$\Psi_k$ Newsletter

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

Number 44 April 2001

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# Contents

# 1 Editorial

This *Psi-k Newsletter* we start with a letter by Mike Finnis and Jürgen Hafner on *"Publishing in European Journals"*. In the **TMR2** and **ESF** sections we have two reports on recent workshops, both containing also abstracts of the presented talks and posters. Several conference/school/workshop announcements can be found in the **TMR2**, **ESF**, and General Workshop/Conference Announcements sections. All information on the available postdoctoral and Ph. D. positions is in the **General Job Announcements** section. The reports on the collaborative visits are in the **ESF** section. There we also give this year's budget for collaborative visits and encourage all who are eligible to apply for funding. As always abstracts of newly submitted papers are placed in the usual **Abstracts** section. The *Newsletter* is finished with the scientific highlight of the month by L. Benco, T. Demuth, and J. Hafner (*University of Vienna*), F. Hutachka (*Total Raffinage Distribution, France*), and H. Toulhoat (*IFP, France*) on **Ab initio simulation of proton dynamics in zeolites"**. Please see the table of contents for further details.

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

**http://psi-k.dl.ac.uk/**

The above contains information on the Psi-k 2001 workshops and hands-on courses. In these pages you can also find information on how to apply for funding to make collaborative visits.

**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 $\Psi_k$ community** |

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

# 2 General News

## 2.1 Publishing in European Journals

In our last proposals to the EU Commission and to the European Science Foundation for creating the $\Psi_k$-TMR Networks and the $\Psi_k$-ESF Research Programme we were proud enough to claim that in our field Europe is producing some of the best research in the world. On the other hand we continue to send the best of our work to American Journals such as Physical Review Letters, Physical Review, Journal of Chemical Physics, etc. Europhysics Letters or the Letters sections of the Journal of Physics or of the new European Journal of Physics are sometimes considered as a second stop, if the authors are unlucky with referees the first time around. In the meantime priority may be lost.

Should we not become more self-confident in the publication of our results, and contribute in the process to the survival of European scientific journals? As a former member of the Executive Board of the Journal of Physics: Condensed Matter and as a Co-Editor of Europhysics Letters we have been empowered to decide rapidly on the publication of Letters for those Journals sent directly to us. A letter communicated by us with a recommendation to publish will be accepted immediately and if the authors supply a TeX source code (including any variant - LaTeX, AMS-TeX, REV-TeX, etc.) it will be published on the Web in the next available issue, which usually means within days. One concern of authors is that if they publish their work in European journals it will not be read by Americans. To counter this, if authors of the articles we communicate send a list of e-mail addresses of people working in the field (especially Americans) the publishers will send these readers an e-mail alert when the article is published on the Web. All Letters in JPCM (along with other IOP journals) are available free on the Web as part of Physics Expresss Letters, which again adds to their visibility. We invite the $\Psi_k$ community to take advantage of this opportunity. Of course we are vitally interested in maintaining a very high standard - in the interest of our journals as well as in the interest of the community.

Mike Finnis
former member of Executive Board, Journal of Physics: Condensed Matter

Jürgen Hafner
Co-Editor, Europhysics Letters

# 3 News from the TMR1 Network

# "Interface Magnetism"

## 3.1 Reports on Visits to Conferences/Workshops

### Report on a Conference Participation:
### TMS Annual Meeting, New Orleans
### February 11-15, 2001

The 2001 Annual Meeting and Exhibition of the Minerals, Metals and Materials Society (TMS) took place in New Orleans, February 11-15, 2001. This Society awards annually among others the Hume-Rothery prize and organizes with this a symposium on **"Electronic Structure and Alloy Properties"**. This year's prize winner was **Prof. B.L. Gyorffy** of the University of Bristol, UK. Previous prize winner include such distinguished personalities as A.G. Khachaturyan, R. Kikuci, D.G. Pettifor, J.W. Cahn, J.C. Phillips, A.J. Guinier, D. Turnbull, R.E. Watson, H. Ehrenreich, A.R. Miedema, T.B. Massalski, K.A. Gschneidner, Jr, J. Friedel.

This year's Hume-Rothery symposium was organised by Tony Gonis and Patrice Turchi (LLNL). The scientific scope of the symposium reflected the many scientific interests of the award winner. In his Hume-Rothery award lecture Balazs Gyorffy reported on the progress made in the description of the quasiparticle spectra of superconducting random alloys. In particular, he stressed the cases of exotic pairings such as d- and p-wave superconductivity. The topic of superconductivity featured also in the invited talks by Dzidka Szotek (Daresbury Laboratory, UK) and Adri Lodders (Amsterdam). The invited talk by Ole Andersen (MPI Stuttgart) reviewed the development of muffin-tin orbitals accurate to arbitrary order and also the methodologies to construct low energy Hamiltonians into which many-body effects, beyond LSD, could be incorporated. Magnetism featured prominently at this meeting with the invited talks by Josef Kudrnovsky Prague) on the calculation of the interlayer exchange coupling in magnetic multilayers, Hubert Ebert (Munich) on the relativistic calculation of the magnetic linear response function, and Julie Staunton (Warwick, UK) who discussed the effects on the magnetic anisotropy of magnetic annealing transition. Aspects of the electronic properties of alloys were addressed in the invited talks by J.S. Faulkner (Boca Raton, FL), A.V. Ruban (Copenhagen), I. Abrikosov (Uppsala), P.A. Korzhavyi (Uppsala), C. Wolverton (Dearborn, MI), Jack Kirkaldy (Hamilton, Ontario). There were also invited talks on angle resolved photoemission spectroscopies of magnetic systems by Paul Strange (Keele, UK) and Walter Temmerman (Daresbury Laboratory, UK). Three invited talks covered the physics of actinides, and Pu in particular, by F.E. Gibbs (Golden, CO), M.E. Manley (Los Alamos), and Walter Temmerman (Daresbury Laboratory, UK). All in all, this symposium gave a good cross-section of the phenomena of strongly interacting electron systems where Balazs Gyorffy's contributions featured very prominently.

Finally, we would like to acknowledge partial funding by TMR1- and TMR2 Networks which made our visit to the 2001 TMS Annual Meeting possible.

Walter Temmerman and Dzidka Szotek

# 4 News from the Research Training Network (RTN)

## COMPUTATIONAL MAGNETOELECTRONICS

## 4.1 Workshop Announcements

### 4.1.1 EGSCM PRAGUE'01

### European Graduate School on Condensed Matter (EGSCM)

### "Physics of Magnetic Multilayers - Theory and Experiment"

We remind you that the web-site of the European Graduate School on Condensed Matter (EGSCM) in Prague on the subject 'Physics of Magnetic Multilayers - Theory and Experiment' is available and continuously updated at the address:

`http://195.113.32.128/EGSCM_Prague.htm \\`

The organizers

V. Sechovsky, V. Drchal, J. Kudrnovsky, and I. Turek

# 5 News from the TMR2 Network

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

## 5.1 Workshop/Conference Announcements

### 5.1.1 Workshop on Physics of f-Electron Systems

# The Physics of f-Electron Systems

**Daresbury Laboratory, Tower Seminar Room**
**6-8 April 2001**

## Programme:

- **Friday April 6th.**

| | |
|---|---|
| **10:00-13:30** | *Coffee and Buffet Lunch in Science Center* |
| **13:30-14:20** | **B. Johansson** |
| **14:20-15:10** | **P. Wachter** *The physics of the actinide tellurides up to AmTe* |
| **15:10-15:40** | *Coffee* |
| **15:40-16:30** | **P. Oppeneer** *Theoretical results on the Pu monochalcogenides and on intermetallic U compounds* |
| **16:30-17:20** | **L. Petit** *SIC-LSD theory of Actinide Pnictides and Chalcogenides* |
| **17:20-18:10** | **R. Ahuja** *Structural properties of Am under Pressure: Theory* |
| **19:30-Closing Time** | *Daresbury Ring of Bells Pub* |

- **Saturday April 7th.**

| | |
|---|---|
| **9:00- 9:50** | **A. Georges** *Dynamical Mean Field Theory* |
| **9.50-10:20** | *Coffee* |
| **10:20-11:10** | **J. Lægsgaard** *DMFT description of CeP* |
| **11:10-12:00** | **B. Gyorffy** |
| **12:00-13:00** | *Buffet Lunch* |
| **13:00-13:50** | **P. Wachter** *Recent developments in the $\delta$ phase of Pu metal* |

| | |
|---|---|
| **13:50-14:40** | **G. Kotliar** *DMFT of Plutonium* |
| **14:40-15:30** | **T. Gouder** *Pu thin films* |
| **15:30-16:00** | *Coffee* |
| **16:00-16:50** | **G. Lander** *X-ray Magnetic Scattering from f-electron materials* |
| **16:50-17:40** | **P. Söderlind** *GGA+OP theory for f-electron metals* |
| **17:40-18:30** | **M. Brooks** *Exchange enhanced spin-orbit interaction and screened exchange interactions* |
| **19:30- Closing Time** | *Conference Dinner at Daresbury Cantina* |

- **Sunday April 8th.**

| | |
|---|---|
| **9:00- 9:50** | **V. Antonov** *The electronic structure and magneto-optical Kerr effect of Tm monochalcogenides* |
| **9:50-10:20** | *Coffee* |
| **10:20-11:10** | **Z. Henkie** *Nonmagnetic Kondo like behaviour in Actinides: Atomic disorder versus band structure tuning effect* |
| **11:10-12:00** | **M. Biasini** *Positron annihilation experiments in f-electron systems* |
| **12:00-12:50** | **U. Lundin** *Using perturbation theory from the atomic limit in electronic structure calculations* |
| **12:50** | *End of meeting (Lunch available at Cantina)* |

- **Satellite Meeting: Sunday April 8th.**

| | |
|---|---|
| **14:00-17:00** | *Informal Discussions on the Dynamical Mean Field Approach to f-electron systems* |

## 5.2 Reports on Workshops/Conferences

### 5.2.1 Report on Noncollinear Magnetism Workshop

# WORKSHOP

# "NONCOLLINEAR MAGNETISM"

### Universität Wien, March 8-10, 2001

The workshop has been organized and supported by:

EUROPEAN SCIENCE FOUNDATION – RESEARCH PROGRAMME
“ELECTRONIC STRUCTURE CALCULATIONS FOR ELUCIDATING
THE COMPLEX ATOMISTIC BEHAVIOUR OF SOLIDS AND SURFACES”
(STRUC-$\Psi_k$)

TMR NETWORK
"ELECTRONIC STRUCTURE CALCULATIONS OF MATERIALS
PROPERTIES AND PROCESSES FOR INDUSTRY AND BASIC SCIENCES"

RESEARCH CENTER AND SCIENCE COLLEGE
"COMPUTATIONAL MATERIALS SCIENCE"
(AUSTRIAN SCIENCE FUNDS)

INSTITUTE FOR MATERIALS PHYSICS, UNIVERSITÄT WIEN

Local organization:

J. Hafner , R. Lorenz, D. Spišák, T.Branis

The workshop "Noncollinear magnetism" assembled about thirty scientists form the European $\Psi_k$ Community, from the US and from Japan working in the field of complex noncollinear magnetic structures of materials. The presentations ranged from basic aspects of density functional theory applied to noncollinear magnetism and its implementation at various degrees of sophistication into the main electronic structures codes to applications ranging from spin-spiral states in $\gamma$-Fe and the noncollinear ground-sate in the complex $\alpha$-phase of Mn over noncollinear or canted magnetic structures in systems as different as invar-alloys, disordered colossal-magnetosresistance manganites and liquid oxygen to the ab-initio calculation of spin-waves. The abstracts of all contributions are listed below.

# FUNDAMENTALS

Thursday 13:30

## Density Functional Theory of Magnetic Systems Revisited

Helmut Eschrig[1] and Warren Pickett[2]
[1] *IFW Dresden, P.O.B. 27 00 16, D-01171 Dresden, Germany*
[2] *Department of Physics, University of California, Davis, CA 95616*

### Abstract

The first Hohenberg-Kohn (HK) theorem of density functional theory states the existence of a unique map

$$n(\mathbf{r}) \mapsto v(\mathbf{r}) \text{ mod (constant)}.^1$$

According to the second HK theorem, the ground state energy and density are obtained as the solution to a variational principle:

$$E[v-\mu] = \min_n\{F[n] + \textstyle\int n(v-\mu)d^3r\},^2$$

with $\mu$ the chemical potential. Although the variational principle has been put on a basis later on independent of (1) due to Levy and Lieb, the uniqueness of the map (1) remains an important prerequisite for the correctness of the application of Euler's equation to (2): $\delta F/\delta n = -(v-\mu)$, namely the uniqueness of the functional derivative. It is commonly assumed that the theorems readily apply to the more general case of spin dependent potentials, that is of external magnetic fields coupling to the spin only (as a non-relativistic approximation). The simple case of an atom in an eigenstate of $S_z$ is a trivial counterexample, however: its ground state itself and hence its ground state density does not change under an external homogeneous field $\mathbf{B}=B_z\mathbf{e}_z$ as long as the Zeeman energy does not lead to crossing of the discrete atomic energy levels. In this contribution we construct a more revealing generalization of the HK theorem, obtain explicitly the conditions that allow half metallicity, and demonstrate some unexpected consequences.

14:10

## Symmetry principle of the stability of complex magnetic structures

L.M. Sandratskii
*Institut für Festkörperphysik, Technische Universität,*
*D-64289 Darmstadt, Germany*

### Abstract

I use the notion of symmetry constraint in the density functional theory to introduce the symmetry principle of the stability of regular features of magnetic structures. Development of the symmetry approach is illustrated by the examples of the noncollinear one-sublattice ferromagnetism of $U_3X_4$ [1], noncollienar two-sublattice ferromagnetism of $UFe_4Al_8$ [2], noncollinear induced magnetism in $UX_3$ [3], helical magnetic structure in UPtGe [4], magnetism of atomically disordered Fe [5].

1. L. M. Sandratskii and J. Kübler, PRL 75, 946 (1995)
2. L. M. Sandratskii and J. Kübler, PR B 60, R6961 (1999)
3. S. Demuynck, L. M. Sandratskii, S. Cottenier, J. Meersschaut and M. Rots, J. Phys.: Condens. Matter, 12 (2000) 4629
4. L. M. Sandratskii and G. Lander, PR B 63, April (2001)
5. L. M. Sandratskii (to be published)

14:50

# Non-collinear ab-initio calculations with the FLAPW method

G. Bihlmayer, Ph. Kurz, F. Förster and S. Blügel
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*D-52425 Jülich, Germany*

### Abstract

We present a detailed account of the implementation of a formalism that allows to calculate non-collinear magnetic structures in the FLEUR code, a program based on the full-potential linearised augmented planewave (FLAPW) method. This formalism relies on a vector spin-density description with a (locally) collinear magnetic exchange-field in the vicinity of the atoms. This approximation of the collinear exchange-field will be discussed in detail. At present three approaches to deal with non-collinear magnetism are implemented: (i) arbitrary commensurate spin-structures by employing a (intra-atomic non-collinear) constraint-field, (ii) incommensurate spin-spirals and (iii) the relaxation of the spin directions. Technical aspects, like the parallelisation of the code as well as several recent results of calculations, e.g. of fcc-Fe, Mn(100) and (111) monolayers are presented. Apart from commensurate spin structures we also discuss the calculation of materials with incommensurate spin spirals. We show explicitly how to explore the magnetic phase diagrams by relaxation of the spin directions and calculations with constrained spin directions. Special emphasis will be put on a systematic approach to the investigation of the magnetic ground-state of a system by combining model Hamiltonians with ab-initio calculations.

16:00

# Fully unconstrained noncollinear magnetism within the projector augmented wave method

D. Hobbs, G. Kresse, and J. Hafner
*Institut für Materialphysik and Center for Computational*
*Material Science, Sensengasse 8, A-1090 Wien, Austria*

## Abstract

Spin-polarized calculations in solids have generally been confined to a global quantization axis to simplify both the theoretical model and its implementation in self-consistent codes. This approximation is justified as many materials exhibit a collinear magnetic order. However, in recent years much interest has been directed towards noncollinear magnetism in which the magnetization density is a continuous vector variable of position. In this paper we develop the all-electron projector augmented wave (PAW) method for noncollinear magnetic structures, based on a generalized local-spin-density theory. The method allows both the atomic and magnetic structures to relax simultaneously and self-consistently. The algorithms have been implemented within a powerful package called VASP (Vienna *ab-initio* simulation package), which has been used successfully for a large variety of different systems such as crystalline and amorphous semiconductors, simple liquids and transition metals. The approach has been used to study small clusters of Fe and Cr and triangular antiferromagnetic monolayers. Some of the clusters show noncollinear magnetic arrangements. For triangular Cr layers (both unsupported and grown on Cu(111) substrates, the ground state is noncollinear, it shows a $\sqrt{3} \times \sqrt{3}$ periodicity with ±120° angles between magnetic moments on neighbouring sites. Mn monolayers on the other hand have a collinear ground state with antiferromagnetically coupled rows of parallel moments.

This work has been supported by the TMR Network "Electronic Structure ($\Psi_k$).

16:30

# Ab-initio treatment of noncollinear spin structures within the atomic-sphere approximation and beyond, and application to spin waves

C. Ederer, O. Grotheer, and M. Fähnle
*Max-Planck-Institut für Metallforschung*
*Heisenbergstr. 1, D-70569 Stuttgart*

## Abstract

The properties of noncollinear magnets are often calculated within the framework of density-functional theory in local-spin-density approximation with the additional use of the atomic-sphere approximation for the spin directions. Thereby the intra-atomic noncollinearity is neglected for the calculation of the exchange-correlation energy by taking into account only those components of the spin density which are parallel to spin quantization axes (SQAs) defined for the whole atomic spheres. When the magnetic moment directions are calculated in a self-consistent manner, e.g., for systems with intrinsic noncollinearity or when calculating the response of the system to a weak external field with components perpendicular to the moment directions, the SQAs are conventionally chosen to be parallel to the magnetic moments. We present both theoretical arguments and test calculations showing that this choice of SQAs is not the best and may in certain situations lead to wrong results. As a consequence of our arguments we can suggest a better choice of SQAs. Furthermore, a new version of the linear-muffin-tin-orbital method is presented where the atomic-sphere approximation for the spin directions and the introduction of local SQAs are not required so that the intraatomic noncollinearity appears already in the basis functions.

As an application, a powerful method for the ab-initio calculation of adiabatic spin waves via the transverse susceptibility is developed, which may be used for systems with large and small exchange fields and for which the number of calculations required to obtain the spin wave spectrum scales linearly with the number of basis atoms in the supercell. Results are given for Fe, Co, Ni, $Ni_3Fe$ and CoFe.

17:00

# Non-collinear magnetic polarization on the basis of Density Functional Theory

Vito D.P. Servedio
*IFW Dresden*

### Abstract

The Local Spin Density Approximation (LSDA), despite its simplicity, has almost never been fully analyzed. It is being always used in connection with the intra-atomic spin-collinearity approximation, i.e. the vector spin density inside an atom was always considered parallel to a given axis.

From a relativistic treatment of the theory, it comes out that the effective field which governs the behaviour of the vector spin density, the XC-field, must be a transversal field.

Atomic numerical calculations, mainly involving isolated rare earth atoms and ions, will be presented using a fully non-collinear LSDA, as well as a new defined *ad hoc* transversal XC-field functional.

17:30

# Simple rules for determining the valencies of f electron systems

L. Petit[1], A. Svane[1], Z. Szotek[2], P. Strange[3], H. Winter[4] and W.M. Temmerman[2]
[1]*Institute of Physics and Astronomy, University of Aarhus,*
*DK-8000 Aarhus C, Denmark*
[2]*Daresbury Laboratory, Daresbury, Warrington WA4 4AD, United Kingdom*
[3]*Department of Physics, Keele University,*
*Keele, Staffordshire ST5 5DY, United Kingdom*
[4]*INFP, Forschungszentrum Karlsruhe, Postfach 3640,*
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### Abstract

The electronic structure of $f$-electron systems is calculated with the self-interaction corrected local-spin-density approximation. This scheme allows for a splitting of the $f$ electron manifold into an integral number of localized electrons and self-consistently determined fractional number of band electrons. Therefore, in comparison with the LSD, where all $f$ states are pinned at the Fermi energy, only maximum one $f$ band is left at the Fermi energy. We show that this band is partially occupied with occupancy $n_f$, and the $f$-electron fluctuations are reduced compared with the LSD. When $n_f$ exceeds a critical value of approximately 0.6, it becomes energetically more favourable to localize this state and the number of valence bands is reduced by one.

## ITINERANT MAGNETISM I

Friday 9:00

# Full potential studies of noncollinear states in $\gamma$-Fe

Elisabeth Sjöstedt, Lars Nordström
*Condensed Matter Theory Group, Physics Department,*
*Uppsala University, S-75121 Uppsala, Sweden*

### Abstract

Accurate density functional calculations have been performed for the fcc-based frustrated antiferromagnet $\gamma$-Fe. Several competing collinear as well as noncollinear magnetic structures have been considered, e.g. ferromagnetism, **1k**, **2k**, **3k** and double layered type I antiferromagnetism, as well as non-commensurate helices.The calculated ground state is found to vary with volume, and depends on whether a local or gradient corrected approximation to the exchange-correlation functional is adopted.

In contrast to standard noncollinear methods, our scheme treats the magnetization density as a vector field which is free to change both in magnitude as well as direction throughout space. This noncollinear scheme is implemented into an alternative linearization of the the full-potential augmented-plane-wave method (APW+lo), proved to be as accurate as the conventional linear-augmented-plane-wave method (LAPW), but computationally more efficient.

The obtained results are analyzed and compared with earlier calulations and existing experiments.

9:30

## Iron chains in Copper

Markus Eisenbach, Balazs L Gyorffy, G Malcolm Stocks
*H H Wills Physics Laboratory, Tyndall Avenue*
*Bristol BS8 1TL, United Kingdom*

### Abstract

We investigate the magnetic ground states of iron inclusions embedded in fcc copper using first principles calculations. Of main interest are linear monoatomic chains of atoms aligned along different directions in this Cu matrix. The method of calculation we employ is the locally selfconsistent multiple scattering (LSMS) real space method for solving the LDA Kohn-Sham equation. With this approach we find that depending on the orientation of the atoms along the 100 or 110 direction in copper the ground state orientation of the magnetic moments in the chain is either ferromagnetic or antiferromagnetic. Furthermore we have extended our code to perform fully relativistic calculations to enable us to investigate the spin orbit coupling effects leading to anisotropies and potentially non colinear ordering of magnetic moments in these systems of magnetic inclusions in copper.

10:00

## Unusual magnetism and magnetocrystalline anisotropy of $CrPt_3$

P. M. Oppeneer,[1] I. Galanakis,[2] and O. Eriksson[3]
[1]*Institute of Solid State and Materials Research, P.O. Box 270016,*
*D-01171 Dresden, Germany*
[2]*Institute für Festkörperforschung, Forschungszentrum Jülich,*
*D-52425 Jülich, Germany*
[3]*Department of Physics, Uppsala University,*
*Box 530, S-75112 Uppsala, Sweden*

### Abstract

We investigate computationally the origin of the unusual magnetic properties of $CrPt_3$. $CrPt_3$ is a metallic ferromagnet which recently attracted attention, because it was discovered that thin crystalline $CrPt_3$ films exhibit an unusually large magnetocrystalline anisotropy energy (MAE). This is unexpected, because $CrPt_3$ crystallizes in the cubic $AuCu_3$ structure. The easy axis is the (111) axis, and in $CrPt_3$ films suitably grown along this axis a strong perpendicular anisotropy was discovered, which together with the $T_C$ of 500 K makes $CrPt_3$ promising for perpendicular recording. In our investigations we find that there exist a profound Cr $3d$–Pt $5d$ hybridization, such that a large orbital moment of $0.15\,\mu_B$ develops *parallel* to the Cr spin moment of $2.73\,\mu_B$. Thus, Hund's 3rd rule is violated, due to the influence of the ligand states on the Cr site. This behavior is similar to what we recently discovered for $VAu_4$. We shall discuss various computed quantities, including the magnetic anisotropy. We calculate the (111) axis to be the easy axis. The calculated MAE is, with about 0.55 meV/unit cell, very large for a cubic transition metal compound. The computed MAE is larger than the experimental value of 0.3 meV/unit cell.

11:00

# Noncollinear magnetism in random transition metal alloys

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

### Abstract

Magnetic properties of random transition metal alloys have always been a subject of great scientific and practical interest. However, in most applications they were studied within a collinear spin model. On the other hand, in certain cases a treatment that includes only collinear spins may be not sufficient to describe a physical situation in a material, the most noticeable example being the Invar effect in Fe-Ni alloys (M. van Schilfgaarde, I. A. Abrikosov, and B. Johansson, Nature **400**, 46 (1999)). I breafly discuss an extension of the first-principles calculations for random alloys to the case of noncollinear magnets, as well as limitations of different approximations and techniques.

The effect of noncollinearity on the properties of a transition metal alloy are illustrated for the case of the fcc Fe-Ni Invar. Recently, it was found that the transition from the high-volume high-spin state to the low-volume low-spin state proceeds as a continuous transition to a disordered noncollinear configuration. The noncollinearity gives rise to an anomalous volume dependence of the binding energy curve, and explains the well-known peculiarities of Invar systems. I discuss a recent experiment (L. Dubrovinsky *et al.*, to be published) that provide a support for this theory. I also discuss exchange interactions in the 3d-transition metals and their alloys, and show that they favor noncollinear spin alignment in Invar alloys.

11:30

# Ab-initio density-functional study of non-collinear magnetism in $\alpha$-Mn

D. Hobbs and J. Hafner
*Institut für Materialphysik and Center for Computational Materials Science,*
*Universität Wien, Sensengasse 8/12, A-1090 Wien, Austria*

### Abstract

The crystalline and magnetic structures of all known polymorphs of Mn have been investigated using ab-initio local-spin-density functional theory (including generalized gradient corrections), with special attention to the occurence of a noncollinear magnetic structure in $\alpha$-Mn. We find that at atomic volumes smaller than 12 Å$^3$, the magnetic ground-state is collinear with large magnetic moments on sites I and II, small moments on sites III and nonmagnetic atoms on sites IV. At larger atomic volumes, a metastable collinear configuration coexists with a stable noncollinear state. The noncollinearity of the magnetic structure is driven by the appearence of magnetic moments on sites IV, leading to a frustration of exchange-interactions in the coordination shells of sites I and II. We also predict a slight tetragonal distortion, in agreement with experiment. In the metastable collinear configuration, magnetic moments on sites IV remain small and the frustration is reduced by a much stronger tetragonal distortion of the crystalline lattice. A similar situation is found in $\beta$-Mn, with a collinear structure with substantial moments on sites I, but nonmagnetic moments on sites II. The $\alpha$-phase is found to be stable over a wide range of volumes, under compression a phase-transition to hexagonal $\epsilon$-Mn is predicted.

This work has been supported by the TMR-Network "Electronic Structure ($\Psi_k$)".

# ITINERANT MAGNETISM II

13:30

# Noncollinear magnetism in ordered and disordered FeMn alloy: Order through disorder

D. Spišák and J. Hafner
*Institut für Materialphysik and Center for Computational Materials Science,*
*Universität Wien, Sensengasse 8/12, A-1090 Wien, Austria*

### Abstract

The results of calculations of the magnetic properties of ordered and disordered $\gamma$-FeMn using a self-consistent k-space tight-binding linearized muffin-tin orbital approach without any constraint on magnitude or direction of magnetic moments are presented. In an ordered $Fe_{0.5}Mn_{0.5}$ compound a noncollinear ground-state with parallel Fe moments and canted Mn moments forming an angle of 128° and with transverse components distributed in a plane perpendicular to the average Fe moment is found. If substitutional disorder is present in the system, a uniform collinear type-I antiferromagnetic order builds up. A possible explanation of this result is proposed referring to the phenomenon of ordering due to disorder.

14:00

# Exchange interactions in itinerant magnets: A Stoner model analysis

I. Turek
*Institute of Physics of Materials, Acad. Sci. Czech Rep.,*
*Žižkova 22, CZ-61662 Brno, Czech Republic*
*and*
*Department of Electronic Systems, Charles University,*
*Ke Karlovu 5, CZ-12116 Prague 2, Czech Republic*

### Abstract

A critical comparison of existing methods to evaluate the parameters $J_{ij}$ of the effective classical Heisenberg Hamiltonian from selfconsistent local spin density calculations is presented. The contribution concentrates on approaches based on: (i) constrained magnetic moments, (ii) a linear response theory, and (iii) the magnetic force theorem. The analysis is carried out in terms of a single-band Stoner model of non-collinear itinerant magnetism. It is shown that the parameters $J_{ij}$ yielded by the magnetic force theorem differ in general from those obtained by the constrained-moment procedure and by the linear response theory. Consequences of this discrepancy for reliable determination of quantities like the Curie temperatures or the spin-wave stiffness constants of metallic ferromagnets are discussed as well.

14:30

# A first principles theory of Bloch Walls in ferro magnets

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[2] *Technical University of Budapest*

### Abstract

We present a first-principles account of Bloch Walls in itinerant ferromagnets on the basis of fully relativistic Spin-Density Functional Theory in the Local Density Approximation(LDA). We argue and demonstrate that calculations based on this description will provide useful and novel information about the physics of this important element micro-magnetics. To illustrate the points we wish to make we implement the proposed calculations for Fe and determine the Bloch Wall thickness l(BW). Moreover,we comment on the features of the electronic structure, such as the layered and spin resolved density of states,which arise due to the presence of a Bloch Wall.

## CRITICAL TEMPERATURES

15:30

### First principles calculations and Monte Carlo simulations for calculating critical temperatures of ferromagnets

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**Abstract**

Calculations of critical temperatures of ferromagnets have been performed by employing classical Monte Carlo simulations. By calculating spin spiral energies using noncollinear density functional theory in the local spin density approximation, within the tight-binding linear muffin-tin orbital method and subsequently fitting the first principles data to a generalized Heisenberg expression for magnetic ordering, we have extracted the exchange parameters needed for the Monte Carlo simulations. So far the method has been tested on bcc-Fe, fcc-Co and fcc-Ni, where the calculated critical temparatures are in fair agreement with experimental data.

16:00

### Oscillatory Curie temperature of 2D ferromagnets

Josef Kudrnovský, P. Bruno, V. Drchal, M. Pajda, and I. Turek
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**Abstract**

We have determined the effective exchange interactions (EEIs) of magnetic overlayers Fe/Cu(001) and Co/Cu(001) covered by a Cu-cap layer of varying thickness (1-15 monolayers) in real space from first principles. The electronic structure was determined within the tight-binding linear muffin-tin orbital method combined with the surface Green function technique. We employ the so-called magnetic force theorem and construct the effective two-dimensional Heisenberg Hamiltonian which is then used to determine magnon dispersion laws, spin-wave stiffness constants, and overlayer Curie temperatures, the latter within both the mean-field (MFA) and random-phase (RPA) approximations. The approach is first tested for the case of bulk bcc-Fe and fcc-Co, Ni ferromagnets and we obtain a good agreement of calculated spin-wave stiffness constants and RPA-Curie temperatures with available experimental data. The RPA correctly obeys the Mermin-Wagner theorem for the two-dimensional case and small relativistic effects have to be therefore considered in order to obtain a non-vanishing value of $T_c^{RPA}$. Calculations give an oscillatory Curie temperature of magnetic overlayer as a function of the cap-layer thickness in a qualitative agreement with recent experiments and its values are in better agreement with experiment as compared to $T_c^{MFA}$. The origin of these oscillations can be traced down to quantum-well states formed in the Cu-cap layer sandwiched by the magnetic layer and by the vacuum which, in turn, influence properties of the magnetic layer.

# LOCALIZED MOMENTS

16:30

## Symmetry and noncollinear magnetism of $UFe_5Al_7$

C. Cardoso[1], L. M. Sandratskii[2], T. Gasche[1], 3, M. M. Godinho[1]
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### Abstract

The $UFe_5Al_7$ compound belongs to a very interesting series of $UFe_xAl_{12-x}$ compounds where the magnetic structure changes drastically with composition [1]. For example, the magnetic structure of $UFe_4Al_8$ is characterized by two types of the magnetic noncollinearity: the moments of the Fe and U atoms are almost orthogonal and, additionally, there is a canting of the magnetic moments within the Fe sublattice. On the other hand, the magnetic structure of $UFe_5Al_7$ was proposed to be collinear ferromagnetic.

Recent band structure calculations [2] allowed to explain the unusual magnetism of $UFe_4Al_8$. Here we extend the theoretical study of the $UFe_xAl_{12-x}$ series to the $UFe_5Al_7$ compound. On the basis of the symmetry analysis we show that the magnetic structure of $UFe_5Al_7$ is noncollinear since the magnetic moments of some of the Fe atoms must deviate from the magnetization axis. The first-principles relativistic calculations with the use of the ASW method confirmed the results of the symmetry analysis. The Fe magnetic moments deviated from the initial direction and formed a noncollinear magnetic configuration. Detailed results of the symmetry analysis and first-principles calculations are present. The role

of the orbital polarization correction is studied.

1. M. Kuznietz, A. Gonçalves, J.-C. Waerenborgh, M. Almeida, C. Cardoso, M. M. Cruz, M. Godinho, Phys. Rev. B, 60 (1999) 9494
2. L. M. Sandratskii and J. Kübler Phys. Rev. B 60 (1999) R6961

17:00

## Ab-initio molecular dynamics simulation of liquid oxygen

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### Abstract

Using a framework in which the magnitude and the orientation of the magnetization are allowed to vary with position,† we carried out *ab inito* molecular dynamics of liquid oxygen. Our scheme offers the possibility of following *simultaneously* the evolution of the magnetic and structural properties of this system. Liquid oxygen is modeled by a periodic system containing 32 oxygen molecules at the experimental density of 1.14 g/cm$^3$. The simulation is carried out near the boiling point at a temperature of 90 K. Liquid oxygen is a molecular liquid constituted of $O_2$ molecules which preserve their structural and magnetic identity. These features are indeed reproduced by the simulation. The radial distribution functions and the mean square displacement, extracted from the atomic trajectories, show that the structural and diffusive properties of this system ressemble those of a normal liquid. The magnetic structure is monitored during the simulation by calculating the local magnetic moments on every oxygen molecule. The oxygen molecules are found to preserve individually their spin triplet state during the course of the simulation. Preliminar analyses of correlations between structural and magnetic properties indicate that oxygen molecules show the tendency of dimerizing in an antiferromagnetic fashion.

† T. Oda, A. Pasquarello, and R. Car, Phys. Rev. Lett. **80**, 3622 (1998).

17:30

## Density functional studies of magnetic lamellar organic-inorganic materials: the case of solid copper hydroxonitrate

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### Abstract

The linear correlation found between the exchange coupling constant J and the Cu-O-Cu bond angle $\theta$ in hydroxo-bridged Cu(II) molecular complexes has long been established (1). It results in an antiferromagnetic (ferromagnetic) coupling for complexes with Cu-O-Cu bond angle $\theta$ larger (smaller) than 98°. These predictions have been corroborated by intensive theoretical investigations performed within density functional theory where, in addition to Cu-O-Cu bond angle, the out-of- plane displacement of the hydrogen atom of the hydroxo group was also found to play a major role in determining the sign of the magnetic interactions (2,3). The question arises whether the same scheme can be employed to describe not only molecular complexes but also solid-state periodic structures. Solid copper hydroxonitrate $Cu_2(NO_3)(OH)_3$ can be considered as one of the extended system counterparts (4) of the molecular complexes studied in Ref. 2 and Ref. 3. This system is a prototypical example of layered solid characterized by a planar array of transition metal ions arranged in a triangular fashion. Susceptibility measurements in the range $T < 350$ K are suggestive of an antiferromagnetic character within each plane. In a recent paper (5) we have resorted to density functional theory combined with a plane-wave approach to investigate spin topology and magnetic interactions in solid $Cu_2(NO_3)(OH)_3$. The results have shown that no clear correlation was found between the nature of the bridging groups and the sign of the exchange interactions, and this irrespective of the specific Cu-O-Cu exchange pathways. Indeed, both parallel and antiparallel alignments between spin densities occur for the Cu(1) or the Cu(2) pairs along the **b** direction, as well as for Cu(1)-Cu(2) pairs lying on adjacent rows along the **b** direction. This finding is at odds with the conjectures of phenomelogical models which associate one specific sign for the exchange coupling to each pair of Cu(1)-Cu(1) and/or Cu(2)-Cu(2) centers. Moreover, it suggests that models for magnetism relying on only one single, isolated layer, are insufficient for this compound. We are currently working on the extension of these investigations to the account of non-collinear effects, as developed in (6).

REFERENCES
(1) V. H. Crawford, H. V. Richardson, J. R. Wasson, D. J. Hodgson and W. E. Hatfield, Inorg. Chem. 15, 2107 (1976).
(2) E. Ruiz, P. Alemany, S. Alvarez and J. Cano, J. Am. Chem. Soc. 119, 25 (1997).
(3) E. Ruiz, P. Alemany, S. Alvarez and J. Cano, Inorg. Chem. 36, 3683 (1997).
(4) V. Laget, C. Hornick, P. Rabu, M. Drllon, P. Turek and R. Ziessel, Adv. Mater. 10, 1024 (1998).
(5) C. Massobrio, P. Rabu, M. Drillon and C. Rovira, J. Phys. Chem. B 103, 9387 (1999).
(6) T. Oda, A. Pasquarello and R. Car, Phys. Rev. Lett. 80, 3622 (1998).

# SPIN DYNAMICS

Saturday 9:00

## Spin Dynamics in Itinerant Magnetic System

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### Abstract

Calculations based on an unconstrained spin density functional method will be presented together with a brief description of the implementation in the FP-LAPW method. Some focus will be on the dynamics of these spin densities. This will be demonstrated with results of calculations for the spin-wave spectra of Fe, Ni, and Co.

9:30

# "Local" magnetic moments and magnetic correlations in thin films and multilayers above the Curie temperature: a study of bcc-Fe/W(100), fcc-Fe/Cu(100) and fcc-Co/Cu(100)

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### Abstract

We present a microscopic theory of magnetic correlations in materials of reduced dimensions at finite temperatures within the framework of a first-principles electronic structure scheme. We use the spin-polarised screened Korringa-Kohn-Rostoker method and describe the magnetic correlations at finite temperatures within a mean-field disordered local moment picture in conjunction with the inhomogeneous coherent-potential approximation. We show that the paramagnetic spin susceptibility of the films and multilayers is layer dependent, and therefore, in principle the type of magnetic correlations can be different in different layers. Using this scheme we study the magnetic correlations and the Curie temperatures in bcc-Fe thin films on W(001), fcc-Fe thin films and fcc-Co thin films on Cu(100) substrates. The Curie temperature of the thin films approaches that of the bulk when the number of layers $\geq 7$.

10:00

# Non-collinear magnetic states in FeMn: Application of first principles spin dynamics

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### Abstract

Although a subject of great venerability, metallic magnetism is currently undergoing a renaissance. The proposed spin dynamics (SD) of Antropov *et al.** which offers the possibility to treat the dynamics of magnetic moment reorientations on a first principles basis. In this presentation we show that 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. The formalism is than implemented in the Locally Selfconsistent Multiple Scattering Theory (LSMS), and applied to study the ground state properties of FeMn random binary alloys. It is beleived, that fcc Fe and FeMn (at the appropriate lattice constant) have a non-collinear ground state called the "3Q" state. We find that this is a ground state only on the "average".

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

Work supported by DOE Office of Science BES-DMSE and OASCR-MICS, under subcontract DE-AC05-00OR22725. Oak Ridge National Laboratory (ORNL) is operated by UT-Battelle, LLC for the U.S. Department of Energy.

## SPECTROSCOPY

10:30

# Treatment of non-collinear spin-structures in electron spectroscopy

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### Abstract

Many magnetic compounds posses a spin-structure that is non-collinear, i.e. the spin magnetic moments may be oriented with respect to one another in an arbitrary way. When dealing with the electronic structure of such systems this situation can be accounted for in a straight forward way when using the relativistic version of multiple scattering theory for spin-polarised systems (SPR-KKR). The corresponding formalism is extended to deal with various kinds of electronic spectroscopy. This is demonstrated in some detail for the valence band photoemission as well as the X-ray absorption. Corresponding results will be presented for the system FeMn for which various spin configurations have been investigated. It will be shown that the magnetic linear dichroism in X-ray absorption (XMLD) should allow to identify the spin configuration of the ground state.

11:00

## Optical and magneto-optical spectroscopy of noncollinear magnets: application to $U_3P_4$

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### Abstract

The method [1] to calculate the optical and magnetooptical properties of noncollinear magnets is discussed. Application to the noncollinear magnetic configurations in $U_3P_4$ is considered. The dependence of the spectra on the angle between the U magnetic moments is studied and related to the character of the U 5f states in this compound.

1. J. Köhler, L.M. Sandratskii, J. Kübler, Phys. Rev. B55, R10153 (1997); Physica B 253, 222 (1998).

# OXIDES

11:30

## Novel Properties of Metallic Oxides

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### Abstract

This talk discusses two transition metal oxide systems, particularly magnetic ruthenates and spinel $LiV_2O_4$. Magnetism is not expected in 4$d$ and 5$d$ oxides, particularly metallic ones. However, it has been known for some time that perovskite $SrRuO_3$ is an exception, being ferromagnetic with $T_C = 165$K. Furthermore, recent investigations have established the existence of a whole family of related perovskite and layered perovskite ruthenates that show an unusually diverse range of magnetic properties. Even more unexpectedly, spinel structure $LiV_2O_4$ was discovered to be a heavy Fermion compound. In this talk, density functional studies of these materials are presented. Transition metal oxygen covalency plays an unusually important role in the ruthenates leading to strong magnetoelastic effects and complex magnetic phase diagrams. $LiV_2O_4$ is found to be a metal with local moment magnetic character and antiferromagnetic interactions. The moments are formed from the $a_g$ component of the V $t_{2g}$ manifold. The remainder of the V $t_{2g}$ orbitals participate in itinerant lighter mass bands. This has superficial similarities to $f$-band heavy fermions, but closer examination reveals that a direct mapping is not possible due to off-diagonal effects, particularly Hund's coupling and Coulomb correlation, arising because the local moments and conduction bands are derived from the same atomic $d$ shell. This opens the door to other explanations of the heavy fermion behavior related to geometrical frustration and non-collinear spin arrangments.

12:00

## Canted spin structures in GMR manganites

R. Lorenz and J. Hafner
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### Abstract

Magnetization, electronic and structural properties of $La_{1-x}Sr_xMnO_3$ and $La_{1-x}Sr_xMnO_3$ are reported for the range $0 \leq x \leq 1$. The results are obtained using self–consistent local spin–density electronic–structure methods that include full geometrical relaxation. The aim of this work is to investigate possible non–collinear spinstructures and to explain the discrepancy of recent experimental studies for the magnetic and structural groundstate of $LaMnO_3$ and lightly doped $La_{1-x}Sr(Ca)_xMnO_3$.

The samples have been relaxed to the groundstate structure using an ab–initio PAW (vasp) method. The non–collinear calculations are based on a Linear-Muffin-Tin-Orbital (LMTO) Method in the Atomic Sphere Approximation (ASA) in k–space allowing for non-collinear spin-directions. To overcome the well known problems in treating the Oxygen d–states we used downfolding algorithm, also for the non–collinear case. The investigations use both LSDA and GGA for the exchange correlation potential.

It is shown, that pure $LaMnO_3$ shows a complex magnetic phase diagram with a structure induced metastable antiferromagnetic configuration. Non–collinear spinstructures are only found in the region $0 < x < 0.15$ for both systems.

# Optical properties of $\alpha'$-NaV$_2$O$_5$

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V.N. Antonov
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## Abstract

We have studied the optical properties of the ladder compound $\alpha'$-NaV$_2$O$_5$ using the LDA+$U$ approach. Firstly, the calculations were performed assuming an anti-ferromagnetic alignment of the V magnetic moments along the ladders. Then, the effect of the absence of the long-range anti-ferromagnetic order in the high-temperature phase was modelled by performing the calculations for spiral magnetic structures defined by a $q$ vector parallel to $b$ crystal axis. The calculated optical conductivity agrees well with the experimental one derived from the loss function measured using electron energy-loss spectroscopy. The decomposition of the calculated optical conductivity into contributions from transitions between the electronic states of different character reveals the origin of the observed anisotropy of the optical conductivity.

# 6 News from the ESF Programme

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

### 6.1 Budget for Collaborative Visits

We have a budget of 100,000 FF for up to a month long collaborative visits. If you belong to one of the 17 European countries contributing to the above ESF Programme (Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Hungary, Ireland, Italy, Poland, Portugal, Slovenia, Spain, Sweden, Switzerland, and UK) you are invited to apply for financial support to psik-management@dl.ac.uk, supplying a short scientific proposal, duration and cost of the visit you plan to make and the affiliations of your and host institutions. Details are given on the web-site at:

http://psi-k.dl.ac.uk/

under the heading 'How to Collaborate'.

## 6.2 Reports on Collaborative Visits

# Report on a Collaborative Visit of Carla Molteni (Theory of Condensed Matter group, University of Cambridge) to the Max-Planck-Institut für Festkörperforschung, Stuttgart

25 – 29 January 2001

I visited Prof. Michele Parrinello and his group at the Max-Planck-Institut für Festkörperforschung in Stuttgart (Germany) from 25 to 29 January 2001.

The goal of my visit was to discuss recent results and future developments of on-going collaborations on structural phase transformations in semiconductor nanocrystals.

The visit has benefited from the presence, at the same time, of Dr Roman Martonak from the Slovak Technical University of Bratislava who is involved in the nanocrystal project.

We have developed and applied a new constant pressure molecular dynamics method suitable for studying, within a density functional theory or tight-binding scheme, non-periodic systems under pressure, which cannot be simulated with the usual techniques for periodic systems. [R. Martonak, C. Molteni and M.Parrinello, Phys. Rev. Lett. **84**, 682 (2000), *"Ab-initio molecular dynamics with a classical pressure reservoir: simulation of pressure-induced amorphization in a* $Si_{35}H_{36}$ *cluster"*].

In particular during this visit we have discussed new results on large silicon clusters obtain with tight-binding molecular dynamics, and on CdS clusters treated within density functional theory. Ideas about how to lengthen the time scale of structural phase transformation simulations have also been analyzed.

The visit has been very useful to discuss new ideas for future calculations and outline a couple of publications with the most recent results.

I am very grateful to the network for its support.

Carla Molteni

Cavendish Laboratory, Cambridge

# Report on a Collaborative Visit of Pablo Ordejón (Institute of Materials Science of Barcelona) to Jorge Kohanoff (Queen's University of Belfast)

Feb 14 – Feb 28, 2001

I visited Dr. Jorge Kohanoff, and the rest of the Atomistic Simulation Group at the Queen's University of Belfast (QUB), from February 14 to February 18, 2001. The aim of my visit was to continue an ongoing collaboration with Dr. Kohanoff, on ab initio calculations of ferroelectricity in hydrogen-bonded materials, and also to start new collaborations with other members of the group (mainly, Prof. Mike Finnis).

We have recently developed (D. Sanchez-Portal, P. Ordejón, E. Artacho and J. M. Soler, International Journal of Quantum Chemistry **65**, 453 (1997)) the SIESTA package for electronic structure calculations on systems with a large number of atoms. The group at QUB has been using the serial version of this code during the past two years for a variety of problems, including ferroelectric materials, metal/metal interfaces, and biologically relevant systems.

A parallel version of the code, developed mainly by J. Gale (Imperial College, London) and A. García (UPV, Bilbao) is about to become available to the SIESTA users. This will allow to attack larger problems which are also beyond the capabilities of the usual (parallel) plane wave codes (FPMD, CPMD and FEMD) used by the QUB group. The group will start to use it on an experimental basis; this will allow to detect possible problems and bugs, while allowing the group to study larger and more complex systems.

During my visit, I helped in the installation of the parallel version in the computers available to the group at QUB, and instructed the researchers, postdocs and students on the theory, implementation and usage of the code. We also advanced in established collaborations between our groups on hydrogen-bonded ferroelectric materials (KDP), and started new collaboration on the simulation of oxides, namely zirconia, alumina, and related systems

Pablo Ordejón

## 6.3 Reports on Workshops/Conferences

### 6.3.1 Report on WideGap2001 Workshop

# Doping Issues in Wide Band-Gap Semiconductors

## University of Exeter, United Kingdom

## 21-23 March 2001

## http://widegap2001.ex.ac.uk/main.html

## widegap2001@excc.ex.ac.uk

## Organising Committee

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The conference was attended by 74 people from 15 counties. Its aim was to discuss the successes and problems of doping wide-bandgap semiconductors.

The conference opened by a talk by Bechstedt (Germany) on deep level defects in SiC especially vacancies and complexes with boron. This was followed by several talks on SiC by Nieminen (Finland), Deak (Hungary), Svensson (Sweden) and Steeds (UK): all of which highlighted the problems of doping and the formation of compensation centres such as vacancies. Hydrogen was singled out as an important impurity while Steeds emphasised the likely role of carbon interstitials in luminescence. Nieminen emphasised that corrections to the total energies of charged defects found in supercell methods were very important.

Donot As (Germany) gave a talk on carbon doping of MBE grown cubic GaAs leading to the incorporation of $10^{20}$ $\text{cm}^{-3}$ carbon atoms although the activation efficiency was only about 1%. A red luminescence was correlated with the compensating centre. The importance of dislocations was emphasised by Martin (UK) in experiments on AlGaN/GaN HFETs. Conduction parallel and perpendicular to the growth axis was quite different. HPHT growth of GaN was discussed by Krukowski (Poland) where oxygen was incorporated as a donor. Mg was readily introduced but Be doping was a problem. Van de Walle (USA) and Nieminen independently argued that Be might favour an interstitial site with a $\text{Be}_i$-$\text{Be}_s$ pair readily formed. This would explain its low doping efficiency.Saarinen (Finland) highlighted the use of positrons in identifying vacancies.

Robinson (UK) discussed tetrahedral amorphous diamond where intricate details of its structure coould be deduced from Raman measurements. The problem of doping with nitrogen was described which is found to be inefficient in spite of a level resonant with the conduction band. However, the low carrier mobility of the amorphous material would always limit any electronic application. Nebel (Germany) reported sulphur doping of diamond where (0/+) and (+/++) levels were found at 370 and 480 meV respectively. Ven der Walle reviewed ZnO comparing H donor levels in a wide range of materials. His talk was nicely followed by King (UK) on muon spin spectroscopy confirming his prediction of a donor level at $E_c - 0.019$ eV. Auret (S. Africa) used DLTS to describe deeper levels in ZnO while Clerjaud (France) showed what could be extracted from local mode spectroscopy of GaN, finding modes for Mg and Be complexes possibly linked with oxygen. Monemar (Sweden) gave a nice talk on what had been learned from PL of shallow dopants. Si, O and Mg bound excitons were identified. No Be bound exciton PL has been confirmed.

Katayama-Yoshida (Japan) gave an interesting talk on his theory on codoping where shallow level defects might be made in wideband gap materials by complexes. Examples include P-P-H and S-H defects in diamond, N-N-Al defects in ZnO, and Mg-O-Mg defects in GaN. There is experimental evidence that Mg+O codoping increases the hole concentration in GaN. A striking feature of Katayama-Yoshida's talk was the number of patents secured for the effect. Neugebauer (Germany) gave the results of an impressive set of calculations on dopant-surface effects nicely explaining why rough and smooth faces occur under different conditions. These calculations may pave the way to an alternative theory of codoping of say Mg+O in GaN, where the presence of surface oxygen would encourage the incorporation of Mg. This would be especially true if oxygen and Mg had surfactant and anti-surfactant roles respectively.

Pereira (Portugal) showed that EPR could lead to assignments of the levels of defect with respect to band edges and illustrated it with Ni and Ni-N centres in diamond. An adsorbate model for the high surface conductivity in hydrogenated diamond was discussed by Ristein (Germany) which was supported by the first-principles calculations of Goss (UK). The transfer doping effect apparent here might be important in other materials.

Kucheyev (Australia) highlighted the difficulties of eliminating lattice damage from ion implantation in GaN while Svensson showed that ion implantation was the method of choice for selective area nitrogen doping of SiC. However, unknown compensation centres were created which were difficult to anneal out. Speck (USA) impressed the conference with MBE growth studies of GaN under Ga rich and N rich conditions and the success of introducing *p*-dopants like Mg with resulting high hole mobilities. Finally, Berzina (Latvia) discussed optical centres in AlN highlighting the importance of $V_{Al}$ and $O_N$ centres.

There were exciting posters as well and Van de Walle summed up the meeting as one which had successfully brought together groups having interests in different material and experience with different ways of doping. It will be judged successful if the tricks used in one area are used in others. Certainly, co-doping will be tried in SiC and possibly diamond and theorists encouraged to analyse the difficult problems of dopant incorporation and surface effects.

**List of participants follows.**

| | |
|---|---|
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# Conference Programme

## Wednesday 21 March 2001

*Session I, chairman: R. Jones*
Engineering building, Harrison lecture theatre

09:00-09:15 **Welcome address**
R. Jones, University of Exeter

09:15-10:00 **Native Defects and Self-Doping in SiC**
*Invited* Friedhelm Bechstedt, Friedrich-Schiller-Universität, Jena, Germany

10:00-10:45 **Boron and Aluminum Doping in SiC and its Passivation by Hydrogen**
*Invited* Peter Deák, Budapest University of Technology and Economics, Hungary

*Session II, chairman: Bo Monemar*
Engineering building, Harrison lecture theatre

11:15-12:00 **Computational studies of defects and doping in GaN and SiC**
*Invited* Risto M. Nieminen, Helsinki University of Technology, Finland

12:00-12:30 **Carbon - an Alternative Acceptor for Cubic GaN**
Donat As, University of Paderborn, Germany

12:30-13:00 **Conduction in Undoped GaN Grown by MOVPE**
Trevor Martin, DERA, United Kingdom

*Session III: chairman: Bernard Clerjaud*
Engineering building, Harrison lecture theatre

14:00-14:30 **Temperature Dependent Hole Transport in GaN**
D. Lancefield, University of Surrey, UK

14:30-15:00 **Effective Electron and Hole Masses in Intrinsic and Heavily $n$-type Doped GaN and AlN**
Clas Persson, University of Uppsala, Sweden

15:00-15:30 **Influence of Si Doping on Optical Properties of Wurtzite GaN**
Antonio Ferreira da Silva, Universidade Federal da Bahia, Brasil

*Session IV, chairman: Bengt Svensson*
Engineering building, Harrison lecture theatre

16:00-16:45 **High Nitrogen Pressure Growth of GaN Single Crystals: Doping and Physical Properties**
*Invited* Stanislaw Krukowski, High Pressure Research Center, Poland

16:45-17:30 **Vacancies in the Growth and Doping of Gallium Nitride**
*Invited* Kimmo Saarinen, Helsinki University of Technology, Finland

17:30-19:30 Poster Session & Industrial Exhibits
Engineering building, rooms 101-103

## Thursday 22 March 2001

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| 09:00-09:45 | **Electronic Structure of Wide-gap Diamond-like Carbons** |
| *Invited* | John Robertson, Cambridge University, UK |
| 09:45-10:30 | ***N*-type Doping of CVD Diamond by Sulfur** |
| *Invited* | Christoph Nebel, Walter Schottky Institut, Garching, Germany |
| | *(talk sponsored by Oxford Instruments)* |
| | *Session VI, chairman: Risto Nieminen* |
| | Engineering building, Harrison lecture theatre |
| 11:00-11:45 | **Photoluminescence microscopy of TEM irradiated diamond and SiC—a new route to high spatial resolution information about point defects at the ppm level and below** |
| | John Steeds, University of Bristol, UK |
| 11:45-12:30 | **Dopant engineering in wide-band-gap semiconductors** |
| *Invited* | Chris G. Van de Walle, Xerox PARC, Palo Alto, USA |
| | *Session VII: chairman: Joerg Neugebauer* |
| | Engineering building, Harrison lecture theatre |
| 14:00-14:45 | **Shallow versus deep hydrogen states in ZnO and HgO** |
| | P. J. C. King, Rutherford Appleton Laboratory, UK |
| 14:45-15:30 | **Electrical Characterisation of Defects in As-Grown and Proton Irradiated n-Type ZnO** |
| *Invited* | Danie Auret, University of Pretoria, South Africa |
| | *Session VIII, chairman: Kimmo Saarinen* |
| | Engineering building, Harrison lecture theatre |
| 16:00-16:45 | **Beryllium and Magnesium Dopants in GaN and their Interactions with Oxygen and Hydrogen** |
| *Invited* | Bernard Clerjaud, Université Pierre et Marie Curie, France |
| 16:45-17:30 | **Shallow Dopants in GaN** |
| *Invited* | Bo Monemar, Linköping University, Sweden |

## Friday 23 March 2001

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| 09:00-09:45 | **Codoping method for the fabrication of low-resistivity wide bandgap semiconductors: prediction vs. experiment** |
| *Invited* | Hiroshi Katayama-Yoshida, Osaka University, Japan |
| 09:45-10:30 | **Dopants on GaN surfaces: Incorporation mechanisms and effect on surface morphology** |
| *Invited* | Joerg Neugebauer, Fritz-Haber-Institut, Germany |
| | *Session X, chairman: Christoph Nebel* |
| | Engineering building, Harrison lecture theatre |
| 11:00-11:30 | **Determination of Nickel-Related Defect Levels in the Diamond Gap** |
| | Rui Nuno Pereira, Technical University Berlin, Germany |
| 11:30-12:15 | **Surface doping: a special feature of diamond** |
| *Invited* | Jürgen Ristein, University of Erlangen, Germany |
| 12:15-12:45 | ***P*-type surface doping of diamond: a first principles study** |
| | Jonathan Goss, University of Exeter, UK |
| | *Session XI: chairman: John Robertson* |
| | Engineering building, Harrison lecture theatre |
| 14:00-14:30 | **Problems of Doping GaN by Ion Implantation** |
| | Sergei Kucheyev, The Australian National University |
| 14:30-15:15 | **Ion Implantation and Doping of Silicon Carbide** |
| *Invited* | Bengt Svensson, Oslo University, Norway |
| | *Session XII, chairman: Chris Van de Walle* |
| | Engineering building, Harrison lecture theatre |
| 15:45-16:15 | **Optimization of p-doping in the MBE growth of GaN** |
| | James Speck, University of California, USA |
| 16:15-16:45 | **Natural Dopants and their Spectral Characteristics in the AlN crystalline lattice** |
| | Baiba Berzina, University of Latvia |
| 16:45-17:00 | **Concluding remarks** |
| | R. Jones, University of Exeter, UK |

# Talks

### NATIVE DEFECTS AND SELF-DOPING IN SiC

*Friedhelm Bechstedt*
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The physical properties of silicon carbide (SiC) make the material well suited for high temperature, high power, and high frequency applications. A striking property of SiC is its polytypism. The compound exists in several different polytypes of which the 3C, 4H, 6H, and 15R structures are the most common ones. The accompanying variation of the fundamental gap between 2.39

eV (3C) and 3.26 eV (4H) makes SiC interesting for heterostructure devices. Native defects play an important role in the modification of the material properties. They occur in as-grown crystals and layers but, in particular, in irradiated samples. In the paper the monovacancies are considered as prototypical native defects in the prototypical polytypes 3C and 4H. However, antisites and complexes of vacancies with impurities, e.g. boron, are also discussed.

The energetics, structure, and electronic states are investigated via *ab initio* calculations based on density functional theory and local spin density approximation. The generation of the C-site vacancies is generally accompanied by a remarkable Jahn-Teller distortion towards $D_{2d}$ symmetry. Therefore a negative $U$ behaviour is predicted. Due to the strong localization of the C dangling bonds, the Si-site vacancies exhibit an outward breathing relaxation and high-spin configurations except for the neutral vacancy. According to the formation energies the carbon vacancy, which is a double donor, dominates in $p$-type material independent of the polytype. In C-rich 3C-SiC, however, the electrically inactive $C_{Si}$ antisite is the dominant native effect in the thermal equilibrium, at least for $n$-type conditions.

The Si vacancies give rise to ionization levels close to the valence band maximum of both 3C and 4H. Taking into account the inaccuracy of the calculations of about 0.1 eV and the binding energy of about 0.05 eV, the (+/0) ionization level may be related to the donor $D_1$ bound exciton. The $L_1$ photoluminescence (PL) line can be interpreted as a transition $V_{Si}^{+}$ + electron $\rightarrow V_{Si}^{0}$. It explains the polytype dependence and the occurrence of only one line in 4H, despite of the inequivalent lattice sites. The charge states of the vacancies can be also used to explain the characteristic PL lines at 1.12 eV (3C) and 1.35/1.44 eV (4H) in the infrared spectral region. The weak polytype dependence, the spin states, and the transition energies are related to intravacancy transitions between an excited state and the ground state of a charged Si vacancy.

The deep boron acceptor in hexagonal SiC is interpreted by a boron on a silicon position with an adjacent carbon vacancy. In addition, a shallow boron acceptor is discussed. In this paper we suggest to study the atomic geometry and the electronic structure of B adsorption on SiC(111)/(0001) surfaces, in order to understand bulk doping. We predict a $B_{Si} - V_C$ ($B_C$) adsorption configuration under carbon (Si)-rich preparation conditions, in agreement with coimplantation experiments. It induces a surface band in a midgap position (close to the valence band maximum).

## BORON AND ALUMINUM DOPING IN SiC AND ITS PASSIVATION BY HYDROGEN

*Peter Deák, Balint Aradi, and Adam Gali*
Budapest University of Technology and Economics, Department of Atomic Physics, Budafoki út 8, Budapest, H-1111, Hungary

Since diffusion is too slow in SiC under 1300°C, doping is carried out either by implantation or in growth. Both procedures involve problems with activation. The substitutional incorporation of the dopant atom in one or the other sublattice is promoted by tuning the Si/C ratio in growth or by co-implantation of Si or C (site competition). While, among the $p$-type dopants, the behavior of Al is relatively predictable, boron produces both a shallow and a deep acceptor center, along with at least one more paramagnetic center distinct from these two acceptors. Hydrogen is a natural contaminant of the SiC growth processes, and may occur in large quantities in as grown crystals. The presence of hydrogen might affect doping efficiency by influencing the site competition process, by passivating or compensating the dopants or by passivating vacancy related traps. Decrease of the free carrier concentration upon hydrogenation has only been observed in *p*-type samples. Passivation by complex formation with hydrogen has been proven both for Al and B, however, the experimentally observed reactivation energy of these complexes seems to differ by about 1 eV.

Extensive calculations regarding the formation energy of interstitial hydrogen and hydrogen - vacancy complexes in different charge states have been carried out using the Local Density Approximation to ab initio Density Functional Theory with a plane-wave basis and norm-conserving pseudopotentials on supercells of cubic (3C) SiC. Based on these results the hydrogen concentration of as-grown or variously treated SiC is estimated and its effect on the net carrier concentration is given. Incorporation of B and Al in or without the presence of hydrogen has been investigated in hexagonal (4H) SiC supercells. Possible origins of the shallow and deep boron acceptors is discussed. It is found that the presence of boron promotes hydrogen incorporation during growth in form of passive B+H complexes. The same is not true for Al. If Al+H complexes are formed (say, after H-plasma treatment), the structure of this complex is different from that of the B+H complexes. The calculated difference between the dissociation energies is 0.9 eV.

## COMPUTATIONAL STUDIES OF DEFECTS AND DOPING IN GaN AND SiC

*Risto M. Nieminen*
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This talk summarizes results of computational studies, based on density-functional theory and planewave- pseudopotential methods, of point defects and defect- dopant complexes in GaN, AlN and SiC. Among the properties considered are formation energies, ionisation levels, structural parameters and vibrational frequencies. The results will be used to discuss a number defect-related experimental findings.

This work has been done in collaboration with Leena Torpo, Torsten Staab, Chris Latham and Meri Marlo.

## CARBON - AN ALTERNATIVE ACCEPTOR FOR CUBIC GaN

*D. J. As and U. Köhler*
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Controlled *p*-type doping is crucial for the development of electronic and optoelectronic devices based on the group III-V nitrides. Up to now Mg has been the commonly used *p*-type dopant in molecular beam epitaxy (MBE) of both hexagonal and cubic phase GaN and is the only acceptor in GaN that reproducibly generates useful *p* conduction. Despite this breakthrough the hole concentration in GaN:Mg has remained low ($p_{max} = 6 \times 10^{17}$ cm$^{-3}$) due to the large Mg-acceptor ionization energy and compensation effects [1]. MBE-growth further showed that Mg is very volatile, and requires low substrate temperatures and N-rich growth conditions. Both conditions are disadvantageous for high quality epilayers, especially for the cubic phase, where N-rich conditions deteriorate the phase purity. In this contribution we studied in detail the incorporation of C in cubic phase GaN and demonstrate the practicability of C as an alternative acceptor for *p*-type doping. Cubic GaN (c-GaN) were grown by rf-plasma assisted molecular beam epitaxy (MBE) on semi-insulating GaAs (001) substrates [2]. C-doping of the c-GaN was achieved by e-beam evaporation of a graphite rode through adjusting the power between 0 and 400 W. The C-flux was externally calibrated through the growth of C-doped GaAs epilayers assuming a sticking coefficient of one for both GaAs and c-GaN and measuring the hole concentration by Hall-effect measurements at room temperature. In this way a maximum C-concentration of about $10^{20}$ cm$^{-3}$ was achievable in c-GaN, as confirmed by additional secondary ion mass spectroscopy (SIMS) measurements. At room temperature Hall-effect measurements showed a hole concentration of the c-GaN epilayer of $6 \times 10^{17}$ cm$^{-3}$ with a mobility of 200 cm$^2$/Vs. With increasing e-beam evaporation power a new photoluminescence line at 3.08 eV appeared at 2 K. Temperature dependent measurements of the 3.08 eV line showed a thermalization above 100 K, which is typical for a donor acceptor ($D^0A^0$) transition. From the spectral energy the binding energy of the C acceptor is estimated to be about $E_C$ = 0.210 eV. Our experiments demonstrate that C indeed introduces a shallow acceptor in c-GaN and that the binding energy of C is about 15 meV lower than that observed for the Mg acceptor in c-GaN [3]. [1] U. Kaufmann, P. Schlotter, H. Obloh, K. Köhler, and M. Maier, Phys. Rev. B 62 (2000) 10867

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## CONDUCTION IN UNDOPED GaN GROWN BY MOVPE

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AlGaN/GaN HFETs offer 5-10 times higher power at microwave frequencies than conventional solid-state devices. The conventional structure relies on piezoelectric and spontaneous polarisation to form the 2DEG, with no need for modulation doping of the structure. A key feature of the structure is that there should be no parallel conduction through the GaN layer. Experimentally it is found that some growth conditions lead to insulating GaN. However, it is not entirely clear what defect or mechanism leads to this insulating material [1]. This paper indicates that transport in this insulating layer can have both *n*- and *p*-type nature, and can potentially be explained by the high dislocation density of the material.

An HFET layer structure of 28nm $Al_{0.23}Ga_{0.77}N$ on $\sim 1\mu$m GaN (all undoped) was grown by MOVPE in a Thomas-Swan Epitor reactor. The substrate was a conducting, nitrogen doped, *n*-type, 4H, on-axis SiC wafer from Cree Inc. There is intense interest in growth on SiC because of its high thermal conductivity compared to sapphire. The conducting nature of the SiC allows a substrate bias to be applied to the device giving the opportunity to change the 2DEG concentration and obtain information about the electrically active centres in the GaN.

Temperature dependent conductivity measurements made between adjacent etched mesa isolated devices, showed that the conductivity of the GaN layer was ohmic and extremely low (typically $< 1$nS at 350°C), with an activation energy of 0.9eV. Similar conductivity behaviour and activation energy was obtained with HFET layers grown on sapphire. The fact that the conduction between two isolated 2DEG regions was ohmic suggested that the material was *n*-type, with transport likely to be via conduction band electrons with a compensated deep level at 0.9eV. The conductivity was too low for us to carry out Hall measurement to check carrier type.

The effect of varying substrate bias on the HFET gate transfer characteristic has been studied and showed a shift in pinch-off voltage as a result of a reduction in 2DEG carrier density as the substrate bias was made more negative. The pinch-off voltage shifts with the square root of the substrate bias, suggesting that a depletion region of roughly constant doping with exposed negative charge is being formed in the GaN. The fact that the substrate leakage was insignificant (nA level), and the presence of a depletion region implies that the GaN layer has a *p*-type nature, with an acceptor doping of $1.6 \times 10^{17}$ cm$^{-3}$. If the substrate had an *n*-type nature, space charge limited behaviour would normally result and depletion would not be seen.

One model which could reconcile these observations relies on the inhomogeneous nature of the GaN layer. AFM indicates that these layers typically have a dislocation density of $\sim 10^9$ cm$^{-2}$. It is expected that the dislocations and grain boundaries can accept high concentrations of electrons [2]. Since these dislocations will extend vertically from the 2DEG to the GaN/SiC interface, it is possible that hole conduction can occur along the dislocation cores, with tunnelling, or defect mediated transfer, across the GaN/SiC interface to the SiC conduction band, allowing the GaN to appear *p*-type for vertical transport. If there is a background of acceptors at 0.9eV below the conduction band and a smaller concentration of compensating donors in the bulk of the GaN, the material would behave as *n*-type for conduction between mesas. Where a dislocation core intersected with a 2DEG, there would be a small region surrounding the dislocation which would be depleted, resulting in a small reduction in the effective mobility.

This work was carried out as part of Technology Groups 7 and 9 of the UK MoD Corporate Research Programme. Crown Copyright 2001.

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## TEMPERATURE DEPENDENT HOLE TRANSPORT IN GaN

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The transport properties of Mg doped, p-type GaN films grown by MOCVD have been measured using Hall effect and resistivity measurements over a temperature range from 400–50K.

The mobility is found to increase slowly over the temperature range from 400 to 200K. Below this temperature the mobility is seen to decrease rapidly, while the corresponding Hall carrier density goes through a minimum before increasing to lower temperatures. These results have been analysed, using a two-band model. This incorporates a simple valence band model, calculated using a relaxation time approximation, and additional transport within an acceptor impurity band. A good fit has been obtained self-consistently to both the mobility and carrier density over a temperature range of 400–120K. We find that neutral impurity scattering plays an important role in limiting the hole mobility while the best fits are obtained assuming an acoustic-deformation potential of ∼20eV.

## EFFECTIVE ELECTRON AND HOLE MASSES IN INTRINSIC AND HEAVILY *N*-TYPE DOPED GaN AND AlN

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The effective masses are fundamental quantities of semiconductors, used in various experimental and theoretical investigations. We present calculations of the electronic structure near the band edges in intrinsic and heavily n-type doped GaN and AlN, for both the wurtzite and the zincblende polytypes. The electronic structures of the intrinsic materials were obtained from a full-potential linearized augmented plane wave (FPLAPW) method within the generalized gradient approximation (GGA). We show the importance of performing a fully relativistic calculation. For instance, the hole mass in cubic AlN is a very large and negative quantity if the spin-orbit coupling is excluded, whereas the fully relativistic calculation gives a relatively small and positive value. The electron-phonon coupling was taken into account according to the Fröhlich Hamiltonian for large polarons, resulting in the effective polaron masses. The effects on the masses due to doping were investigated by using a zero-temperature Green's function formalism within the random phase approximation (RPA).

## INFLUENCE OF Si DOPING ON OPTICAL PROPERTIES OF WURTZITE GaN

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The influence of doping in semiconductor materials leads to a band gap shift (BGS) causing a remarkable effect on the efficiency of optic-electronic devices. We have investigated the BGS of the Si-doped wurtzite GaN for impurity concentrations spanning the insulating to the metallic regimes. The calculations were carried out within a framework of the random phase approximation and the electron-electron, electron-optical phonon, and electron-ion interactions have been taken into account. In the wake of a very recent photoluminescence measurements, we have showed and discussed the possible transitions involved in the present scenario.

## HIGH NITROGEN PRESSURE GROWTH OF GaN SINGLE CRYSTALS: DOPING AND PHYSICAL PROPERTIES

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Growth of GaN under high pressure-high temperature conditions allows to obtain large size high quality GaN single crystals. These crystals have high concentration of free electrons, most likely due to high concentration of O impurity replacing nitrogen in N sublattice. Incorporation of oxygen impurity during high pressure growth of GaN single crystals will be investigated. It will be shown that the dissolution of oxygen in liquid gallium leads to dissociation of $O_2$ molecule. The dissociation process proceeds without energy barrier. Doping of Mg during growth leads to change of electric properties of GaN crystals - they become highly resistive. Mg-doping changes morphology of GaN plate-like crystals. The physical properties of GaN:Mg crystals will be reviewed and compared with undoped GaN crystals. Beryllium doping is considered as an alternative route to *p*-type of GaN. The doping with Be during growth increases resistivity of Be doped GaN. However optical properties of Be doped GaN crystals are different. These properties will be compared with Ng-doped and undoped GaN crystals.

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## VACANCIES IN THE GROWTH AND DOPING OF GALLIUM NITRIDE

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Positron annihilation spectroscopy can be used to identify vacancy defects in bulk semiconductor crystals and epitaxial layers. It yields quantitative information on vacancy concentrations in the range $10^{15}$–$10^{20}$ cm$^{-3}$. Positron localization into the hydrogenic states around negative centers can be applied to study also acceptors that have no open volume.

Positron experiments detect Ga vacancies as dominant intrinsic acceptor defects in *n*-type GaN bulk crystals and in layers grown by MOCVD, MBE and HVPE. Doping with Si impurities instead of oxygen decreases the concentration of Ga vacancies by an order of magnitude. The concentration of $V_{Ga}$ decreases with increasing Mg doping and no Ga vacancies are observed in *p*-type or semi-insulating layers doped with Mg. These trends agree well with the theoretical calculations, which predict that the formation energy of Ga vacancy is high in *p*-type and semi-insulating material, but greatly reduced in *n*-type GaN, and even further reduced due to the formation of $V_{Ga}{-}O_N$ complexes.

Thermal stability of Ga vacancies was studied in GaN bulk crystals after 2 MeV electron irradiation at 300 K. The isolated Ga vacancies recover in long-range migration processes at 500–600 K with an estimated migration energy of 1.5(2) eV. Since the native Ga vacancies in as-grown GaN survive up to much higher temperatures (1300–1500 K), we conclude that they are stabilized by forming $V_{Ga}{-}O_N$ complexes. The estimated binding energy of 2.2(4) eV of such complexes is in good agreement with the results of theoretical calculations.

In addition to doping, the presence of open-volume defects in GaN layers depends on the growth conditions. The concentrations of Ga vacancies increases strongly when more N rich stoichiometry is applied in the MOCVD growth. On the other hand, the lattice mismatch and associated dislocation density seem to have less influence on the formation of point defects than doping and stoichiometry—at least at distances $> 0.5\ \mu$m from the layer/substrate interface. This suggests that the formation of point defects in both epitaxial layers and bulk crystals follows mainly the trends expected for defects in thermal equilibrium.

## ELECTRONIC STRUCTURE OF WIDE-GAP DIAMOND-LIKE CARBONS

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Diamond-like carbon is an amorphous, $sp^3$ bonded, wide band gap material with potential as a large area electronic material. There are various types of DLC, depending on $sp^3$ content and hydrogen content. The band gap can be up to 3.6 eV. The talk will describe the nature of band edge states, defects, and our ability to dope the material. To date, the mobility of DLC based transistors has been quite low. Nitrogen is a weak dopant, but it also induces $sp^2$ formation. Applications for field emission are also discussed.

## *N*-TYPE DOPING OF CVD DIAMOND BY SULFUR

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Diamond has been recognized as a promising semiconductor material for electronic applications due to its unmatched electronic properties. Natural diamond, high pressure high temperature (HPHT) diamonds and meanwhile also CVD-diamond are available with intrinsic and p-type properties where boron acts as deep acceptor about 370 meV above the valence band edge. *n*-type doping of diamond is, however, still elusive. In analogy to donors in silicon group V (N, P, As) and VI-elements (S) in diamond are expected to act as donors if incorporated on substitutional sites. *N*-type doping by adding phosphine ($PH_3$) to the $CH_4/H_2$ gas mixture in a microwave assisted plasma deposition has been demonstrated. Phosphorus is, however, a very deep donor with an ionization energy of 604 meV.

In this paper we show that homo-epitaxially grown CVD-diamond where $H_2S$ has been added to the $CH_4/H_2$-gas mixture during the growth also shows *n*-type conductivity. We apply Hall experiments, photoconductivity and photo-thermal ionization spectroscopy experiments to investigate the donor properties of sulfur. The results show that Sulfur is a double donor with ionization energies of the S (0/+)-transition (single ionization) of 370 meV and of the S (+/++)-transition (double ionization) of 480 meV. Both donor levels exhibit five detectable excited states that were studied from oscillatory photocurrent and photo-thermal ionization experiments. These data demonstrate that sulfur is an effective mass center in diamond. The LO-phonon energy is determined to be 161±1 meV in agreement with indirect optical transitions at the conduction band minimum at $k_{min}$=(0, 0, 0.76). After annealing the sample at temperatures >500 K the donor is fully compensated by deep defects, giving rise to an onset of optical absorption for photon energies $h\nu \geq 1$ eV.

# PHOTOLUMINESCENCE MICROSCOPY OF TEM IRRADIATED DIAMOND AND SiC - A NEW ROUTE TO HIGH SPATIAL RESOLUTION INFORMATION ABOUT POINT DEFECTS AT THE PPM LEVEL AND BELOW

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The aim of this talk is to introduce a new technique with considerable promise for studying point defects at the ppm level and below in wide band-gap semiconductors and devices. There are many advantages of using a TEM for electron irradiation. These include efficiency, flexibility and control. Efficiency because many irradiations can be carried out on a specimen (bulk mainly at present but it could also be electron transparent) during one three-hour electron microscope session. Flexibility because of the ability to vary dose, dose rate, specimen temperature, crystallographic orientation and area. Control because the electron accelerating voltage can be set and measured to any desired accuracy so that damage may be introduced very close to the displacement threshold for any chosen sub-species in the lattice.

Subsequent examination of the specimens is carried out at liquid helium temperatures using an Oxford Instruments continuous flow cryostat attached to the microscope stage of Renishaw micro-Raman spectrometers (experiments have been carried out using 244, 325, 457.9, 488, 514.5 and 633 nm laser as excitation sources). By control of the electron energy the displacement thresholds for Si and C displacements in 6H and 4H SiC have been determined. By comparing the spectra obtained from within the irradiated regions to those obtained outside, species that migrate under the conditions of irradiation can be identified. By use of isotopes the involvement of a particular dopant in the optical centre can be identified and the dumbbell form of certain interstitial related centres can be deduced.

# DOPANT ENGINEERING IN WIDE-BAND-GAP SEMICONDUCTORS

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Lack of control over the conductivity of wide-band-gap semiconductors still presents a serious obstacle to optimum device performance. After describing the first-principles approach we have developed to address these problems, I will focus on three issues: acceptor doping of nitrides, conductivity control in ZnO, and the role of hydrogen in dopant engineering of semiconductors in general. *p*-type doping of nitrides still relies entirely on magnesium. Our recent investigations indicate that beryllium could be a promising alternative, provided compensation by beryllium interstitials can be brought under control. I will describe two strategies for achieving this, one being post-growth drift of interstitial Be (for which we have generated the required knowledge about its diffusion characteristics), the other the use of H as a codopant to suppress compensation by interstitials. The beauty of using H as a codopant is that it can be neutralized or removed from the *p*-type layer after growth, resulting in acceptor activation. The challenges involved in using other codopants, such as oxygen, will be discussed. When H is incorporated, acceptor-hydrogen complexes are formed, and their detection forms a powerful means of monitoring the activation process.

We have studied the vibrational modes of these complexes in detail, including anharmonic effects. In the process, we have identified a configuration of the Mg-H complex that is consistent with the recent IR spectroscopy results of Clerjaud *et al.* [1]. Turning to ZnO, we are confronted with the same problems that GaN faced about a decade ago: lack of understanding about unintentional $n$-type doping, and inability to achieve $p$-type. I will summarize our current thinking about the source of $n$-type conductivity, and the prospects for achieving $p$-type doping. Finally, since hydrogen plays an important role in many of these phenomena, I will discuss our present understanding of the electronic behavior of hydrogen in semiconductors and oxides in general. Our initially startling discovery that hydrogen acts as a *donor* in ZnO and in InN can actually be consistently explained in this broader context.

This work was supported in part by ONR (Contract No. N00014-99-C-0161) and by AFOSR (Contract No. F4920-00-C-0019). [1] B. Clerjaud, D. Côte, A. Lebkiri, C. Naud, J. M. Baranowski, K. Paula, D. Wasik, and T. Suski, Phys. Rev. B **61** (2000) 8238

## SHALLOW VERSUS DEEP HYDROGEN STATES IN ZnO AND HgO

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The muonium states mimicking interstitial hydrogen in ZnO and HgO are compared. Whereas in ZnO the predicted shallow donor state [1] is confirmed [2], in HgO we find a considerably deeper state, more akin to Mu* and the AA9 centre in Si. The respective ionization temperatures are around 40 K and 150 K and the donor ionization energies are 32±3 and 155±2 eV, deduced from the temperature dependence of the $\mu$SR signal amplitudes. (On the assumption of thermodynamic equilibrium, the donor–level depths would be twice these values.) The $\mu$SR spectra provide a comprehensive characterization of the undissociated paramagnetic states. The hyperfine parameters, which measure the electron spin density on and near the muon, differ by a factor of $\sim$50, defining a hydrogenic radius of 1.1 nm in ZnO and indicating a much more localized state in HgO. Both show a degree of anisotropy in the hyperfine tensor which could provide further clues to site and local electronic structure. These data should largely carry over to hydrogen and provide stringent tests of further calculations. We speculate on the causes of the switch from shallow to deep behaviour, and on the competition and coexistence of shallow and deep muonium states in other wide–gap II–VI compounds. [1] C. G. Van de Walle, Phys.

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## ELECTRICAL CHARACTERISATION OF DEFECTS IN AS-GROWN AND PROTON IRRADIATED N-TYPE ZnO

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We have fabricated rectifying Au contacts to n-type vapour phase grown ZnO. From capacitance-voltage (C-V) measurements, the free carrier density of the ZnO was found to be $3.0 \pm 0.3 \times 10^{16}$ $cm^{-3}$. TSCAP measurements in the region 20–300K showed that the diode capacitance, *i.e.* the number of ionised donors, reduces rapidly below 50K, consistent with the presence of shallow donor(s) extracted from Hall measurements. We have used deep level transient spectroscopy (DLTS) to study the electrical properties of electron traps introduced in the ZnO during growth and subsequent high-energy proton irradiation. Four electron traps with DLTS peaks below 300K could be detected in the as-grown ZnO. The most prominent of these, E1, is located at $E_c$ - 0.12 eV and has an estimated concentration, $N_t$, of about $10^{16}$ $cm^{-3}$. For the second most prominent level, E3, we have determined $E_c$ - 0.29 eV and $N_t = 10^{14}$ $cm^{-3}$. Two less prominent defects, E2 and E4, with energy levels at 0.10 and 0.57 eV, respectively, were also characterised. After irradiation with 1.8 MeV protons at room temperature, the two most prominent defects detected were Ep1 and Ep2. Ep1 has approximately the same DLTS signature as E4 and for Ep2 we found $E_c$ - 0.29 eV. A comparison of the introduction rates of electron traps introduced in GaAs, GaN and ZnO by proton irradiation revealed that ZnO is remarkably radiation hard compared to the other two semiconductors.

## BERYLLIUM AND MAGNESIUM DOPANTS IN GaN AND THEIR INTERACTIONS WITH OXYGEN AND HYDROGEN

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Local vibrational mode (LVM) spectroscopy is a direct method for the identification of important impurities as well as their complexes in semiconductor matrices. In this work, we concentrate on studies of Mg and Be acceptors in GaN semiconductor and their interactions with oxygen and hydrogen.

Bulk, high-pressure grown GaN crystals doped intentionally with Mg or/and Be are investigated by Fourier transform infrared spectroscopy and electrical measurements. Mg doped samples exhibit either slightly *p*-type or semi-insulating behaviour. Be-doped and Be+Mg co-doped samples are always semi-insulating. Bulk GaN crystals grown by means of high-pressure synthesis contain oxygen donors in relatively large concentrations ($\sim 5 \times 10^{19}$ cm$^{-3}$). We believe that these donors are responsible for the high compensation rate of the investigated materials.

In beryllium doped samples, a local vibrational mode at 789 cm$^{-1}$ is observed. It is attributed to "isolated" electrically active beryllium. This mode is the analogue of the 656 cm$^{-1}$ mode observed by Raman spectroscopy in magnesium doped GaN and assigned to "isolated" Mg [1, 2]. In magnesium doped GaN, several correlated modes are attributed to magnesium-oxygen complexes. In beryllium doped samples, evidences of beryllium-oxygen complexes are also observed. In Mg+Be co-doped samples both of these features together with the 789 cm$^{-1}$ mode can be seen.

The complexing of magnesium with hydrogen in GaN is well established in MOVPE as grown materials; it gives rise to a local vibrational mode at 3125 cm$^{-1}$ [3]. This mode is rarely observed in GaN:Mg as grown crystals elaborated by high-pressure synthesis whereas it is clearly observed in samples annealed in hydrogen ambient. The analogue mode in beryllium doped samples has not been detected even in samples annealed under hydrogen atmosphere.

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## SHALLOW DOPANTS IN GaN

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Recent data on shallow donors and acceptors in GaN will be discussed, with emphasis on optical experiments. The identification of optical signatures for shallow donors and acceptors, in particular bound exciton spectra, with the corresponding shallow impurity is still not final, and will be discussed. The main shallow impurities are Si, O, Be and Mg. Comparison will be made between results from HVPE and MOVPE grown GaN. Available magnetic resonance data will be discussed in connection with the optical data. The possible origin of some deep level spectra related to shallow dopants and intrinsic defects will briefly be discussed.

## CODOPING METHOD FOR THE FABRICATION OF LOW-RESISTIVITY WIDE BANDGAP SEMICONDUCTORS: PREDICTION VS. EXPERIMENT

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It is well known that the fabrication of both low-resistivity *n*- and *p*-type wide bandgap (Eg) semiconductors is difficult (uni-polarity), because of the so called compensation and deep energy levels of the dopants in the wide bandgap semiconductors, such as GaN (Eg = 3.4 eV), AlN (Eg = 6.2 eV), and Diamond (Eg = 5.4 eV). The origin of the difficulty to fabricate the low-resistivity wide bandgap semiconductors are the compensation and the deep energy levels of dopants with increasing Eg (decreasing the dielectric constant), for example, GaN:Mg (200 meV), AlN:C (500 meV), and Diamond:P (430 meV). In order to fabricate the low-resistivity wide bandgap semiconductors, (i) we should avoid compensation with increasing solubility of the dopant, (ii) we should increase the mobility of the carriers and (iii) we should reduce the energy level of dopants by using codoping. To do so, we propose an effective new valence control method by using thermal non-equilibrium crystal growth method, which is so called the codoping method (using both *n*- and *p*-type reactive codopants at the same time), for the fabrication of low-resistivity *p*-type GaN, *p*-type AlN and *n*-type Diamond based upon ab initio electronic structure calculations. We discuss that the codoping increase the solubility, decrease the energy levels and increase the mobility of the carriers. We review our new valence control method of codoping for the fabrication of low-resistivity *p*-type GaN, AlN, and *n*-type Diamond. We propose the following codoping method to fabricate a low-resistivity *p*-type wide bandgap semiconductors (a) GaN: [Si+2Mg(or Be), H+2Mg(or Be), and O+2Mg(or Be)], (b) AlN: [O+2C]. We also review the codoping method for the fabrication of low-resistivity *n*-type Diamond (c) Diamond:[H+S, B+2N, H+2P]. We compare our predictions of codoping with the recent successful codoping experiments for the fabrication of the low-resistivity wide bandgap semiconductors.

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## DOPANTS ON GaN SURFACES: INCORPORATION MECHANISMS AND EFFECT ON SURFACE MORPHOLOGY

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Most studies on dopant issues have focused on their properties in bulk. However, recent experiments indicate that dopants may significantly affect the growth morphology (and thus the material quality) and also the bulk concentration. Examples are the anti-surfactant behavior of Si on GaN(0001) surfaces (which leads to the formation of quantum dot like structures) or the reduction in the oxygen concentration when going from the GaN($000\bar{1}$) to the (0001) surface.

In order to get some insight into the mechanisms causing these effects we have studied the adsorption and incorporation of dopants on GaN surfaces employing density-functional theory. In the present talk we will focus mainly on two dopant impurities—oxygen and silicon—which both are well known to act as shallow donors in GaN. We have thereto calculated the surface energy, atomic geometry and electronic structure for a large number of possible surface reconstructions where we have varied the ratio between Ga, N and impurity atoms. Based on these results we construct a phase diagram which gives all stable surfaces as a function of the chemical potentials.

Using these results we find a qualitatively different behavior for oxygen and silicon. Oxygen has a strong tendency to segregate to the surface: the oxygen concentration on the surface will be therefore significantly higher than in bulk. Also, the incorporation of oxygen on GaN surfaces is highly stable against the formation of the solubility limiting phase $Ga_2O_3$. In contrast, silicon is more stable in the bulk than on the surface and almost all silicon induced surface structures are unstable against the formation of $Si_3N_4$. These results give immediate insight into recent experiments. In particular, we identify the conditions under which Si acts as an anti-surfactant, we discuss how the doping efficiency of silicon can be increased, and we explain why the oxygen concentration on (0001) is lower than on ($000\bar{1}$).

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## DETERMINATION OF NICKEL-RELATED DEFECT LEVELS IN THE DIAMOND GAP

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When Ni alloys are used as solvent-catalysts in the synthesis of diamond under high-pressure and high-temperature conditions (HPHT), Ni becomes incorporated as a dispersed impurity and produces various defects. Beside the isolated substitutional $\mathrm{Ni}_s^-$ (W8) [1] which is the dominant paramagnetic Ni-defect in such diamond samples, many Ni-related defects were observed by electron paramagnetic resonance (EPR) [2-5]. Recently, five new nickel-related paramagnetic centres (AB1-AB5) have been detected in HPHT diamond samples annealed at 1600°C [4,5]. In this work we present for the first time photo-EPR investigations on the AB5 centre together with new photo-EPR results on the W8 and the P1 (substitutional $\mathrm{N}_s^0$) centres as well as latest findings concerning the formation conditions of the AB5 centre. Among the AB centres, only AB5 is an $S = 1$ centre. It was tentatively assigned to a nickel-nitrogen pair in the negative charge state [4]. Our EPR study of a set of as-grown and annealed diamonds grown using Ni (or a Ni alloy) as solvent/catalyst reveals that AB5 is always present in samples grown without a nitrogen getter. The photo-EPR investigations were performed in the Q-band (34GHz). In order to avoid any unwanted infrared irradiation of the sample, we used a bath cryostat. In samples with a strong W8 signal and a relatively weak P1 spectrum, we measured the W8 EPR signal intensity behaviour for different photoexcitation energies, and we observed two complementary photoionisation transitions (PTs) involving the W8 energy level: a photoinduced quenching at about 2.5 eV in agreement with [6] and a photoinduced enhancement at 3.0 eV. In order to determine the nature of these two PTs, we also investigated the behaviour of the deep nitrogen donor $N^0$. We found a recharging of this donor for photon energies higher than 2.5 eV. This indicates directly that the photoionisation transition of the $Ni_s^-$ (W8) centre at 2.5 eV is caused by the excitation of electrons to the conduction band. Relating this recharging processes to the observed photoinduced changes of the AB5 EPR signal intensity we determine the level position of this centre to be $E = E_c - 1.88 \pm 0.03$ eV.

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## AN ELECTROCHEMICAL MODEL FOR THE SURFACE CONDUCTIVITY OF DIAMOND

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Diamond despite being a bona fide insulator with a gap of 5.4 eV exhibits a special kind of surface conductivity (SC) of the order of $10^{-5}$ $W^{-1}$. The conductivity is confined to a surface layer of a few tens of nm and is carried by an areal hole concentration of about $10^{13}$ $cm^{-2}$. The SC can be controlled by a gate electrode and has therefore been utilized in the form of a unique kind of field effect transistor. Despite ten years of research the mechanism responsible for the hole accumulation layer remained unsolved. The only reliable fact was that surface hydrogenation is required to induce SC. Consequently, a number of publications have suggested that an as yet unspecified hydrogen related subsurface defect acts as acceptor that provides the necessary hole concentration.

We have combined conductivity measurements in ultra high vacuum (UHV) and under atmospheric conditions with spectroscopic methods such as photoelectron emission spectroscopy and infrared (ir) spectroscopy in the attenuated total reflection (ATR) mode to elucidate the connection between surface conditions and SC. We find that surface hydrogenation is a necessary but not a sufficient condition for SC. In addition, species from the atmosphere are required that act as acceptors. Furthermore, the acceptor level has to coincide with the valence band maximum (VBM) in order to induce the surface band bending that is connected with the subsurface hole concentration referred to above, *i.e.*, the VBM has to coincide with the Fermi level. This in turn requires that the adsorbate has an electron affinity of at least 4.2 eV which is higher than that of the most electronegative adsorbates imaginable, namely halogen atoms. However, charge exchange between diamond and a thin water layer as it forms automatically on all surfaces exposed to air is possible by the neutralisation of oxonium ions according to the reaction $2\ H_3O^+ + 2\ e^- \rightarrow H_2 + 2\ H_2O$. The electrochemical potential of this reaction turns out to be of the correct magnitude (4.2 eV below the vacuum level for a pH of 6 that is maintained by dissolved CO2 from the atmosphere) to allow electron transfer from the diamond to the water layer (electrolyte). The holes remaining in the VB induce an upward band bending and form the subsurface accumulation layer. The electron transfer comes to a halt when the band bending has reached a degree such that the Fermi level of diamond and the electrochemical potential are aligned (the electrochemical potential is tied to the vacuum level and thus to the VBM of diamond). At this point the hole concentration has the value of $10^{13}$ cm$^{-2}$ required for the SC. The neutralizing negative charges reside in the form of anions, presumably carbonate ($HCO_3^-$) in the electrolyte and they can even reside on the surface after the sample is brought into UHV and other species have desorbed from the surface. By this the surface conductivity is maintained in a metastable configuration and can be gradually removed by thermal annealing. The hydrogenation of diamond is necessary in this scenario because it results in the lowering of the vacuum level (negative electron affinity of diamond) such that the ionisation energy (vacuum level-VBM) reaches a value (4.2 eV) comparable with the electrochemical potential of a slightly acidic water layer. It is this last point that makes hydrogenated diamond unique. No other semiconductor has such low ionisation energy.

## *P*-TYPE SURFACE DOPING OF DIAMOND: A FIRST PRINCIPLES STUDY

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Recent experiments have shown that diamond can become *p*-type by the addition of an aqueous solution, probably of carbonic acid, to a hydrogenated surface. Models for the mechanism behind the conduction suggest that an electronegative molecule close to the surface can accept an electron from the diamond valence band, leaving a hole. The subsequent conduction is stable at modest temperatures (~100°C), and is removed by annealing to >200°C. This implies that the species are relatively weakly bound to the surface, *i.e.*, physisorbed rather than chemisorbed.

We present the results of first principles calculations examining the binding energy and electronic structures of candidate molecules on various diamond surfaces.

The results strongly support the principle of *p*-type surface conduction via the donation of valence electrons to physisorbed molecules, but indicate that a wide range of molecules should give rise to this effect, contrary to observation. It is suggested that, in contrast to carbonic acid, some other species either chemisorb to the surface or remove surface hydrogen leaving compensating sites.

## PROBLEMS OF DOPING GaN BY ION IMPLANTATION

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In the fabrication of GaN-based devices, ion implantation represents a very attractive processing tool for several technological steps such as selective-area doping, dry etching, and electrical isolation. However, lattice disorder is always a concomitant (and often undesirable) effect of ion bombardment. Our recent studies have revealed that, unlike the situation for mature semiconductors such as Si and GaAs, GaN exhibits a range of intriguing behavior involving extreme property changes under ion bombardment. In this presentation, we discuss opportunities and highlight current problems, associated with implantation disorder, which may hinder a successful application of ion implantation in the fabrication of GaN-based devices. In particular, the following problems will be discussed: (i) a complex and somewhat unexpected damage buildup behavior; (ii) preferential loss of nitrogen from the GaN surface during bombardment; (iii) formation of extended defects which appear to be difficult (or even impossible) to anneal; (iv) ion-beam-induced porosity due to material dissociation with the formation of nitrogen gas bubbles; (v) anomalous surface erosion during ion bombardment at elevated temperatures; (vi) a dramatic effect of implantation disorder on mechanical properties, affecting contact damage; and (vii) current problems with annealing of amorphous GaN. Emphasis is given to understanding physical mechanisms responsible for such a somewhat extreme behavior of GaN under ion bombardment.

## ION IMPLANTATION AND DOPING OF SILICON CARBIDE

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Controlled doping of bulk crystals and epitaxial layers of SiC can be performed in-situ during growth, and for instance, using chemical vapour deposition dopant concentrations over a wide range are accessible. However, for genuine SiC device processing a planar technology enabling selective area doping is required. In principle, ion implantation is ideally suited for this because

of the possibility to accurately control the distribution of dopants in three dimensions without chemical or thermodynamical constraints. A major drawback is, however, the generation of damage destroying the crystalline structure of the implanted layer. The damage can vary from point defects caused by single collision cascades at low ion doses to amorphization at high enough doses. Post-implant annealing is thus necessary to restore the crystal structure and electrically activate the implanted dopants as shallow acceptors or donors.

For SiC, our knowledge and understanding of the damage build-up during implantation is severely limited and the same is true for the post-implant annealing processes. In this contribution, a survey is given of the current status, and issues like implantation temperature, defect evolution as a function of dose and dose rate, dopant compensation, co-implantation and electrical activation of dopants, evolution of structural defects during post-implant annealing, and transient enhanced dopant diffusion are addressed. Finally, recent results regarding the interaction between hydrogen and $p$-type dopants will be discussed.

## OPTIMIZATION OF P-DOPING IN THE MBE GROWTH OF GaN

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In this talk, we cover three main results from our work on the optimization of MBE grown Mg-doped GaN: (1) optimization of growth conditions and resulting morphology; (2) transport properties and abruptness of doping; and (3) polarity inversion as a result of Mg doping. For these studies Mg layers were grown by plasma-assisted molecular-beam epitaxy at 650°C. In the plasma-assisted MBE growth of nitrides, we show that optimal growth is realized for Ga-rich conditions at the cross-over from a Ga-wetting layer on the surface to conditions that give rise to droplets on the GaN surface. Growth under N-rich conditions resulted in either semi-insulating or $n$-type material. Secondary-ion-mass-spectroscopy measurements reveal uniform Mg doping profiles with very sharp boundaries. The amount of incorporated Mg atoms changes approximately linearly with incident Mg flux. Hall measurements on $p$-type GaN:Mg layers show that about 1–2% of all Mg atoms are ionized at room temperature. The hole mobility depends strongly on the hole concentration, varying from $\mu_p = 24$ cm$^2$/Vs for $p = 1.8 \times 10^{17}$ cm$^{-3}$ to $\mu_p = 7.5$ cm$^2$/Vs for $p = 1.4 \times 10^{18}$ cm$^{-3}$. We have carried extensive studies on the polarity inversion that results from Mg-doping. We show that under N-rich conditions, the polarity can be completed inverted by Mg, whereas Ga-rich conditions result in the formation of ‘spiked-shape’ inversion domains.

## NATURAL DOPANTS AND THEIR SPECTRAL CHARACTERISTICS IN THE AlN CRYSTALLINE LATTICE

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Aluminum nitride is a wide band-gap (6.2 eV) material having a wurtzite structure. Oxygen is a well-known natural dopant for this material [1]. Oxygen ions can substitute the nitrogen or form some more complicated structures of defects in the crystalline lattice. The energy levels of oxygen-related defects are usually situated inside the band-gap and their spectral characteristics fall into the spectral region of ultraviolet (UV), visible (V) or near infrared (IR) light. The present work is aimed with a study of some natural defect structure in AlN. Complex investigation of spectral characteristics was performed. The spectra of luminescence and its photoexcitation, luminescence kinetics as well as photostimulated luminescence (PSL) of photorecharged defects were studied. The AlN ceramics sintered at different conditions were used. A structure of a complex oxygen-related defect consisting of the oxygen ions and an aluminium vacancy is proposed [2,3]. This defect complex is responsible for the UV-blue luminescence, which is predominant in the UV-V spectral region caused by the recombination-tunneling mechanism. Investigation of other defects responsible for 600 nm and 1000 nm luminescence bands of AlN are in progress.

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## Posters

### COMPUTATIONAL STUDY OF THE EFFECT OF Al AND In ON THE FORMATION ENERGIES AND ACCEPTOR LEVELS OF Mg AND C DOPANTS IN GaN

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The effect of aluminium and indium on the formation energies and acceptor levels of magnesium and carbon dopants in GaN have been calculated using a density functional approach. Single aluminium and indium atoms are incorporated into the lattice at a minimal distance from the acceptor species. The formation energies are obtained as a function of the Fermi level position. In the absence of aluminium or indium, magnesium in a charge neutral state is found to have a formation energy of 1.1 eV whereas carbon has a formation energy of 2.6 eV. In the presence of indium, the magnesium formation energy rises to 1.6 eV whereas the addition of aluminium has no effect. For carbon, the presence of aluminium and indium increases the formation energy by 0.4 and 0.3 eV respectively. Furthermore, the calculations predict that the magnesium acceptor level becomes more shallow by the addition of aluminium (from 0.14 to 0.01 eV above the valence band maximum) but is made deeper by indium (from 0.14 to 0.27 eV above the valence band maximum). The carbon acceptor level is found to remain approximately unchanged with aluminium and indium doping. These results are compared to experimental data and the effect of various approximations in the calculations is discussed.

## DEFECTS IN BERYLLIUM DOPED GaN MODELLED BY LOCAL DENSITY FUNCTIONAL THEORY

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The problem of beryllium doping in gallium nitride has been investigated using the AIMPRO local-density-functional theory based method. Three defects are considered: substitional beryllium acceptors, interstitial beryllium atoms, and a beryllium pair near to a vacant gallium lattice site. The formation energy of a neutral Be acceptor is found to be approximately 2.4 eV, in good agreement with the value of 2.2 eV calculated earlier by Neugebauer and Van de Walle [1]. Interstitial Be lies very close to the hexagonal site on a nitrogen plane. The substitutional-interstitial pair is very strongly bound with an energy of approximately 4.2 eV. It is a deep donor; thus its formation provides a possible explaination the poor doping efficiency of Be in GaN. [1] J. Neugebauer and C. G. Van de Walle, J. Appl. Phys. **85** (1999) 3003–3005

## COMPENSATION MECHANISM IN MBE AND MOVPE GROWN GaN:Mg

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*P*-type conduction of GaN is typically obtained by Mg doping which acts as an acceptor. High acceptor concentrations are necessary for many applications but compensation effects limit the achievable free hole concentrations, especially in the samples grown by metal organic vapour phase epitaxy (MOVPE). We studied several series of GaN samples grown by MOVPE and Molecular beam epitaxy (MBE) doped with different Mg concentrations by photoluminescence (PL), Hall and SIMS measurements. For the MOVPE samples a saturation of the hole density vs Mg concentration was observed. The PL was strongly dependent on the Mg concentration. For low doped samples the donor acceptor pair recombination at 3.26 eV was observed, while in the medium/highly doped samples a band at 2.9/2.7 eV dominated. In the MBE samples, independent of the Mg concentration, both bands were seen with rather constant intensity ratios. Also no saturation of the free hole concentration was observed. A first model to gain understanding on the compensation behaviour in MOVPE GaN:Mg was developed by Kaufmann *et al* [1]. We extended these calculations by considering the formation energies of defects such as VN, VNH and H [2] and also by taking into account the differences between these two growth processes (like temperature and hydrogen presence). The good agreement, between these calculations and our experimental results, allows us to formulate a model explaining the compensation mechanism in MOVPE and also in MBE GaN:Mg. [1] U. Kaufmann, P. Schlotter,

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## PECULIARITIES OF DOPANTS ACTIVATION IN PRESSURE-GROWN GaN:Mg CRYSTALS

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We measured and analyzed, at the temperature up to 750 C, the electrical properties (resistivity) of gallium nitride crystals grown from Mg-rich Ga melt under high $N_2$ pressure. The studied material is characterized by high background concentration of O donors ($\sim 5\times10^{19}$ cm$^{-3}$), which compensate Mg acceptors. Generally, the resistivity of as-grown crystals is high, due to nearly perfect compensation of dopants. We have studied the thermally activated time-depending processes leading to activation of dopants (*i.e.* annealing, leading to irreversible increase of conductivity) as well as characteristic temperature dependencies of resistivity at different stage of these processes. We found that:

1. The electrical properties can be described by two impurity/defect levels: For the adequate explanation of the resistivity behavior, (especially above 500 C), beside the shallow Mg acceptor level ($E_v$ + 0.1 eV), a second level lying at $E_v$ + 0.9 eV should be introduced.

2. There are two different thermoactivated processes which lead to the activation of the corresponding defect/impurity centers.

The first process, which lead to appearance of shallow Mg acceptors, is observed at temperatures as low as ~300 C and terminates below 600 C (we find a rough estimate of activation energy characteristic for this process as equal to about 1.5 eV ). We find however that the number of Mg acceptors activated in this process does not exceed 1% of the total Mg concentration present in the material. In the second process, observed above 600 C, the considerable concentration of the deep centers of unknown nature is generated. The possible nature of the centers as well as the mechanisms of their activation is discussed. The low-temperature annealing process might be tentatively attributed to the dissociation of Mg-H complexes *i.e.* to the mechanism observed in MOCVD grown layers (the presence of hydrogen in our material is confirmed by SIMS), although in the case of MOCVD samples such process starts at more elevated temperature. The second process seems to be worthy of further studies for two reasons:

- it results in generation of important concentration of defects (comparable to this of the main dopants)

- it is observed in the temperature range usually employed to activation of Mg acceptors in MOCVD grown nitride layers.

## AB INITIO THEORY OF NATIVE DEFECTS IN ALLOYS: APPLICATION TO CHARGED N VACANCIES IN $Al_xGa_{1-x}N$

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Semiconductor alloys with varying compositions have attracted considerable interest in the last years due to their applications in microelectronic and optoelectronic devices. The electrical and optical properties of these materials are to a great extent determined by native defects such as antisites and vacancies. We present calculations of the electronic and atomic structures of neutral and charged nitrogen vacancies in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}$ alloys using a combination of first-principles methods which enables us to treat point defects in ternary alloys on the same level as they are treated in binary compounds. The treatment of the alloys is based on the generalized quasi-chemical approach [1] to disorder and composition effects and a cluster expansion to account for the various configurations [2]. The point defects are modelled by supercells which are multiples of the alloy clusters. The total energy and electronic structure calculations are performed within the density functional theory and the local spin density approximation. Explicitly a pseudopotential-plane-wave code is used. We study the atomic geometry, the energetics, and the charge-dependent vacancy states for the clusters and the alloys versus cation numbers or composition $x$. [1] A. Sher, M. van Schilfgaarde, A. B. Chen, and W. Chen, Phys. Rev. B **36** (1987) 4279
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## 60-DEGREE DISLOCATIONS IN GaN AND THEIR DISSOCIATION

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Dislocations in GaN have influence on its electronic properties. On one hand electrically active point defects might be accumulated at the dislocation core and on the other hand some dislocations introduce deep levels in the gap resulting from either strong distortion or unreconstructed dangling bonds. The undissociated 60-degree dislocation is a good example for the latter. We investigated the atomic and electronic structure of 60-degree dislocations in cubic GaN using self-consistent-charge DFT-based Tight Binding (scc-DFTB) combined with the pseudopotential method AIMPRO. Furthermore the dissociation of those dislocations into 30- and 90-degree partials is considered.

## STRUCTURE AND ENERGY OF THE 90° PARTIAL DISLOCATION IN WURTZITE-GaN

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GaN/InGaN/AlGa structures are important as blue light-emitting diodes and lasers. Their success in this role is achieved in spite of low material quality (threading defects exceeding $10^9$–$10^{10}$ cm$^{-2}$) compared with that required by, for example, GaAs optoelectronic devices [1]. Dislocations have been associated with the yellow luminescence $\sim 2.2\,\mathrm{eV}$ of these materials [2], while other evidence suggests that threading dislocations act as nonradiative recombination

centres [3], thereby reducing luminescent efficiency. Theoretical dislocation studies in the last 5 years have focussed on the core geometry and electronic structure of threading dislocations (see review [4]). Glide dislocations have been relatively neglected, in spite of their importance for stress relaxation and experimental evidence for glide driven by stresses generated during cooling after growth [1].

In parallel with studies of glide dislocations in cubic GaN [4] we have undertaken a study of glide dislocations in hex GaN. We choose the simplest such dislocation: the 90° glide partial, one of the constituents of dissociated dislocations with Burgers vector $\frac{1}{3}\langle 11\bar{2}0\rangle$. Here we report first principles total energies and structures for supercells containing either a dipole of partials, or individual partials within a hydrogenated boundary. We use AIMPRO within local-density functional method, norm-conserving pseudopotentials with non-local core corrections [5]. We apply conjugate gradient optimisation to initial positions from isotropic elasticity theory in a 144 atom supercell $L \approx 32.8$ Å, $D \approx 15.5$ Å, and the thickness of the cell is $\approx 3.2$ Å. The optimised lattice constants of hex GaN are $a = 3.162$ Å and $c = 5.143$ Å. We investigated the effects of adding different translations to the lattice vectors in the climb direction. These change the global dislocation pattern but do not affect the average dislocation density in the crystal.

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## MICRO-RAMAN AND LOW TEMPERATURE PHOTOLUMINESCENCE INVESTIGATION OF CUBIC BORON NITRIDE SINGLE CRYSTALS

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A number of reasonably small (250 $\mu$m x 250 $\mu$m x 100 $\mu$m) single crystals of HPHT cubic boron nitride have been studied by micro Raman spectroscopy and low temperature photoluminescence microscopy using 325 nm and 488 nm laser excitation. The crystals were grown with the aid of various catalysts so as to produce samples that varied from B-rich to N-rich stoichiometries. Raman spectra were investigated as a function of stoichiometry and specimen temperature up to 1300 °C. Fine structure associated with the TO and LO Raman peaks was noted and its possible relationship to extended defects in the material is under investigation. Two new optical systems have been discovered and the results are currently being analysed. Particularly fine examples of the 387 nm centre have been encountered and the phonon coupling is associated with unusually low energy phonons. A tentative explanation of this coupling will be presented in terms of a resonant mode caused by tungsten, used as a catalyst, incorporated into the BN lattice. TEM, EELS and CBED investigations confirm that the samples are uncontaminated by hexagonal BN.

# PASSIVATION OF BERYLLIUM AND MAGNESIUM BY HYDROGEN IN BORON NITRIDE

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In the past few years, the III-V nitrides have received a great deal of attention. This is due, of course, to the famous blue LED based on GaN. The fundamental problem that was overcome was the efficient p-type doping. Many theoretical and experimental papers have been published in the literature searching for new dopant sources.[1,2,3] What hasn't been addressed in great detail is the interaction of hydrogen with these dopants. Hydrogen plays and important role in the nitride family passivating defects such as grain boundaries and vacancies rendering them in most cases neutral and inactive. It is always present in large quantities due to it being part of the growth procedure in normal CVD grown crystals. Passivation of dopants is not new in other materials, such as silicon, but in the nitrides our knowledge is still limited. The most well known case of passivation in the nitride family is the passivation of magnesium by hydrogen in GaN[4,5]. Although well known there is still no consensus on the microscopic structure of the center. Passivation of magnesium has not been understood if at all studied in the other nitrides.

We present ab initio total energy calculations using Density Functional Theory of Mg-N-H and Be-B-H complexes. All calculations use wave functions that are expanded in terms of gaussian-like orbitals ($s$, $p$, and $d$ components) and they are used in both super-cells and hydrogen terminated clusters of BN. The lowest energy structures are determined by sampling possible configurations and allowing them to relax. The relaxation is done by a conjugate-gradient method, in which the forces are determined using the Hellmann-Feynman theorem and include a Pulay term due to due to the basis set being dependent on the nuclear sites. Various configurations of the hydrogen atom where studied as well as the influence on the complexes gap levels. Local vibrational modes have also been calculated for the lowest energy configurations.

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# CONTROLLABLE DOPING AS A WAY TO IMPROVE DOSIMETRIC PROPERTIES OF AlN CERAMICS

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Aluminum nitride AlN is a wide-gap crystalline material ($E_g = 6.2$ eV). Due to its hardness, thermal and chemical stability and high thermal conductivity it is widely used in microelectronics in the form of thin layers and ceramics. We have studied AlN ceramics using methods of optical spectroscopy, thermally stimulated luminescence (TSL) and optically stimulated luminescence (OSL). AlN grains are characterized by a lattice of wurtzite type easily incorporating oxygen as a natural dopant, which substitutes nitrogen in the regular lattice site during the crystallization process forming several types of oxygen-related defects. Charge transfer processes between the oxygen-related defects occur under irradiation with both ultraviolet radiation (UVR) and ionizing radiation producing donor and acceptor pairs with different separation distances. Recombination of close donor-acceptor pairs during irradiation process and shortly after its ceasing is accompanied by a strong luminescence emission peaking around 400 nm. The donor - acceptor pairs with larger separation distances survive until their recombination is initiated by heating or illuminating the sample with visible or infrared light, producing TL or OSL, respectively. These phenomena form the basis for the application of AlN as a dosimetric material.

The properties of TL and OSL of AlN ceramics were studied after exposure both to ionising radiation and UVR. The TL signal of the irradiated material is characterized with a very high sensitivity, 5 decades wide linear dynamic dose range, good repeatability of measurements and a minor influence of the heating rate on the TL. Though the OSL signal was found to be much weaker than the TL response, it is still high enough to be used for dosimetric applications. This material has a spectral sensitivity in a broad region from 200 to 360 nm covering almost the whole UVR spectrum. In the UV-A and UV-B regions of the solar emission (280-360 nm) the character of the AlN spectral sensitivity is in good agreement with the human skin erythemal response, making the material potentially applicable for personal UV dosimetry.

A practical application of the AlN ceramics for dosimetry is hampered by the serious disadvantage of the material - the high fading rate of the TL and OSL signals after exposure to ionising radiation and UVR during storage at room temperature. The fading of the stimulated signal is explained by the uncontrollable recombination of the donor-acceptor pair due to charge carriers release from the trapping centres. Introducing additional dopants, providing stable deep trap levels inside energy gap could eliminate the fading process. The search for such impurities improving dosimetric properties of the material is the aim of further study.

## FIRST-PRINCIPLE CALCULATIONS OF DIELECTRIC FUNCTION IN CUBIC AND HEXAGONAL InN

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The imaginary part of the dielectric function of InN have been calculated using a full-potential linearized augmented plane wave method. Both the zinc-blende and the wurtzite structures have been investigated. From the Kramers-Kronig dispersion relations the real part of the dielectric function has been obtained, presuming a quasi-particle band-gap correction according to Bechstedt and Del Sole. We have found that it is necessary to have a good treatment of the band gap in order to obtain the low-frequency optical properties. We present the longitudinal as well as the transverse components in wurtzite InN, showing that the anisotropy is small.

# INVESTIGATION OF THE LOW DOPED SUBLIMATION GROWN EPI-LAYERS OF *P*-6H-SiC

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In SiC rectifying diodes the base region as usual has *n*-type conductivity and layers of such conductivity type is more detailed investigated. But for developing bipolar transistors and thyristors, *i.e.* for optimization of the multi-layers structures it is necessary to do detailed investigation of *p*-type SiC with different doping level. The aim of the present study is the investigation of low doped *p*-6H-SiC layers, which have no special doping of acceptor impurity, and are only doped by background impurity from graphite crucible. Epitaxial layers were grown by sublimation in vacuum. Schottky diodes and ohmic contacts were formed by magnetron sputtering on the sample surface of Ni or Al+Ti respectively. The diode diameter was in range 120-1200 $\mu$m. The doping level (and its profile) of the layers, hole mobility value, parameters and ionization degree of the main acceptor centers at the different temperatures (DLTS) are investigated. Also values of Schottky barrier height and diffusion potentials for pn junctions formed on the base of these layers were measured. For investigation of the hole mobility on the base of these samples JFET transistors with D-channel were formed.

# HYDROGEN PASSIVATION AND REACTIVATION OF THE Al-ACCEPTORS IN P-TYPE 6H-SiC

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We report on the passivation by hydrogen and the subsequent thermal reactivation of the acceptors in Al-doped *p*-type 6H-SiC. In order to introduce hydrogen into the SiC, Schottky barriers were formed by evaporating a thin film of ruthenium through a contact mask. The Schottky barrier diodes were then exposed to a remote hydrogen plasma at 200°C. Ru was chosen as the Schottky barrier metal for both its permeability to hydrogen as well as its thermal stability [1]. The Ru film also serves to protect the SiC surface from possible damage related to the plasma exposure. Capacitance-voltage measurements revealed that the near-surface free carrier concentration was reduced by at least an order of magnitude after the hydrogen plasma treatment.

The thermal stability of the Al-H complex in the hydrogenated SiC was investigated through a series of isothermal anneals at temperatures ranging from 200°C to 275°C, while applying a reverse bias to the Ru Schottky barrier. The electric field associated with the applied reverse bias caused the dissociated hydrogen to drift deeper into the material, thereby confirming the positive charge state of atomic H in *p*-type SiC. The reactivation process was found to obey first-order kinetics for temperatures above 225°C. From an analysis of the reactivation process we were able to determine the dissociation energy for the Al-H complex. [1] M. E. Samiji, E. van Wyk, L. Wu, A. Venter and A. W. R. Leitch, Mater. Sci. Forum **353–356** (2001) 607

## HYDROGEN INTERSTITIALS IN SILICON CARBIDE POLYTYPES

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Of the silicon carbide polytypes, perhaps the 4H is considered as the most appropriate for high power applications: it has a large gap ($\approx$ 3.3 eV) combined with high carrier mobility ($\mu_e \approx 1000 \frac{cm^2}{Vs}$ at room temperature) [1-3]. Understanding the role of hydrogen in SiC is important because it is typically incorporated into SiC during the growth (by chemical vapor deposition), or via ion implantation for instance in the Smart Cut process. We study hydrogen in 4H-SiC and in other common polytypes (with a reasonable cell size) cubic, 2H, 4H and 6H [4]. *Ab initio* techniques in the local density approximation are applied. The lowest energy configurations for various charge states of a single interstitial hydrogen atom are found. The positions of the electronic gap levels are investigated, and diffusion energies are estimated in particular cases.

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## RADIOTRACER INVESTIGATION OF A DEEP Be-RELATED BAND GAP STATE IN 4H-SiC

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The group II-element Beryllium is expected to act as a doubly charged acceptor in silicon carbide (SiC). Although two acceptor levels at 0.42 eV and 0.60 eV above the valence band edge have been found in Be-doped SiC [1], Be is, alternatively, known to create compensation when introduced in p-doped crystals [2]. Recently, Deep Level Transient Spectroscopy (DLTS) experiments have been performed using the stable $^9$Be isotope [3, 4] revealing several deep band gap states whose assignment to Be-correlated defects is, however, still uncertain. To identify Be-related deep levels in the band gap of SiC, DLTS measurements were performed repeatedly during the elemental transmutation of $^7$Be to $^7$Li. The radioactive isotope $^7$Be was recoil-implanted into *p*-type as well as *n*-type 4H-SiC for radiotracer experiments. The DLTS spectra of *p*-type 4H-SiC exhibit one peak of time-dependent height. It describes the decreasing concentration of the element Be with the half-life of the nuclear decay ($T_{1/2}$ = 53.3d). Thus, one level at 1.06(5) eV above the valence band edge is identified to be Be-correlated. In *n*-type 4H-SiC, neither Be- nor Li-correlated deep levels have been found in the investigated part of the band gap within the measurement accuracy. [1] Yu. P. Maslakovets, E. N. Mokhov,

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## NANOCRYSTAL FORMATION AFTER Er IMPLANTATION IN 6H-SiC

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Properties of bulk materials are modified significantly if the material is manipulated on a nanometer scale [1]. SiC polytypes are promising candidates as matrices for nanocrystals because of the large band gap, the easy formation of good Ohmic contacts and the stability of the bulk materials in harsh environmental conditions. In previous studies, parameters for nanocrystal formation after Ge implantation into hexagonal SiC have been determined [2] and their nature has been revealed [3]. Similar implantation parameters were used for the present study on Er ions resulting in the formation of Er-containing nanocrystals. Specifically, *n*-type 6H-SiC was implanted with 400 keV Er-ions with a fluence of $5 \times 10^{15}$ cm$^{-2}$ at 700°C and subsequently annealed at 1500°C for 30 min in an Argon atmosphere.

Bright-field TEM images of the sample prior to annealing show three distinct regions with different contrast variations due to strain formations: in the near surface region I (vanishing Er-concentration) no contrast variations are observable. Strong strain contrasts are present in the region II from 70 to 140 nm beneath the surface (with high Er-concentration, detected by EDX chemical profiling), originating from point defect clusters and extended defects. In region III (140 to 200 nm) the profiling shows no detectable Er, and therefore the observed strain contrast may be associated with the presence of point defects alone [4,5]. It should be noticed that near the interface of region I and II, a substantial Er content has been measured, however, it does not appear to cause strain contrast. After annealing the following differences can be deduced: Voids have been formed in region I, the point defect clusters which were present in region II either out-diffused, diffused more deeply into the matrix or recombined, while Er has been collected in region I forming nanocrystals. From Fourier transform pattern of high-resolution images of the nanocrystals one type could be assigned to $ErSi_2$.

Studying the damaged SiC matrix in high-resolution transmission electron microscopy a number of planar defects were found in the unannealed as well as in the annealed specimens. By an extended HRTEM study of the planar defects some of them are identified as originating from 0001 extra planes (Frank loops, extra SiC plane) showing a quite pronounced strain field at the ends of their intersection. Another type of planar defects originates from stacking faults, which may be caused by single Er atom clusters. For this type of defects strain measurements from HRTEM images using the geometrical phase approach show that strain fields do not surround them. This work has been supported by the Sonderforschungsbereich 196 of the DFG. [1] L. Pavebi, L. DalNegro, C. Mozzoleni, G. Franco, F. Priolo, Nature **408** (2000) 440–445

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## ANNEALING PROCESSES WITHIN DIAMOND-LIKE CARBON

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Tetrahedral amorphous carbon films have attracted considerable interest because they can be used as an inexpensive and easily produced wide band-gap semiconductor (2.0-2.7 eV) in the fabrication of heterojunction devices, thin film transistors and large area flat-emitter display materials [1]. Relaxation processes are vital for useful diamond or diamond-like films, which usually have large grown-in stresses. Stress relief reduces the chances of delamination. Post-growth annealing also changes the band gap. There is a supposition for diamond-like films that the reduction in band gap with post-growth annealing can be attributed to the encroachment of the gap by aromatic $\pi$-$\pi^*$ states. It is argued that the $\pi$-$\pi^*$ gap in DLC decreases as the size of the aromatic system increases, in the same way as it does for polyaromatic molecules. All sp$^3$ systems eventually graphitise with temperature (sp$^3$ to sp$^2$ conversion), but there is evidence that sp$^2$ carbon atoms can effectively aggregate during annealing, without further conversion of sp$^3$ atoms [2].

We have used dislocations in crystalline diamond as models for some of the environments and processes occurring within diamond-like carbon and tetrahedral amorphous carbon. Our justification is that a dislocation core shares some of the features of the amorphous state (i.e. non-crystalline ring statistics) and that structural changes are easily identified with dislocation motion. Clearly, the model has most applicability for films with a density approaching that of diamond.

We have investigated the possibilities that the cores of dislocations in diamond are graphitised, and that dislocations can glide together to form climb dipoles which nucleate graphitic regions. Furthermore, we draw on previous work which gave the activation energy for motion of dislocations in the presence and in the absence of hydrogen to deduce the activation energies of the process of sp$^2$ aggregation within an sp$^3$ carbon network [3]. [1] K. Zellama, Current opinion in Solid State and Materials Science **4** (1999) 34

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## DISPLACED SUBSTITUTIONAL ACCEPTORS IN SEMICONDUCTORS OF ZINCBLENDE STRUCTURE

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An intriguing aspect of substitutional acceptors in binary semiconductors of zincblende structure is their exact local symmetry. It has been conjectured that there are cases in which the acceptor atom lies not exactly at the substitutional site but slightly off-centre and, furthermore, that the position adopted can be influenced by material factors such as strain and the level of doping. There are very few methods by which this local environment can be investigated. The most promising approach is to study the behaviour in a magnetic field, notably by magnetic resonance or by spin flip Raman scattering (SFRS). We have previously used SFRS extensively to study nitrogen and lithium acceptor centres in wide bandgap II-VI heterostructures and have found that the acceptor centres have the symmetry of the host material, reduced by the biaxial strains induced as a result of lattice mismatch and/or differential thermal contraction. In contrast, we report here work on ZnSe that contains phosphorus: here the SFR spectra from the acceptors show the presence of a strong trigonal field which is additional to the tetragonal field expected due to the biaxial strain of the layer as a whole. The g-values nevertheless remain characteristic of a shallow (valence-band related) hole centre. The most likely explanation is that the acceptor is displaced from the substitutional site towards or away from the nearest cation neighbour. We believe that this is the first unequivocal demonstration of this type of behaviour in such semiconductors.

## CONTRIBUTION OF STATISTICAL FLUCTUATIONS TO THE CO-DOPING EFFECT

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The co-doping process usually involves high concentrations of donor and acceptor impurities. This situation naturally leads to large random fluctuations of the impurity concentrations from place to place around the average values. These fluctuations in return cause a spatial modulation of the charged impurity potential. These potential fluctuations affect both the band edges and the impurity energy levels. As a result, the occupancy of deep impurity levels fluctuates, with a mean ionisation rate higher than the one obtained without fluctuations. We present a phenomenological analysis of the above effect by considering Gaussian fluctuations. The probability distribution of the potential has a standard deviation which is related to a screening length as formulated by Shklovskii and Efros for compensated semiconductors. The local density of states in the continuum is assumed to take its classical form. The average neutrality equation is then solved self consistently to yield the Fermi energy level. The total number of free carriers in the band is finally calculated. The results are plotted as a function of the parameters of the problem: concentration (Na) and ionisation energy (Ea) of the majority impurity, concentration (Nd) of the compensating impurity. A clear positive effect of co-doping appears in the high concentration range (Na = $10^{19}$, $10^{20}$ $\mathrm{cm}^{-3}$) and for deep impurity level (Ea = 0.25 eV), with a maximum doping enhancement occuring at Nd = Na/2. The increase in free carrier concentration due to co-doping is thus fifteenfold for Na = $1.5 \times 10^{20}$ $\mathrm{cm}^{-3}$ and threefold for Na = $10^{19}$ $\mathrm{cm}^{-3}$. In conclusion, potential fluctuations at high doping levels could play an important role in the enhancement of dopant activation due to co-doping.

## 6.4 Workshop/Conference Announcements

### 6.4.1 DFT Conference in Madrid

SECOND ANNOUNCEMENT

# 9th International Conference on the Applications of the Density Functional Theory in Chemistry and Physics

**September, 10-14, 2001**
**San Lorenzo del Escorial, Madrid, SPAIN**
**http://www.uam.es/dft2001**
**E-mail: dft2001@uam.es**

The Organizing Committee of the Applications of the Density Functional Theory in Chemistry and Physics is pleased to announce the opening of the Registration Period for the "9th International Conference on the Applications of the Density Functional Theory in Chemistry and Physics" and looks forward to your participation.

To register just access our web page and fill in the Registration Form following the instructions provided therein.

To achieve maximal representation in this Meeting, please forward this circular to interested colleagues at your institution and elsewhere.

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U. Rothlisberger (Zurich)
A. Rubio (Valladolid)
A. Savin (Paris)
M. Scheffler (Berlin)
J. Schofield (Toronto)
M. Teter (Cornell)

SCOPE OF THE CONFERENCE:

The Conference will be devoted to a broad and balanced overview of new results, emerging trends, and perspectives pertaining to the applications of Density Functional Theory to Chemistry and Physics. The main topics covered by the Conference will be new and recent advances on:

-Methodological developments. New exchange-correlation and kinetic energy functionals. Excited states.
-Computational advances. New codes.
-Isolated systems: molecules, reactivity, dynamics, small clusters.
-Condensed phases: mesoscopic systems, solids, assembled materials.
-Complex molecular systems: biomolecules, molecular materials.
-Electric and magnetic properties.

FORMAT:

The scientific Program will consist of thematic sessions where plenary talks, invited lectures, and some oral contributions (selected from the submitted Abstracts) will be presented. In addition there will be poster sessions, scheduled for optimal viewing and discussion.

Further information about the abstracts format can be found in HTTP://www.uam.es/dft2001

LOCATION:

Colegio Universitario Maria Cristina, in San Lorenzo del Escorial, 50 Km from Madrid. San Lorenzo del Escorial is a picturesque village near the mountains of Sierra de Guadarrama, easily accesible from Madrid. It is also an important historical site, with its famous Monastery.

ACCOMMODATION:

It is expected that most participants will be lodged in single rooms at the Colegio Universitario Maria Cristina and at the Residencia Sagrados Corazones. They provide confortable and modern installations and we have negociated very reasonable prices for full board accomodation from the evening of Sunday (September 9th) until Saturday (September 15th), after breakfast. No fractions of this special global package can be offered. Alternative accomodations can be found in several hotels in town.

REGISTRATION FEE:

Before June 1: 325 Euros.
After June 1: 375 Euros.

LODGING FEE:

Full board (accommodation and meals): 450 Euros.

GRANTS:

A number of Grants covering lodging and/or part of the Registration Fees are available for Graduate students. Applications, submitted by mail or FAX, must be received before May 1st. A letter from the Research supervisor or Head of Department is required.

REGISTRATION:

Registration Form is available on web site

(http://www.uam.es/dft2001).

DEADLINES:

Oral presentations(*): April 1st.
Abstract submission: June 1st.
Grants applications: May 1st.

(*) Notice: only a small number of contributions can be selected for oral presentations.

Updates and pertinent details will be placed periodically on the web site:

http://www.uam.es/dft2001

### 6.4.2 Workshop on Local Orbitals

## Local orbitals and linear-scaling ab initio calculations

CECAM, Lyon, France

3–7 September 2001

`http://www.tcm.phy.cam.ac.uk/LocalOrbital/`

### Aim

This workshop, jointly supported by CECAM and the ESF STRUC-$\Psi_k$ Programme, aims to bring together scientists from a wide variety of communities who use local-orbital techniques for electronic structure calculations and atomistic simulations, with a particular emphasis on linear-scaling methods. This follows on from the successful workshop on localized orbitals held at CECAM in 1998.

Five sessions have been planned:

1. Atomic type orbitals
2. Gaussian type orbitals
3. Real space grid methods
4. Optimized orbitals
5. Linear-scaling methods

### Invited speakers

Jerzy Bernholc, North Carolina State University, USA
Matt Challacombe, LANL, USA
Roberto Dovesi, Turin, Italy
Julian Gale, Imperial College, UK
Giulia Galli, LLNL, USA
Mike Gillan, University College London, UK

Stefan Goedecker, CEA Grenoble, France
Martin Head-Gordon, UC Berkeley, USA
Andrew Horsfield, Fujitsu ECIT, UK
Jürg Hutter, U. Zürich, Switzerland
Walter Kohn, UC Santa Barbara, USA
Richard Martin, UIUC, USA
Nicola Marzari, Princeton, USA
Pablo Ordejón, ICMAB-CSIC, Barcelona, Spain
Chris Pickard, Cambridge, UK
Gustavo Scuseria, Rice, USA
Gotthard Seifert, Paderborn, Germany
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Mark van Schilfgaarde, Sandia, USA

**Organizers**

**Peter Haynes**
Theory of Condensed Matter
Cavendish Laboratory
Madingley Road
Cambridge CB3 0HE, UK

**David Bowler**
Department of Physics and Astronomy
University College
London WC1E 6BT, UK

**Emilio Artacho**
Dep. Física de la Materia Condensada
Universidad Autónoma de Madrid
C-III, 28049 Madrid, Spain

### 6.4.3 FHImd Hands-on Workshop

## APPLICATION OF DENSITY-FUNCTIONAL THEORY IN CONDENSED MATTER PHYSICS, SURFACE PHYSICS, CHEMISTRY, ENGINEERING AND BIOLOGY

**23 July - 1 August 2001, Berlin**

**http://www.fhi-berlin.mpg.de/th/Meetings/FHImd2001/**

**Sponsored by the Fritz-Haber-Institut der Max-Planck-Gesellschaft and the Psi-k Network**

This hands-on course focuses on the application of density-functional theory to electronic-structure calculations in different scientific fields and provides a practical introduction to the handling of pertinent software packages. As a specific example we consider the computer code FHImd. The workshop programme combines morning lectures, which elucidate the theoretical concepts and numerical procedures, with practical sessions in the computer laboratory where realistic research problems are tackled. In addition to condensed matter physics, special emphasis is placed on nontraditional fields like biology and surface chemistry. The workshop is part of a biennial series and follows previous events in Berlin (1995, 1997) and Trieste (1999).

Applications for this workshop should be submitted until 31 March 2001. Further details and instructions how to apply are available at

http://www.fhi-berlin.mpg.de/th/Meetings/FHImd2001/

# 7 General Workshop/Conference Announcements

## 7.1 Summer School on DFT

### 2nd circular
### 2nd Summer School on Computational Physics

The Centre of Computational Physics of the University of Coimbra is organizing the 2nd Summer School on Computational Physics. The school will take place at Caramulo, Portugal, between August 28 and September 1, 2001. There will be both theoretical (18 hours) and practical sessions (8 hours). Students are also invited to present a short summary of their research project.

Topics covered:

- Introduction to DFT, exchange and correlation functionals
- Excited states in DFT, Time Dependent DFT, DFT beyond the Born-Oppenheimer approximation
- Orbital dependent functionals in DFT, van der Waals interactions
- Relativistic DFT
- Computational aspects in DFT, pseudopotentials, Car-Parrinello Molecular Dynamics
- Fundamental problems in DFT, Many-Body versus DFT methods
- Relativistic DFT, future prospects of DFT

Lecturers:

- Reiner Dreizler, Goethe Universitaet, Frankfurt-am Main, Germany
- John P. Perdew, Tulane University, New Orleans, USA
- Jos Luis Martins, Instituto Superior Tcnico, Lisboa, Portugal
- Rex Godby, University of York, UK
- E. K. U. Gross, Universitaet Wuerzburg, Germany
- Eberhardt Engel, Goethe Universitaet, Frankfurt-am Main, Germany

Webpage:

http://cfc.fis.uc.pt/events/DFT2001

Payment and registration:

See the webpage.

Warning: The school will have a limited number of participants.

## 7.2 HLCS - EUROCONFERENCE

### XI WORKSHOP ON COMPUTATIONAL MATERIALS SCIENCE

**17 - 23 September 2001**
**Sofitel Timi Ama, Villasimius (CA), Sardinia, Italy**

**web page: http://www.dsf.unica.it/CMS2001**
**e-mail: workshop@dsf.unica.it**

**with the sponsorship of**
**European Commission-Community Research**
**High-Level Scientific Conferences**

**under the patronage of UNESCO**

**organized by: The Physics Department, Università di Cagliari, and the Cagliari Research Unit of Istituto Nazionale per la Fisica della Materia**

**An international workshop on computational techniques and applications to materials science**

See TENTATIVE INVITED SPEAKERS and INFO below.

FORMAT: About 20 invited lectures plus TALK (~12) and POSTER contributed session.

VENUE: Sofitel Timi Ama at Villasimius (CA), an attractive sea resort on the south-eastern coast of Sardinia, providing comforts and an informal atmosphere.

CONTACT: For scientific and logistic queries: workshop@dsf.unica.it

CONTRIBUTIONS AND PROCEEDINGS:

Contributions in poster format are invited. ALL contributions (after refereeing) will be published probably in a special issue of the journal Computational Materials Science. Deadline for abstract submission: June 30, 2001. Contact V. Fiorentini at +39 070 6754912 or P. Ruggerone at +39 070 6754847 or at workshop@dsf.unica.it for further details. Camera ready manuscripts will be due at the Workshop, LaTeX templates can be downloaded from the Workshop homepage:

http://www.dsf.unica.it/CMS2001

INVITED SPEAKERS

H. Brune (Lausanne, Switzerland)
A.J. Freeman (Evanston, USA)
W. Hanke (Wuerzburg, Germany) (*)
D. Helbing (Dresden, Germany)
L. Kubin (Chatillon, France) (*)
J. Majewski (Munich, Germany)
F. Mauri (Paris, France) (*)
B. Persson (Juelich, Germany) (*)
U. Roethlisberger (Zurich, Switzerland)
A. Rubio (Valladolid, Spain)
A. Ruini (Modena, Italy)
F. Seno (Padova, Italy)
L. Serrano (Heidelberg, Germany) (*)
J. Soler (Madrid, Spain)
A. Zunger (NREL, USA)

(*) not yet confirmed

REGISTRATION

The REGISTRATION form can be sent directly from the Workshop homepage

http://www.dsf.unica.it/CMS2001).

The deadline is June 1, 2001.

The registration should be accompanied by payment receipt of the CONFERENCE FEE (by FAX: ++39-070-510171). The fee includes full-board lodging at Hotel Sofitel Timi Ama from 17/9 afternoon to 23/9 lunch, coffee breaks, refreshments, social trip (or banquet), and amounts to

Double or triple room lodging It.Lire 1400000 (~US$ 670)/person Single room lodging It.Lire 1600000 (~US$ 760)/person.

PAYMENT should be effected by bank money transfer on the bank account # 22698 of Comitato Organizzatore di Attività di Fisica Computazionale, at Banco di Sardegna, Sede di Cagliari, Codice ABI 1015/7 - CAB 04800.

No fee is requested from the invited speakers.

The Organizing Committee is able to offer support (from 50% up to 100% of the conference fees plus travel costs in some cases) to a limited number (~50) of young scientists, preferrably PhD students. The deadline for the request of financial support is May 1, 2001. The committee will comunicate its decision on May 20, 2001.

Series Chairman : prof. A. Baldereschi - EPFL Lausanne

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

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

## 7.3 EuroConference on PARTICLE - SOLID INTERACTIONS

### PARTICLE - SOLID INTERACTIONS

bf EuroConference on the Deposition of Atoms, Ions and Clusters at Surfaces
Supported by the European Commission, Research DG, Human Potential Programme High-Level Scientific Conferences (Contract No: HPCF-CT-2000- 00230)
San Sebastian, Spain, 11-16 September 2001
Chairperson: Risto M. Nieminen (Helsinki University of Technology, FIN)
Vice- Archie Howie (Cambridge Chairperson: University, UK)
Organised in association with the European Physical Society
and Donostia Encounters on Particle-Solid Interactions (President of the series: Pedro Miguel Etxenike)
Preliminary Programme On line at:
http://www.esf.org/euresco/01/pc01081a.htm

This conference belongs to the series of Donostia Conferences arranged biannually. The programme will be built around a number of invited talks, with ample time for discussion and workshop sessions. A number of contributed papers will be included as posters.

The topics of the sessions include various aspects of particle- surface interactions, such as ion implantation and processing, surface modification and characterisation, morphology, atomic manipulation and imaging, cluster deposition, electronic excitations and charge transfer.The conference will elucidate the basic physics and chemistry of nanoscale structures at and near solid surfaces, which is a rapidly advancing area of materials science. Experimental, theoretical and computational topics will be presented.

Speakers will include:

Robert Averback (Illinois, US)
*Ion irradiation induced nanostructures in metals*

Florian Banhart (Ulm University, D)
*The generation of new carbon nanoparticles umder irradiation*

Flemming Besenbacher (Aarhus, DK)
*title to be announced*

Andrei Borisov (Paris, F)
*Quantum size effects in charge transfer between a projectile and the surface of a thin metal film*

Eleanor Campbell (Chalmers, S)
*Ion implantation of fullerenes*

Luciano Colombo (Cagliari, I)
*Theoretical investigations of low-energy recoils in silicon*

Kristen Fichthorn (Penn State University, US)
*Surface-mediated adsorbate interactions: quantification and ramifications for nanostructures at surfaces*

Thomas Frauenheim (Paderborn University, D)
*Density-functional approach to nanoscale materials and processes*

Jim Gimzewski (UCLA, US
*title to be announced*

Hannu Hkkinen (Georgia Tech., US)
*First-principles investigations of chemical reactivity of supported metal catalysts*

Per Hyldgaard (Chalmers, S)
*Nature and consequences of long-range interactions at surfaces*

Matti Manninen (Jyväskylä, FIN)
*Interplay of the geometry and the electronic structure in free and deposited metal clusters*

Thomas Michely (Aachen University, D)
*Atomic processes in damage and erosion of surfaces by low- energy ions*

Michel Moseler (Freiburg University, D)
*Surface processing with cluster beams and liquid nanojets*

Kai Nordlund (Helsinki, FIN)
*Surface modification and erosion by ions and clusters*

Richard Palmer (Birmingham, UK)
*Fabrication of nanostructural surfaces from clusters*

Markus Rauscher (Cornell, US)
*Energetic beam deposition and processing of thin films*

Angel Rubio (Valladolid, E)
*title to be announced*

Bengt Svensson (Oslo, NO)
*Diffusion and defect reactions in silicon-based semiconductors*

Massimiliano di Ventra (Virginia, US)
*Electronic transport in molecular clusters*

Pedro Zeijlmans van Emmichoven (Utrecht, NL)
*Thermal metastable He atoms interacting with single crystal surfaces*

## 7.4 School on COMPUTATIONAL MATERIALS SCIENCE

### NATO ADVANCED STUDIES INSTITUTE

## COMPUTATIONAL MATERIALS SCIENCE
## Il Ciocco, Italy – 9 - 22 September 2001

The School will survey the main techniques and applications in the growing and exciting area of materials modelling using computational techniques. All aspects of the field will be considered, including modern electronic structure methods, static and dynamical atomistic simulation methods and the interface between atomistic and mesoscale modelling methods. Lecturers include the following:

I Abarenkov (St Petersburg, Russia)
V Anatov (Kiev, Ukraine)
CRA Catlow (London, UK)
A Cormack (Alfred, USA)
P Deak (Budapest, Hungary)
R Dovesi (Turin, Italy)
R Evarestov (St Petersburg, Russia)
N Harrison (Daresbury, UK)
F Illas (Barcelona, Spain)
E Kotomin (Riga, Latvia)
C Noguerra (Paris, France)
A Postnikov (Yekaterinburg, Russia)
D Wolf (Argonne Laboratory, USA)
S Yip (MIT, USA)
G Zhidimirov (Novosibirsk, Russia)

The school will be held in the Il Ciocco conference centre, which is beautifully located in the Tuscan Hills north of Pisa. It is aimed at graduate students and post-docs working in relevant areas of materials science, chemistry and physics, and to more experienced scientists who wish to obtain a grounding in the field.

Information and application forms are available on our web site:

http://cems.alfred.edu/NATO

or from

Professor CRA Catlow,
The Royal Institution,

21 Albemarle Street,
London W1S 4BS, UK,
Email: asi2001@ri.ac.uk

Closing date for applications: 21st May, 2001

# 8 General Job Announcements

## Postdoctoral Research Associate in Computational Material Science

## Clausthal University of Technology, Institute of Theoretical Physics

Applications are invited for a postdoctoral research position. The successful candidate will investigate oxide properties and oxide growth on silicon using ab-initio molecular dynamics simulations. The research is part of an European project with several partner institutions from industry and academia. The project aims to develop a key technology for future generations of semiconductor technology, namely new gate oxides and their integration into commercial processes.

The position is currently planned for 2 years. Salary is according to BATIIa (roughly 5000 DM/month). Candidates should have a PhD in physics or chemistry.

Please send applications and inquiries to Prof. Peter Bloechl (address is given below).

Prof. Peter E. Bloechl
Institute of Theoretical Physics
Clausthal University of Technology
Leibnizstr. 10
D-38678 Clausthal-Zellerfeld
Germany
email: Peter.Bloechl@tu-clausthal.de
phone: +49(5323)722021
phone: +49(5323)722555 (Secretary)
fax: +49(5323)723116
http://www.pt.tu-clausthal.de/atp/

### RESEARCH ASSOCIATE POSITION

## in Ab Initio Molecular Dynamics Theoretical Chemistry, Ruhr-Universitaet Bochum

Applications are invited for a postdoctoral research associate position (German nomenclature: promovierter wiss. Mitarbeiter, BAT IIa, including full social benefits). The appointment will be for two years in the first instance, however the position is available for a total of five years - independent of external funding. Starting date will be May 2001 or as soon as possible thereafter.

Applicants are expected to hold a doctorate in physics or a related discipline. The ideal candidate would have significant experience in density functional calculations, ab initio molecular dynamics, programming, and computational techniques in general. He or she would be involved in a number of diverse and challenging research projects including both method development and large-scale applications. The broad interests of the group are covered in the review article: http://www.fz-juelich.de/nic-series/Volume1/marx.ps or ...pdf.

Candidates should send a detailed resume including an outline of their research interests and the names and email addresses of academic referees as soon as possible to

Dominik Marx
Lehrstuhl fuer Theoretische Chemie
Ruhr-Universitaet Bochum
44780 Bochum, Germany
Email : dominik.marx@theochem.ruhr-uni-bochum.de
Phone : ++49 234 32 28083 (direct)
++49 234 32 26485 (office)
Fax : ++49 234 32 14045
Web : http://www.theochem.ruhr-uni-bochum.de

The University particularly welcomes applications from women.

# Postdoctoral Positions in Computational Physics
# North Carolina State University, Raleigh

Applications are invited for postdoctoral research associate positions in computational physics. Successful candidates will be involved in the development of advanced methods such as quantum Monte Carlo and their applications to forefront research problems in electronic structure of nanoscale and solid state systems. The candidate's PhD should be in physics or quantum chemistry. Programming and computational experience is expected. The positions will be for one year initially and are renewable up to three years based upon mutual agreement and availability of funds. The beginning is anticipated in early spring, summer or fall of 2001, at the latest. Publications from our recent projects are listed at http://altair.physics.ncsu.edu/lubos/main.html .

Please send the application with CV, copies of two recent papers, max. one page of research interests/plans, and contact information (address, phone and email) of three references to: Prof. Lubos Mitas, Dept. of Physics, North Carolina State University, Raleigh, NC 27695-8202, USA or email me: lmitas@unity.ncsu.edu
or contact me at the APS March Meeting in Seattle, March 12-14, 2001.

More information is at:

http://altair.physics.ncsu.edu/lubos/group/pdra.html
http://altair.physics.ncsu.edu/lubos/main.html

## POSTDOCTORAL POSITION

# Groupe de Physique des Materiaux

# Departement de Physique
# Universite de Liege, Belgium

A postdoctoral position is available at the Universite de Liege (Belgium) to study theoretically the electronic structure and the magnetic and optical properties of small clusters and nanoparticles. Experience in handling semiempirical (Hückel, Pariser-Parr-Pople) and ab initio (DFT) methods to compute the electronic structure of small clusters will be appreciated. The position is a one-year appointment, starting from April 2001 and is opened to physicists and chemists. The research will be carried out jointly with Prof. Ph. Ghosez and Dr. F. Remacle.

Applications including (i) a curriculum vitae and (ii) two confidential letters of recommendation should be addressed to

Prof. Ph. Ghosez,
Institut de Physique (B5),
Allee du 6-aout 17,
B-4000 Sart Tilman,
Belgium

Phone: 32/4/366 3611,
Fax: 32/4/366 2990,
E-mail: Philippe.Ghosez@ulg.ac.be

# Research Jobs In Physics and Chemistry
# DIRECTION DES SCIENCES DE LA MATIERE
# DRFMC -Commissariat a lÉnergie Atomique
# Grenoble FRANCE

The Department of Fundamental Research on Condensed Matter (DRFMC), a laboratory of the French Atomic Energy Commission (CEA), is located in Grenoble, France. At the DRFMC, a permanent staff of 400 people (150 researchers and 70 PhD students) are working in fields that range from the advancement of basic knowledge in condensed matter physics and chemistry to applications in new materials, new technologies and biology. The laboratory consists of five groups: Physics of Materials and Microstructures, Magnetism, Superconductivity and Statistical Physics, Interfaces, Molecules and Molecular Materials, Inorganic and Biological Chemistry, Low Temperatures. The DRFMC is currently inviting applications for **six** permanent research positions. All these positions require a PhD or equivalent qualification, and candidates with postdoctoral experience would normally be preferred.

Theory in condensed matter physics (Jan 2002). The appointee should have a confirmed experience in statistical physics. A knowledge in magnetism and/or superconductivity would be an advantage, as well as an interest in mesoscopic physics.

A letter of application with CV, list of publications, at least two referees' names and addresses, should be sent to:

A. Chamberod
DRFMC
CEA-Grenoble
38054 GRENOBLE cedex 9
France

Tél: 33 476 88 34 98
Fax: 33 476 88 51 53
E-mail: chamber@drfmc.ceng.cea.fr

# Postdoctoral Position
# University of Zürich, Switzerland

An opening for a postdoc is available in my group at the University of Zurich. Candidates should have a background in method development for electronic structure theory or molecular dynamics simulations. Good programming skills and experience with Unix programming tools are expected.

The position is within a research project to develop new methods for ab initio molecular dynamics in electronically excited states. We plan to incorporate excited states DFT methods within our plane wave and atomic orbital based programs to investigate molecular excitations in condensed systems.

Description of codes and methods:

D. Marx and J. Hutter, Ab initio molecular dynamics: Theory and implementation; Modern Methods and Algorithms of Quantum Chemistry, J. Grotendorst (Ed.), Forschungszentrum Julich, NIC Series, Vol. 1, (2000)

G. Lippert, J. Hutter, and M. Parrinello, Theor. Chem. Accounts 103, p124 (1999)

I. Frank, J. Hutter, D. Marx, and M. Parrinello, JCP 108 p4060 (1998)

The position is available starting April 2001 for two years. The appointment is originally for one year, but an extension to the second year is possible with mutual agreement. Candidates should send a CV with publication list and two contacts for references (preferably by e-mail).

Juerg Hutter
Institute of Organic Chemistry
University of Zürich
Winterthurerstrasse 190
CH-8057 Zürich, Switzerland

Phone : ++41 1 635 4211
FAX : ++41 1 635 6836
E-mail: hutter@oci.unizh.ch

# Postdoctoral Research Position in Computational Material Science
# National Renewable Energy Laboratory, Golden, Colorado

We at the National Renewable Energy Laboratory (one of the DOE's prestige National Laboratories) invites applications for a postdoctoral research position, available immediately. This position is for one year, but renewable upon mutual agreement and available funding up to two more years. The research objective is to study the electronic properties of atomic ordering in III-V alloys and the surface reconstructions that lead to such ordering. The starting salary is US$40-50 K/year depending on qualification. NREL is located near the beautiful Rocky Mountains, a gate to the wild west and ski resorts. We have outstanding computational facilities, excellent basic-research atmosphere, and the postdoc is expected to interact extensively with the experimental groups at NREL on the related subjects. Candidate should send a curriculum vitae, list of publications (including preprints of unpublished papers, if possible) and list of three references to

Dr. Shengbai Zhang
Computational Materials Science Group
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, CO 80401, USA

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

# Postdoctoral Positions at Computational Materials Theory Center
# California State University, Northridge

The Computational Material Theory Center at California State University, Northridge invites applications for two postdoctoral positions available immediately. The research areas include first principles electronic structure calculations and model simulations to study 1) mechanical properties in metals and intermetallics and 2)electronic transport in metal/ceramic interfaces.

The candidate should have experience in ab initio/atomistic methods and/or transport phenomena. The position will be for 2 years and can be extended for a third year.

Interested candidates should send their resume and two letters of references to Nicholas Kioussis at Department of Physics and Astronomy California State University Northridge, 18111 Nordhoff Street, CA 91330-8268, or through email to nick.kioussis@csun.edu.

## POST-DOCTORAL/RESEARCH ASSOCIATE POSITION IN COMPUTATIONAL MATERIALS SCIENCE

## Department of Chemical Engineering and Materials Science

## Minnesota Supercomputer Institute for Digital Technology University of Minnesota

The computational Materials Science Group at the Department of Chemical Engineering and Materials Science and Minnesota Supercomputer Institute for Digital Technology at the U. of Minnesota will have a openings for postdoctoral research associate positions in the Fall of 2001. Research in the group develops around first principles theory of structural, electronic, and thermodynamical properties of oxide solids. The group has close interactions with the Physics Department in the area of magnetoresistive oxides (MRSEC funded research), and with the Geology and Geophysics Department at U. of MN and other institutions (NSF/EAR funded research) in the are of high pressure mineral physics. Candidates are expected to have exceptional background in first principle calculations and be committed to excellency in research. Salary is commensurate with experience. Application material or enquiries may be sent to this e-mail address or to:

Renata M. Wentzcovitch
Department of Chemical Engineering and Materials Science
421 Washington Ave. SE
Minneapolis, MN 55455
USA

# Vacancies at SISSA, Trieste, Italy
# Theory of Condensed Matter and Computer Simulation

Come and learn how to do state-of-the-art research in a beautiful place!

Our faculty includes: S. Baroni, P. Carloni, S. de Gironcoli, F. Ercolessi, M. Fabrizio, S. Fantoni, M. Marsili, A. Maritan, G. Santoro, S. Scandolo, and S. Sorella.

Our group leader is E. Tosatti.

We do theoretical modeling and computer simulations of materials properties, quantum fluids, statistical mechanics, strongly correlated many-body systems, surface physics, theoretical biophysics and structural biology.

Find more about our research menu at: http://www.sissa.it/cm/

Additional details on these positions:

http://www.sissa.it/cm/students2001.html

## Ph. D. Positions
## Institut Francais du Petrole (IFP), France

IFP and IFP-School are offering 46 PhD positions in 2001 (of which 40 are still open).

All information can be found on the web site:

http://www.ifp-school.com/uk/pages/theses.html

The subject promoted by Pascal Raybaud (and myself in the background) within the Applied Chemistry and Physical Chemistry Division is particularly relevant to the psi-k audience (ab intio simulations with VASP).

Many other subjects might be of interest for students with skills in computational physics.

Herve TOULHOAT
Adjoint au Directeur Scientifique
Directeur de Recherche Associe (Modelisation Moleculaire)
INSTITUT FRANCAIS DU PETROLE (IFP)
1 & 4 Avenue de Bois-Preau
92852 RUEIL-MALMAISON Cedex
France

Tel: +33-01-47-52-73-50
Fax: +33-01-47-52-70-22
E-mail: herve.toulhoat@ifp.fr

## UNIVERSITY COLLEGE LONDON

# Condensed Matter and Materials Physics EU-funded and other research studentships

The Condensed Matter and Materials Physics group at University College London invites enquiries from well qualified UK and non-UK students interested in doing a Ph.D. A number of three-year studentships are available to start in October 2001. The following is a selection of the studentships available:

Two PhD Scholarships are available to work with Dr. Alexander Shluger on the following projects:

1. Theoretical studies of defects in oxides and thin oxide films on silicon.

$Al_2O_3$, $ZrO_2$, $HfO_2$ and some other dielectrics are considered as alternatives to silicon dioxide for memory and logic devices. Point defects, such as vacancies and impurities and more complex structural imperfections associated with growth of these materials on silicon and other processes, will determine the performance of future devices. This project is a part of a concerted effort involving several industrial partners and funded by the EU. It will involve the development of quantum-mechanical methods for calculation of defects in dielectric materials and their application to studies of particular systems. Applicants should have strong undergraduate background in quantum mechanics and solid state physics. Experience in programming and applications of quantum-chemistry or periodic band structure calculation codes would be an advantage. Willingness to collaborate with experimental groups and industrial partners is essential. A substantial increase of a scholarship over the usual EPSRC level is possible dependent on performance.

2.Theory of Atomic Force Microscopy on insulators.

Atomic Force Microscopy (AFM) is the only method available for imaging insulating surfaces with atomic resolution. Strong interaction between experiment and theory is necessary for the understanding of experimentally observed images and development of new AFM techniques. The group at UCL is one of the world leaders in theoretical modelling of AFM. This project, which is funded by EPSRC, will focus on studies of oxide surfaces and molecular adsorption and chemical reactions at these surfaces. We would like to image and stimulate molecular processes at oxide surfaces using AFM. This will involve the development of new methods for calculations of the AFM tip - surface interaction and extensive computer modelling of AFM images. Strong collaboration with several leading experimental groups will be essential. A substantial increase of a scholarship over the usual EPSRC level is possible dependent on performance.

Enquiries about the above two projects should be made direct to Dr. Alexander Shluger (a.shluger@ucl.ac.uk).

A Ph.D. studentship is available to work with Professor Keith McEwen on research involving experiments in magnetism, superconductivity and neutron scattering in a joint project with Dr Gerry Lander at the EU-funded Karlsruhe Institute for Actinides (in Germany) and Dr Jiri Kulda at the Institut Laue-Langevin in Grenoble (France).

The student would be registered for a PhD at UCL, and probably spend the first year in London, and then 2 years in Grenoble.

The nationality requirements are that the student must be a national of an EU country, but must definitely not be British or French. The studentship is very attractive financially, being a tax-free salary of about 2000 euro/month, more than twice as much as an EPSRC studentship, although the student has to pay his/her fees from this (but these have been at a part-time rate for the time in Grenoble). Candidates should expect to get a first or good upper second class MSci/MPhys degree. The studentship would be for 3 years, starting in October 2001, or soon after.

The Institut Laue-Langevin (ILL) is a very exciting place to work. It is a joint UK-French-German-Italian-Spanish-Austrian-Swiss research center for physics, chemistry, materials science using neutron scattering, and is the world leader in the field. On the same site as the ILL is the European Synchrotron Radiation Facility (ESRF), the world's best source of X-rays. Some experiments would also be done here. Grenoble is on the edge of the Alps, and a very attractive place to live, especially if you like mountains! The ability to speak French is not essential, but is obviously desirable. The working language amongst the scientists is English. You can find information about the ILL and ESRF at their web sites: www.ill.fr and www.esrf.fr

The project would involve fundamental studies of novel metallic materials which have unusual electronic and magnetic properties. Examples include the recently-discovered heavy-fermion systems, which often display an (as-yet!) unexplained coexistence of superconductivity and magnetism.

If you are interested in this possibility, please contact Professor Keith McEwen as soon as possible (email:k.mcewen@ucl.ac.uk).

Please also send names and addresses (email address if possible) of 2 people who can give me a reference about you.

# PHD POSITIONS - MATERIALS MODELLING
# NSTITUTE FOR MATERIALS RESEARCH
# UNIVERSITY OF SALFORD

Applications are invited for Ph.D positions in the area of first principles modelling of materials in the neutron scattering and materials modelling group at Salford. The group uses state of the art methods in electronic structure theory to model structure and properties of complex materials. Emphasis is placed on the interpretation of neutron spectra of such materials. Current activities include first principles simulations of proton dynamics in metal hydrides, structure and dynamics of molecular solids/clusters and magnetic phase transitions in metal hydrides. Computational facilities available to the group include numerous local workstations and a 17.2 GFlop IBM SP.

A number of funding routes exist including EPSRC awards (EU nationals) and ORS awards with University bursaries (non - EU nationals).

Interested parties should contact:

Dr. Ian Morrison
Joule Physics Laboratory and Institute for Materials Research
University of Salford tel: 0161 2955303
email: i.morrison@salford.ac.uk

# 9 Abstracts

## Resolving Complex Atomic-Scale Spin-Structures by SP-STM

D. Wortmann[†], S. Heinze[†,¶], Ph. Kurz[†], G. Bihlmayer[†], and S. Blügel[†]
[†]*Institut für Festkörperforschung, Forschungszentrum Jülich,*
*D-52425 Jülich, Germany*
[¶]*Zentrum für Mikrostrukturforschung, Universität Hamburg,*
*D-20355 Hamburg, Germany*

### Abstract

The spinpolarized scanning tunneling microscope (SP-STM) operated in the constant current mode is proposed as a powerful tool to investigate complex atomic-scale magnetic structures of otherwise chemically equivalent atoms. The potential of this approach is demonstrated by successfully resolving the magnetic structure of Cr/Ag(111), which is predicted on the basis of *ab initio* vector spin-density calculations to be a coplanar non-collinear periodic 120° Néel structure. Different operating modes of the SP-STM are discussed on the basis of the model of Tersoff and Hamann.

(Accepted by Phys. Rev. Lett.)
Copy available from: d.wortmann@fz-juelich.de

# High-pressure phases in the Al2SiO5 system and the problem of aluminous phase in the Earth's lower mantle: ab initio calculations

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### Abstract

One of the main uncertainties in mineralogical models of the Earth's lower mantle is the nature of the aluminous mineral : it is not clear whether Al forms its own minerals or is mainly contained in (Mg,Fe)$SiO_3$-perovskite. This question is very important, since it is known that if Al were mainly hosted by perovskite, it would radically change Fe/Mg-partitioning and phase equilibria between mantle minerals, and also alter many physical and chemical properties of perovskite, which is currently believed to comprise ca 70 % of the volume of the lower mantle. This, in turn, would require us to reconsider many of our geochemical and geophysical models for the lower mantle.

This work considers the possibility of a $V_3O_5$-type structured modification of $Al_2SiO_5$ to be the main host of Al in the lower mantle, as proposed by Ahmed-Zaid and Madon (1991; 1995). We report ab initio calculations, based on density functional theory within the generalised gradient approximation (GGA) with plane wave basis set and nonlocal pseudopotentials. We consider polymorphs of $Al_2SiO_5$ (kyanite, andalusite, sillimanite, and hypothetical $V_3O_5$-like and pseudobrookite-like phases), $SiO_2$ (stishovite, quartz) and $Al_2O_3$ (corundum). Computational conditions (e.g., plane-wave energy cutoff, Brillouin zone sampling) were carefully chosen in order to reproduce small energy changes associated with phase transitions between the $Al_2SiO_5$ polymorphs. Good agreement of crystal structures, bulk moduli, atomisation energies and the phase diagram of $Al_2SiO_5$ with experimental data was found. Strong disagreement between the calculated lattice parameters and density of $V_3O_5$-like phase of $Al_2SiO_5$ and the experimental values (Ahmed-Zaid and Madon 1991) suggests that the phase studied in the latter work is not a $V_3O_5$-structured phase of $Al_2SiO_5$. In addition, we found that the most stable high-pressure assembly in $Al_2SiO_5$ system is corundumstishovite, and the value of the transition pressure at T=O K (113 kbar) is in excellent agreement with experimental estimates (95-150 kbar). We explain the instability of octahedrally coordinated silicates of Al to decomposition on the basis of Pauling's second rule.

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# Magnetic Phase Diagram of $Ca_{2-x}Sr_xRuO_4$ Governed by Structural Distortions

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### Abstract

We constructed, by the first-principles calculations, a magnetic phase diagram of $Sr_2RuO_4$ in the space spanned by structural distortions. Our phase diagram can qualitatively explain the experimental one for $Ca_{2-x}Sr_xRuO_4$. We found that the rotation and the tilting of $RuO_6$ octahedron are responsible for the ferro- and antiferro-magnetism, respectively, while the flattening of $RuO_6$ is the key factor to stabilize those magnetic ground states. Our results imply that the magnetic and the structural instabilities in $Sr_2RuO_4$ are closely correlated cooperatively rather than competitively.

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# Strong ferromagnetism and weak antiferromagnetism in double perovskites: $Sr_2FeMO_6$ ($M$=Mo, W, and Re)

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### Abstract

Double perovskites $Sr_2FeMO_6$ ($M$=Mo and Re) exhibit significant colossal magnetoresistance even at room temperature due to the high Curie Temperature (419K and 401K). However, such a high Curie Temperature is puzzling, given the large separation between magnetic elements (Fe). Moreover, with $M$=W, the electronic and magnetic properties suddenly change to insulating and antiferromagnetic with the Néel temperature of only 16~37 K. Based on detailed electronic structure calculations, a new mechanism is proposed which stabilizes the strong ferromagnetic state for $M$=Mo and Re and is passivated for $M$=W.

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# Surface Magnetic Phase Diagram of Tetragonal Manganites

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### Abstract

To gain insights into the fundamental and characteristic features of the surface of doped manganites, we constructed a general magnetic phase diagram of $La_{1-x}Sr_xMnO_3$ (001) surfaces in the plane spanned by $x$ and the bulk tetragonal distortion $c/a$, from the first-principles calculations. We found that the surfaces are quite different from the bulk in the sense that both the (La, Sr)O and $MnO_2$ terminated surfaces show strong tendency toward antiferromagnetism (A-type and C-type respectively). The basic physics governing the phase diagram can be understood in terms of the surface orbital polarizations. It is also found that the strong surface segregation of Sr atoms is mostly caused by the electrostatic interaction and will further enhance the tendency to surface antiferromagnetism.

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# Spin and orbital polarizations around oxygen vacancies on the (001) surfaces of $SrTiO_3$

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### Abstract

The (001) surfaces of $SrTiO_3$ with oxygen vacancy were studied with the first-principles calculations based on the generalized gradient approximation (GGA) supplemented by the LDA+U method. Strong local spin and orbital polarization of the Ti 3d electrons induced by oxygen vacancy are found. For SrO-terminated case, the occupied Ti 3d orbital has strong 3z2-r2 character, while for TiO2-terminated case, one of the t2g orbitals perpendicular to the surface is occupied on each of the two neighboring Ti atoms. By allowing the spin polarization, the calculated electronic structures of TiO2-terminated surface can well explain the scanning tunneling microscopy (STM) and spectroscopy (STS) data.

Surf. Sci. **470**, L75 (2001).
Latex-file available from zfang@jrcat.or.jp

# Effects of Resonant Interface States on Tunneling Magnetoresistance

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### Abstract

Based on model and *ab initio* calculations we discuss the effect of resonant interface states on the conductance of epitaxial tunnel junctions. In particular we show that the 'hot spots' found by several groups in *ab initio* calculations of the $\mathbf{k}_{||}$-resolved conductance can be explained by the formation of bonding and antibonding hybrids between the interface states on both sides of the barrier. If the resonance condition for these hybrid states is met, the electron tunnels through the barrier without attenuation. Only when both hybrid states move together and form a single resonance, normal attenuation sets in. The effect explains, why for intermediate barrier thicknesses the tunneling conductance can be dominated by interface states, although hot spots only occur in a tiny fraction of the surface Brillouin zone.

submitted to: Phys. Rev. Lett.
Manuscripts available from: O. Wunnicke (o.wunnicke@fz-juelich.de)

# Reaction-limited island nucleation in molecular beam epitaxy of compound semiconductors

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**Abstract**

Kinetic Monte Carlo simulations on the basis of rates derived from density-functional calculations are used to investigate the atomic processes in molecular beam epitaxy of GaAs. This novel approach puts us in a position to describe island nucleation and growth in all relevant atomistic detail by bridging the gap in length and time scales between the mesoscopic scale of growth morphology and the atomic scale. We observe a non-monotonic dependence of the island density on growth temperature related to a reversible surface reaction of $As_2$ with Ga adatoms.

(submitted to: Phys. Rev. Lett.)
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# GaAs(2 5 11) - A new stable surface inside the stereographic triangle

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## Abstract

The atomic structure of GaAs(2 5 11), a hitherto unknown stable surface, has been determined by *in situ* scanning tunneling microscopy (STM) and first-principles electronic structure calculations. This orientation is located inside the stereographic triangle, i.e. far away from all low-index surfaces. A low-energy (1×1) reconstruction containing arsenic dimers forms on the surface. The analysis of the surface structure shows that, for semiconductor surfaces, the gain in stability due to minimization of the number of dangling bonds is more important than the gain from rendering a semiconducting ground state.

(submitted to: Phys. Rev. Lett.)

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# Effect of strain on surface diffusion in semiconductor heteroepitaxy

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### Abstract

We present a first-principles analysis of the strain renormalization of the cation diffusivity on the GaAs(001) surface. For the example of In/GaAs(001)-$c(4\times4)$ it is shown that the binding of In is increased when the substrate lattice is expanded. The diffusion barrier $\Delta E(\varepsilon)$ has a non-monotonic strain dependence with a maximum at compressive strain values ($\varepsilon < 0$), while being a decreasing function for any tensile strain ($\varepsilon > 0$) studied. We discuss the consequences of spatial variations of both the binding energy and the diffusion barrier of an adatom caused by the strain field around a heteroepitaxial island. For a simplified geometry, we evaluate the speed of growth of two coherently strained islands on the GaAs(001) surface and identify a growth regime where island sizes tend to equalize during growth due to the strain dependence of surface diffusion.

(submitted to: Phys. Rev. B)

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# Island dissolution during capping layer growth interruption

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### Abstract

A possible scenario for the dissolution of partially capped quantum dots has been investigated. This model is based on the consideration of the total free energy being a sum of elastic and surface energies as the quantum-dot material redistributes itself as a second wetting layer on top of the capping layer. Quantitative results have been obtained for the case of InAs/GaAs quantum dots that are partially capped by GaAs. We compare our results with supporting experimental evidence.

(submitted to: Appl. Phys. A)
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# The role of electronic correlation in the Si(100) reconstruction: a quantum Monte Carlo study

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## Abstract

Recent low-temperature scanning tunneling experiments have challenged the generally accepted picture of buckled silicon dimers as the ground state reconstruction of the Si(100) surface. Together with the symmetric dimer model of the surface suggested by quantum chemistry calculations on small clusters, these findings question our general understanding of electronic correlations at surfaces and its proper description within density functional theory. We present quantum Monte Carlo calculations on large cluster models of the symmetric and buckled surface, and conclude that buckling remains energetically more favorable even when the present-day best treatment of electronic correlation is employed.

(submitted to: Phys. Rev. Lett.)

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# Atomistic description of oxide formation on metal surfaces: The example of ruthenium

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## Abstract

Presently very little is known or understood about the microscopic processes actuating the formation of oxides on metal surfaces. Using density-functional theory we investigate the oxidation of a Ru(0001) surface, from the initial O adsorption, subsequent O incorporation into the metal, sub-surface nucleation, to the transition to the oxide film. The different chemical properties of such corroded surfaces are crucial to understand the catalytic activity of metals at realistic pressures and temperatures.

(submitted to: Phys. Rev. Lett.)
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# Reorientation phase transitions in thin magnetic films: a review of the classical vector spin model within the mean field approach

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**Abstract**

The ground state and the finite temperature phase diagrams with respect to magnetic configurations are studied systematically for thin magnetic films in terms of a classical Heisenberg model including magnetic dipole-dipole interaction and uniaxial anisotropy. Simple relations are derived for the occurrence of the various phase boundaries between the different regions of the magnetic orientations. In particular, the range of the first and second order reorientation phase transitions are determined for bi- and trilayers.

(To be published in Phil. Mag. B)
Preprints are available from A. Vernes (`av@cms.tuwien.ac.at`).

# Ab initio simulation of the proton dynamics in zeolites[1]

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### Abstract

Ab-initio density-functional molecular dynamics is used to characterize dynamical processes in zeolites. Simulations performed on the structure of gmelinite show that the proton transfer between the O-sites is a spontaneous process enabled in both Na-free and Na-zeolite by just one water molecule adsorbed to the acid site. A proton attack of the acid zeolite at the hydrocarbon molecule is investigated at increased temperature of 700K. In the protonated molecule a series of proton jumps are observed indicating a high mobility of protons along the hydrocarbon molecule at high temperatures.

## Introduction

Zeolites are microporous crystalline aluminosilicates with a framework formed by a three-dimensional network of corner-sharing Si(Al)$O_4$ tetrahedra [1]. The Al/Si substitution occurring in both natural and synthetic compounds leads to the existence of extra-framework cations. Water-coordinated cations, such as $Na^+$, $K^+$, $Ca^{2+}$, etc., which are located in channels and

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[1] Original contribution to the 13th International Zeolite Conference, Montpellier, France, July 8-13, 2001, extended and adapted for Psi-*k* Newsletters

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cavities of the zeolite framework balance the neutrality of the solid compound perturbed by the Al/Si substitution. Zeolites thus represent a unique combination of relatively rigid covalently bonded aluminosilicate frameworks with weakly ionically bonded exchangeable cations. An ion-exchange into the $NH_4^+$-form with consequent thermal decomposition of $NH_4^+$ into $NH_3$ and $H^+$ ends with the H-form of the zeolite which is free of extra-framework cations with hydrogen atoms connected directly to framework O atoms. Because such a structure with trivalent oxygen atoms is considerably disfavored in energy compared to ionic form, the H-zeolites exhibit strong tendency to liberate protons and behave as typical strong acids. The combination of acidic, sorption and sieving properties makes zeolites good candidates for heterogenous catalysis. Currently zeolites are widely used in chemical and petrochemical industry and the extent of their use is rapidly increasing, because many liquid acid catalysts need to be replaced with environmentally more compatible chemicals.

In spite of the great amount of experimental material collected over several decades of the usage of zeolites as industrial catalysts, the microscopic mechanisms of chemical reactions in zeolites are unclear and have attracted continuous attention of both experimentalists and theoreticians. The characterization of the properties of zeolites, however, represents a difficult task due to the extremal complexity of these inorganic materials. Though zeolites are bulky materials their density is low due to numerous channels and cavities through which any part of the structure is accessible as an internal surface. Surface defects and sorption of small molecules modify both the composition and the structure of the internal surface. Moreover, a treatment of zeolitic samples which leads to higher catalytic activities includes drastic processes like dealumination and removal of adsorbed species at high temperatures. A fraction of released molecules and oxide nanoparticles remains accommodated in structural voids and makes the composition and the structure of internal zeolite surfaces ill-determined. Especially extra-framework aluminum particles (EFAL) are everpresent in zeolite structures. If properties of such particles are similar to those of alumina catalysts the EFAL can play a major role in catalytic processes within zeolites. Unfortunately details of composition, structure and location of such particles are beyond the capabilities of structural methods. Structural studies of the inclusion compounds, like extra-framework particles of ZnO encapsulated in zeolites, represent the leading edge in applications of the up-to-date experimental techniques [2].

First periodic first-principles calculations on zeolites were performed, due to the complexity of zeolite structures, only recently [4, 5, 6, 7]. The increasing performance of computers makes it possible to launch projects on technologically important structures with large unit cells (cf. an application to ZSM-5 with 288 atoms/cell [3] including short-run molecular dynamics (MD) runs. Though ab initio MD is powerful tool for the characterization of elementary steps of chemical reactions, first applications to zeolites [8, 9, 10, 11, 3] have demonstrated that mechanistic applications to complex structures do not automatically deliver solutions to chemical processes which are typically completed on the time-scale of milliseconds. Numerous short-term MD simulations are therefore necessary to scrutinize partial microscopic steps, each of them providing a small picture to the mosaic representing a chemical reaction.

Any conversion of a hydrocarbon within the zeolite matrix starts with proton (or hydride) transfer. This can occur both along the zeolite framework and/or between the zeolite and the adsorbed molecule. We have performed simulations of proton dynamics in gmelinite. This natu-

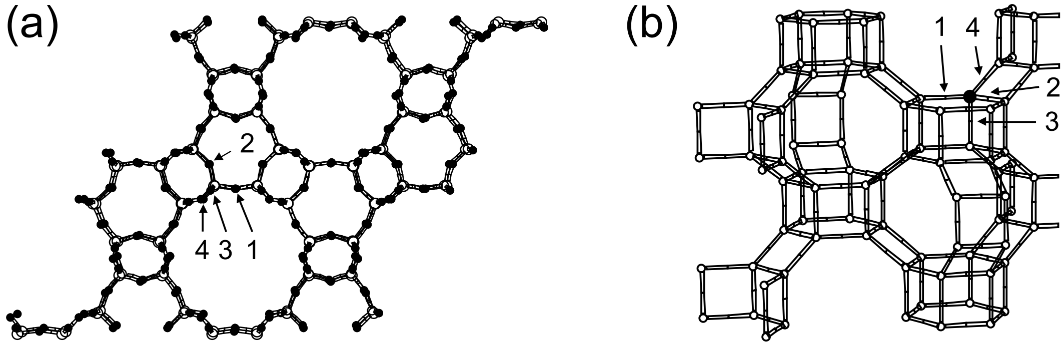

Figure 1: Structure of gmelinite. (a) Top view of the large 12MR channels. (b) Framework structure. Vertices correspond to tetrahedral positions (Si or Al), the O atoms are not displayed. Arrows indicate four inequivalent O positions.

ral zeolite does not itself belong to the technologically important materials. However, structural features such as a hexagonal prism as a building block of the structure and the twelve-membered ring (12MR) are similar to those of the important industrial zeolite faujasite (FAU). The large unit cell of gmelinite containing relatively a small number of atoms make gmelinite a proper candidate for MD simulations. We have performed extensive sampling of dynamical behavior of protons based on full relaxation of atomic positions of selected configurations complemented with short-term MD simulations. Details of the proton transfer are investigated for the migration between O-sites in the zeolite, for the proton attack of the zeolite acid proton on the adsorbed hydrocarbon molecule, as well as for the H transfer along the chain of the protonized hydrocarbon.

## Structure and Computational Details

Simulations are performed on the medium-sized unit cell of gmelinite comprising 24 tetrahedral $SiO_2$ units with a low Si/Al substitution rate (Si/Al=23/1) The secondary building unit is a hexagonal prism whose parallel stacking leads to the hexagonal structure with space group $P6_3mmc$ (Fig. 1). The largest aperture is a $\sim$7 Å channel circumscribed by 12-membered rings (12MR) which runs parallel to $c$ [12]. Periodic ab initio calculations are performed within DFT using the Vienna ab initio simulation package VASP [13] based on pseudopotentials and plane-wave expansion of the wave-functions and using GGA density functionals. Fixed-volume molecular dynamics applies Verlet velocity algorithm in a canonical ensemble with a timestep of $\Delta t = 1$ fs.

## Results

Our first studies based on both static relaxation of zeolite structures and finite-temperature molecular dynamics focus on the properties of the structure of gmelinite [14] and the behavior of the extra-framework particles [15]. Optimizations performed on purely siliceous as well as on Al-substituted structures show that Si/Al substitution in gmelinite induces pronounced local

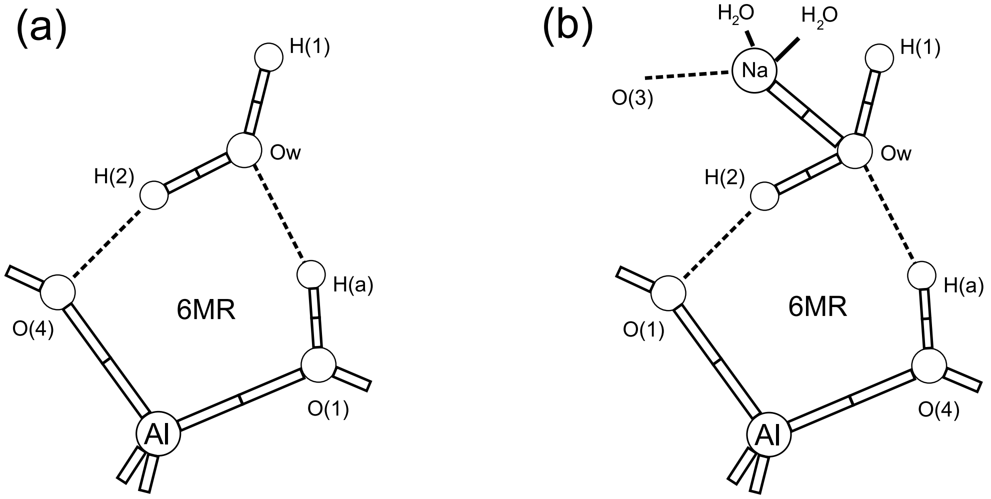

Figure 2: The geometry of the water molecule adsorbed to the acid site in gmelinite. (a) The Na-free zeolite with water adsorbed to proton bound to the O(1) position. (b) The Na-zeolite with water placed between the acid site and the $Na^+$ cation. Adsorbed water typically establishes a six-membered ring (6MR) through two hydrogen bonds. The stronger bond forms between the water oxygen atom Ow and the acid proton Ha and the secondary hydrogen bond between hydrogen of the water molecule and the framework O-atom.

deformations [14] similar to those observed in mordenite [16]. Through protonation the four inequivalent O-sites (Fig. 1) form acid sites of high (O1, O4) and lower stability (O2, O3) positions. The frequency spectra calculated by Fourier-transforming the velocity autocorrelation function shows that the stretching of OH1, OH2 and OH4 hydroxyl groups produces one band of vibrational states located at the high-frequency edge of the O-H stretching region. The protonation of the O2 site produces an OH group extending within the base of the hexagonal prism where it forms weak contacts to the framework O atoms. Due to these weak hydrogen bonds the frequency of the OH2 group is downshifted by $\sim$100 $cm^{-1}$ [14].

## Acidity and proton transfer in zeolites

The most important forms of zeolites are natural cationic species containing a mixture of extra framework cations like $Na^+$, $K^+$, $Ca^{2+}$, etc. and protonated zeolites (H-forms). Protonated forms of zeolites are typical solid acids widely used in industry as acid catalysts. The acidity of the H-zeolite originates from the tendency of the framework to donate the H atom to adsorbed molecules. The connection of the H atom to the framework is energetically considerably disadvantaged compared with the $Na^+$ zeolite [15] as it produces a trivalent O atom. Placing an isolated $H^+$ in the void of the zeolite in analogy with natural zeolites, however, is not possible. The transfer away from the framework can be mediated by molecules of basic character, such as water, methanol, or hydrocarbons. Protonized forms of adsorbed basic molecules are located in voids of zeolites stabilized through hydrogen bonds to zeolite O-sites.

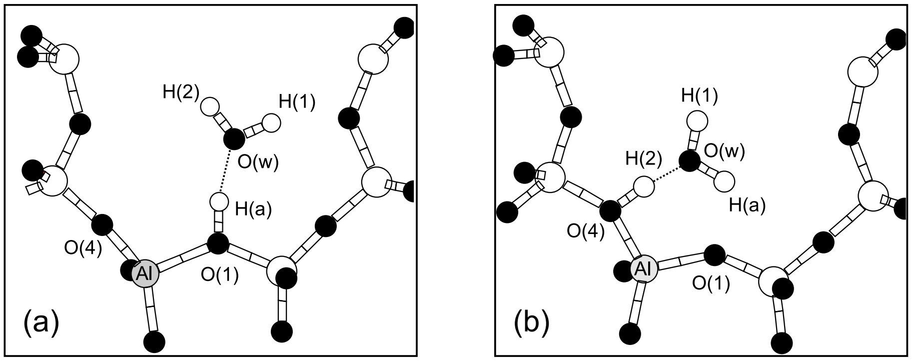

Figure 3: The snapshots of two structures of Na-free zeolite developed in the MD run at 300 K. (a) Water molecule is adsorbed to the acid proton H(a) located at the O(1)-site. (b) Water is adsorbed to the H(2) atom after two proton transfers, (i) H(a) is transferred from O(1) to O(w) and (ii) H(2) goes from O(w) to O(4).

## A. Na-free zeolite

Room-temperature simulations are performed with a single water molecule adsorbed to the acid proton bound in the most stable O1 position. Fig. 2a shows the geometry of a fragment of the structure adopted upon adsorption, where the O1 and O4 atoms are the most stable sites for the protonation of the gmelinite framework [14]. The dynamical simulation leads to the transfer of the acid proton (Ha in Fig. 2a) to the water molecule, thus producing a short-lived $H_3O^+$ cation [17]. The cation is for a short period of time stabilized through two hydrogen bonds which form a six-membered ring (6MR). The decay of the short-lived $H_3O^+$ cation leads either to the same location of proton (O1) or ends with the framework protonated at the O4-site. Fig. 3 shows two MD snapshots displaying the starting location of the acid proton (a) and proton-transferred zeolite framework (b). The decay of the short-lived $H_3O^+$ cation leading to the proton transfer is enabled by the dynamics of both the $H_3O^+$ cation and of the zeolite framework. Both types of proton transfer, (i) from zeolite to $H_2O$ and (ii) from $H_3O^+$ back to the zeolite framework, are accomplished through relatively strong hydrogen bonds O-H...O. A temporary strengthening of the secondary hydrogen bond (H2-to-O4, Fig. 2a) causes the elongation of the Ow-H2 bond. This makes the oxygen atom of the adsorbed water molecule (Ow) more attractive and ends with the transfer of the acid proton (Ha) to Ow. Characteristic of the hydrogen bond strengthening is the increase of the O-H-O angle up to a value close to $180^o$ for which the hydrogen bond is the most effective. The time evolution of both O-H-O angles of the 6MR (cf. Fig. 2, left) is displayed in Fig. 4a. The strengthening of the secondary hydrogen bond corresponds to the maximum of the O4-H2-Ow angle at $\sim$ 1165 fs. The response to changes within the secondary hydrogen bond leads to the strengthening of the primary hydrogen bond and induces the proton transfer. This occurs during the quasi-linear arrangement of O1-Ha-Ow at $\sim$1185 fs (cf. first arrow in Fig. 4a). During approximately 70 fs the acid proton is detached from the zeolite and the neutrality of the negatively charged framework is balanced by the positive charge of the $H_3O^+$ cation. Such a configuration is similar to the most stable forms of zeolites in which cations like $Na^+$, $K^+$, $Ca^{2+}$, etc. are located at distances of several Å from the framework. A singly charged $H_3O^+$ particle represents, however, only a transition state with limited lifetime. A stabilization

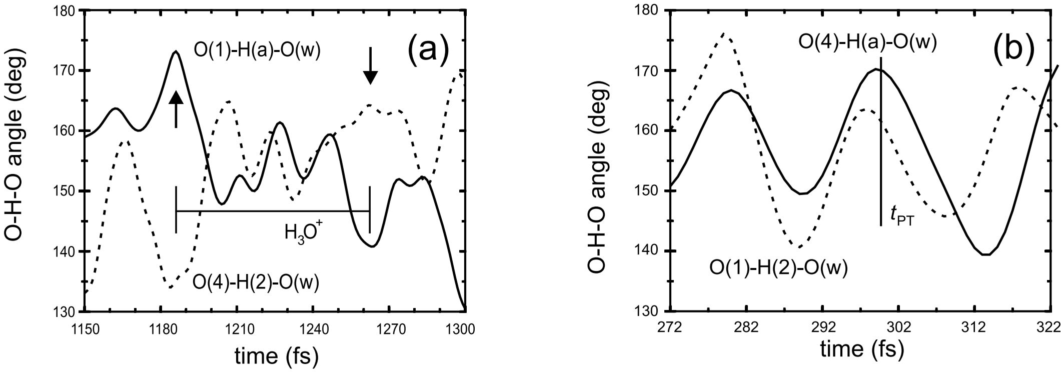

Figure 4: The time evolution of the O-H-O angles within hydrogen bonds (cf. Fig. 2) (a) in the Na-free zeolite and (b) in the Na zeolite.

of the charged particle within the voids of the zeolite takes place at higher loadings, leading to a clustering of adsorbed molecules [9, 18]. The decay of the configuration with separated charges occurs via proton transfer back to the zeolite, thus restoring the neutrality of both the zeolite and the adsorbed molecule. In Fig. 4a the arrow at ~1260 fs indicates the back-transfer of the proton to zeolite. Because the back transfer occurs via the strengthening of the secondary hydrogen bond (cf. the maximum value of the O4-H2-Ow angle in Fig. 4a), the decay of $H_3O^+$ ends with the neutral zeolite protonized at the O4-site. Fig. 3 displays both the O1-protonized zeolite before the $H_3O^+$ cation is formed (a) and the O4-protonized structure after the decay of $H_3O^+$ as simulated for the contact of the acid site with one water molecule. Our simulation indicates that in zeolites a fast exchange of protons between the most stable O-sites is enabled by even very low concentrations (traces) of adsorbed water molecules.

## B. Na-zeolite

Both cations and the acid sites of H-zeolites are strong attractive centers for the adsorption of small molecules. Because zeolites pretreated for technological purposes can contain both extra framework cations and acid sites we have investigated the adsorption of water molecules in such zeolite structures to figure out the influence of extra framework cations on the proton transfer observed in Na-free zeolites. The effective interaction with either of the centers requires a proper reorientation of the adsorbed molecule. Because the creation of a $H_3O^+$ cation is not possible without water being adsorbed to the acid site, the presence of Na appears to counteract the formation of the $H_3O^+$ and the process of the proton transfer in zeolites.

The MD simulations of a zeolite containing both an acid site and a Na atom are performed for gmelinite with a Si/Al ratio of 11 with two Al atoms per cell. One Al atom is compensated by the acid proton and the second by the Na atom coordinated by three water molecules (cf. Fig. 2b). The Na atom is typically localized in the main channel next to the framework O3-site (cf. Fig. 1) with three water molecules coordinated from the side of the main channel. The competition of the two centers for the water molecules is observed for the geometry displayed in Fig. 2b where the acid proton is located at the O4-site [19]. In this arrangement one water molecule is placed between the acid site and the Na atom and connects to both centers. The water molecule forms two hydrogen bonds to the zeolite framework and establishes a 6MR in

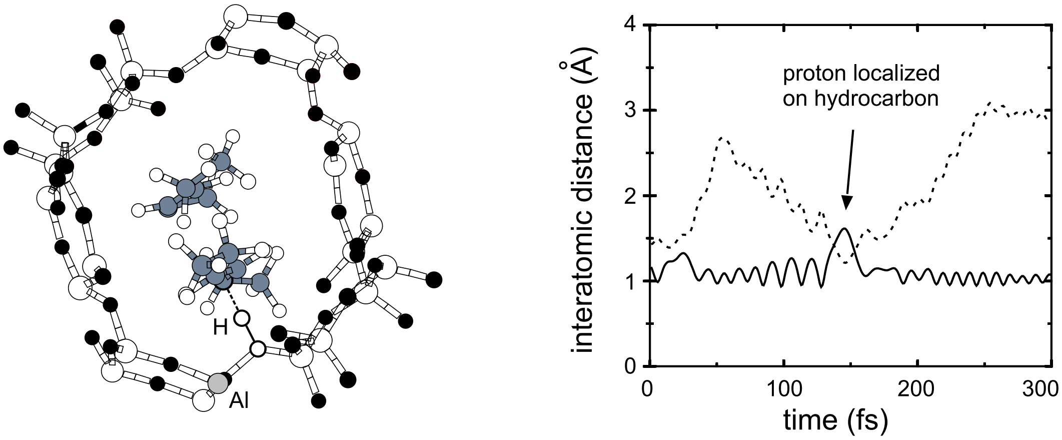

Figure 5: The contact of the zeolitic acid proton (H) with the hydrocarbon molecule 2E Left, the placement of the molecules inside the channel. Right, the time development of the location of the acid proton. Full line shows the distance between proton and the zeolite O-site and dashed line shows that between the H atom and the C atom of the hydrocarbon molecule. The arrow indicates the proton transfer to the adsorbed molecule.

Na-free zeolite (cf. Figs. 2b and 2a). Induced by the dynamics of the lattice two proton transfers are observed. The Ha proton is transferred to the water molecule and the H2 proton is donated to the O1 framework site. Because the creation of a $H_3O^+$ cation in close proximity to the extra-framework cation ($Na^+$) is energetically disfavored, the two proton transfers occur almost simultaneously. The display of the O-H-O angles (Fig. 4b) shows that maximum values of both angles practically coincide. This means that maximum strength of the two hydrogen bonds is achieved at the same time and the transfer of two protons occurs as a correlated two-particle phenomenon. Both protons are located close to the water oxygen atom just for a short period of time (∼5 fs).

## Conversion of hydrocarbons in zeolites

The catalytic conversion of hydrocarbons in acid zeolites is one of the most important processes in the oil refining industry. In spite of the huge research effort aimed at a detailed understanding of the reaction mechanisms, there are still areas requiring deeper knowledge, including both the initiation and propagation of the chemical reaction.

### A. Proton transfer to hydrocarbon molecule

It is generally accepted that the initial step of the reaction is the attack of the acid proton on the reactant molecule. We investigate the acid attack at a linear C6 molecule adsorbed in a zeolite at 700K. The hydrocarbon molecule is placed in the main channel of the zeolite parallel to the *c* lattice vector (Fig. 5, left). A high temperature simulation is performed for both saturated and unsaturated molecules. For the latter the role of an increased concentration of adsorbate is tested for two and three molecules per cell, respectively. At a temperature of 700 K the hexane molecule is not adsorbed at the inner surface of the zeolite. It moves laterally (not

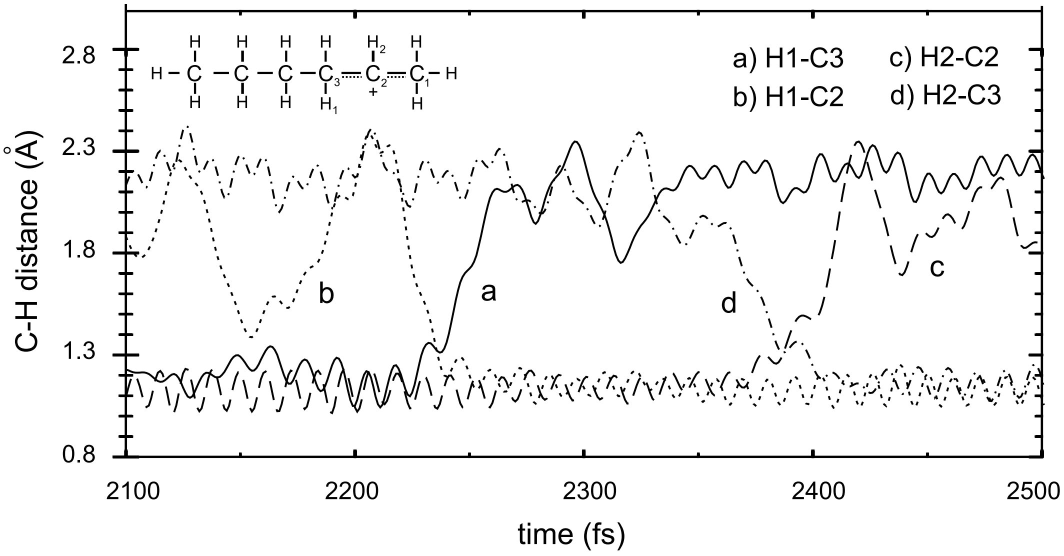

Figure 6: Migration of H atoms along the protonated hexene molecule.

vertically) in the main channel making only weak periodic contacts with the zeolite acid proton [20]. The calculated vibrational spectrum shows a down-shift of the OH stretching frequency by ~130 $cm^{-1}$ compared with that of the adsorbate-free zeolite. A much stronger interaction is expected for an unsaturated molecule (3-hexene). The shift of the OH stretching frequency, however, is similar to that obtained for the adsorption of the saturated molecule. During the high-temperature simulation of the adsorption of both saturated and unsaturated molecules the acid proton resides on the zeolite framework [20]. With increased loading of the unsaturated molecules (two per cell) the proton affinity of the adsorbed molecules increases considerably. The contact between the acid site and the hydrocarbon molecule is more tight. The acid proton is more intensively attracted by the electron density of the double bond, but it is still resides on the more electronegative framework O-site. The dynamics of both the O-H stretching and of the kinetic movement of the adsorbed molecule supports the proton transfer. The simulation reveals that for short periods of time the acid proton can be transferred to the hydrocarbon molecule. Two events of the intensive attraction are displayed in Fig. 5, right. During the first contact (0-30 fs) when the hydrocarbon molecule closely approaches the acid proton, this is pulled away from the zeolite to a distance of ~1.4 Å, but remains bonded to the O-site. During the second contact (~130-160 fs), however, the proton is transferred to the double bond of 3-hexene. Further increase of the loading (three molecules per cell) leads to the formation of rather compact cluster of the adsorbed molecules, considerably decreasing the mobility of the adsorbed molecules and making the proton transfer more difficult [20].

### B. Migration of protons in protonated hydrocarbon

The nature of the elementary steps of hydrocarbon conversion is still strongly debated. Two possible reaction pathways consider i/ conversion through stabilized carbenium ions and ii/ conversion through alkoxy species covalently bonded to the zeolite framework [21]. Because our simulations indicate that at high temperatures hydrocarbon molecules are not anchored at the surface of the zeolite we performed a simulation of the behavior of the protonated hydrocarbon (carbenium ion). The simulation shows that a protonated hydrocarbon does not approach the inner surface of the zeolite. It is long-lived and resides in the centre of the channel, stabilized by the long-range electrostatic interactions. Compared to the neutral molecule the cation is more mobile and moves along the main channel [21]. This vertical movement induces consecutive transfers of the H atoms leading to the migration of the positive charge along the hydrocarbon chain. The location of the positive charge on the hydrocarbon is correlated to the position of the Al-site within the zeolite framework. Following the vertical displacement of the hydrocarbon a transfer of the H atom occurs which allows for a more effective contact between the positive charge localized on the molecule and the negative charge localized on the framework. The migration of the H atoms is visualized in Fig. 6 through the time development of the C-H distances. The starting location of the positive charge is on the C2 atom (cf. inset in Fig. 6, top left). The line displaying the H1-C3 distance shows that the H1 atom jumps from the C3 atom at ~2230 fs. Line b shows that this H1 atom goes to C2. Note that first unsuccessful attempt to move H1 from C3 to C1 occurred already at ~2150 fs. Together with the H atom the electron density corresponding to two electrons is transferred. The phenomenon of the migration of the H atom is therefore better characterized as a hydride transfer. Shortly later, at ~2380 fs, another hydride transfer follows, restoring the location of the positive charge on the C2 atom. Note, however, that another H atom is transferred back to the C3 atom. The two hydride transfers displayed in Fig. 6 thus lead to the mutual exchange of the positions of the H1 and H2 atoms on the chain of the protonated hexene molecule which is stabilized in the channel of the zeolite.

## Conclusions

Ab initio MD simulations are performed to investigate the dynamics of protons within zeolites, the proton transfer from zeolite to an adsorbed hydrocarbon and the hydride transfer within the protonized hydrocarbon molecule. Spontaneous proton transfer between O-sites is observed, induced by the dynamics of the lattice and mediated by an adsorbed water molecule. The MD simulations show that spontaneous proton transfer occurs in the hydrated forms of both Na-free and Na-zeolites. The presence of the extra-framework cation does not suppress the proton transfer. Considerably influenced, however, is the lifetime of the $H_3O^+$. In Na-zeolites it is extremely short (~5 fs), whereas for Na-free zeolites much longer lifetimes are observed (~70 fs).

An attack of the acidic proton on the hydrocarbon is investigated for a saturated linear hexane molecule and for unsaturated 3-hexene at different loadings. Due to the tight contact between the acid site and the adsorbate molecule at the high loading a the short-time proton transfer to the double bond of the hexene molecule is observed.

A protonated hydrocarbon molecule is shown to be long-lived in the channel of a zeolite. It resides approximately in the centre of the channel, stabilized by long-range electrostatic interactions. During the movement of the adsorbed molecule along the channel the interaction of the positive charge of the protonized molecule and the negative charge localized around the Al-site of the framework induces a series of hydride transfers along the hydrocarbon molecule. The hydride transfer leads to an instantaneous location of the proton which retains an effective contact between the mobile positive charge on the molecule and the fixed negative charge on the zeolite framework.

Our simulations demonstrate that ab initio molecular dynamics is maturing into a powerful tool for investigation of technologically important chemical processes.

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