surface of the film as well the interface with the substrate. Remarkably, the calculated coupling parameters are consistent with the antiferromagnetic ground states of Fe_n/Cu(001) obtained by total energy calculations.

We then used the calculated parameters in a simple statistical mean-field approach to determine theoretical Curie temperatures, T_C. Interestingly, we obtained that for ferromagnetic couplings T_C increases, while for antiferromagnetic couplings T_C decreases as the number of layers increases. Our results compare qualitatively well to available experimental data.

MAE – 9

Magnetic Surface Alloys: Recent progress

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In the past years we investigated by means of the *ab initio* total energy and force calculations the role of magnetism for the formation of surface alloys. We arrived at the conclusion that i) magnetism acts against interdiffusion. At low coverage, where the magnetism of Cr and Mn is very large, interdiffusion is suppressed. ii) Magnetism reduces clustering and promotes alloy formation. For Mn we find a strong tendency for alloy formation. ¿From i) + ii) we concluded for the case of the Cu and Ni substrate the existence of thermodynamically stable, two dimensional surface alloys: $c(2 \times 2)$MnCu/Cu(100), $c(2 \times 2)$MnCu/Cu(110), and $c(2 \times 2)$MnNi/Ni(100). We present recent investigations for the Pd and Ag substrate and if time permits results on Cu(111).

MAE – 10

Role of surface orientation on the ferromagnetism of $3d$, $4d$ and $5d$ transition-metal monolayers on Ag

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We report systematic spin-polarized *ab initio* calculations for the electronic structure and magnetic moments of $3d$ (Ti, V, Cr, Mn, Fe, Co, and Ni), $4d$ (Mo, Tc, Ru, Rh, Pd) and $5d$ (Re, Os, Ir) transition-metal monolayers on the Ag(100) and Ag(111) substrate. Allowing for ferromagnetic ordering nonvanishing magnetic moments were calculated for all $3d$ metals, Tc, Ru and Rh among the $4d$ metals and Os and Ir among the $5d$ series. The comparison of the magnetic moments between the monolayers on the Ag(100) and the Ag(111) substrates illustrates the dependence of the magnetism of monolayers on the substrate orientation and local atomic coordination.

MAE – 11

Electronic structure and magnetic properties of Fe-Cr multilayers

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GMR – 1

Magnetic properties of impurities and impurity pairs in magnetic multilayers

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Spin-dependent scattering is considered to be the origin of Giant MagnetoResistance (GMR) in magnetic multilayers, although the role of bulk or interface defects is still under discussion.
We present ab initio calculations of spin-dependent impurity scattering potentials as a function of the impurity position in a Co/Cu-multilayer. The calculations are performed within spin density functional theory using a Green function method (TB-KKR).
It will be shown that the impurity potential depends strongly on the impurity position which is reflected in local densities of states and local impurity moments.
Furthermore, calculations of magnetic properties of impurity pairs are presented and compared with results for single impurities with respect to the interfaces.

GMR – 2

Non-equilibrium spins and Coulomb charging in ferromagnetic double barrier junctions

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We consider transport through a ferromagnetic double barrier structure. The non-equilibrium spin accumulation in the island is shown to govern the transport in small structures. The transport properties are described by a generalization of the theory of the Coulomb blockade. The magnetoresistance is expressed in terms of the spin polarizations of the ferromagnets and

the spin-flip relaxation life-time. The spin accumulation enhances the magnetoresistance. The long-time response is dominated by the spin dynamics. This can be used as an experimental signature of the spin-accumulation.

GMR – 3

GMR of interdiffused Co/Cu layered systems

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The resistivity and magnetoresistance (MR) of $(Cu_3Ni_3)_n$ embedded in Cu(100), $n \leq 11$, that originates from the band structure of these finite, yet otherwise perfect, systems is calculated for currents in the plane of the layers (CIP) by using the Kubo-Greenwood formula for semi-infinite systems and the fully relativistic, spin-polarized Screened Korringa-Kohn-Rostoker method. We find that for this repeated structure the CIP resistivity decreases as the number of repeats is increased, while the MR ratio approaches towards a saturation value.

GMR – 4

Spin-polarized electron tunneling in the Co/Al_2O_3 interface

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In order to elucidate the mechanism of spin-polarized electron tunnelling in thin-film ferromagnet-insulator junctions, self-consistent total energy calculations of the Co/Al2O3 interface have been performed within the framework of the density functional theory. Since the results of the calculations are very sensitive to the distance between the Co and Al (or O) planes, we have minimised the total energy with respect to this distance. Our calculations show that at the Fermi energy, a strong bonding between the 3d-electrons of Co with the sp-electrons of Al (or O) at the interface can have an important influence on the spin polarization of the layer-projected density of states (LPDOS) of inner Al and O layers. Since the Fermi energy lies within the minority-spin d-band of Co but above the majority-spin d-band, the sp-d bonding results in a smaller LPDOS of the

minority-spin electrons of the interfacial Al layers in comparison to that of the majority-spin electrons. This asymmetry in the LPDOS extends to the inner Al2O3 layers implying a positive spin polarization of the tunnelling density of states. The result is consistent with the experimental observations on tunnelling from cobalt through alumina where positive values of the spin polarization of the tunnelling current were measured.

SPEC – 1

Calculated magneto-optical spectra of 3d elements and compounds

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Using a first-principles full-potential linear muffin-tin orbital method, we have calculated the polar magneto-optical Kerr signal for tetragonal and cubic Fe, Co, and Ni. Our calculations indicate that for all three metals, the amplitudes and positions of the peaks in the Kerr spectra change due to the tetragonal distortion, but the effect is not dramatic. Since the magnitude of the magnetic moment changes very little as a function of the tetragonal distortion in these systems, much less than the Kerr spectra, our results indicate that the calculated changes in the Kerr spectra are to a large extent unrelated to the change in the magnetic moment.

Also, magneto-optic Faraday and polar Kerr spectra of the manganese pnictides MnAs, MnSb, and MnBi have been calculated using the same method. We are able to reproduce the experimentally observed second peak in our Kerr rotation spectra of MnBi, albeit at a lower energy than experimentally observed. Although the MO property is a rather complicated function of the diagonal and off-diagonal elements of the optical conductivity tensor, present theory nevertheless provides very practical insight about its origin in these compounds. The systematic increase in the MO effect as one goes from MnAs to MnBi is seen to be due to the enhancement of magnetic moment on the Mn site as well as the increasing spin-orbit coupling strength of the pnictogen.

SPEC – 2

A theoretical description of spin-resolved Appearance Potential Spectroscopy of magnetic surface layer systems

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The theoretical description of spin-resolved Appearance Potential Spectroscopy (APS) for bulk systems has been extended to deal with magnetic surface layer systems. Applications for Fe-layers on top of a (001)-oriented Cu- as well as Au-surface are presented and compared with available experimental data. For a most detailed discussion of the results the layer-resolved contributions to the total APS signal are used. This is particularly helpful in the case of Fe on top of a Cu-substrate for which non-ferromagnetic spin-structures are very important.

SPEC – 3

A scheme to deal with the magneto-optical properties of surface layer systems

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In order to investigate the magneto-optical Kerr effect (MOKE) for surface layer systems, a calculational scheme for the optical conductivity based on the Kubo formalism for linear response is presented. In view of the spin-orbit coupling being the origin of the MOKE, all calculations are based on a newly developed fully relativistic KKR-ASA-program for surface layer systems. In the future, the program will be extended to allow for full-potential calculations and metallic alloys via the Coherent Potential Approximation (CPA). Furthermore, the scheme is flexible enough to be extended to deal with nonlinear response. This way a sound basis for the investigation of the non-linear Kerr-effect of surface layer systems can be achieved.

SPEC – 4

Real-space non-relativistic angle-resolved photoemission

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A real-space non-relativistic angle-resolved photoemission code has been developed in the independent particle approximation. The method is formulated in terms of the multiple scattering

theory using a real-space representation of the Green's function. The advantage of this approach is in the simplification of the study of complex solids. The Green's functions are calculated in the following two ways. The first one is a real-space cluster method to obtain the τ-matrix. This method is simple at the expense of accuracy due to the finite size of the KKR-matrix, which can lead to errors in the contribution from atoms lying far away from the center of the cluster. The convergence is determined by the size of the KKR-matrix, that can be inverted for the calculation of the photocurrent. The other approach is the calculation of the Fourier transformed structure constants using two dimensional periodicity. After inversion of the KKR-matrix in the two dimensional k-space the τ-matrix in real-space can be evaluated by the Brillouin zone integration. This KKR-matrix has a substantially smaller size, and can be inverted for a variety of boundary conditions, referring to bulk, surface, *etc.* We illustrate our approach on the example of the angle-resolved photoemission study of Cu.

SPEC – 5

Magnetic circular dichroism in Gadolinium metal: The L edges.

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The LMTO-ASA method is employed to obtain self-consistent potentials for bulk *hcp* Gadolinium. The validity of the LSDA and PBE is investigated and the relationship between the magnetic and physical structure is explored for both ferromagnetic and antiferromagnetic structures. The self-consistent potentials are used in spin-polarised relativistic KKR-band structure calculations to determine the X-ray absorption and magnetic X-ray dichroic spectra for the $L1$, $L2$ and $L3$ edges. A study of the calculated dichroic signal, at a fixed volume, indicates that the dichroic signal is not highly sensitive to variation in c/a ratio of the unit cell. The layer-by-layer dichroic signal for a Gadolinium slab is also presented for various relaxations of the surface layer and the dichroic signal within the slab is related to the calculations presented for the bulk.

SPEC – 6

Spin-polarized XE spectroscopy for disordered semi-infinite systems

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X-ray emission spectroscopy (XES) of $Fe_x Co_{1-x}/Cu(100)$ is presented in terms of first-principles calculations. Based on spinpolarized fully relativistic multiple scattering theory a theoretical

description of valence band XES is used to emphasize new features in comparison to a non-spinpolarized description. Variations in the calculated Co and Fe spectra with respect to the concentrations are explained by means of electronic structure calculations using the screened Korringa-Kohn-Rostoker method. XES for ferromagnetic and antiferromagnetic aligned films are compared.

KKR – 1

Screened real space study of the magnetic properties of Co and Ni

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We have implemented screening in the fully relativistic spin-polarized version of the real space KKR method [1]. Exploiting the resulting sparsity, we were able to considerably accelerate the matrix inversions. The factors determining the convergence of the method as a function of shells in the atomic cluster are discussed, and we show the results obtained for the magnetic moment and the magneto-crystalline anisotropy of the transition metals Co and Ni.

[1] S.V. Beiden, W.M. Temmerman, Z. Szotek, G.A. Gehring, G.M. Stocks, Yang Wang, D.M.C. Nicholson, W.A. Shelton and H. Ebert, PRB 01 June 1998.

KKR – 2

Screened KKR with hard core potentials

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We developed a selfconsistent Screend-KKR method in an *ab-initio* Tight-Binding formulation. The Screened-KKR is especially advantageous for layered structures. It allows the consideration of the electronic structure of systems with up to 500 atoms per unit cell. The reduction of the numerical effort in comparison to the standard KKR is caused by the choice of a suitable reference system. Following the idea of Zeller et al. /1/ we consider reference systems with muffin-tin-potentials of constant height. This paper is dedicated to reference potentials of infinite height, so-called hard core potentials. It will be demonstarted that the advantage of the analytical solution of the scattering problem is accompanied by reduced accuracy of the

Screened-KKR method.

[1] R. Zeller, P.H. Dederichs, B. Újfalussy, L. Szunyogh, and P. Weinberger, Phys. Rev. B **52**, 8807 (1995).

KKR – 3

Total energy calculations with the Full-Potential KKR method

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We present total-energy calculations for Al, Ni, Fe and Cu based on the full-potential (FP) Korringa-Kohn-Rostoker (KKR) Green-function (GF) method. We show that calculated lattice constants and bulk moduli are in excellent agreement with the values obtained by other FP methods. We focus on the difference between the local-spin-density and generalized-gradient approximations (LSDA and GGA) and show that GGA values for lattice constants and bulk moduli agree very well with experiment. We also discuss some technical details concerning the numerical accuracy of the FP-KKR-GF method.

KKR – 4

Layer Screening transformations for two-dimensional structure constants

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By making explicit use of the so-called "Kambe structure constants", originally formulated for a theoretical description of Low Energy Electron Diffraction (LEED), the Screened KKR Surface Green's function (*SKKR-SGF-*) method for layered systems can conceptually be extended to multilayer systems corresponding to complex two-dimensional lattices and to layer relaxation

at interfaces (surfaces). In the present paper the screening properties of the "Kambe structure constants" are illustrated.

LMTO − 2

A real-space full-potential LMTO method for non-collinear magnetism

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We have constructed a complete basis set for a real-space full-potential localized linear muffin-tin orbital method. The physical concepts that are fulfilled by our method and the development of corresponding algorithms and their implementation will be highlighted. In particular, we discuss the implementation of (1) the Lanczos recursion method to obtain the greens function, (2) the non-collinear magnetism, (3) the spin-orbit coupling. Suggestions for computational improvement and better accuracy will be given in relation to existing **k**-space methods. Principal aspects of the structure of the final code, and particular difficulties will be presented. A particular emphasis will be given to the the preference of studying non-collinear magnetism in metallic clusters and surfaces in real space.

LMTO − 3

Induced V polarization at the interface with Fe: Fe_nV_m superlattices and thin V_m films on Fe substrate

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Recent experimental and theoretical studies have displayed induced V polarization in Fe_nV_m superlattices and thin V_m films on Fe substrate. Tomaz et al [1] have shown a long-range induced polarization in Fe_5V_m multilayers. Walker and Hopster [2] and Fuchs et al [3] have displayed an oscillatory behavior of V thin film polarization on Fe(001).

We have performed TB-LMTO calculations of Fe_5V_m following the experimental configuration of Tomaz et al. We found a short-range induced polarization of V in agreement with ASW calculations of Coehoorn [4] but in disagreement with Tomaz et al. Both (001) and (011) crystallographic orientations have been studied. We have also made TB-LMTO calculations for thin V_m films on semi-infinite Fe(001) and Fe(011) substrates. For V_1/Fe(001) we obtained

perfect agreement with FLAPW of Handschuh and Blügel [5]. For thicker coverages an oscillation of V polarization is found in qualitative agreement with the experimental studies.

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[3] P. Fuchs, K. Totland and M. Landolt, Phys. Rev. B53, 9123 (1996)

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[5] S. Handschuh and S. Blügel, Solid State Comm. 105, 633 (1998)

LMTO – 4

Non collinear magnetism of large systems studied by semi empirical tight binding method

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The theoretical study of the non collinear behaviour of ferromagnetic/antiferro-magnetic multi-layers (like Fe/Cr and FeCo/Mn) realised since more than 3 years in our group, is now nearly achieved. The FeCo/Mn multilayers are particularly interesting from their experimental behaviour (strong biquadratic couplings, net non collinear magnetisation of the Mn spacer) but also from a theoretical viewpoint because they allow to study the magnetic properties of thin Mn layers with varying boundaries conditions by varying the Fe concentration. The aim of this paper is to present the major results we have obtained. In order to determine the vectorial magnetic moments map of complex systems (containing up to 300 unequivalent sites) from their electronic structure, we use a tight binding modelisation and the real space recursion technique. We have first focussed our attention on multilayers with perfect interfaces and done a systematic study of the magnetic ordering and interlayer magnetic couplings as a function of the spacer thickness varying the Fe concentrations in the FeCo/Mn case. Surprisingly, a strong non collinear character of the Mn spacer is obtained for small Fe concentrations even for situations where only collinear solutions are expected which is not the case for Fe/Cr systems. We show that the interlayer coupling energy, as a function of the angle between successive ferromagnetic magnetisations, follows a parabolic law as expected. The second part of our work is devoted to the role of interfacial monoatomic steps on the magnetic ordering in such multilayers. Even if this study is not completely achieved, preliminar results show that non collinear magnetic arrangements are induced by such interfacial imperfections. We present the vectorial magnetic

moments maps obtained for particular step sizes and Fe concentrations.

LMTO − 5

Electronic and Optical Properties of FeS$_2$ and CoS$_2$

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We have used the linear muffin-tin orbital method, without geometrical constraints on the electron density or potential, to calculate the electronic structure of FeS$_2$ and CoS$_2$. ¿From the self-consistent potential we have computed the energy bands and the frequency dependent dielectric function. The calculated dielectric function is found to be in good agreement with available experimental data.

O − 1

Towards a constrained local moment model for first principle spin dynamics [1]

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Although a subject of great venerability, metallic magnetism is currently undergoing a renaissance. A contributor to the renewed interest is the recently proposed spin dynamics (SD) of Antropov *et al.*[1] which offers the possibility to treat the dynamics of magnetic moment reorientations on a first principles basis. In this presentation we show that, has currently proposed, the general non-collinear states, whose time evolution are the subject of SD, are not well defined ground states within LDA. To properly formulate SD within density functional theory, we develop a constrained density functional theory of general non-collinear spin systems. In the resulting constrained local moment (CLM) model the specific orientational configuration is maintained by local transverse constraining fields that are obtained selfconsistently. We illustrate the CLM states by explicit examples corresponding to the rotation of moments in Fe and

[1]V. P. Antropov et al. Phys. Rev. **54**, 1019, (1996)

a large cell disordered local moment model of paramagnetic bcc Fe calculated using the the $O[N]$ locally selfconsistent multiple scattering (LSMS) method[2]. Finally, we assess the outlook for developing first principles, LSMS based, spin dynamics as a practical procedure for real systems.

O − 2

The stability of the $Cu_xZn_yAl_{100-x-y}$ alloys

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The ab initio total energy calculations for $Cu_xZn_yAl_{100-x-y}$ random alloys were done for both the FCC and BCC structure for the whole concentration range. The most stable FCC alloys are on tha Cu-Al axes at 25 at% Cu, and the most stable BCC alloys on tha Cu-Zn axes at 40 at% Cu. The Al atoms produce no extra bonding but favorized the FCC structure against the BCC structure especially for small and large values of Cu concentrations. The solubility lines and spinodal surfaces were also computed . The martensitic behavior was found in the range of 60 to 70 at% Cu and spinodal decomposition in the Al rich part of the phase diagram. In the limit of $x = 0$; for Zn_yAl_{100-y} the energy of the concentration waves, in the [001] direction, were calculated using supercells in the limit of short wave length and in the presence of small vacancy concentrations. It was found that the vacancies favorized the spinodal structures but strongly depending on the concentration of the components. For some alloys the Fermi surface was investigated by calculating the Bloch spectral functions at the Fermi energy. All calculations were done using the fast KKR-CPA method in the scalar-relativistic approximation together with the GGA-form for the exchange and correlation potential and energy.

O − 3

Hyperfine fields of probe atoms on the Fe and Ni(001) surface

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Motivated by recent experiments for [77]Se adatoms on the surface of Ni [1], we present first-principles calculations of the electronic structure and hyperfine fields of $3d$ and $4sp$ impurities

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[2]Yang Wang et al. Phy. Rev. Letters **75**, 2867,(1995)

on the (001) surfaces of Ni and Fe. The calculations are based on local-spin-density-functional theory and employ a Korringa-Kohn-Rostoker Green's function method for impurities at surfaces. The systematic behaviour obtained for the hyperfine fields of the $4sp$ adatoms or impurities in the first surface layer is completely different from that found in the bulk. Instead of a single maximum with a very large hyperfine-field value at about the end of an sp series, the adatoms exhibit two maxima with a pronounced minimum in between. This behaviour can be traced back to the reduced coordination number of the adatoms which leads to a much smaller relative splitting of the bonding and antibonding peaks, and to the lower symmetry at the surface which results in an on-site s-p_z hybridization. The hyperfine fields found for the $3d$-impurities are basically determined by the ferro- or antiferromagnetic coupling of the local impurity moment to the substrate magnetization. Therefore they are similar to the results of bulk impurities, though the effects are modified due to the surface enhancement of the moments.

[1] H. Granzer, H. H. Bertschat, H. Haas, W.-D. Zeitz, J. Lohmüller, and G. Schatz, Phys. Rev. Lett. **77**, 4261 (1996).

O − 4

Indirect exchange and magnetic ordering in elemental and layered heavy rare earth systems

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Employing spin spiral symmetry in a non collinear version of density functional theory we have calculated the magnetic and electronic properties of several late rare earth (RE) metals and alloys. All calculations are done in the experimental (hcp) crystal structure using the local density approximation to yield an effective one electron potential. Treating the chemically inert but unfilled 4f shells as localized states the conduction electrons are polarized through the influence of

an internal magnetic field produced by the open core. This way we attempt to deal with the indirect exchange interaction between spin moments on different crystal sites as it is mediated by the spin polarized conduction electrons. The indirect exchange interaction is known to be oscillatory and of long range order. Experimentally well established are a variety of periodic spin structures such as helical order in the basal plane, distorted helicals or ferrimagnetic antiphase domains. For the elemental metals our calculated magnetic "phase diagram" at T = 0 is in good agreement with experiment. Further the behaviour of the turn angle in systems consisting of a single magnetic element interleaved with a non magnetic one is studied.

O − 5

Growth mode of Cr on Fe(001) described by ab-initio interactions

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The Fe/Cr interface has been widely experimentally studied providing a model system to confront theoretical approaches. For instance the growth mode of Cr on Fe(001) has revealed unexpected bahaviour: strong interdiffusion of Cr into Fe and a Cr-Cr nearest neighbour repulsion have been reported. Simple arguments based on phenomenological schemes cannot be invoked and thus more detailled study is necessary.

In this work a Solid-on-Solid model is used to simulate the growth of Cr on Fe(001). The key ingredients are the so-called Effective Cluster Interactions (ECI) combined with a Monte Carlo study. Point and Pair Interactions are taken into account. The values of these ECI are obtained by a KKR-Green's function method in the dilute limit. These parameters are then used in a Monte Carlo simulation of deposition and diffusion. Rapid diffusion of Cr into the bulk is observed in agreement with experiments. Snapshots for a range of deposition parameters are used to elucidate the various structures. The consequences for the magnetic properties of this system will also be briefly discussed.

O − 6

Application of $O(N)$ LSGF method for calculation of systems with noncollinear magnetic configurations

I.A.Abrikosov and B.Johansson

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We discuss an extension of the locally self-consistent Green's function method (LSGF) (I. A. Abrikosov *et al.*, Phys. Rev. Lett. **76**, 4203 (1996); Phys. Rev. B **56**, 9319 (1997).) to the case of large magnetic systems with arbitrary orientations of local spin moments. The 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. The order-N scaling is achieved by associating each atom in the system with its so-called local interaction zone (LIZ). Inside each LIZ the multiple scattering problem is solved exactly. The accuracy of

the LSGF calculations is controlled by the size of the LIZ, and its minimal size is ensured by embedding the LIZ into a self-consistent mean-field CPA-like effective medium. We show how this effective medium can be constructed for an alloy with noncollinear spins. Our technique is demonstrated by calculating ground state magnetic structures of bcc and fcc Fe.

O − 7

The Effect of Hydrogenation on the Magnetic State in Pd_3Mn

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We have, with the use of the linear augmented plane wave method (LAPW) in the local density approximation (LDA), calculated the magnetic state in Pd_3Mn and the effect of hydrogenation. Before hydrogenation the system is in a tetragonal Al_3Zr phase and a hydrogen induced phase transition leaves the system in a cubic Cu_3Au phase in which it remains after the hydrogen has been removed.

The from experiment suggested magnetic structure is a trigonal non-commen-surate spin-spiral with $\mathbf{q}$=(0.0972, 0.0972, 0.0972) and an opening angle of the co nes of $\sim 55°$. We reproduce this state with very good accuracy, $\mathbf{q} = (0.10, 0.10, 0.10)$ and an angle of $49°$. For the hydrogenated system we get a tetragonal spin-spiral with $\mathbf{q}$=(0.38, 0.38, 0.38). The result is anal yzed and the magnetic structure is matched with structures in the Fermi surface.

The energy difference between the different magnetic states are of the order of 0.5 meV so temperature effects and defects in the sample can play a major role but still we can reproduce the ground state with good precision.

O − 8

Interface magnetism of 3d transition metals

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The layered resolved magnetic spin moments of magnetic 3d bilayer interfaces are calculated by means of a first principle's Green's function method. It is shown how the magnetic profiles around the bilayer interfaces and surfaces directly can be used to predict the magnetization of more complex systems such as magnetic multilayers and clusters. Furthermore, it is shown how the magnetic interface moments can be estimated from data of the corresponding binary bulk

alloys.

O − 9

Electronic structure of a realistic STM - tip: the role of different apex atoms

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In view of interpreting images obtained by scanning tunneling microscopes with perturbation methods the electronic properties of the STM tip are of utmost importance. We have calculated with a first-principles method the spin-resolved electronic structure of a tungsten (100) surface with different apex atoms. The results presented show that the electronic states in the vacuum region above the tip are in each case a mixture of states with s, p, and d-type symmetries. The relevance of this result for STM imaging and the calculation of the tunneling current by numerical methods is discussed briefly.

O − 10

Theoretical tensile strength in metals and intermetallics

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Fully self-consistent ab initio electronic structure calculation of the theoretical tensile strength of single-crystalline tungsten and NiAl loaded uniaxially along [001] and [111] directions is performed using the full-potential LAPW method. Although tungsten is elastically nearly isotropic ($C_{44} \approx C'$), theoretical tensile strength exhibits a marked anisotropy. Similarly, in NiAl, the "hard" orientation [001] differs very significantly from the [111] orientation. This anisotropy is explained in terms of higher-symmetry structures present or absent along the deformation paths.

O − 11

Spinordering in $Fe_{3-x}Mn_xSi$ Heusler alloys

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Applying the Augmented Spherical Wave method, the Heusler alloy $Fe_{3-x}Mn_xSi$ is studied for integer values of x where it forms fairly well ordered intermetallic compounds. In our calculation we allow for non collinear spin ordering. It is found that the magnetic groundstate changes from a ferromagnet for Fe_3Si to a long wavelength spin spiral for Mn_3Si which is close to a [111] antiferromagnet. Our results are in excellent agreement with experiment, which is particularily true for Fe_2MnSi where our calculations confirm the experimental conjecture of a [111] antiferromagnet with a ferromagnetic component due to a canting of the spins off the [111] axis.

O − 12

The energetics of steps on transition metal surfaces

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We have applied our recently established database of surface free energies and surface free energy anisotropies of low-index surfaces in a study of the energetics of surface steps for cubic transition metals. The first-principles results from the database are used for a cluster expansion of the surface free energy which is subsequently used for high-index surfaces. The accuracy of the expansion is established by a comparison with first-principles results for a few high-index surfaces. Using the cluster expansion for the surface energy of vicinal surfaces we derive the monoatomic step-formation energies for different close packed *bcc* and *fcc* surface facets. Trends in the anisotropy of the step energy are also discussed.

4 News from the TMR2 Network and ESF Programme

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

4.1 Report on Industry Workshop

European Science Foundation (ESF)
Research Programme
"Electronic Structure Calculations for Elucidating the Complex Atomistic Behaviour of Solids and Surfaces"

Training and Mobility of Researchers (TMR) Network **"Electronic Structure Calculations of Materials Properties and Processes for Industry and Basic Sciences"**

Workshop
"Electronic Structure Calculations for Industry and Basic Sciences"
Technische Universität Wien
June 3-4, 1998

Scientific Programme and Abstracts

The need to coordinate the European research efforts in the field of electronic structure theory on a broad basis and to focus these methodologies on industrially important problems has recently lead to two mutually re-inforcing European programmes, namely a broad programme supported by the European Science Foundation (ESF) and a focused research effort within the framework "Training and Mobility of Researchers" (TMR) funded by the European Commission. As initialisation of these programmes, the workshop "Electronic Structure Calculations

for Industry and Basic Sciences" had three major objectives, namely (i) to review the present industrial needs, (ii) to strengthen the impact of current electronic structure methodology in these areas, and (iii) to provide a stimulus for new methodological developments.

At the beginning of this year, the European Science Foundation decided the creation of a Research Programme on *"Electronic Structure* - (Struc-$\Psi_{\vec{k}}$)" supported by the national research agencies of sixteen European countries (Austria, Belgium, Denmark, Finland, France, Germany, Hungary, Ireland, Italy, Poland, Portugal, Slovenia, Sweden, Switzerland, Spain (to be confirmed), United Kingdom). The aim of this Programme is to promote research on electronic structure of materials on a very broad level.

At the same time, the contract with the European Commission on the creation of a TMR Network on *"Electronic Structure Calculations of Materials Properties and Processes for Industry and Basic Sciences"* was signed. In this network seven international teams focus on the following areas: molecular processes on surfaces (Molecular Simulations, s.a.r.l., France), f-electron systems (Univ. of Aarhus, Denmark), interfaces (Queens University Belfast), magnetism (Technische Universität Wien), development of the the LAPW method (Forschungszentrum Jülich), electronic excitations (Helsinki University of Technology), and superconductivity (Universität Würzburg). An additional team, lead by Daresbury Laboratory, is in charge of specific training programmes and dissemination.

These programmes continue the fruitful cooperations initiated through the Human Capital and Mobility (HCM) $\Psi_{\vec{k}}$-Network "Electronic Structure".

To mark the starting point of both initiatives was the aim of the joint workshop on "Electronic Structure Calculations for Industry and Basic Sciences". The idea was to bring scientists from industry and academia together. We expected the participants from industry to formulate the challenges arising from application-oriented industrial research and to point out where ab-initio simulations are necessary to achieve deeper insight and to supplement information that would otherwise not be available. Selected speakers from academia presented the state-of-the-art in ab-initio simulations. The hope was that the confrontation of the necessities of industrial research with the possibilities offered by front-line academic research would initialize a fruitful dialog.

J. Hafner, W. Temmerman *(ESF-Programme)*
E. Wimmer, A. Svane *TMR-Network)*

Wednesday, June 3

10:00	Opening
10:10	**E. Wimmer (MSI Paris)**
	Presentation of the TMR-Network
10:25	**J. Hafner (TU Wien)**
	Presentation of the ESF-Programme
10:40	**S. Mengel (VDI Technologiezentrum)**
	What Can Magnetism Contribute to Electronics ?
11:20	**J. Wecker (Siemens Erlangen)**
	Future of Permanent Magnet and Magnetic Thin Film Devices
12:00	**I. Mertig (TU Dresden)**
	An Insight into Interlayer Exchange Coupling and
	Giant Magnetoresistance from Ab-initio Calculations
12:30	*Lunch break*
14:00	**H. Toulhoat (Institut Français du Pétrole, Rueil)**
	Surfaces and Interfaces in Oil and Gas Sciences:
	Tasks and Challenges for Electronic Structure Calculations
14:40	**C. Stampfl (Fritz-Haber Institut, Berlin)**
	Why is the Chemical Reactivity of Ruthenium Special ?
	An Analysis of the Catalytic CO Oxidation at Ru (0001)
15:10	*Coffee break*
15:30	**R. Meier (DSM Research Gelen)**
	Some Applications of First-Priciples Molecular Dynamics in Chemistry

and Polymer Science

16:10	*End of Session*
16:20	Meeting of the Steering Group of the ESF Programme

Thursday, June 4

8:30	Meeting of the Management Board of the TMR Network

10:00   **B. Clausen (Haldor Topsoe SA)**
Application of Theory and Modelling in the Development of Catalysts

10:40   **Ch. Werner (Siemens München)**
Ab-initio Simulations for Chemical Vapour Deposition in
Semiconductor Technology

11:20   *Coffee break*

11:40   **J. Nørskov (DTU Lyngby)**
Nitrogen Fixation in Industry and in Nature

12:10   **F. Hutschka (TOTAL Raffinage et Distribution)**
Molecular Modelling in TOTAL: Industrial Experience in an Oil and
Gas Company and Future Needs in Electronic Structure Calculations

12:50   *Lunch break*

14:00   **O. Anttila (Okmetic)**
Halfway from Sand to Supercomputers: Practical Needs for
Improving Silicon Wafer Quality

14:40   **G. Kresse (TU Wien)**
Ab-initio Molecular Dynamics Applied to Catalysis

15:20   *Coffee break*

15:40   **P. Erk (BASF)**
Crystal Design of Pigments - Simulations of Industrial Relevance

16:20   **M. Finnis (Queens Univ. Belfast)**
Theory of Metal/Oxide Bonding

16:50   **R. Nieminen (Helsinki Univ. of Technology)**
Semiconductor Processing: Challenges for Materials Modelling

17:20   Closing remarks

17:30   *End of Session*

Abstracts of invited contributions

What can magnetism contribute to electronics?

Stefan Mengel

VDI Technology Center, Association of German Engineers, Düsseldorf, Germany

New technologies initiate innovation. Basic research is in general the source for completely new technologies based on new effects and findings. However, new technologies do not emerge by themselves from their laboratory origins. They have to be identified and the information has to be communicated to decision-makers in industry, research management and the political administration in order to keep pace with international competition. How can potential be identified? Which results give rise to a really new technological paradigm? How can one assess conditions for the success of a future technology?

In order to deal with such issues, methods are required first for drawing rational conclusions and secondly for disseminating information. The technology forecasting carried out at VDI Technology Center aims to seek options for new technologies at the advanced fundamental research stage.

As an example technology forecasting methods are demonstrated for a technology screening in the field of magnetism. Magnet technologies are widely used in many fields of applications such as electrical devices, data storage and medical diagnosis. Are there new findings in research for improvement innovations? Are there in particular new findings with potential for basic innovations? Recently discovered new effects in magnetism allow for the first time the efficient control of electrical currents by magnetic means. This enables the creation of elementary electronic functions by using magnetic systems instead of or complementary to semiconductors. There are good arguments that magnetoelectronics will play a major role in the future development of nanoelectronics.

The future of permanent magnets and magnetic thin film devices

Joachim Wecker

Siemens AG, Corporate Technology, Erlangen, Germany

Modern permanent magnets are based on rare-earth transition metal compounds like $SmCo_5$,

Sm_2Co_{17} or $Nd_2Fe_{14}B$. These intermetallics exhibit strong magnetic uniaxial anisotropy in combination with reasonable saturation polarisation and Curie temperatures. Equally important favourable processing routes are available which allow the fabrication of magnets with high coercivities. Since the discovery of $Nd_2Fe_{14}B$ in 1983, however, the search for novel phases with improved magnetic properties has been unsuccessful. The talk will outline the requirements put on new materials from an application point of view and will discuss possible development strategies.

With respect to magnetic thin films the phenomenon of giant magnetoresistance (GMR) i.e. the extraordinarily large change in resistance of magnetic multilayers under an applied magnetic field has led to the development of a variety of thin film devices like recording heads or magnetic sensors. Here, a novel GMR-sensor will be described which was designed for the contactless measurement of angles or positions. Emphasis will be put on problems which have to be solved in order to further improve the sensor performance. Finally, magnetic tunnel junctions will be addressed which may form the basis of new magnetoelectronic devices like non-volatile memories.

An insight into interlayer exchange coupling and giant magnetoresistance from ab-initio calculations

Ingrid Mertig

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The discovery of Interlayer Exchange Coupling (IEC) and Giant MagnetoResistance (GMR) in magnetic multilayers initiated experimental and theoretical work to elucidate the microscopic origin of the phenomena. Among other theoretical attemps like RKKY theory for IEC and free electron models for GMR the ab initio calculations play an important role since they are able to account for general aspects and specific properties of the considered materials.

As a result of the ab-initio calculations it was shown that quantum confinement in layered systems is extremely important to understand IEC and GMR. In particular, it was pointed out that selected quantum-well states in growth direction (at stationary points) are responsible for IEC whereas quantum well and interface states cause the intrinsic GMR.

Furthermore, defects in layered systems like impurities (especially at the interface), interface alloys and interface roughness influence the phenomena sensitively. The amplitude of IEC is drastically reduced by interface roughness and alloying, GMR, however, can be enhanced, reduced or even inverted by these defects.

Surface and interfaces in oil and gas sciences:
Tasks and challenges for electronic structure calculations

Hervé Toulhoat

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I will present a few major issues for oil and gas industry, which can be translated into scientific problems of relevance for electronic structure calculations: heterogeneous catalysis, gas-solid adsorption, wetting of minerals by oil or water, crystallization of solids from a liquid phase. In all cases, the simulation of phenomena at solid-fluid interfaces is central.

In some of these fields, I will briefly survey results recently obtained at IFP with different state-of-the-art methods: (1) Hydrodesulfurization on MoS_2-based catalysts, (2) Poisoning of noble metal based catalysts by sulfur, and de-poisoning by halogens, (3) Calcite wettability changes induced by adsorption of organics, (4) Morphology of boehmite precipitated in aqueous solutions.

Beyond these rather encouraging results, I will try to outline the present limitations which in my opinion call for improved or new methodological approaches:
- Of course, dealing with surfaces and interfaces implies low symetries and therefore large models; Catalysis by zeolites might be the exception at first sight, but unfortunately (large pores) industrially relevant zeolites show the largest unit-cells: ever increasing the reach of accurate electronic structure calculations, in terms of number of atoms and electrons handled should remain a primary goal for still a long time. Order N methods, embedded cluster methods, and other promising techniques will therefore always be welcomed with interest for validation benchmarks.
- In support of the interpretation of experimental characterizations practiced on dispersed materials, new or improved ab initio spectroscopic calculations of various kinds should add much value: while vibrational spectra seem to be quite reasonably predicted by present days DFT/GGA MD techniques for instance, electronic spectra still come with some questionmarks. The simulation of XANES would be particularly useful. This requirement implies a proper treatment of excited states and one would hope openings along that way.
- Tools for the evaluation of quadrupolar moments at nuclei and hence NMR shifts should be included in the kits supplementing well appraised electronic structure codes for solids and interfaces, as well as other aids for translating an electron density or wavefunction into concepts intelligible to the chemist: fitted atomic charges, gradient analysis of electronic localisation functions, etc...
- Intermolecular interactions: we need them badly, either to build better forcefields, or to treat consistently ab initio all condensed matter problems. Which part is accounted for by DFT seems still rather obscure and functionals-dependent. Of special interest for the oil and gas industries are $\pi - \pi$ attractive forces between aromatic planes, and London-VdW forces. In his theory of the latter (5) Lifshits derived the attractive potential from the reduction in Gibbs energy resulting from the correlation of local electronic density fluctuations: it is, maybe too naively,

speculated that a revisitation of this approach in the framework of modern electronic structure methods might bring in useful results.

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Why is the chemical reactivity of Ruthenium special?
An analysis of the catalytic CO oxidation at Ru (0001)

Catherine Stampfl and Matthias Scheffler

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New methodological developments enable *ab initio* (from the electronic structure) calculations of poly-atomic complexes with extensive statistics (e.g. *ab initio* molecular dynamics with 10,000 and more trajectories [1]), and of adsorption/desorption thermodynamics. In this way contact with the "real world" and realistic process simulations are becoming possible.

This talk gives

- a brief description of recent methodological advancements (hybrid methods "from electron orbitals to surface thermodynamics")

- as an example of this methodology and recent impact of *ab initio* calculations on surface reactions we discuss the catalytic oxidation of carbon monoxide at ruthenium.

The carbon monoxide oxidation reaction over Ru (0001) exhibits somewhat anomalous behavior: under ultra high vacuum conditions, Ru is by far the *poorest* catalyst, yet under "realistic working conditions" (e.g. high O_2 partial gas pressures and elevated temperatures) the rate of the catalytic carbon monoxide oxidation reaction is notably *higher* at ruthenium than at other transition metal surfaces [2].

Using density functional theory, detailed information can be obtained on a *microscopic* level which affords an undertanding of the apparent "pressure gap" behavior of this system. Important is found to be the fact that Ru (0001) can support a high coverage, and more weakly chemisorbed,

monolayer O structure [3] which, however, can only be achieved for high O_2 gas pressures (or with the use of atomic oxygen, e.g. NO_2) due to kinetic hindering for O_2 dissociation. We investigate the catalytic reaction $CO+1/2O_2 \rightarrow CO_2$, for both a scattering reaction of CO at the O-covered surface (Eley-Rideal mechanism) [4] as well as for the Langmuir-Hinshelwood mechanism. With respect to O on Ru (0001), we show how a realistic description of the thermodynamic and kinetic properties of the adsorbate can be obtained by combining *ab initio* and phenomenological theories, in particular, by constructing a lattice gas hamiltonian on the basis of density functional theory.

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Some applications of first principles molecular dynamics in chemistry and polymer science

Rob Meier

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First-principles dynamics methods of the Car-Parrinello type have recently allowed efficient computation of various processes relevant to polymers and polymer synthesis. Using this approach, for the first time the ultimate elastic modulus of a crystalline polymer, i.e. polyethylene, could be calculated on a first-principles basis [1]. In this contribution the specific value of exploring the dynamics of chemically reacting systems studied by first principles molecular dynamics methods will be highlighted.

In a series of publications we have reported on the insertion of ethylene in bis-cyclopentadienyl metallocenes, as well as in mono-Cp* systems [2-5]. Such simulations, which show the entire molecular dynamics of such reactions, have explicitly revealed the importance of the agostic interaction for olefin insertion to proceed. Moreover, despite their stability as corroborated from static simulations, the dynamics of the agostic interactions is significant. In addition, the flexibility of the species involved was much greater than expected, in particular the floppiness of the Cp ring system.

The insertion of olefins into metal-hydrogen (M-H) bonds is important to olefin isomerisations, hydroformylations and hydrogenation reactions. It is in this wider context that we have extended

our work in this area with application of the Car-Parrinello method to ethylene insertion in the PtII-H bond of $(H)Pt(PX3)_2$ species [7]. Contrary to the metallocenes, these systems have a relatively rigid structure with the P-Pt-P showing little variation.

The bis-phosphine $Cl_2(PH_3)_2Ru=CH_2$ complex and its mono-phosphine equivalent were taken as model compounds for the Grubbs metathesis catalyst [7]. Depending on temperature conditions set in the molecular dynamics simulations, the interaction of these ruthenium-phosphine catalysts with ethylene revealed insertion, the formation of a metallacyclobutane, or a pure metathesis reaction [8]. A comparison with recent experimental results from Grubbs et al. [7] shows that some of the preliminary interpretation presented in that work is supported by our calculations. Examples are the ability for carbene rotation, the relative easiness of Cl-Ru-Cl cis-trans configurational exchange and the presence of small fraction of the mono-phosphine complex. Furthermore, the simulations indicate that energy stored in the Ru-P bond, or otherwise the lability of the Ru-P bond, is of crucial importance for the metathesis reaction to proceed. The requirement to store excess energy in the Ru-P bonds agrees with the higher activity of the mono-phosphine system compared to bis-phosphines complexes. In addition, the fact that ruthenium-carbene complexes based on sterically-crowded phosphines gives higher metathesis activity, can be rationalized by their intrinsically more labile Ru-P bonds as indicated by longer Ru-P bond lengths.

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Application of theory and modelling in the development of catalysts

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Theory has in the last few years reached a level where it has predictive power and together with the development of faster computers more realistic systems can now be treated. Thus,

theory and modelling find increasing use at Haldor Topsoe to guide the development of new and improved heterogeneous catalysts. Examples of catalyst systems where this new strategy for development of catalysts has been used will be addressed in the talk.

One recent example is the design of a new steam reforming catalyst. The traditional catalyst which is based on nickel on a refractory, high surface area support is used in a very important industrial reaction, where hydrocarbons are reacted with steam at high temperatures, giving hydrogen and CO. If the reaction is operated at a too low O/C ratio, the tendency for carbon formation is high, and graphite is formed at the nickel surface. Carbon formation decreases the activity of the catalyst and might cause spalling, pressure drop over the reactor, and even pulverization of the catalyst pellets. DFT calculations have shown that the reactivity of the nickel surface atoms towards carbon formation can be altered by introducing fractions of a monolayer of gold in the topmost surface layer [1]. Although a lower reactivity towards methane dissociation is predicted, this is counterbalanced by a higher resistance towards carbon formation. These predictions have been verified by molecular beam scattering experiments on well-defined single crystals [2]. These observations were indeed found to be valid for real nickel catalyst systems. Several techniques were used to characterize the high surface area Ni and Ni/Au samples. The carbon resistance was determined in a standard TGA setup operating under steam reforming conditions. The results revealed that the carbon resistance is increased significantly by adding Au to the Ni catalysts. In situ EXAFS measurements performed under typical steam reforming conditions showed that the Au atoms have Ni nearest neighbors. This verifies that the Au is indeed alloyed into the Ni crystallites and is not present as a separate phase. Thus, the combination of the fundamental understanding of surface physics and chemistry and in situ EXAFS studies of real catalysts have made possible the design a new catalyst for steam reforming [3]. The test of this novel catalyst system is presently being tested under more industrial relevant conditions.

Another example of the application of theory is within hydrotreating catalysts which are used to remove heteroatoms from fossil fuels in the refineries. The exact structure of the active phase is not understood in detail but DFT calculations have added significant new insight into the nature of the active sites which are sulfur vacancies at the edges of the MoS_2-type structures. The presence of Co or other promoters at the edges leads to an increase in the vacancy concentration and may thus explain the promoting role of Co and other transition metal [4]. A better understanding of the active structure and the role of the promoter atoms is essential for the design of the next generation of highly active hydrotreating catalysts.

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Ab initio simulations for chemical vapor deposition processes in semiconductor technology

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Chemical Vapor Deposition is one of the key technologies in the manufacturing process of modern Integrated Circuits. Therefore it is very important to achieve a thorough understanding of the basic chemical reactions, which determine the uniformity and the composition of all the various metal, insulator and semiconductor films that influence the electrical performance of the circuit.

In this talk some results of ab-initio density functional calculations with DMOL will be presented, that were extremely helpful in developing a better understanding of the chemical pathways that play a role in our deposition processes.

The examples to be discussed include:

- Surface reactions of Dichlorosilane and Germane on a Si(100) surface

- Gas phase reactions in the deposition of Ferroelectric insulator films from Barium-, Bismuth- and Titanium precursors

- Adsorption of different Titanium precursor molecules on a Strontium titanate surface

In this presentation we will also point out the shortcomings of present state of the art as well as the challenges for future development from the industrial users' point of view.

Nitrogen fixation in industry and in nature

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The adsorption, dissociation and hydrogenation of N_2 on Fe and Ru surfaces is studied using density functional theory and a non-local description of the exchange-correlation energy. On Ru(0001) a molecularly adsorbed state is identified, and the barrier for dissociation is high (1.2 eV). On Fe(111), on the other hand, four stable molecular states are found and the barrier to dissociation is low (0.1 eV). The calculations allow us to rationalize the vast amount of experimental information for these systems and to understand the different characteristics of Ru and Fe as ammonia synthesis catalysts. In this connection we also study the influence of promotors (Na, Cs) and poisons (S). We show that adsorbed alkali metal atoms lower the barrier

for N_2 dissociation through an electrostatic interaction. Adsorbed S atoms increase the barrier through a combination of direct and indirect (through metal d electrons) interactions with the dissociating N_2 molecule. Ammonia synthesis takes place in nature in the enzyme nitrogenase, and we study a $MoFe_6S_9$ compound chosen to be a close model of the active part of of the enzyme. Here we find adsorbed N_2 to hydrogenate directly instead of dissociating first as on the metal surfaces. A mechanism of the biological N_2 fixation process is proposed on this basis. The model is in good agreement with available kinetic and spectroscopic data.

Molecular modelling in TOTAL: industrial experence in an oil and gas

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The present talk deals with the experience of an oil and gas company in molecular modelling tools, especially with quantum-mechanic based programs for the calculation of electronic features of molecules and molecules that react at the solid surface. We will present a summary of results related to our industrial approach of the use of this young technology in terms of validation works (i.e. what is the best tool to use).

Among the problems studied are the following:

- Proton affinity calculation to demonstrate the ability of Density Functional Theory (DFT) to scale molecules and models of catalysts (e.g. zeolites).

- Exploration of the chemical reactivity of thiophene (C_4H_4S) on zeolite clusters using a DFT based program (i.e. a collaborative study with Gaussian 94, Prof. R. Van Santen and X. Saintigny, University of Eindhoven, to be published).

But the main purpose of the presentation is to highlight the present and future aims we should achieve in terms of methodological development to bring up molecular modelling to a routinely stage in industry. As an example among the multiple objectives we will present the study of local phenomena of the adsorption of corrosion inhibitors on steel-based surfaces in a distillation unit as a representative example that is, by now, out of the possibilities of molecular modelling tools but of today industrial importance. We hope then to give inputs of industrial relevance that could help theoriticians in physics and chemistry to orient their developments and collaborative works.

Halfway from Sand to Supercomputers: Practical Needs for Improving Silicon Wafer Quality

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Silicon crystals, grown from silica crucibles using Czochralski (CZ) method , and subsequently sliced to thin wafers, form the material basis to modern electronic systems. The raw material, elemental silicon, is very abundant in earth's crust, but a plethora of process steps are needed before the billions of submicron sized semiconductor components are ready to serve a physicist inside a modern supercomputer.

This talk will give a short overview to the manufacturing process from a source of quartz sand through high purity polycrystalline silicon and single crystal dislocation free silicon to semiconductor wafers. The wafers are then processed further to produce integrated circuits like CPU's and memories, and the end products, electronic systems. The market value of the end products approaches one trillion USD annually. The emphasis will be in crystal growth through wafer production.

The bulk of the crystals produced today are 150 and 200 mm in diameter and from 60 to 140 kg in weight, 300 mm diameter crystals weighing up to more than 300 kg being in pilot production. The quality requirements get more stringent for each generation of IC circuitry of $2\frac{1}{2}$–3 years. In crystal growth, extensive modeling support is needed to help to control thermal distributions, three dimensional time dependent melt flows, as well as gas flow behavior. Magnetic fields are increasingly applied to modify melt flows. In addition to typical yields and productivity issues, vacancy and interstitial related defects are the largest challenge today. Analytical methods, e.g., measuring the small concentrations of the above mentioned intrinsic point defects, their properties and behavior, as well as metallic contaminants to below 100 ppqa levels, are largely lacking. An important aspect of the crystal material quality is the dissolved oxygen, originating from the silica crucible, which the crystal contains in 10-15 ppma range. Oxygen strengthens the silicon lattice in subsequent high temperature anneals, as well creates small defects which act as gettering sites during device processing. The control of these defects is of prime importance.

The sliced wafers face stringent requirements concerning their geometrical properties, e.g., warp and flatness, as well as the quality and cleanliness of the surfaces. Modern circuit manufacturing processes are sensitive to 0.1 μm particles and metallic contaminants in few millionths of a monolayer range. The surfaces must be damage free to prevent slippage in the high temperature processes. The surface roughness after wafer polishing is typically about 1 Å (rms. value, compare with lattice constant of 5.4 Å). Etching, polishing and cleaning of the wafers may benefit immensely from appropriate modeling efforts, not only through faster and easier optimization of those processes, but more by adding understanding about the important phenomena controlling them.

An increasing number of wafers are experiencing epitaxial growth of silicon on top of the substrate, before integrated circuit manufacture. Another, closely related process is the growth of a polysilicon layer at the backside of the wafer, to act as a gettering layer and/or to reduce backside originated autodoping during subsequent epitaxy. The polysilicon layer may be further

sealed using a low temperature oxide (LTO) layer. The uniformity and structural properties of these chemical vapor deposited layers are of increasing significance.

Ab-initio molecular dynamics applied to catalysis

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The talk reviews the current status of development of the Vienna Ab-initio Simulation Package (VASP). VASP is a plane-wave-based pseudopotential code, which is distributed with optimized ultrasoft Vanderbilt type pseudopotential for s, p and d-elements allowing the treatment of systems with up to 200 atoms on workstations. Recent improvements of the code are briefly discussed:

- The projector augmented wave method proposed by P. Blöchl [1] has been implemented in a form applicable to large metallic systems [2]. This allows to evaluate the all-electron wavefunctions and improves the precision of calculations for transition metals considerably.

- More efficient algorithms for the evaluation of the electronic groundstate during *molecular dynamics* using the dielectric functions evaluated in previous time steps are briefly presented. For surfaces, the performance is increased typically a factor of 2-3 in comparison to more traditional methods.

In the second part of the talk the oxidation of CO on the Pt(111) surface is discussed as a typical case study. 6 different oxidation mechanisms are explored, including the oxidation of CO by atomic "nascent" oxygen, and chemisorbed O_2. Reaction barriers and transition state are calculated using the "nudged elastic band" method [3]. It is shown that at coverages of $\theta_O \sim 0.5$ the co-adsorption of CO stabilizes the chemisorbed molecular precursor of O_2 over the dissociated atomically adsorbed oxygen. The barrier for the reaction between the co-adsorbed molecules is lowest if first the molecular O_2 bond is broken (E_{barr}=1.18 eV). At the transition-state the nascent O atoms are only bridge- or top-bonded and therefore quite reactive. After desorption of CO_2, the remaining adsorbed O atom can react with a second CO molecule via a transition state similar to that for the molecular reaction, but with a much lower barrier (E_{barr}=0.38 eV). The difference in the barrier heights is comparable to the dissociation barrier for the molecular precursor ($E_{diss} \sim 0.88$ eV, see Ref. [3]. The common principle determining the transition state with the lowest barrier is to minimize the number of broken adsorbate-substrate bonds.

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Crystal design of pigments : Simulations of industrial relevance

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During the last decades material science has grown up as an interdisciplinary research domain, that developed from a mainly descriptive and analytical to a highly creative discipline. Theoretical methods for the understanding and prediction of materials properties were a dominant driving force in that process.

Crystal Design condenses the vision of manipulating crystal structures and crystal morphologies on a rational base of calculated microscopic and mesoscopic characteristics. The industrial significance of these approaches originates from the value added through solid state properties to many performance products. Polymorphism, crystal habit, and crystal size strongly influence technical and application properties of crystalline products, e.g. sugars, fats, catalysts, agrochemicals, drugs, and pigments.

Pigments are - by definition - insoluble colorants, and therefore optical properties of pigments are a sensitive measure for property changes induced by structure and morphology, thus offering a challenge to simulation methods. The significance of structural and morphological properties of organic and inorganic pigments will be discussed with respect to experimental and computational methods regarded as being useful in outlining new technological solutions.

Structural Properties: Crystal structures of organic pigments are well understood and to some extend predictable without any experimental knowledge on the basis of atomic simulations. Structure related color changes can be explained by low dimensional band models or via exciton theory. Up to now no generalized simulation strategies for the ab initio prediction of complex inorganic crystal structures exist - they do not even appear at the horizon. DF- and HF-methods are proven to calculate inorganic crystal structures with high accuracy, but are still to costly to do excessive searches in crystalline phase space. Electronic properties may be derived from various methods. Results are usually sufficient to interpret absorption mechanisms and to follow trends in structure related color changes.

Morphological Properties: Morphology prediction based on pure lattice information is known for more than sixty years. More advanced methods taking the anisotropy of specific interactions between atoms or molecules into account have been developed starting in the 1950ies and are now taken to fully automatization for molecular crystals. Simulations of crystal habits give access to surface structures and surface properties, providing the information needed to modify growth forms by the use of tailor-made additives. Morphologies of inorganic materials may be

derived according to similar techniques, calculating surface energies by an appropriate method. However, surface relaxation is considered to play an important role and no simple concept comparable to the *tailor-made additives* is available to modify crystal habits. Experimentally the addition of ions in the crystallization process has a strong impact on the growth kinetics of inorganic materials, resulting in extremely different morphologies. Unfortunately, none of the available simulation methods offers theoretical access to these phenomena.

The theory of oxide-metal interfaces

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The interfaces between oxides and metals play an active part in the properties of materials ranging from high temperature alloys and metal-ceramic composites, to catalyst supports and microelectronic components. Important questions relate to the effects of impurities or additives on these properties. The "Psi-k" approach of using density functional theory to solve for the electronic structure, atomic positions and bonding strength is beginning to shed light on the nature of the bonding at such interfaces in simple model systems [1,2]. Particular interfaces of the oxides MgO and Al2O3 and spinel with metals have been studied, and their electronic structure and works of adhesion calculated. At the same time simpler, faster approaches to the problem of total energy calculation have been proposed, with a view to studying systems larger than the tens to hundreds of atoms accessible to the density functional method. One such approach (the Discrete Classical Model) is based on the classical image potential. Another more recent approach is a self-consistent tight- binding model for oxides [3], which complements the use of tight-binding as an approximate description of transition metal bonding. Both these simple approaches can be derived as approximations to the density functional theory and have their own advantages and disadvantages. Future work will evaluate them for interface calculations.

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Semiconductor Processing: Challenges for Materials Modelling

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With the shrinking of device features, the ability to control the composition and quality of semiconductor materials in near-atomistic length scales and over vastly different time scales is increasingly more important. Process simulation has to draw on accurate treatment of microscopic phenomena governed by quantum mechanics. This talk surveys some of the outstanding challenges in view of modern, atomistic materials modelling. In particular, the role of lattice defects, introduced either during crystal growth or in wafer processing, is emphasised. The predictive calculation of basic defect parameters, such as their energetics, charge states and mobility barriers. The questions of doping efficiency, defect metastability and defect-dopant clustering are also addressed. The main emphasis is on silicon processing, but some special aspects of compound semiconductors are considered as well.

Posters presented at the workshop

Multiscale Modelling of Diamond CVD

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WIEN97 Calculations of Solids

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Oxides and Li-intercalated Derivative for Lithium Intercalation Batteries: A First-Principles Study

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Quasiparticle Calculations of Valence-band Ofsets in AlN/GaN Superlattices

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Calculation of Phonons from Ab-initio Force-Field Software

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Magnetism in Häusler Alloys: Ni_2MnGa and Co_2MnGa

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Adsorption of CO on NiAl

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Summary of ChiPPs 1997

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Theoretical Tensile Strength in Metals and Intermetallics

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Electronic Structure Calculations for Industry and Basic Sciences

Technische Universität Wien

June 3-4, 1998

An increasing number of industrially relevant problems can now be solved using advanced electronic structure calculations. Therefore, industrial scientists show a growing interest in this methododology, they start to apply these approaches, and notice the aspects which need to be improved. Developers of electronic structure methods, who are working predominantly in academic or government research organisations, are keen to see their methods applied to industrial problems and are eager to receive feedback in order to orient their new developments. The success of the Ψ_k workshop "Electronic Structure Calculations for Industry and Basic Sciences" held June 3-4, 1998 at the Technische Universität Wien was a clear testimony of the timeliness of this dialogue between industrial researchers and developers of electronic structure methods.

Given the breadth of possible industrial applications in chemistry, physics, and materials science, the workshop was also very helpful in setting priorities in terms of the best match between industrial impact and current computational capabilities. Four application areas have found particular industrial resonance and thus have been addressed at the Workshop, namely

- **heterogeneous catalysis**

- **semiconductor processing**

- **magnetoelectronics**

- **crystal engineering for pigments**

In comparison with these areas, industry appears to be less ready to adopt electronic structure methods related to the thermal and mechanical properties of materials including high-performance alloys, corrosion, and fatigue. Although these areas are the topic of major academic research efforts, they did not constitute a focus of this Industry Workshop.

Exploring surface reaction mechanism

Seven of the fifteen invited lectures were dedicated to catalysis. A common theme connected these contributions: electronic structure methods, originating from solid state physics, have emerged as an extremely useful tool to unravel reaction mechanisms on surfaces. The following highlights illustrate this point.

Hydrodesulfurisation. The petrochemical industry (including petroleum refining and processing) is responding to increasingly stringent environmental regulations on sulfur (e.g. in Diesel fuel). In reviewing the challenges for electronic structure calculations on surfaces and interfaces from the perspective of the oil and gas industry, Hervé Toulhoat from the "Institut Français du Pétrole" showed that advanced electronic structure calculations helped to establish the adsorption geometry of thiophene on a surface model of the molybdenum sulfide based industrial catalyst, thereby revealing how the edges of the molybdenum sulfide sheets can bind thiophene molecules quite strongly, deform the molecule and thereby activate the C-S bonds for cleavage by hydrogen.

In his comments about industrial requirements, Toulhoat pointed out the need to treat systems with a larger number of atoms, to have more accurate and also faster methods. Furthermore, methods using embedding techniques would be helpful in order to treat each area of the system at the appropriate level of theory. For many chemical questions, a good description of π-π and van-der-Waals interactions is critical. To this end, current density functional approximations are perhaps not yet accurate enough. Electronic structure calculations are valuable for the interpretation of experiment. Therefore, computer programs should make it easy to calculate these spectroscopic properties. Finally, the computations should also provide convenient chemical descriptors such as charge decompositions which would facilitate the dialogue with synthetic chemists.

Unusual Oxidation on Ru(0001). Another example related to surface reaction mechanisms was discussed in a contribution by Catherine Stampfl and Matthias Scheffler. They demonstrated the ability of electronic structure calculations to help explain the unusual behaviour of Ru in the catalytic oxidation of CO. The ability of Ru to form a dense, but weakly adsorbed layer of oxygen atoms on its (0001) surface was found to be critical for the excellent performance of this metal as oxidation catalyst at high oxygen pressures. The absence of this oxygen layer at low pressure causes a rather poor performance of this catalyst. Furthermore, the calculations demonstrate that the predominant mechanism proceeds via adsorbed CO species (Langmuir-Hinshelwood mechanism) rather than reactive scattering of gas-phase CO molecules (Eley-Rideal mechanism).

Uncovering the details of homogeneous catalytic reactions. Polyolefins such as polyethylene and polypropylene are the world's most widely used polymers. So far, these materials are being synthesized via well established catalytic processes based on Ziegler-Natta catalysts. The introduction of metallocenes such as bis-cyclopentadienyl- titanium as alternative catalysts has major technological and business implications in the chemical

and petrochemical industry. The interest in metallocene catalysts is based on the fact that these so-called single-site catalysts allow a better control of polymer properties such as tacticity, chain length, and branching ratio, which determine the macroscopic visco-elastic and thermo-mechanical materials behaviour. Since the polymer properties such as tacticity can be manipulated by the molecular architecture of the catalytic centre, the detailed understanding of the reaction mechanism holds the key to innovation and improvements. The ability of density functional methods to treat transition metals as well as organic molecules makes this approach well suited for the study of reactions on metallocene catalysts.

Rob Meier from DSM, a major chemical producer in the Netherlands, demonstrated the usefulness of *ab initio* molecular dynamics simulations for the study of metallocene cata-lysts. The simulations revealed a surprising flexibility of the cyclopentadienyl rings thus offering new aspects for improvements. Furthermore, the so-called agostic interaction of hydrogen becomes clearly evident from these electronic structure calculations. (In an agostic interaction, a hydrogen atom from the ethylene molecule shows a bonding interac-tion to the metal atom.) A number of other important industrial reaction mechanisms are being studied using this approach, such as insertion of olefins in metal-hydrogen bonds (important for olefin isomerisation, hydroformylations, and hydrogenation reactions), and metathesis reactions. Based on electronic structure calculations, the key aspects of reac-tion mechanisms can be identified, thus helping to create new ideas and to focus experi-mental efforts.

Improving resistance of metal catalysts. Bjerne Clausen from the Danish catalyst manufacturer Haldor Topsoe demonstrated in his contribution how theory and modelling find increasing use to guide the development of new and improved heterogeneous cata-lysts. Graphite formation on nickel catalysts pose a serious problem for steam reforming catalysts, where hydrocarbons react with steam to form hydrogen and carbon monoxide. DFT calculations showed that a fraction of a monolayer of gold in the surface can make the catalyst more resistant to graphite formation, even though a lower reactivity towards methane dissociation is predicted. Surface experiments on single crystals confirmed these predictions. Importantly, these surface modifications proved to be valid also for the real catalysts and thus an improvement in the catalytic systems was achieved.

Learning from enzymes. Using enzymes as models and inspirations for designing in-dustrial heterogeneous catalysts represents a most fascinating path to innovation. For this approach to succeed, one needs to have a thorough understanding of the enzymatic reaction mechanisms. In his presentation, Jens Nørskov demonstrated how DFT calcula-tions can be used to achieve this goal for nitrogen fixation by the enzyme nitrogenase. It was found that the compound $MoFe_6S_9$ captures the essence of the active site and thus represents a viable model for the biological fixation of molecular nitrogen.

DFT practiced at TOTAL. One of the major European petrochemical companies, TO-TAL, is using molecular modeling since 1993. François Hutschka explained how electronic structure calculations using DFT have become an integral part of the research activities at TOTAL providing valuable contributions in areas such as zeolite catalysts and desulfurisation catalysts. He also pointed to corrosion a as major remaining challenge. For example, corrosion by CO_2 and H_2S as well as scale formation are serious problems in the production of natural oil and gas. The design of effective corrosion and scale inhibitors is urgent. Present quantum mechanical tools are not yet ready to tackle this type of problems. Difficulties in creating viable surface models, the complexity of surface reactions involving the formation of new phases, and the potentially long time scales involved in these reactions are enormous challenges. Encouraged by the successes of electronic structure methods in the treatment of catalytic reactions, one should envision corrosion phenomena as a new target.

Oxidation mechanisms on platinum. Georg Kresse from the group of Jürgen Hafner in Vienna presented the results of detailed studies of catalytic surface processes such as the oxidation of CO on a Pt(111) surface. This contribution added another strong piece of evidence that electronic structure calculations are a viable and highly useful tool for establishing reaction mechanism on surfaces.

Electronic structure calculations to help in semiconductor processing

Chemical vapour deposition (CVD) plays a central role in the processing of semiconductor devices. Despite this importance, it is probably safe to say that only few - if any - surface reaction mechanisms underlying CVD processes are well understood. Yet a clear understanding of the chemical pathways is critical for building a process model with predictive capabilities outside a narrow range, which is typically obtained if only empirically fitted data are used in the model construction. The contribution by Christoph Werner from Siemens gave an illustrative example of the capabilites of present density functional methods to determine possible reaction pathways and to exclude others.

Growth of Si-Ge. In the growth of Si-Ge alloys for microelectronic device applications, it has been observed that the presence of germane, GeH_4, increases the growth rate of silicon. In this reaction, dichlorosilane (DCS) is used as source for silicon. This "catalytic" effect of germane is somewhat surprising. One could imagine two explanations, namely an overall change of the surface structure (e.g. a surface reconstruction or other long-range effects) which modifies the reactivity of surface silicon atoms or, alternatively, some local effects due to the presence of germanium atoms on the surface. It is known that the rate limiting step in the growth of pure silicon from DCS is the desorption of hydrogen. A computational study of the energetics of hydrogen interaction with silicon and germanium shows that the desorption energy of hydrogen from germanium is lower than from silicon. In the presence of germanium, one could therefore imagine a mechanism whereby hydrogen

atoms blocking silicon sites first diffuse to germanium atoms and then desorb from the germanium site. In order for this process to occur, the energy barriers for lateral hydrogen diffusion on the surface needs to be smaller than the barriers involved in the desorption of hydrogen. DFT calculations revealed that this is indeed the case. By using this reaction pathway in a reaction model, an excellent fit over a wide range of process conditions could be achieved, thereby creating a significantly improved process model. Encouraged by this success, researchers at Siemens are now applying this approach to the CVD of $SrTiO_3$, which is a new class of dielectric materials needed for the coming generations of integrated circuits. One of the questions is the design of new organometallic gas-phase precursors such as $Ti(O\text{-}C_3H_7)_4$. These precursors need to be volatile and thermally decompose at the surface, but not in the gas phase. To this end, one needs computational tools which allow the investigation of reactions in the gas phase and on surfaces at the same level of theory. Localised orbital DFT methods seem to be a good choice. However, the large size of the organometallic compounds makes it challenging to describe their interaction with surfaces since large surface models (supercells or clusters) are required for an adequate description. Clearly, there is a need for improved methods which can treat large models.

Helping in the processing of silicon wafers. Computer technology is in a phase of rapid evolution with performance and capacity increasing at a rate of doubling every 18 months. Processing of silicon wafers of large diameter (200 mm today with 300 mm in the pilot stage) together with reduced feature sizes in the sub-micron range are the key to this development. Producers of silicon wafers are thus faced with unprecedented requirements for purity and flatness. O. Anttila from Okmetic (Finland), a specialised manufacturer of silicon wafers, described these requirements and outlined opportunities for atomistic simulations. The control of impurities, notably oxygen, but also Fe, Ni, Cu and Zn is critical. Given the extremely low concentrations of these impurities, analytical methods are too blunt for providing a clear picture of their influence on the silicon lattice. Atomistic simulations can play an important role in understanding defect mechanisms such as clustering around oxygen impurities. Accurate calculations can also provide materials data which are difficult to obtain experimentally such as solubilities and transport properties. A flatness of better than 1 Å of the wafer surface requires advanced polishing methods. To this end, organic additives are used. The improvement of the polishing process and the additives would greatly benefit from a more detailed understanding of the molecular processes on the silicon surface. Thus, edging and polishing of silicon wafers represent fruitful application areas for electronic structure calculations and atomistic simulations.

Challenges for electronic structure methods. In his review of the challenges for materials modeling in semiconductor processing, Risto Nieminen stressed the need for building bridges between microscopic and macroscopic simulations. For certain questions such as the silicon vacancy formation energy some of the most reliable numbers originate from first-principles calculations. This demonstrates that links between the atomistic and continuum domains can be established, but more of it has to be done. Reaching

out to the finite element world will thus be an important theme as electronic structure methods become applicable to larger and more complex systems. The urgent problems to be tackled include oxygen diffusion in silicon, clustering of defects, the simulation of the growth process, a better understanding of copper diffusion and electromigration in silicon in view of the replacement of aluminium by copper, as well as the understanding of III-V semiconductors such as GaN.

Magnetoelectronics - an emerging technology

Besides catalysis and microelectronics, magnetic materials were the third major topic of the Workshop. Stefan Mengel from the Association of German Engineers presented an overview of the promising field of magnetoelectronics, i.e. the connection of electronic and magnetic components to form an integrated device. So-called MRAM devices exploiting tunneling magnetoresistance have recently been demonstrated and offer an exciting technological opportunity. During the past decade, the prediction of magnetic properties has been one of the great successes of first-principles electronic structure calculations. Therefore, the stage is set for applying these tools to the development and improvement of magnetic and magnetoelectronic materials with applications including sensors, magnetic read/write heads, MRAM, and possibly spin transistors.

Since the discovery of $Nd_2Fe_{14}B$ in 1983, the search for novel phases and materials for improved permanent magnets has been unsuccessful, said Joachim Wecker from Siemens in reviewing the future of permanent magnets and magnetic thin film devices. Given the uncertainties for immediate success, industrial research laboratories are perhaps reluctant to carry out such a search for new phases. Wecker stressed the point that experimental efforts need to by guided by electronic structure calculations. Finally, magnetic tunnel junctions as the basis for new magnetoelectronic devices like non-volatile memories present major research opportunities, where theory can play an important role.

Electronic structure methods are clearly making an important contribution in the research and development of materials exhibiting giant magnetoresistance (GMR). This was beautifully demonstrated in the contribution form Ingrid Mertig from the TU Dresden, who showed how *ab initio* calculations revealed quantum confinement in layered systems to be extremely important to understand interlayer exchange coupling (IEF) and GMR.

Interfaces - a major problem in materials science.

A generic problem in the study of many materials is the understanding of interface phenomena. Often, experimental techniques are not suitable to probe the structural, electronic, and magnetic properties of buried interfaces, yet they play a critical role in materials science. Mike Finnis from the University of Belfast demonstrated how the "Ψ_k approach", i.e. the use of electronic structure methods, can deepen our understanding of

interfaces in terms of atomic positions, bonding mechanisms. He illustrated this point by discussing the prototypical cases such as the interfaces of MgO and Al_2O_3 with metals. In the face of the complexity of such oxide/metal interfaces, Finnis showed the usefulness of more approximate methods such as the "Discrete Classical Model" using classical image potentials and, more recenly, self-consistent tight-binding methods.

Crystal design

The chemical industry continues to be a pillar of the European economy. In a global market, the creation of high-value added chemical products is critical for sustaining a leading position. Peter Erk from BASF illustrated this point for the area of crystal design of pigments. BASF is a major producer of high-performance pigments for the car indus- try, which poses demanding requirements on performance and consistent product quality. While the prediction of crystal structures of organic pigments can be accomplished fairly well with today's quasi-classical force-fields, this cannot be said for inorganic crystals. It would be most useful to have a set of tools including accurate electronic structure calcula- tions which would allow the prediction of inorganic crystal structures. In these materials, the interplay between electronic and crystallographic structure precludes for the most part the use of empirical potentials. While ab initio electronic structure methods are starting to offer sufficient accuracy for predicting crystal structures, they are still too demand- ing computationally to allow the exploration of the vast conformational space of crystal packing. On the other hand, electronic structure methods are now capable of predict- ing optical spectra which allows the interpretation of optical absorption mechanisms and to follow trends in structure related colour changes. Because of the great technological relevance of crystal habits, the control of crystal sizes and morphology has stimulated a variety of theoretical approaches ranging from simple rules to models based on calculated surface and attachment energies. In the realm of organic crystals, it is possible to employ computational methods for designing additives which control crystal habits. The same is not true for inorganic crystals, where surface relaxation and electronic structure effects can play decisive roles, thus pointing to another important development need.

The Ψ_k Industry Workshop held in Vienna on June 3-4, 1998 was clearly a successful start. A fruitful dialogue between industrial researchers from leading European companies and academic researchers in the field of advanced electronic structure methods has been es- tablished. The industrial speakers have stated clear development priorities, notably in the are of reaction mechanisms on surfaces, in the field of electronic materials, magneto- electronics, and crystal engineering. The stage is set for a successful implementation of the ambitious research programmes of the Ψ_k network.

(Erich Wimmer)

5 Workshop/Conference Announcements of the ESF Programme

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

5.1 Conference on 'COMPUTATIONAL PHYSICS FOR NANOTECHNOLOGY'

19-24 SEPTEMBER

It is still not too late to register for the ESF European Research Conference 'Computational Physics for Nanotechnology', which will be held in the Il Ciocco conference centre in Tuscany from 19 to 24 September. The meeting is the successor to the 'Electronic Structure of Solids' Euroconferences that ran from 1992 to 1995; it will concentrate on the interface between the modern 'Psi-k' techniques of computational electronic structure theory, and the rapidly experimental advances in the field of nanotechnology. This is one of the places where the length scales of experiment and electronic structure theory coincide; we shall be discussing how our theoretical methods can be used to calculate the quantities that are crucial for further progress in this field on

- Semiconductor systems, including quantum dots

- Scanning probe microscopies

- Understanding surface properties and processes in real environments

- Surface reactions and aassembly of structures on surfaces

- Nanoscale and molecular-scale wires

For more information on the programme and location, and to register online, see the conference website at

http://www.cmmp.ucl.ac.uk/ ajf/conference/

Some financial assistance is available for young scientists wishing to attend the conference. This support comes from the European Science Foundation (from the Euroconferences activity and from the programme 'Electronic Structure Calculations for Elucidating the Complex Atomistic Behaviour of Solids and Surfaces'), from the UK Engineering and Physical Sciences Research Council and from the Thin Films and Surfaces Group of the Institute of Physics.

ESF Workshop

Structures and properties of inorganic crystals from theory and experiment
Kiel, FRG, 28.09 - 03.10.1998
Workshop within the ESF Programme
Electronic Structure Calculations for Elucidating the Complex Atomistic Behaviour of Solids and Surfaces

The aim of this workshop is to bring together experimentalists from the chemistry, mineralogy, physics and material science communities with developers of quantum mechanic codes so that the state-of-the-art in computer simulations can be compared to the requirements in precision and accuracy in 'computational crystallography'-studies.

The main topics are therefore studies of structural phase transitions, phonons, electric field gradients etc. of small inorganic compounds.

This workshop is currently planned by Björn Winkler (Kiel) (`bjoern@min.uni-kiel.de`) and Victor Milman (MSI/Cambridge)(`vmilman@msicam.co.uk`).

Further information is given at :
`http://www.min.uni-kiel.de/kristallographie/esf/seite1.html`

Deadline for registration is the 31st August.

There will be only a small registration fee.
Contributors will be eligible for financial support provided through the ESF programme.

5.3   Workshop in Sardinia

The Physics Department, Universita' di Cagliari, and the Cagliari Research Unit of Istituto Nazionale per la Fisica della Materia

—- with the sponsorship of —-

Regione Autonoma Sardegna

European Science Foundation Programme "Electronic Structure Calculations for Elucidating the Complex Atomistic Behaviour of Solids and Surfaces"

organize the

VIII WORKSHOP ON COMPUTATIONAL MATERIALS SCIENCE

18 - 22 September 1998

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

An international workshop on computational techniques and applications to materials science

Please see PROGRAM and REGISTRATION INFO below.

FORMAT: 20 invited lectures plus POSTER contributed session.

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

CONTACT: For scientific queries: vincenzo.fiorentini@dsf.unica.it

For logistics: Corsi&Congressi, Cagliari, corsieco@tin.it

CONTRIBUTIONS AND PROCEEDINGS: Contributions in poster format are invited. ALL contributions will be published in a dedicated volume of the Conference Proceedings Series of the Italian Physical Society.

Deadline for submission: Aug 31, 1998. Contact V. Fiorentini or P. Ruggerone at +39 70 6754865 or at vincenzo.fiorentini@dsf.unica.it/paolo.ruggerone@dsf.unica.it for further details. Camera ready manuscripts will be due at the Workshop, LaTeX templates will be circulated to all scientific participants in due time.

PROGRAM

FRIDAY SEPTEMBER 18

MORNING: arrivals

AFTERNOON: working session 1 - **AB INITIO VS SEMIEMPIRICAL SIMULATIONS**

17.30 W. Andreoni (Zuerich): *Ab-initio molecular dynamics in materials science I*

18.30 H. Jonsson (Seattle): *DFT and empirical potential calculations of minimum energy paths for Si atom diffusion in bulk Si using the Nudged Elastic Band method*

21.00 Get-together party

SATURDAY SEPTEMBER 19

MORNING: working session 2 – **SIMULATIONS OF COMPLEX SYSTEMS**

9.00 W. Andreoni (Zuerich) *Ab-initio molecular dynamics in materials science II*

10.00 G. Barkema (Utrecht): *Towards Long-Time Simulations of Disordered Materials*

11.00 Coffee break

11.30 J. Hafner (Vienna)

AFTERNOON: working session 3 – **DEVICES: SIMULATION AND EXPERIMENT**

17.30 F. Beltram (Pisa): *Some results on advanced semiconductor "devices"*

18.30 A. Di Carlo (Roma): *Tight-binding methods applied to semiconductor nanostructures and device*s

SUNDAY SEPTEMBER 20

MORNING: working session 4 - **SURFACES: REACTIONS,ADSORPTION,DIFFUSION**

9.00 J. Hafner (Vienna)

10.00 B. Persson (Juelich): *Ordered Structures and Phase Transitions in Adsorbed Layer*s

11.00 Coffee break

11.30 H. Jonsson (Seattle): *Adsorption, diffusion and island formation of water molecules on the surface of proton disordered ice Ih*

AFTERNOON: free

21.00 POSTER SESSION with refreshments

MONDAY SEPTEMBER 21

MORNING: working session 5 - **SCALING AND CRITICALITY IN CONDENSED MATTER**

9.00 A. Vespignani (Trieste): *Avalanche processes in collective transport phenomena*

10.00 S. Zapperi (Paris): *The Barkhausen effect: A new perspective for an old problem*

11.00 Coffee break

11.30 G. Barkema (Utrecht): *Simulation of Models for Polymer Reptation*

AFTERNOON: working session 6 - **SURFACE GROWTH**

17.30 K.H. Rieder (Berlin): *Structuring of surfaces using STM*

18.30 A. Pimpinelli (Clermont-Ferrand): *Evolution of epitaxial island morphologies at and out of equilibrium*

21.00 Social dinner

TUESDAY SEPTEMBER 22

MORNING: working session 7 - **CORRELATION AT SURFACES: CHARGE DENSITY WAVES**

9.00 G. Santoro (Trieste): *Surface charge density waves and Mott insulators for adlayer structures on semiconductors.*

10.00 K.H. Rieder (Berlin): *Charge density effects visualized with STM*

11.00 Coffee break

11.30 B. Persson (Juelich): *Sliding Friction: Physical Principles and Applications*

AFTERNOON: departures

REGISTRATION

Please send the REGISTRATION form by fax or e-mail, before July 31, 1998 to Corsi&Congressi via Ghibli 8, I-09126 Cagliari tel +39 70 383373 fax +39 70 3837102 e-mail: corsieco@tin.it The registration should be accompanied by payment receipt of the CONFERENCE FEE. The fee includes full-board lodging at Hotel Costa dei Fiori from 18/9 afternoon to 22/9 lunch, coffee breaks, refreshments, social banquet, and amounts to Double room lodging It.Lire 850000 (~US $ 475)/person Single room lodging It.Lire 950000 (~US $ 535)/person. PAYMENT should be effected by bank money transfer on the bank account # 11080620154 of Corsi&Congressi, at Banca Commerciale Italiana, Sede di Cagliari, Codice ABI 2002 - CAB 43950. No fee is requested from the invited speakers. The Organizing Committee hopes to be able to offer partial support to a limited number of young scientists, preferrably PhD students. Since this possibility depends on funds availability, support will be decided upon shortly before the workshop.

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REGISTRATION FORM

Name ....

Institution ....

e-mail address ....

Arrival date: / /98 - Departure date: / /98

Accomodation: Single room [_] Double room [_]

Plan to present a poster entitled:

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Series Chairman : prof. A. Baldereschi - EPFL Lausanne

Workshop Chairman : prof. F. Meloni - INFM and Universita' di Cagliari

Scientific Secretariat: dr. V. Fiorentini - dr. P. Ruggerone INFM and Universita' di Cagliari

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6 General Workshop/Conference Reports

6.1 Report on Workshop in Melbourne

CSIRO Workshop on Electronic Structure Computations
and Theoretical Methods
for Materials Sciences, Minerals and Industry

Marek T. Michalewicz
Joint Bureau of Meteorology – CSIRO
High Performance Computing and Communication Centre
CSIRO Mathematical and Information Sciences
24th Floor, 150 Lonsdale St., Melbourne, Victoria 3000, Australia
Marek.Michalewicz@hpc.csiro.au

and

Mukunda P. Das
Department of Theoretical Physics
Institute of Advanced Studies
The Australian National University
Canberra, ACT 0200, Australia
mukunda.das@anu.edu.au

Exploration, mining and processing of minerals is one of Australia's main industries and export earners. Number of groups and divisions in Commonwealth Scientific and Industrial Research Organisation (CSIRO) are directly involved in materials and minerals research. Traditionally more emphasis is placed on rapid delivery of workable solutions for the local industry, and experimental methods. Computational methods developed in solid state physics and quantum chemistry are gaining wide acceptance in materials sciences, metallurgy and minerals science. This is well recognised in Europe and the USA, but there is still lots to be done to achieve similar level of acceptance for computational materials science in Australia.

To address some of these problems an intensive two day CSIRO Workshop on Electronic Structure Computations and Theoretical Methods for Materials Sciences, Minerals amd Industry took place on 8th and 9th July at the CSIRO Molecular Sciences in Clayton, Victoria, Australia.

One of peculiar characteristics of Australian research scene is a very low 'critical mass' of research activities. In most cases there are only individual researchers studying any given topic, sometimes working with graduate students, less often with post-docs. They are dispersed in different Universities, with little or no contacts.

This meeting aimed at encouraging more collaboration between the Acedemia and CSIRO, was able to establish contacts in the small community of electronic structure specialist in Australia and to make CSIRO scientists more aware of new and promising methods of computational and theoretical studies of materials and minerals

The workshop was attended by 64 researchers: half of them from CSIRO, several from the BHP and the rest from eight universities (Victoria, ACT,Qld, NSW). The workshop was sponsored by HPCCC, CSIRO Minerals and CSIRO Molecular Sciences.

CSIRO is uniquely placed to encourage and deliver computational science. It operates, jointly with Bureau of Meteorology in Melbourne, the largest supercomputer in the country, NEC SX-4 with 32 CPU's and 8 GB Main memory. At the workshop we planned to solicit ideas and suggestions regarding the most desirable, suitable and affordable software for this class of problems to be installed on NEC SX-4 for CSIRO researchers.

During the Workshop 19 talks on various topics on electronic and atomic structure computations, and properties of materials were presented. Basic philosophy of ab-initio theories and computational approaches was discussed displaying their relative strength and weaknesses. Details of Density functional theory, tight binding Green function method, molecular dynamics, quantum chemical methods (HF+CI) etc. with numerous applications were presented.

Lecturers and topics are detailed below.

Dr Mukunda P. Das, ANU
Density functional approach: a standard model for low energy physics

A/Prof. John Dobson, Griffith U.
Density Functional Theory of Many-Electron Systems

Dr U. Faul, Research School of Earth Sciences, ANU
Structure and properties of grain boundaries

Dr Stephen Fletcher, CSIRO Minerals
Some opportunities for molecular simulation in mineral processing

Dr Frederic Green, CSIRO Telecommunications and Industrial Physics
Current noise as a probe of electronic structure

Ian Harrowfield, C MacRae, N Scarlett, N Wilson, CSIRO Minerals
X-ray and Electron Microcharacterisation of Minerals and Materials

Dr Ian Jackson, Research School of Earth Sciences, ANU
Oxide and silicate minerals at high P and T: Thermodynamical behavior and physical properties

Dr Anatoli Kheifets, ANU
Calculation of energy-momentum distribution of electrons in solids and electron momentum spectroscopy of crystalline and disordered materials

Dr Michael Ling, Monash University
Computational Materials Science: from Schroedinger equation to alloy design

Dr Marek Michalewicz, CSIRO Mathematical and Information Sciences, HPCCC
How to deal with defects? Electronic structure methods for non-perfect materials

Dr Andrew Smith, Monash U.
Plasmons. When are they observed? How can they be calculated?

Dr Brian Smith, CSIRO Molecular Sciences
Methods for Accurate Energies

A/Prof. Phil V. Smith, U. of Newcastle
Lattice dynamical and electronic structure calculations on clean and chemisorbed semiconductor surfaces

Prof Ian Snook, RMIT
The use of computer simulation methods to investigate materials structure and crystallisation

Dr Billy Todd, CSIRO Molecular Science
Indefinite-time molecular dynamics simulations of elongational flow

Dr Feng Wang, U. of Melbourne
Electronic structural investigation of excited and ionized species: An introduction to MOLPRO

Dr Dave Winkler, CSIRO Molecular Sciences
'Orbital Imaging' of Strained Organic Molecules using Density Functional Theory and Electron Momentum Spectroscopy

Dr Alf Uhlherr, CSIRO Molecular Sciences
Computational Polymer Science: a Game of Mix'n Match

Dr Ling Zhang, CSIRO Minerals
Molecular Dynamics Simulation of Silicate Melts

The workshop web page containing the abstracts of all talks is:

http://www.mel.dit.csiro.au/ marek/el_structure/el_str_workshop.html

Commonwealth Scientific and Industrial Research Organisation (CSIRO) is the largest federally funded, multidisciplinary, national research organisation serving the scientific and research needs of Australian industry. CSIRO web page can be found at: http://www.csiro.au/.

Dr Ling Zhang, CSIRO Minerals
Molecular Dynamics Simulation of Silicate Melts

7 Job Announcements

'HOCHSCHULASSISTENT'
Department of Physics and Chemistry of Minerals
Institute for Geosciences at the Christian-Albrechts-University
of Kiel, Germany

A position as

'HOCHSCHULASSISTENT',

beginning 01.04.1999, is available in the 'Computational Mineralogy' group within the departement 'Physics and Chemistry of Minerals' in the Institute for Geosciences at the Christian-Albrechts- Universitaet, Kiel, Germany.

The official advertisment can be found at
http://www.min.uni-kiel.de/stellenangebote/ausschreibung.html

The following is aimed at providing information for candidates not familiar with the German University system:

The aim of the position of a Hochschulassistent is to offer the opportunity to obtain the Habilitation, which is generally a prerequisite for becoming a Professor at a German University. The position is therefore intended for researchers who already have some previous post-doc experience, and who are capable of establishing, within the framework of the group, their own research programme.

The position is initially available for 3 years, and can be renewed for a further 3 years, subject to satisfactory progress. If the Habilitation is completed within the first 6 years, there maybe a possibility to extend the position for another 4 years at the level of an 'Oberassistent'.

To aquire teaching experience, the succesful candidate will be required to teach 4 hours/week per semester.

The succesful candidate is expected to contribute to the research of the 'Computational Mineralogy/Crystallography' group, headed by B. Winkler. There is currently a strong interest in our group in adapting density functional codes, so that they can be used to address problems relevant to vibrational and optical spectroscopy, nuclear magnetic resonance experiments, and inelastic magnetic neutron scattering. Our aim is to strengthen the collaboration with experimental groups within and outside the departement.

The Hochschulassistent will also be required to help maintaining our computational facilites and provide help and advice to other members of the institute with respect to computer simulations.

Preference will be given to female candidates, as the policy of the University is to increase the number of women in research and teaching positions. Physically challenged candidates will also be treated preferentially.

We would like to point out that there have been recent precendes in our Institute where the Habilitationsschrift was written in English.

The salary for the position is very reasonable.

Further information can be obtained from:

Bjoern Winkler (bjoern@min.uni-kiel.de) or Prof. Depmeier (wd@min.uni-kiel.de).

Applications should be sent before 15.09.98 to:

Prof. Dr. W. Depmeier
Universität Kiel
Institut für Geowissenscahften/Mineralogie
Olshausenstr. 40
D-24098 Kiel

LECTURER IN HIGH PERFORMANCE COMPUTING
UNIVERSITY OF DUBLIN TRINITY COLLEGE

Applications are invited for the above post in the School of Mathematics at Trinity College, Dublin. The appointment, which will be made on contract for a period of five years, will be tenable from 1st October, 1998 or as soon as possible thereafter.

The School of Mathematics has recently instituted a new taught Master's programme in High Performance Computing. This programme includes elements in high performance computing hardware and software technology, classical simulation techniques in mathematics and physics, and emerging applications such as financial analysis, data-base mining, and optimisation. The successful applicant will be responsible for the design and teaching of appropriate elements within this programme. The Lecturer will also be expected to contribute to the computational research programme within the School of Mathematics. This research programme includes Lattice QCD, Quantum Field Theory, Relativity, Fluid Mechanics and Numerical Analysis. Available resources include a departmental UNIX cluster and access to a 48-node IBM parallel computer recently installed by the Centre for Supercomputing in Ireland.

Salary Scales:

Lecturer Grade II: 15,531-24,636 Irish Pounds
Lecturer Grade I : 31,347-40,384 Irish Pounds

Appointment will be made on the Lecturer Grade II scale within the range 15,531-21,915 Irish Pounds per annum at a point to accord with qualifications and experience to date.

Application forms and further particulars relating to this post may be obtained from:

Establishment Officer
Staff Office
Trinity College
Dublin 2
Tel: +353-1-608-1678
FAX: +353-1-677-2169
email: recruit@tcd.ie

Informal requests for information can be addressed to:

Dr. James Sexton
School of Mathematics
Tel: +353-1-608-2285
email: sexton@maths.tcd.ie

The closing date for receipt of completed applications will be Friday, 28th August, 1998.

TRINITY COLLEGE IS AN EQUAL OPPORTUNITIES EMPLOYER.

8   Abstracts

Role of Symmetry Reduction in the Polarization Dependence of the Optical Absorption in Non-Common Atom Superlattices

Rita Magri and Stefano Ossicini

Istituto Nazionale per la Fisica della Materia (INFM)

Dipartimento di Fisica, Università di Modena,

Via Campi 213/A, 41100 Modena, Italy

Abstract

In this paper we provide an explanation which accounts for both the intensity and the shape of the experimentally observed giant polarization anisotropy of the optical absorption in non common atom superlattices. By first-principles self-consistent calculations of the superlattice crystal potential and of the dielectric tensor elements we derive a "selection rule" by which the radiation polarization along the 110 and -110 directions *choose* only one optical transition of the doublet corresponding to transitions to the conduction band from the two upper crystal field splitted hole states which are degenerate in common atom superlattices. However, due to the similar intensity of the oscillator strenght of these transitions, it turns out that the magnitude of the anistropy depends *only* on the magnitude of the energy gap between the splitted states. Thus the inclusion of strain in the calculation increases the anisotropic effect by an order of magnitude. This effect is likely to be shown also by other systems with broken degeneracies and suggests ways to enhance the anisotropy through manipulation of interface structure or chemistry or strain condition.

First-principles optical properties of Si/CaF$_2$ multi-quantum wells

Elena Degoli and Stefano Ossicini
Istituto Nazionale per la Fisica della Materia (INFM)
Dipartimento di Fisica, Università di Modena,
Via Campi 213/A, 41100 Modena, Italy

Abstract

The optical properties of Si/CaF$_2$ multiple quantum wells are studied ab-initio by means of the Linear Muffin Thin Orbital method. In particular we investigate the dependence of the optoelectronic properties on the thickness of the Si wells. We find that below well width of $\sim$ 20 Å , new transitions appear in the optical region with an evident polarization dependence. The oscillator strength of these transitions shows a dramatic increase as the width of the Si well decreases. A comparison is made with recent experimental work on similar systems. Our results show that quantum confinement and passivation are necessary in order to have photoluminescence in confined silicon based materials.

Optical properties of confined Si structures

Stefano Ossicini
Istituto Nazionale per la Fisica della Materia (INFM)
Dipartimento di Fisica, Università di Modena,
Via Campi 213/A, 41100 Modena, Italy

Abstract

The optical properties of bulk silicon are deeply modified if the material is manipulated at the nanometre scale. In particular the growth of Si nanostructures constitutes today one promising approach for the development of silicon-based light emitting devices. In this context I discuss theoretical results on the optoelectronic properties of low-dimensional silicon structures, e.g. Si quantum wells, quantum wires, quantum dots. The results are compared with recent experimental data.

Pressure-induced phase transitions in solid Si, SiO$_2$, and Fe: Performance of LSD and GGA density functionals

Aleš Zupan

Department of Physical and Organic Chemistry, Jožef Stefan Institute,
Jamova 39, 1000 Ljubljana, Slovenia

Peter Blaha, Karlheinz Schwarz

Institute for Technical Electrochemistry, Technical University Vienna,
Getreidemarkt 9/158, A-1060 Vienna, Austria

John P. Perdew

Department of Physics and Quantum Theory Group, Tulane University,
New Orleans, LA 70118, U.S.A.

Abstract

We focus on a particular shortcoming of the local spin density (LSD) approximation for the exchange-correlation energy of a many-electron system: underestimation of the transition pressure p_t at pressure-induced structural phase transitions in solids. We have performed selfconsistent full-potential LAPW calculations, with full structure optimization, for three cases - silicon (Si), silica (SiO$_2$), and iron (Fe). In agreement with previous calculations, we find that gradient corrections to LSD over-correct the equilibrium volumes in Si and SiO$_2$, but correct or slightly under-correct the volume in Fe and the transition pressures in all three materials. We apply a thermodynamic-like inequality [A. Zupan *et al.*, J. Chem. Phys. **106**, 10184 (1997)] to our results to explain why the generalized gradient approximation (GGA) expands the equilibrium volume and increases the value of p_t over LSD. In all three cases, gradient corrections to LSD tend to stabilize the low-pressure phase because of its more inhomogeneous electron density.

Hyperfine fields of sp impurities on Ni and Fe surfaces

Ph. Mavropoulos and N. Stefanou

Section of Solid State Physics, University of Athens,

Panepistimioupolis, GR-15784 Zografos, Athens, Greece

B. Nonas, R. Zeller, and P. H. Dederichs

Institut für Festkörperforschung, Forschungszentrum Jülich,

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Abstract

Motivated by recent experiments for ^{77}Se adatoms on the surface of Ni, we present first-principles calculations of the electronic structure and hyperfine fields of $4sp$ impurities on the (001) surfaces of Ni and Fe. The calculations are based on the local-spin-density-functional theory and employ a Korringa-Kohn-Rostoker Green's function method for impurities at surfaces. The systematic behavior obtained for the hyperfine fields of adatoms or impurities in the first surface layer is completely different from that found in the bulk, mainly due the reduction of the symmetry and the coordination number at the surface. Our results explain the surprisingly small hyperfine-field values measured for Se adatoms and provide challenging predictions to be confirmed by future experiments.

Hyperfine fields of probe atoms on the (001) surface of Ni

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Abstract

We present first-principles calculations of the electronic structure and hyperfine fields of $3d$ and $4sp$ impurities on the (001) surface of Ni. The calculations are based on the local-spin-density-functional theory and employ a Korringa-Kohn-Rostoker Green's function method for impurities at surfaces. The systematic behaviour obtained for the hyperfine fields of the $4sp$ adatoms or impurities in the first surface layer is completely different from that found in the bulk. Instead of a single maximum with a very large hyperfine-field value at about the end of an sp series, the adatoms exhibit two maxima with a pronounced minimum in between. This behaviour can be traced back to the reduced coordination number of the adatoms which leads to a much smaller relative splitting of the bonding and antibonding peaks, and to the lower symmetry at the surface which results in an on-site s-p_z hybridization. The hyperfine fields found for the $3d$ adatoms are basically determined by the ferro- or antiferromagnetic coupling of the local impurity moment to the substrate magnetization and are therefore more or less similar to the results for bulk impurities, except that they appear somewhat reduced.

Fast, parallel electronic structure computations

for up to 7.6 million atoms non-periodic and disordered systems

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Abstract

Extremely fast implementation of the equation-of-motion method for the electronic structure computations is presented. The program can be applied to non-periodic, disordered nanocrystalline samples, metals, transition metal oxides and other systems.

It scales linearly, O(N), runs with a speed of up to 43 GFLOPS/s on NEC SX-4 vector-parallel supercomputer with 32 processors and computes electronic densities of states for multi-million atom samples in mere minutes.

The largest test computation performed was for the electronic density of states (DOS) for the TiO2 sample consisting of 7,623,000 atoms. Mathematically, this is equivalent to obtaining a spectrum of an n x n Hermitian operator (Hamiltonian) where n = 38,115,000. We briefly discuss practical implications of being able to perform electronic structure computations of this great speed and scale.

Lattice relaxation driven reorientation transition in $Ni_n/Cu(100)$

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Abstract

The magnetic anisotropy energy of $Ni_n/Cu(100)$ is calculated in terms of the spin-polarized fully relativistic Korringa-Kohn-Rostoker method including surface relaxation by using 2D structure constants originally described for LEED calculations. Investigating different relaxations, an explanation for the reorientation transition from in-plane to perpendicular can be given. For a relaxation of -5.5% (c/a=0.945) this reorientation occurs at about 7 layers of Ni and yields second order terms to the magnetic anisotropy energy that are in excellent agreement with experiment.

Comparison of ab initio theory and scanning tunneling microscopy for (110) surfaces of III-V semiconductors

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Abstract

We compare results of ab initio electronic structure calculations using density functional theory with measured scanning tunneling microscopy (STM) images for the clean (110) surface of III-V semiconductors. A detailed analysis is made of the nature of the wavefunctions contributing to STM images. The atomic structure has been determined by total energy minimization combined with the pseudopotential technique. The nature of the wave functions (surface localization, surface resonance or bulk like) has been determined for energies in the range of 3 eV on both sides of the fundamental gap. In particular, the decay of the density profiles into the vacuum as well as into the bulk has been analyzed. A consistent understanding of the voltage dependent STM images has been obtained. For tunneling out of the occupied states the dangling bond at the anion gives the main contribution for all voltages measured. On the other hand, for tunneling into the empty states the dangling bond at the cation is important only for small voltages. For higher voltages resonances (back bond but also some bridge bond contributions) dominate the STM image, yielding the observed rotation of the apparent row direction.

Temperature dependent surface relaxations of Ag(111)

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Abstract

The temperature dependent surface relaxation of Ag(111) is calculated by density-functional theory. At a given temperature, the equilibrium geometry is determined by minimizing the Helmholtz free energy within the quasiharmonic approximation. To this end, phonon dispersions all over the Brillouin zone are determined from density-functional perturbation theory. We find that the top-layer relaxation of Ag(111) changes from an inward contraction (-0.8%) to an outward expansion $(+6.3\%)$ as the temperature increases from $T = 0$ K to 1150 K, in agreement with experimental findings. Also the calculated surface phonon dispersion curves at room temperature are in good agreement with helium scattering measurements. The mechanism driving this surface expansion is analyzed.

Coadsorption of CO and O on Ru (0001): A structural analysis by density functional theory

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Abstract

Knowledge of the atomic geometry of a surface is a prerequisite for any detailed understanding of the surface's electronic structure and chemical properties. Previous studies have convincingly demonstrated that density functional theory (DFT) yields accurate surface atomic geometries and that reliable predictions concerning stable and metastable phases can be made on the basis of the calculated energetics. In the present work we use DFT to investigate the atomic structure of four ordered coadsorbate phases of carbon monoxide and oxygen on Ru (0001). All of the structures have a (2×2) periodicity with differing concentrations of CO molecules and O atoms. For two of these phases dynamical low-energy electron diffraction (LEED) intensity analyses have been performed and the agreement between our DFT- and the LEED-determined structures is found to be very good. We predict the atomic geometry of the third phase for which no structural determination based on experiments has been made to date. We also predict the stability of a new ordered mixed phase.

First-principles calculation of the thermal properties of silver

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Abstract

The thermal properties of silver are calculated within the quasi-harmonic approximation, by using phonon dispersions from density-functional perturbation theory, and the pseudopotential plane-wave method. The resulting free energy provides predictions for the temperature dependence of various quantities such as the equilibrium lattice parameter, the bulk modulus, and the heat capacity. Our results for the thermal properties are in good agreement with available experimental data in a wide range of temperatures. As a by-product, we calculate phonon frequency and Grüneisen parameter dispersion curves which are also in good agreement with experiment.

Molecular hydrogen in silicon

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Abstract

We present the results of first principle calculations on the behaviour of molecular hydrogen within crystalline silicon, both as an isolated species, and within defects in the material. These results are compared with recent experimental infra-red and Raman data obtained for silicon treated by either hydrogen plasma or soaked in hydrogen gas. The effect of Fermi–level position on the diffusion barrier of molecular hydrogen within silicon is also discussed.

Infra-red activity of molecular hydrogen in silicon

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Abstract

A freely rotating hydrogen molecule is not infra-red active but becomes so when subject to a hindering potential. It is shown that a strong potential leads to a single infra-red active mode for H_2, D_2 and HD whereas a weaker potential leads to three distinct fundamental transitions in each case. It is concluded that with the present evidence that molecules are aligned along [110] directions at tetrahedral interstitial sites in Si.

The structural properties of transition metal hydrogen complexes in silicon

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Abstract

A first-principles spin-polarised local density functional cluster method is used to explore the structural and vibrational properties of several substitutional transition-metal impurities complexed with hydrogen.

The electronic properties of transition metal hydrogen complexes in silicon

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Abstract

The electrical levels of various combinations of transition metal-H_n defects in Si are calculated using spin-polarised local density functional cluster theory with an empirical correction. The shifts of these levels with H can be understood through a displacement and splitting of the gap t_2 manifold of states due to the impurity. Passive defects are identified.

Vacancy-hydrogen complexes in germanium

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Abstract

Local-density-functional pseudopotential theory is used to investigate the structural, electronic and vibrational properties of vacancy-hydrogen complexes in germanium. The results are compared with recent infrared absorption data from proton and deuteron implanted Ge. The acceptor and donor levels of the VH_n defects are derived semi-empirically from the relaxed structures.

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9   SCIENTIFIC HIGHLIGHT OF THE MONTH

Energetics of $3d$ impurities on the (001) surface of iron

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Abstract

Motivated by recent STM results for Cr on Fe(001) we present a detailed ab-initio study of the alloying process in the dilute limit for $3d$ atoms on the Fe(001) surface. The calculations are based on local density functional theory and apply a KKR–Green's function method for impurities on surfaces. For practically all $3d$ transition metal impurities on Fe(001) we find a strong tendency for a direct exchange mechanism into the first surface layer. The early $3d$ impurities V, Cr and Mn strongly repel each other on neighboring positions within the first layer, while Ni and Cu atoms show a moderate repulsion. The ab–initio results are in good agreement with STM studies for Cr/Fe(001) by the NIST group and present valuable predictions for all $3d$/Fe(001) systems.

Over the last years experimental methods like ion field and scanning tunneling microscopy became able to discern individual atoms on surfaces and to observe to a certain extent diffusion and formation processes on the surface of materials. Together with various calculational methods a good understanding of growth modes on an atomic scale has been achieved [1, 2]. The results so far suggest that adsorption and diffusion depend strongly on the combination of materials and that therefore no general rules can be applied. For a few substrate-adsorbate combinations the formation of surface alloys is found even though the adsorbates are principally immiscible in the substrate [3, 4]. In a recent STM study the growth and alloying of Chromium on the Fe(001) surface has been investigated [5]. The aim of this investigation was to understand a number of anomalies in the interlayer exchange coupling of Fe/Cr magnetic multilayers. The authors find that under layer–by–layer growth condition substantial alloying occurs at the Fe/Cr interface. For instance,

adsorbed Cr atoms are directly incorporated into the first layer and also interdiffusion into deeper layers is observed. Further statistical analysis of the data yields direct information about the interactions of Cr atoms in the surface layer; e.g., the absence of nearest neighbor (nn) dimer pairs shows a strong repulsion between neighboring Cr atoms.

Motivated by these STM results for Cr on Fe(001) we present here a detailed ab–initio study of the alloying process for $3d$ atoms on the Fe(001) surface, where we will concentrate on the energetic properties in the dilute limit.
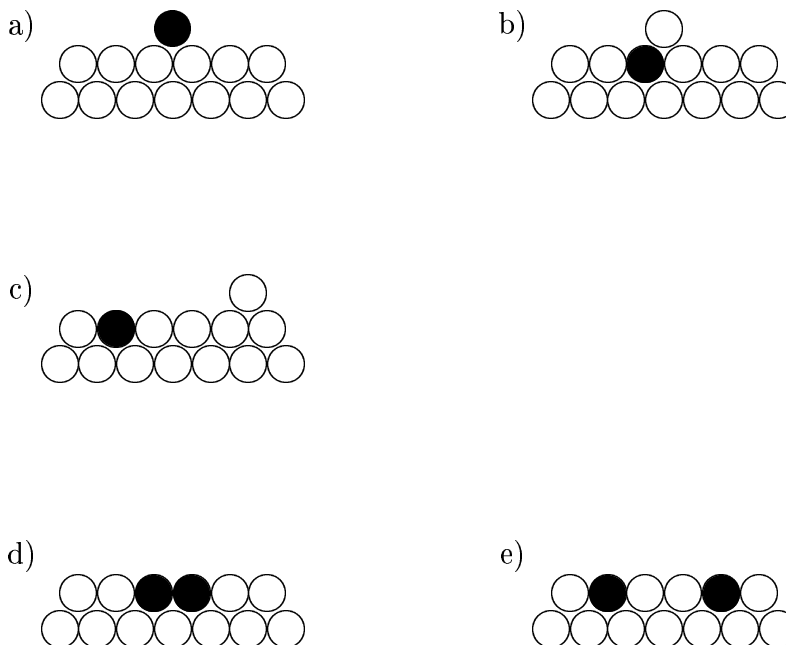
Figure 1: Schematic representation of different configurations of $3d$ impurities (shaded) at the surface: a) $3d$ adatom, b) the direct–exchange complex consisting of a $3d$ surface atom and a neighboring Fe adatom, c) the complete–exchange complex with a "free" Fe adatom, d) two $3d$ surface atoms at nn sites in the first layer and e) two non–interacting $3d$ surface atoms.

In particular we consider the elemental processes sketched in Fig. 1 and ask the following specific questions: Is it for an impurity adatom (Fig. 1a) energetically favorable to exchange with an Fe surface atom ("direct" exchange, Fig. 1b), and is the resulting complex (b) stable or likely to dissociate ("complete" exchange, Fig. 1c), so that effectively a migrating $3d$ adatom (a) is replaced by a migrating Fe adatom as in (c)? Do two $3d$ impurities in the first layer cluster as in (d) or are distant configurations (e) more stable? And finally, does the $3d$ impurity stick to the surface layer or does it interdiffuse into the Fe bulk? We will show, that our results are in excellent agreement with the recent STM–studies for Cr on Fe [5] and represent valuable predictions for the whole $3d$ series on Fe(001).

The calculations are based on density functional theory in the local density approximation

with the parameters of Vosko et al. [6], and apply KKR–Green's function methods for surfaces [7] and impurities on surfaces [8]. The atomic potentials as well as the potentials in the vacuum region are approximated by spherically symmetric ASA–potentials. However the "full" charge density including all non–spherical terms is evaluated and used in the calculation of the total energies. Angular momenta up to $\ell_{\max} = 3$ are included in the expansion of the wave functions (and up to $2\ell_{\max} = 6$ in the charge density expansion). We start from the selfconsistently calculated Green's function of the ideal surface which serves as the unperturbed reference system. To describe the impurity or the impurity dimers on the surface we consider a cluster of perturbed ASA–potentials which includes the potentials of the impurities and the perturbed potentials of several neighbor shells, with typical sizes ranging from 19 perturbed sites for the segregation energies to 58 for the interaction of nn impurities.

To overcome finite size effects due the restricted finite extension of the perturbation, the total energy of the perturbed system is evaluated as the energy difference with respect to the reference system by applying Lloyd's formula (adapted to complex energies [9]). In this way all single particle contributions are summed up in whole space. We checked the accuracy in our calculations by using different cluster sizes and by changing the reference system. In general we find that screening is less efficient at the surface than in the bulk, so that the spatial extent of the perturbed cluster plays a larger role than in the bulk. Nevertheless reliable total energy results can be obtained, if (i) at least two shells of perturbed potentials around each impurity are considered, if (ii) Lloyd's formula is used for the single particle energies, and if (iii) all calculated total energy differences refer to the same cluster sizes. For instance, for the interaction energy of two impurities the larger "dimer–cluster" has also to be used for the energy of the single impurity. Our calculations neglect the lattice relaxations at the surface and around the impurities. For the $3d$ impurities on the Fe surface this should be well justified. For instance, recent calculations for $3d$ impurities in bulk Fe [16] show, that the relaxation energies are very small, e. g. for Cr and Mn impurities 0.02 and 0.002 eV, respectively. At the surface relaxations are in general larger, but the relaxation energies are also small. Recent calculations [15] for $3d$ monolayers on Fe(001) give typical relaxation energies of 0.02 eV, with the largest relaxation energy of 0.04 eV obtained for a Cr monolayer coupling antiferromagnetically to the substrate moments.

Fig. 2 summarizes the calculated energies for the exchange mechanism at the Fe(001) surface. Plotted are both, the energies for the "direct exchange" process defined by the energy difference between the $3d$ adatom configuration shown in Fig. 1a and the exchanged pair configuration of Fig. 1b, as well as the energies for the "complete exchange", defined by the energy difference between configuration (a) and configuration (c) consisting of the $3d$ surface atom and a "free" Fe adatom. Our definition of the exchange energy does not include the additional energy gain due to the possible adsorption of the Fe adatom at a step or an island, since we are only interested in the exchange probability during diffusion on the terrace, which for the present purpose is considered as infinitely large. Moreover we only calculate the equilibrium configuration, but not the activation barrier, which we
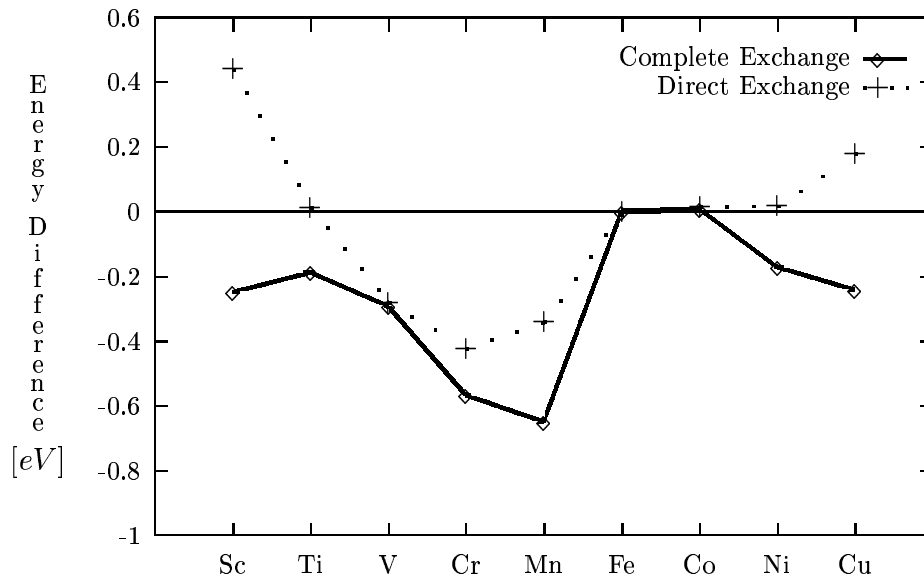
Figure 2: The differences in total energy for the exchange process. The *direct–exchange* energy is the total energy difference between the exchange complex of Fig. 1b and the $3d$ adatom of Fig. 1a. The *complete–exchange* energy includes the dissociation energy of the complex and represents the total energy difference between the configurations 1c and 1a.

assume to be sufficiently small that the exchange process actually occurs. By definition both exchange energies vanish for an Fe "impurity". Surprisingly we find that for all $3d$ impurities the complete–exchange configuration (c) is more stable than the $3d$ adatom (a). The only exception is the Co impurity, which has a nearly vanishing exchange energy and behaves in this respect like an Fe adatom. The energy gain is particularly large for the Cr and Mn adatoms, i. e. 0.57 and 0.65 eV, respectively. Our result for Cr is in excellent agreement with the STM experiments for Cr/Fe(001) [5], which show that all Cr atoms are incorporated directly into the iron surface without moving to steps.

One can see from Fig. 2 that (with the exception of Co and V adatoms) the "direct exchange" configuration (b) is considerably less stable than the "complete exchange" configuration (c), so that substantial energy is gained by breaking up the pair complex. In fact, at both ends of the series, i. e. for Sc and Cu, the pair configuration is energetically higher than the $3d$ adatom configuration. The reason for the instability of this complex will be discussed later on.

The calculated exchange energies are strongly affected by magnetism, which we illustrate for a Mn impurity. The local moment of the Mn adatom couples ferromagnetically to the substrate moments, while for the Mn surface atom the antiferromagnetic configuration [10] is most stable, lying 0.34 eV lower than the ferromagnetic one. Therefore the complete exchange energy of 0.65 eV for Mn is reduced to 0.31 eV, if we consider the transition from the ferromagnetic Mn adatom to the (metastable) ferromagnetic surface atom. While magnetism strongly affects the calculated energies, the local moments of the impurities

do not change much for the different geometries and magnetic configurations.

We now consider the interaction of two $3d$ surface atoms by calculating the interaction energies on nearest neighbor (nn) and next–nearest neighbor (nnn) sites in the surface and comparing with the calculated interaction energies at the same distances in the bulk. The interaction energies are defined as the total energy difference between the dimer complex and two isolated impurities at infinite separation. Thus by construction a negative energy means attraction and a positive energy repulsion between the two atoms. For the single surface impurities the preferred magnetic states are [10]: ferromagnetic coupling (↑) to the substrate for Fe, Co and Ni and antiferromagnetic coupling (↓) for Ti, V, Cr and Mn. Thus for the pairs we can in principle have three different collinear states, the antiferromagnetic configuration (↓↓) with both impurities coupling ferromagnetically to each other, but antiferromagnetically to the substrate, the ferrimagnetic configuration (↑↓) and the ferromagnetic one (↑↑). The last one is realized for the Co and Ni nn–pairs, while the antiferromagnetic configuration is found at the beginning of the series for Ti-, V- and Cr–pairs. Mn and Fe pairs are boundary cases, for which all three configurations exist, with the antiferromagnetic one being most stable for the Mn dimer and the ferromagnetic one for Fe. The interaction energies for all these surface dimers on nn and nnn sites are listed in table 1 together with the corresponding nn dimers in the bulk (in the bulk terminology these are nnn dimers). For Mn and Fe the bold numbers indicate the stable configuration.

	V	Cr	Mn			Fe			Co	Ni	Cu
configuration	(↓↓)	(↓↓)	(↓↓)	(↓↑)	(↑↑)	(↓↓)	(↓↑)	(↑↑)	(↑↑)	(↑↑)	(↑↑)
surface: nn	0.214	0.208	**0.214**	−0.011	−0.010	0.041	0.0	**0.0**	−0.011	0.044	0.067
bulk: nn	0.127	0.082	−	−	−0.031	−	−	**0.0**	−0.016	−0.026	−0.044
surface: nnn	−0.016	0.023	**−0.014**	−	−0.007	−0.059	−	**0.0**	0.003	0.011	−0.03

Table 1: Interaction energies of $3d$ impurities on the nearest neighbor (nn) and next nearest neighbor (nnn) sites in the surface layer of Fe(001) and at the same distance as the surface nn sites in bulk Fe (bulk: nnn). The energies are given in eV with positive energies referring to repulsive interactions.

The most important result of table 1 is, that the interaction for the nn dimers of Ti, V, Cr and Mn is strongly repulsive with a magnitude of about 0.2 eV, while the interaction for the nn dimers of Co, Ni and Cu is relatively weak, being slightly attractive for Co and repulsive for Ni and Cu. A similar trend, in particular the repulsion of the Ti, V and Cr dimers, is also found in the bulk, although the values are reduced due to the better screening in the bulk. The interaction of the nnn surface dimers is much weaker, repulsive for Cr and Ni and attractive for V and Mn. As noted already above for the exchange energies, magnetism plays also a large role for the interaction energy. The repulsion of the (↓↓) configurations is a consequence of frustration: the two atoms would like to couple antiparallel to each other, which can however not been realized due to the strong antiferromagnetic coupling of each atom to the substrate moments.

The above results are in very good agreement with the recent STM studies for the growth process of Cr on the Fe(001) surface [5]. In the statistical analysis of these data, no nn Cr pairs are found, while the probability for the formation of Cr dimers on nnn sites is reduced by 0.4 ± 0.2 as compared to a random distribution, being valid for the non–interacting case. Applying a Boltzmann's formula $\exp E_{\mathrm{Int}}/k_B T$ on our calculated interaction energies E_{Int} with an assumed temperature of $T = 300K$, we obtain a reduction to 0.01 for the nn Cr dimer and a reduction to 0.6 for the nnn dimers which agrees with the above results within the statistical errors.

We now proceed to the calculation of the surface segregation energies, the energy difference between the $3d$ impurity in the first surface layer and in the bulk. The calculated surface segregation energies are plotted in Fig. 3. Negative energies mean that the impurities seg-
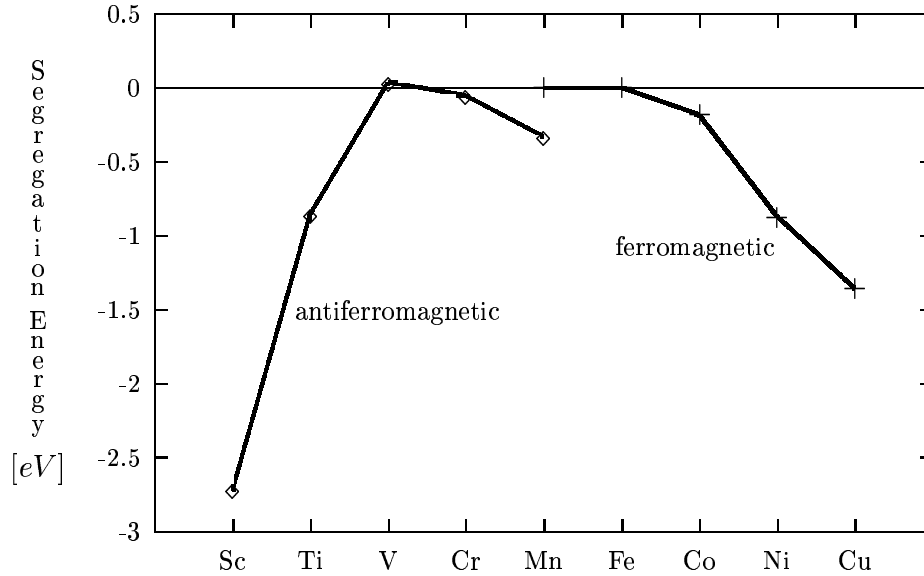

Figure 3: Surface segregation energies of $3d$ impurities with respect to the Fe(001) surface; negative energies mean segregation at the surface.

regate to the surface, while for positive energies the surface position is unfavorable. The results show a parabolic behavior, however with a depletion in the middle of the row. The parabolic behavior with negative values at the beginning and end of the series is expected from simple bonding arguments or from the trend of the surface energies. However instead of the expected maximum with positive values for Cr and Mn, we obtain a slightly negative value for Cr and a stronger negative value for Mn. This anomaly is due to magnetism which also shows up in the two values obtained for the Mn impurities. The stable antiferromagnetic configuration segregates to the surface, while the metastable ferromagnetic one has a vanishing segregation energy. For the well studied case of Cr/Fe(001) Venus and Heinrich [14] report at room temperature an intermixing up to three monolayers, while the STM studies [5] show that in the dilute limit about 25 % of the Cr atoms stay in the first layer. This agrees with the nearly vanishing segregation energy obtained in the calculations which means that there is no energetic driving force to or away from the surface.

Our results also agree reasonably well with the semi–empirical formulas of Miedema [11]. Recent calculations of segregation energies based on the LMTO–CPA method [12] for $3d$ impurities on Fe(110) yield a similar trend as in the present studies. However the results for Ti, V, Cr, Mn, Ni and Cu are about 0.5 eV higher than our values for Fe(001). Most of the difference seems to be due to numerical approximations in evaluating the CPA total energies [13].

The calculated segregation energies offer an easy explanation for the instability of the direct–exchange complex shown in Fig. 1b. The negative surface segregation energy e. g. of the Cu impurity can be modeled by Fe–Cu bonds being weaker than Fe–Fe bonds, since by segregating to the (001) surface 4 nn Fe–Cu bonds are replaced by Fe–Fe bonds. The same process occurs in the dissociation of the complex (b), since one Fe–Cr bond is replaced by an Fe–Fe bond. For this reason we have plotted in Fig. 4 the dissociation
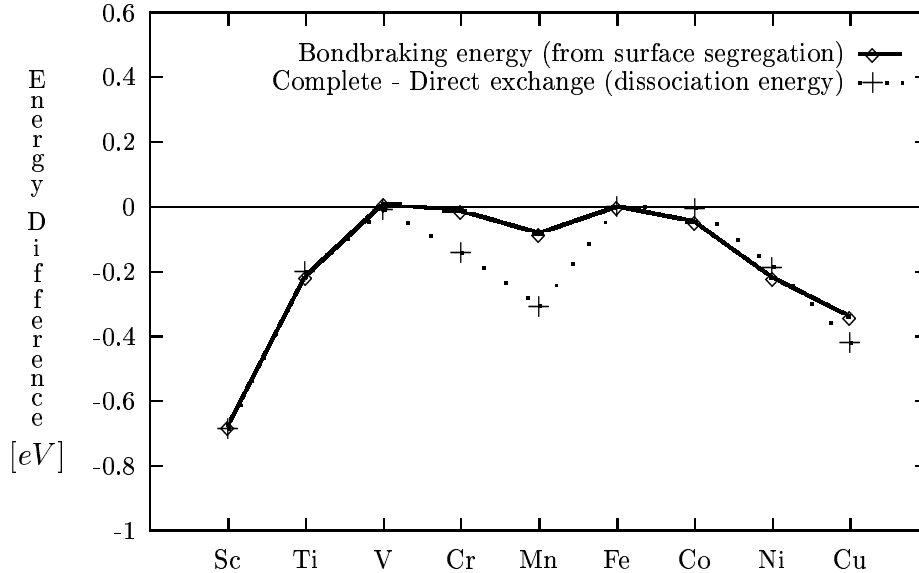

Figure 4: The dissociation energy of the exchange complex (total energy difference between the configurations 1c and 1b) and the energy per broken impurity–iron bond, as calculated from the segregation energy.

energy, as given by the difference of the "complete–exchange" and "direct–exchange" curves in Fig. 2, in comparison to the bond–breaking energy, as defined by 1/4 of the segregation energy. The close agreement supports the simple bond–counting picture.

In summary we have performed ab–initio studies for the energetic behavior of $3d$ impurities on the Fe(001) surface. Using the local density approximation and the KKR Green's function method we calculated the energy gain for the exchange process, the interaction of the impurities within the first layer and the surface segregation energies. The surprising result of our calculation is that with the exception of Co all $3d$ impurities prefer the surface position to the adatom one. Our results for Cr/Fe(001) are in excellent agreement with recent STM studies, showing the stability of the surface configuration, the strong repulsion

of nn pairs, weak repulsion of nnn pairs and a nearly vanishing surface segregation energy.

For the other impurities we predict interesting trends: For V and Mn the incorporation into the surface layer, equally strong repulsion of nn pairs as for Cr, but contrary to Cr weak attraction of nnn pairs, a nearly vanishing segregation energy for V, but a moderate segregation energy for Mn. A Co impurity behaves energetically very much like an Fe atom. On the other hand for Ni and Cu impurities the surface position should be more stable, first neighbors in the surface repel each other, while second neighbors are weakly repulsive for Ni and attractive in the case of Cu. Both Ni and Cu show a strong tendency for surface segregation. We hope that the present calculations encourage further experimental studies of these systems. A slightly shortened version of this paper has been published recently [17].

At present we are collaborating with the group of H. Dreyssé in Strassbourg to gain insight into the growth and alloying process of Cr/Fe(001) at larger Cr coverages [18]. The alloying behavior is investigated by Monte Carlo methods, where the presently calculated ab-initio interaction energies are used to determine the effective cluster interaction parameters [19] needed in this approach.

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