Ψ_k Newsletter

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

Number 46 August 2001

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

Contents

1 Editorial

Similarly to the previous newsletter, we start this newsletter with a call for scientific highlights in the section **General News**. Please do read this and try to respond positively. The sections **News from the RTN Network** and **News from the ESF Programme** contain two large reports on schools and workshops on magnetic multilayers and DFT, respectively. Both reports contain abstracts of presented papers. The workshop/conference announcements can be found in the **News from the ESF Programme** and **General Workshop/Conference Announcements** sections. In addition, in the **ESF** section there is a short write-up by Volker Heine, the chairman of the Programme, on the renewal proposal. In this newsletter we also have news from the UK's electronic structure community, the so-called CCP9 Programme. A number of position announcements can be found in the usual **General Job Announcements** section, which is followed by the **Abstracts** section with abstracts of the recently published or submitted papers. The newsletter is finished with the scientific highlight of the month by Carme Rovira (*Barcelona University*) and Michele Parrinello (*ETH Zürich*) on **First principles simulations of hemeproteins: From the active center to the full protein**. 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 Ψ_k community**

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

2 General News

2.1 Call for Scientific Highlights for 2002

Unfortunately, our last call for scientific highlights for 2002 has been totally unsuccessful, since we have had no response from our readers. Therefore, here we repeat our appeal to all our subscribers in and outside Europe.

As you are fully aware, we publish six Psi-k newsletters a year and in each of them there is a scientific highlight. Six highlights a year may not seem that many, but it is increasingly harder to find volunteers for writing them. In addition, we find that there are only a few European groups who are willing to contribute a highlight from time to time. However, it would be beneficial to the whole community if also, until now, less visible groups would like to share the effort of producing exciting Psi-k newsletters by contributing a scientific highlight. There are many interesting things happening across the Psi-k community and it would be nice if all of it was well represented in the Psi-k newsletters. Note that all scientific highlights published to date can, outside the newsletters, also be viewed at a dedicated web site:
http://psi-k.dl.ac.uk/psi-k/highlights.html.
So, if you feel that you could write a scientific highlight for one of the future newsletters, please contact us on psik-coord@dl.ac.uk suggesting a topic and preferred dates. We shall get back to you with exact dates and other details as soon as possible.

3 News from the Research Training Network (RTN)

COMPUTATIONAL MAGNETOELECTRONICS

3.1 Reports on Workshops/Conferences

3.1.1 Report on a Course on Magnetic Multilayers

The European Graduate School on Condensed Matter (EGSCM Prague'01): Physics of Magnetic Multilayers - Theory and Experiment

Prague, 9th - 16th June 2001

Sponsored by:

ESF Programme:
"Electronic Structure calculations for elucidating the complex
atomistic behaviour of solids and surfaces"

Research Training Network:
"Computational Magnetoelectronics"

Organizers:
Vladimír Sechovský
Václav Drchal, Josef Kudrnovský, Ilja Turek

EGSCM'01: Physics of Magnetic Multilayers

Prague, 9-16 June 2001

The European Graduate School on Condensed Matter (EGSCM'01) on the subject 'Physics of Magnetic Multilayers - Theory and Experiment' was held in Prague from June 9 to 16, 2001. It was organized by the Department of Electronic Structures, Faculty of Mathematics and Physics, Charles University in Prague (V. Sechovský, main organizer) and by the Academy of Sciences of the Czech Republic (Institute of Physics, Prague - V. Drchal and J. Kudrnovský and Institute of Physics of Materials, Brno - I. Turek). The school was sponsored by the ESF Programme and the RT Network.

The aim of this school was to give participants theoretical and experimental background necessary for orientation in the rapidly developing field of the physics of magnetic multilayers. Together 29 invited speakers, mostly the leading persons in the field, gave their lectures to 113 participants coming from 23 different countries all over the world. The lectures were divided into three basic sections:
(i) Electronic structure of multilayers and its experimental study, which included the introduction into electronic structure calculations of magnetic crystals and alloys, both bulk and surfaces (multilayers), which were all based on the density functional theory. In addition, the non-collinear magnetism and the effect of electron correlations on magnetic properties were discussed. Equally important part of this group of lectures was devoted to the structure characterization of magnetic multilayers and to the experimental study of electronic structure of magnetic multilayers using the photoemission.
(ii) Exchange interactions and relativistic effects, like, e.g., magnetic anisotropy, magnetooptical effects, and magnetic dischroism were discussed both theoretically and experimentally;
(iii) Transport properties of magnetic multilayers were key for this school and large number of different theoretical and experimental lectures was presented. The transport across tunnelling junctions and ferromagnet-superconductor interfaces were also discussed.

The theoretical lectures were followed by experimental ones wherever possible. The school lasted one week with six hours of lectures each day and one free day. All lectures were accompanied by intensive discussions at their end as well as at coffee breaks. Two poster sessions were organized allowing the participants to present their recent results and to discuss them with invited speakers and other participants. After intensive program, the city of Prague itself was a beautiful framework for the relaxation.

Communication with speakers and participants was managed predominantly by e-mail and through the EGSCM'01 Web page (http://195.113.32.128/EGSCM_Prague.htm). The Web page contains all necessary information about the School (Organizers, Program, Registration and Practical Info), abstracts of posters and where available also the materials provided by majority of speakers to their lectures.

In conclusion, we believe the EGSCM'01 has reached its main objectives, namely, to give PhD students and young postdocs an overall overview of the field of magnetic multilayers, both theoretical and experimental. Even more important was the possibility to discuss their own results with the leading persons in the field. Last but not least, the school has created new scientific relations among young people from different countries all over the world. Some participants complained that despite of sincere effort of all lecturers to give tutorial talks, some of lectures were difficult to understand fully and that six hours of lectures each day was sometimes too much. However, as a whole, the usefulness of the EGSCM was highly appreciated by most participants.

The organizers:
Vladimír Sechovský, Václav Drchal, Josef Kudrnovský, Ilja Turek

Programme

Programme

· Saturday June 9th

Chair: P.H. Dederichs

08:45 - 9:00 V. Sechovský, I. Turek, P.H. Dederichs "*Opening, general info*"

09:00 - 10:30 B. Velický "*Introduction into the electronic structure*"

10:30 - 11:00 Coffee break, discussion

11:00 - 12:30 H. Eschrig "*Introduction to the Density Functional Theory: magnetic materials*"

12:30 - 14:30 Lunch, poster session

Chair: H. Eschrig

14:30 - 15:30 P. Dederichs "*Electronic structure of magnetic metal surfaces*"

15:30 - 16:30 I. Turek "*Electronic structure of random magnetic metals and their surfaces*"

16:30 - 17:00 Coffee break, discussion

17:00 - 18:00 D. Rafaja "*Structure of multilayers using X-rays*"

· Sunday June 10th

Chair: J. Kirschner

09:00 - 10:00 J. Henk "*LEED and photoemission from ultrathin magnetic films*"

10:00 - 11:00 C. Carbone "*Photoemission from magnetic films*"

11:00 - 11:30 Coffee break, discussion

11:30 - 12:30 J. Hafner "*Non-collinear magnetism*"

12:30 - 14:30 Lunch, poster session

Chair: J. Hafner

14:30 - 16:00 B.L. Gyorffy "*Magnetism of metals*"

16:00 - 16:30 Coffee break, discussion

16:30 - 18:00 J. Kirschner ”*Preparation and properties of magnetic multilayers and nanostructures*”

· Monday June 11th

Chair: P. Weinberger

09:00 - 10:30 P.M. Levy ”*Theory of magnetotransport*”

10:30 - 11:00 Coffee break, discussion

11:00 - 12:30 C. Lambert ”*Ferromagnet-superconductor interfaces: transport*”

12:30 - 14:30 Lunch, poster session

Chair: P.M. Levy

14:30 - 15:30 I. Mertig ”*Ab-initio theory of GMR: Boltzmann equation approach*”

15:30 - 16:30 P. Weinberger ”*Ab-initio theory of GMR: Kubo-Greenwood approach*”

16:30 - 17:00 Coffee break, discussion

17:00 - 18:00 P. Kelly ”*Ab-initio theory of GMR: Landauer-approach*”

· Wednesday June 13th

Chair: A. Fert

09:00 - 10:30 P. Bruno ”*Theory of exchange interactions in metals and multilayers*”

10:30 - 11:00 Coffee break, discussion

11:00 - 12:30 P. Grünberg ”*Interlayer Exchange coupling across metals, semimetals and semiconductors: experiments*”

12:30 - 14:30 Lunch, poster session

Chair: P. Bruno

14:30 - 16:00 S. Blügel ”*Theory of magnetic anisotropy in metals and multilayers*”

16:00 - 16:30 Coffee break, discussion

16:30 - 18:00 R. Allenspach ”*Magnetic Surface Anisotropy: experiment*”

· Thursday June 14th

Chair: B.L. Gyorffy

09:00 - 10:00 A. Lichtenstein ”*Magnetism and correlations*”

10:00 - 11:00 H. Ebert ”*Magnetooptical effects*”

11:00 - 11:30 Coffee break, discussion

11:30 - 12:30 X.F. Jin ”*Magnetism of 3d-metals and alloys on semiconductors: experiment*”

Chair: P. Grünberg

12:30 - 14:30 Lunch, poster session

14:30 - 15:30 J. Mathon "*Theory of tunneling in magnetic multilayers*"

15:30 - 16:30 G. Schmidt "*Spin injection into semiconductors*"

16:30 - 17:00 Coffee break, discussion

17:00 - 18:00 B. Heinrich "*CIP-GMR and spin relaxation processes: experimental point of view*"

19:30 School dinner

· Friday June 15th

Chair: R. Allenspach

0 9:00 - 10:30 A. Fert "*CPP-GMR and tunneling in multilayers: experimental point of view*"

10:30 - 11:00 Coffee break, discussion

11:00 - 12:30 G. van der Laan "*Magnetic circular dichroism: theory*"

12:30 - 14:30 Lunch, poster session

Chair: J. Mathon

14:30 - 15:30 W. Hofer "*Ab-initio theory of STM*"

15:30 - 16:30 P. Varga "*Structure of ultrathin magnetic films determined by high resolution STM*"

16:30 - 17:15 V. Sechovský - Closing of the EGSCM'01

Abstracts of lectures

Introduction to electronic structure

B. Velický
Faculty of Mathematics and Physics, Charles University,
CZ-121 16 Prague 2, Czech Republic

Abstract

This lecture serves to provide an overview of the present status of the electronic structure fom a theoretical point of view. It addresses primarily graduate students working in the field of electronic properties, theoretically or experimentally.
I. Historical prospective: The present impressive state of the electronic structure studies is based on the fundamental work done in the sixties, including development of techniques with

well-known acronyms, like APW, KKR, LDA, GW, introduction of the Hubbard Hamiltonian, etc., on the theoretical side, and establishing techniques for resonance, optical and photoelectron studies on the experimental side. The tasks set for the electronic structure computation, the means available for their handling, and the amount of computational work evolved faster and faster in a parallel manner ever since, from an empirical pseudopotential for simple metal bulk crystals to, say, LSDA-KKR-CPA treatment of tunneling in magnetic alloy multilayers. The basic questions persist, however, across the years: upgrading the computational power to be up to the demands, developing mathematical means for computation, and transforming them into efficient codes, and, above all, improving the many particle treatment of the electronic structure to generate an adequate picture of the phenomena observed.

II. Basic formulation: According to the universally accepted view, a quantum treatment of many particle systems composed of nuclei and electrons with electromagnetic interactions solves, in principle, ALL problems in atomic physics, including all of the chemistry and materials science.

Several comments

- While nobody uses the full QED approach, a simple electrostatic picture is not sufficient and, typically, the one-electron part will today be treated using the Dirac equation, while some QED corrections to the Coulomb force may or may not be included.
- It is mandatory to take the nuclear movements into account. Even in the usual adiabatic approximation, equilibrated positions of the nuclei are determined by minimizing the total energy of the system and this in turn may be decisive for the electronic properties.
- Meaning of "electronic structure" is not obvious. In many particle treatment, the ground state, say, is described by the many particle wave function. This is barely practicable, but also not really needed. For example, by the electrostatic theorem, the equilibrium atomic positions are specified by the spatial electron density as a function of the atomic positions. More generally, we only need properly reduced observables; the actual task of the electronic structure theory has always been to find them *directly*, circumventing the work with the full wave function.

III. Orbital theories: Actual materials stand in between two limits, the localized correlated electrons (Valence Bond in QCh, Heisenberg Hamiltonian in magnetism), and the itinerant independent electrons (LCAO in QCh, Stoner-Slater in magnetism). In condensed matter problems, the orbital point of view prevails ($\sim$ band-like picture). Implicitly, this suggests that the electron quasiparticle states have an "adiabatic", perturbative link to independent electrons. This approach is tremendously productive. A "true" one-electron theory consists of • finding the orbitals as eigenstates of an one-electron Hamiltonian (one-electron part) • finding the occupation numbers (aufbau principle, many-electron part) • constructing the observables (e.g., spin densities, momentum distribution). The same is true for any orbital theory, but there enters a necessary fourth part, construction of the one-electron Hamiltonian. Orbital theories can be classified, according to the method used, as model (semi-empirical, parametrized) theories, and *ab initio* theories, where the Hamiltonian is self-consistent with the electronic structure. A detailed comparison of many popular methods including Hückel, Harrison parametrization, Hartree and HF, DFT, and Green functions is presented.

IV. Orbitals, observables, properties: The orbitals have two uses of a complementary nature. • They can serve to construct the one-particle observables as quantum averages. These are conveniently expressed in terms of the one-electron resolvent. Direct methods for determining the resolvent are often an efficient alternative to an explicit calculation of the orbitals themselves. • The orbitals also help in interpreting the behavior of complex systems in qualitative terms, like quasiatomic levels, bond strength, hybridization, electronegativity etc., in other words, in terms of atomic structure and bonding properties. Again, the resolvent offers a convenient way of describing resonant and bound states in a unified manner, etc.

It is shown on two examples, how the two approaches can be combined to provide general qualitative rules governing some aspects of the electronic structures: one example concerns the relation between atomic states and bands in the 3d series, the other one links LCAO for a diatomic molecule with the Anderson-Newns-Grimley model. Examples: diatomic hydrides vs. chemisorption of hydrogen, adsorption on Al 111 surface.

V. LDA and beyond: Popularity of the orbital theories in CM physics and Materials science is linked with the inception of the LDA, which is computationally simple, practically successful and deceivingly appealing. A pragmatic sketch of the Kohn-Sham equations in the LDA is presented. Then, a qualitative survey of many-electron effects in metals is given, and performance of the LDA is assessed. The aim is to show that the success of LDA is not accidental, and that this method belongs among the "comprehensive" theories (has an exact limit, obeys a variational principle and sum rules for the correlation hole, etc.).

A structured list of important improvements upon the LDA (LSDA, GGA, SIC, gap problem, image potential & dispersive forces) is given in the form of physical questions, which the LDA does not treat adequately, and the question of "good" and "less good" physical properties is addressed. In particular, the meaning of Kohn-Sham orbitals and energies is touched upon.

Two basic routes of reaching beyond the LDA are outlined: • improvements within the density functional theory, which itself is supposedly exact, and • use of other many body techniques, typically Green functions, with LDA providing a starting approximation.

The first approach is illustrated on the Self-Interaction Corrections for polar semi-conductors, where the gap and the shallow core states are corrected in a dramatic way. Then, the GW approximation is qualitatively motivated as a worthy representant of the Green function approach leaving the ground of the DFT. Reference is made to the comparisons between LDA and GW for jellium, and recent results for simple metals are discussed. Finally, the gap problem in LDA, LDA-SIC, and in GW is contrasted.

Introduction into the Density Functional Theory

Helmut Eschrig
IFW Dresden, P.O.Box 27 00 16, D-01171 Dresden, Germany

Abstract

If the ground state energy of a many-electron system in an external potential v,

$$E[v,N] = \min_{\Gamma} \left\{ H_v[\Gamma] \;\middle|\; \int d^3r n[\Gamma] = N \right\},$$

is defined as the minimum of energy expectation values $H_v[\Gamma]$ over all quantum states Γ including ensemble states distributed over particle numbers, then $E[v,N]$ is convex in N for fixed v and concave in v for fixed N. These simple convexity properties together with the equally simple gauge property

$$E[v-\mu,N] = E[v,N] - \mu N, \quad \mu \text{ constant in space}$$

suffice to establish uniquely a density functional $H[n]$ for which the Hohenberg-Kohn variational principle

$$E[v,N] = \min_{n} \left\{ H[\Gamma] + \int d^3r v n \;\middle|\; \int d^3r n = N \right\}$$

holds. This approach is of mathematical rigor without any representability problems. Of course, although $H[n]$ is well defined, its determination is equivalent to the general solution for $E[v,N]$ on grounds of many-body theory. Hence, for practical purposes, $H[n]$ can only be modelled, and density functional theory having been used so far is a model theory.

Fortunately, $H[n]$ is much more local than $E[v,N]$ so that it can effectively be modelled. The generalized Kohn-Sham approach consists of splitting the density functional into two parts:

$$H[n] = K[n] + L[n],$$

$$K[n] = \min_{\{\phi_i, n_i\}} \left\{ k[\phi_i, n_i] \,\middle|\, \sum_i \phi_i n_i \phi_i^* = n \right\},$$

$$L[n] = \int d^3 r n(\mathbf{r}) l(n(\mathbf{r}))$$

with variational Kohn-Sham orbitals ϕ_i and orbital occupation numbers n_i. Variation of the ϕ_i yields the Kohn-Sham equations with the operator part out of K and a local potential out of L, and variation of the occupation numbers yields the aufbau principle for the density.

Examples illustrating the power of the theory are presented.

Surface Magnetism

P.H. Dederichs

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

Abstract

In this lecture we will give an introduction to surface magnetism. After a short reminder to the electronic structure of nonmagnetic metallic surfaces we discuss the surfaces of the elemental ferromagnets Fe, Co and Ni, in particular the role of the coordination number and of the rehybridisation effect in enhancing the moments of the surface layer. In detail we discuss the electronic and magnetic properties of 3d monolayers on noble metal substrates, by covering, among other topics, the competition between ferro- and antiferromagnetism and the occurrence of frustration of the (111) surfaces, which can lead to noncollinear structures. We also present results for the magnetic moments of 4d and 5d monolayers. Finally we discuss the magnetic properties of single transition metal adatoms and small clusters of such adatoms, which, even in the 4d and 5d cases, can have nearly the full atomic moments.

Electronic structure of random magnetic alloys and their surfaces

I. Turek[a,b,c]
[a] *Institute of Physics of Materials AS CR, Brno, Czech Rep.*
[b] *Dept. Elect. Structures, Charles Univ. Prague, Czech Rep.*
[c] *Center for Comput. Mater. Science, TU Wien, Austria*

Abstract

The lecture reviews effects of substitutional disorder on the electronic structure and related properties of bulk alloys and their surfaces. The talk includes following topics:

1) Introduction to the random alloys: general concepts (substitutional disorder, configurational averaging), theoretical approaches (mean field theories - VCA, CPA).

2) Bulk alloys: spin-dependent disorder in binary magnetic alloys, concentration dependence of magnetization, the Invar effect in alloys.

3) Alloy surfaces and metallic interfaces: concentration dependence of magnetization at alloy surfaces, interface interdiffusion and exchange coupling.

4) The disordered local-moment state: paramagnetic state of transition metals, local moment disorder in metallic spin glasses and in diluted magnetic semiconductors.

5) Interatomic interactions in alloys: interplay of magnetism and chemical interactions, the Ising hamiltonian for binary alloys.

Structure of Multilayers seen by X-rays

David Rafaja
Department of Electronic Structures, Faculty of Mathematics and Physics, Charles University, Prague, Ke Karlovu 5, CZ-121 16 Prague, e-mail: rafaja@karlov.mff.cuni.cz

Abstract

The scattering of X-rays is nowadays employed as a standard method for investigation of the real structure of thin films and multilayer structures. In multilayers, it can yield information on thickness, electron density, morphology and atomic ordering in individual layers. The advantages of the X-ray scattering are a low and tunable penetration depth of the radiation into the "bulk" of the sample, its non-destructivity and easy preparation of samples used for the measurement.

The lecture shows advantages and limitations of X-ray scattering used to analyse the real structure of multilayers. Basic principles of the X-ray reflectivity measurements (X-ray scattering at low diffraction angles) are explained using the optical theory and the Parrat optical formalism. It is shown that much more reliable results on the real structure of multilayers can be obtain if the X-ray reflectivity measurement is combined with X-ray diffraction experiments done at higher diffraction angles. The basic principles of the later experimental technique are explained upon the classical kinematical diffraction theory.

The conclusions of the X-ray scattering theory are illustrated on several simulated X-ray reflectivity curves and diffraction patterns. Common models used to describe the real structure of magnetic multilayers are introduced. The applications of the X-ray scattering theory are illustrated on several examples of magnetic multilayers having different degree of interface quality, different morphology and atomic ordering. Besides, typical experimental set-ups are presented.

Theory of Low-Energy Electron Diffraction and Photoemission from Ultrathin Films

Jürgen Henk
Max-Planck-Institut fuer Mikrostrukturphysik, Weinberg 2, D-06120 Halle (Saale), Germany

Abstract

The confinement of electrons to a film grown on a substrate changes significantly the properties of the respective electronic states with regard to those of a semi-infinite system. These properties can for example be investigated by means of low-energy electron diffraction (LEED) or by photoelectron spectroscopy (PES). The lecture gives a comprehensive overview on theories of LEED and PES from ultrathin films. Qualitative results can be obtained for LEED within kinematical theory and for PES by tight-binding as well as interferometer models. Computations based on multiple-scattering theories provide quantitative results that can be directly compared to experimental ones.

Concerning LEED, the manifestation of quantum-well resonances in intensity minima is analyzed for Co/W(110). Confinement effects in PES comprise the weakening of the wave-vector conservation and oscillations of the intensity with film thickness and photon energy. These are investigated for Cu/Co(001) and Ag/Fe(001). The temperature dependence of spin-resolved PES from ferromagnetic Co films on Cu(001) is discussed within the disordered local moment picture.

From oligatomic films to mesoscopic magnets

J. Kirschner
Max-Planck-Institut fuer Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany

Abstract

Thin films and mesoscopic magnetic structures play an increasingly important role in magnetic storage technology, magnetic sensors, non-volatile random access memories, and „magneto-electronics“ in general. In this talk typical surface science approaches, involving adsorption, surface diffusion, epitaxial growth phenomena, and self-organisation will be exploited to produce and characterize films and mesoscopic magnetic structures. Films of a few layers thickness (oligatomic) may have strongly different magnetic properties, depending on their crystalline structure and emorphology. This will be demonstrated for Fe on Cu single crystals. Another example is spin reorientation transition due to strain in the film, which may be manipulated by gas adsorption. Magnetic wires may be made by step edge decoration on stepped single crystal surfaces by tuning surface diffusion. Likewise, magnetic dots may be created by exploiting localized adsorption on reconstructed surfaces. It will be demonstrated, how magnetic pillars with a height-to-diameter ratio of 2:1 can be grown on such a template and that these structures may overcome the "superparamagnetic barrier" in storage technology. A particular challenging task is the magnetic characterization of such structures on the nanometer scale. The use of magnetic x-ray dichroism in photoemission microscopy for element-selective imaging is demonstrated.

Magnetotransport in Multilayered Structures

Peter M. Levy
Department of Physics, New York University, 4 Washington Place, New York, NY 10012, USA

Abstract

The past decade has seen the discovery of a large decrease in the electrical resistance of metallic multilayers, and its' confirmation in magnetic tunnel junctions, when a moderate magnetic field is used to reorient the moments of the magnetic layers. This reorientation alters both the electronic structure and the scattering of the conduction electrons in these structures; these two can alter the resistance by at least a factor of two at room temperature, and even more at low temperatures. While models have been put forth to understand the "giant magnetoresistance" (GMR) observed in metallic multilayers, and the magnetoresistance of magnetic tunnel junctions (TMR), it is necessary to use *ab-initio* calculations of the electronic structure as well of the transport properties to make definitive statements as to the origins of these phenomena. I review the present status of the calculations and indicate the challenges for the future.

The metallic multilayers of interest have either a repeated motif of a magnetic and non-magnetic layer, e.g., Co/Cu, or consist of a trilayer, of two magnetic with a non-magnetic spacer, sandwiched between a substrate, buffer and capping layers. As the contact between layers is metallic the whole structure shares a common Fermi level. In the absence of scattering by defects these metallic structures do not have an indigenous electrical resistance; rather they only have a resistance that comes from their contact with reservoirs. Therefore the resistance obtained from ab-initio calculations done for ballistic transport in metallic structures comes from the boundary conditions used in the calculation rather than an intrinsic property of the multilayer. With this caveat one can nonetheless determine how the relative orientation of the moments of the magnetic layers affects the electrical resistance, i.e., the MR. In the absence of any scattering a multilayer exhibits a magnetoresistance that comes from changes in the electronic structure due to the reorientation of the magnetic layers. However, the metallic multilayers which display GMR have a fair amount of scattering coming from: the alloys used as magnetic layers, e.g., permalloy, impurities, interface roughness and diffusion, magnetic domains and grain boundaries. While the transport in these structures can hardly be characterized as ballistic, it is possible to obtain this in point contact experiments. To discuss the diffusive transport in the more conventional multilayers it is

necessary to include the effects of scattering on transport by using for example the coherent potential approximation (CPA). The principal challenge in doing ab-initio calculations of the resistance and MR of metallic magnetic multilayers lies in the modeling of the defect distribution.

In magnetic tunnel junctions electrons tunnel across an insulating barrier and it is relatively easy to drive the system out of equilibrium and sustain a bias (drop in potential) across the junction. The resistance of the junctions studied to date is overwhelmingly due to the barrier; while it is the electrodes that are responsible for the spin polarization of the current. The minor role played by the electrodes in the resistance leads one to posit an approach which considers ballistic transport across the whole junction should produce realistic estimates of the MR of these junctions. However, from experimental data we are led to focus on the local electronic structure just at the electrode/barrier interface; the remainder of the electrodes are not critical in controlling the MR of magnetic tunnel junctions. This is quite different from metallic multilayers where the MR is determined by the electronic structure and scattering throughout the structure. We will show that estimates of the resistance and MR of tunnel junctions based on ab-initio calculations which consider the transport ballistic across the barrier and diffusive in the electrodes yield higher MR ratios and lower resistances, than those in which transport is ballistic across the entire junction. While it may be possible to produce a junction in which the transport is ballistic, the overwhelming planar magnetic tunnel junctions studied to date should be analyzed by assuming the transport is diffusive in the electrodes;particularly at the electrode/barrier interface.

Research supported by the Defense Advanced Projects Research Agency, Office of Naval Research, National Science Foundation, and NATO.

Ab-initio Calculations of Giant MagnetoResistance

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

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

Abstract

Ab-initio GMR calculations will be presented based on spin density functional theory using a Greens function formalism. All transport calculations are performed solving the quasiclassical Boltzmann equation. Different levels of relaxation time approximations in comparison to the full solution will be discussed. The results are obtained for translational invariant Co/Cu-multilayers and for Co/Cu-multilayer slabs enbedded in vacuum. We consider transport in plane of the layers. It will be demonstrated that GMR is caused by intrinsic and extrinsic properties of the magnetic multilayer. Intrinsic properties which are determined by the electronic structure of the system can be modulated by spin-dependent scattering at nanostructural defects. Consequently, the GMR is enhanced, reduced or inverted.

Interlayer Exchange Coupling and its dependence on the interlayer material: experiments

P. Grünberg
FZ Jülich- IFF, Germany

Abstract

After a brief introduction describing mainly the historical development some remarks on the growth of the samples will be given. This is because it is now well established that the crystalline quality of the samples plays a crucial role in the coupling phenomena. Crystallinity can be demonstrated by means of the resulting magnetic anisotropy for samples floating on water due to surface tension.

The main part of the presentation will be on the qualitative and quantitative determination of the coupling. Antiferromagnetic (AF) type interlayer coupling for example can easily be recogized from the nature of magnetic domains and domain walls. By a similar experiment as just described for the anisotropy, AF coupling can be recognized by means of the reaction of such samples to an external field, resulting in typical rotations. Quantitative information on the coupling can be obtained by means of remagnetization experiments and from the frequencies of coupled spinwave modes. Concerning the coupled modes the similarity between modes in multilayers with antiferromagnetic coupling and antiferromagnetic resonance in natural antiferromagnets will be discussed.

The results obtained so far show that the coupling is generally multiperiodic oscillatory in the case of metallic interlayers and exponentially decaying in the case of semiconducting interlayers. For metallic interlayers the microscopic mechanism is similar to the well known RKKY interaction which can be discussed in terms of spindependent reflectivities of electron waves at the magnetic- nonmagnetic interfaces. Very large coupling strengths obtained for Ru and Rh interlayers can be understood on the basis of bandmatching. For the semiconducting interlayers the mechanism so far is not clear.

Applications of the coupling will also be discussed. They ly in the use of "artificial antiferromagnets" where the atomic planes of natural antiferromagnets are replaced by thin film structures with antiferromagnetic interlayer coupling. These can be used in sensors. Other applications are in magnetic media where such structures can reduce demagnetizing fields and thus stabilize written bits.

Theory of magnetic anisotropy in metals and multilayers

Stefan Blügel
Fachbereich Physik, Universität Osnabrück, D-49069 Osnabrück, Germany

Abstract

This lecture is divided into two parts: i) At first the phenomenological origin of the magnetic anisotropy in terms of shape and magnetocrystalline anisotropy is introduced. A phenomenological expansion of the free energy as function of the magnetic anisotropy is presented for different crystal structures. The concept of volume and surface anisotropy is introduced and examples of spin-reorientation transitions as function of temperature and film thickness are given. ii) In the second part we dwell on the microscopic origin of the magnetic anisotropy. We discuss the contribution of the dipolar energy to the shape and the magnetocrystalline anisotropy energy. Then we look in detail at the various facets of the spin-orbit interaction to the magnetocrystalline anisotropy. At the end some recent results of ab-initio calculations are presented.

Magnetooptical effects

H. Ebert, A. Perlov, and T. Huhne
Institut für Physikalische Chemie, Universität München, Butenandtstr. 5-13, D-81377 München, Germany

Abstract

In the first part an introduction to the theoretical treatment of magneto-optical properties of solids is given. This includes the derivation of the electro-magnetic wave equations in an anisotropic medium from the underlying Maxwell equations, symmetry considerations explaining the presence of a non-diagonal optical conductivity tensor in magnetic solids, the role of the spin-orbit coupling as well as the expressions used to determine the optical conductivity tensor from corresponding electronic band structure data. Some examples for calculated magneto-optical Kerr-spectra are presented in comparison with experiment emphasizing the complex relationship between optical spectra and the underlying electronic structure. Several methods used to discuss this relationship are reviewed and the new concept of the layer resolved optical conductivity is introduced. Examples of its application are shown for a number of multilayer systems that demonstrate that the optical response of these systems is astonishingly local. Finally, a fully relativistic version of the Kubo-formula for the optical conductivity tensor is introduced that allows in combination with the KKR-Green's function method to deal with arbitrary layer systems. This is demonstrated by recent results for the surface layer system Au(001)/Fe/Au.

Epitaxy and magnetism of 3d metals and alloys on semiconductors

Xiaofeng Jin
Department of Physics, Fudan Univeristy, Shanghai 200433, China

Abstract

The 3d transition metals exist in a variety of crystallographic and magnetic phases. Thin-film growth of these materials on crystalline substrates allows the forces present at the interface to drive the film into specific crystalline structures. These structures may be in a thermodynamically stable phase, a known high-pressure or high-temperature phase, or even a phase not previously observed. They greatly increase the variety of magnetic materials by essentially making “new” materials from “old” elements. In this talk, I am going to summarize our recent results on this topic, and to emphasize the strong correlation between the structure and magnetism of 3d metals and alloys, through the examples of Ni/GaAs(001), FeMn/GaAs(001) and Co/Mn/Co/GaAs(001).

Theory of tunneling in magnetic multilayers

J. Mathon
Department of Mathematics, City University, London EC1V OHB, UK

Abstract

• Motivation and experimental background for magnetic tunneling junctions.

• Classical Bardeen theory of a tunneling junction.

• Two-current model for the magnetotransport in magnetic multilayers and its application to magnetic tunneling junctions. Definition of the tunneling magnetoresistance (TMR) and its relationship to the densities of states of the magnetic electrodes - simple Julliere's model of TMR.

• Difficulties of the Bardeen's theory of tunneling when applied to magnetic tunneling junctions. Failure of the Julliere's model to predict the correct sign of the spin polarization of the tunneling current.

• Slonczewski's parabolic band model of a magnetic tunneling junction and its extension to junctions described by a realistic band structure.

• Rigorous Kubo/Landauer formalism for the tunneling current and its relationship to the classical Bardeen theory of tunneling and to the Slonczewski model.

• Green's function method for the calculation of the tunneling current.

• Application of the Kubo/Landauer formalism to a simple single-band tight-binding model of tunneling. Predictions of the simple model for the dependences of the TMR on the height and width of the tunneling barrier.

• Tunneling between two ferromagnetic electrodes across a vacuum gap as a tool for studying the relationship between tunneling and perpendicular magnetoresistance of magnetic trilayers with a nonmagnetic metallic spacer. Fundamental differences between tunneling/ballistic magnetoresistance and the magnetoresistance in the diffusive regime.

• Factors that determine the sign of the spin polarization of the tunneling current in a realistic model of tunneling.

- Application of the formalism to an epitaxial Fe/MgO/Fe tunneling junction.
- Effect of a finite bias on the tunneling magnetoresistance.
- Effect on TMR of a nonmagnetic metallic interlayer inserted between one of the ferromagnetic electrodes and the barrier. Failure of the classical Bardeen theory of tunneling in the case of a junction with a nonmagnetic interlayer. The role of spin-dependent quantum wells in a junction with a nonmagnetic metallic interlayer.

CIP-GMR and spin relaxation processes: experimental point of view.

B. Heinrich
Physics Department, Simon Fraser University, Burnaby, BC, Canada

Abstract

High quality crystalline Fe(001) ultrathin films were grown on (4x6)GaAs(001). Ferromagnetic Resonance (FMR), Brillouin Light Scattering (BLS) and Magneto Optical Kerr Effect (MOKE) were used to investigate the magnetic properties of the individual Fe layers and trilayers consisting of two ferromagnetic layers separated by a non-magnetic spacer. The magnetic properties of the Fe films have anisotropies equal to bulk, modified only by interface anisotropies. The presence of higher order angular terms ($\cos^2(\theta)\sin^2(\theta)$) in the in-plane and out of plane magnetic anisotropies will be discussed. It will be shown that they originate in the interface roughness and inhomogeneous distribution of the intrinsic uniaxial interface anisotropies. In-situ resistance measurements of Fe layers and Au/Fe bilayers were carried out to quantify the electron scattering in the GMR effect of pseudo spin valve structures. Interpretation of the thickness dependence of the conductivity was based on the semi-classical Boltzman equation incorporating first-principles local density functional calculations. Fits to data indicated Fe had a large spin asymmetry with bulk scattering times $\tau_{\downarrow} = 2.9x10^{-14}$ sec and $\tau_{\uparrow} = 2.8x10^{-15}$ sec. Despite the large atomic terraces at the Au/vacuum and Fe/GaAs interfaces the scattering at the outer interfaces was found to be nearly fully diffuse. The origin of MR in GaAs/Fe/Au/Fe/Au(001) structures is found in electron channeling in the Au spacer layer.

The intrinsic magnetic relaxations in metallic films will be discussed. It will be shown that the intrinsic damping mechanism in metals is different from those in magnetic insulators. The Gilbert damping in metals is caused by incoherent scattering of itinerant electron-hole pair excitations by phonons and magnons. The electron-hole excitations are generated by precessing magnetization, and they are either accompanied by the spin-flip or the spin remains unchanged. The spin-flip excitations can be described by the s-d exchange interaction. The non-spin flip excitation are caused by the spin orbit interaction. In magnetic multilayers the dynamic interactions between the itinerant electrons and precessing magnetization can result in non-local relaxation phenomena. Recently Berger showed that the interaction between spin waves and itinerant electrons in multilayers can lead to an interface Gilbert damping. Our Ferromagnetic Resonance (FMR) studies support the Berger prediction of increased interface damping. The FMR studies were carried out by using magnetic single and double layer films. The single layer films were grown by Molecular Beam Epitaxy (MBE) directly on GaAs(001) –4x6 reconstructed substrates and they were covered by a 20ML thick Au(001) film. In double layers, the thin Fe films were separated from a thicker Fe layer (40ML) by a 40ML thick Au(001) spacer. The FMR linewidth for the Fe films in the double layer

structures was found to be always larger than the FMR linewidth measured for the single Fe films having the same thickness. The increase in the FMR linewidth scaled inversely with the film thickness, and was found to increase linearly with increasing microwave frequency. These results are in agreement with Berger's predictions. The measurements of the non-local Gilbert damping offers a possibility to carry out quantitative studies of the relaxation torques caused by the transfer of electron angular momentum between the magnetic layers in the presence of electron-electron exchange interaction.

Ab-initio theory of STM

Werner A. Hofer
Dept. of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT

Abstract

The aim of our lecture is to give an overview of STM tunneling within the general framework of transport theory, and to present the state of the art in the numerical simulations possible today. To this end the introduction gives an overview of working codes and their theoretical background within the Keldysh formalism. It is shown that successive approximations for (i) non-interacting electrons, (ii) high separation between the surface and the tip lead to the Landauer formula and the Bardeen approach, respectively. The effects occuring in everyday measurements are analyzed in five separate case studies. It is shown that we can gain a detailed understanding of all events in the tunneling experiments by employing extensive simulations. Highlights of the lecture are: (i) the presentation of ab initio calculations of forces between tip and sample in realistic tunneling conditions; (ii) the simulation of images of atomic scale magnetism with a spin-polarized STM; and (iii) the corrugation reversal due to quenching of the surface states on a bcc iron surface.

Structure of Ultrathin magnetic films determined by high resolution STM

P.Varga
Vienna Unversity of Technology, Austria, www.iap.ac.at

Abstract

Two systems which are prototype systems for the extrapolation of novel magnetic structures and thin film magnetism have been studied by ST with atomic resolution. besides their relevance for various other films issues, these experiments aim a better understanding of the interrelation between structure and magnetism, which is of increasing importance for the design of special purpose magnetic thin films. In the present study only the crystallographic structure was determined whereas the magnetic structure was taken from literature.

The first system studies was Co on Pt(111) (1) where perpendicular magnetic anisotropy (PMA) have been reported for very thin Co layers and the change in magnetization with

increasing thickness was related to a fcc-to-hcp transition. A linear increase of the PMA as the Co coverage is increased from 0.8.to 3.7 ML was reported (2) and at a coverage between 4-6 ML in-plane and out-of-plane magnetization was found to coexist. The out-of-plane magnetization was observed to decrease to zero at about 6 ML of Co, whereas the in-plane magnetization continued to increase.

In our study we demonstrate that the first Co layer grows preferably in the Pt fcc lattice site, with a high density of defects due to the lattice mismatch. The second layer is found to exhibit a moiré structure, with Co in-plane lattice distance close to that of bulk Co. The growth of thin Co films is observed to be mostly in terms of flat layers (2D9 up to a coverage of about 3.5 ML. At higher coverage, we find that the Co grows in (3D) islands but still in fcc-like stacking. We argue that the reason for the 2D growth mode at low coverage is due to the strained interface between Co and Pt resulting in large number of kinks and corners which facilitate interlayer distribution (3).The implications by these observations on the magnetic properties of the Co/Pt(111) interface system are discussed.

The second system was Fe on Cu(100) which have been studied extensively for the last three decade owing to its apparent ability to stabilize the ferromagnetic fcc phase of Fe. In this talk will be shown that ferromagnetic Fe layers are never fcc or fct but always form nanosized domaines of strained bcc which we call nanomartensite (4). Furthermore a direct view of the very initial stage of the relaxed bcc nucleation on an atomic scale will be presented. The STM images reveal the nucleation centers as nanometer sized bcc crystals, which form free of dislocations and are therefore exposed to a very high strain. They form virtually without mass transfer under conservation of volume(5).

(1) E.Lundgren, B.Stanka, M.Shmid and P.Varga, PRB 62 (2000) 2843
(2)C.S.Shern, J.S.Tsay, H.Y.Her, Y.E.Wu and R.H.Chen, Surf.Sci. 529 (1999) L497
(3)E.Lundgren, B.Stanka, G.Leonardelli, M.Schmid and P.Varga,. PRL 82 (1999) 5068
(4) A.Biedermann, R.Tscheliessnig, M.Schmid and P.Varga, PRL accepted
(5)A.Biedermann, M. Schmid and P.Varga, PRL in print

Abstracts of posters

First-principles study of tetragonally deformed iron

M. Friak, M. Sob, V. Vitek

Abstract

A detailed theoretical study of magnetic behavior of iron along the bcc-fcc (Bain's) transformation paths at various atomic volumes, using both the local spin density approximation (LSDA) and the generalized gradient approximation (GGA), is presented. The total energies are calculated by spin-polarized full-potential linearized augmented plane wave (FLAPW) method and are displayed in contour plots as functions of tetragonal distortion c/a and volume; borderlines between various magnetic phases are shown. Calculated phase boundaries are used to predict the lattice parameters and magnetic states of iron overlayers on various (001) substrates.

Ab initio study of trigonally deformed elements with A7 structure

P. Lazar, M. Friak, D. Legut, M. Sob

Abstract

The trigonal deformation path for three elements with A7 structure (Bi, As, Sb) was simulated by ab initio electronic structure calculations using full potential linearized augmented plane wave method (FLAPW) within the generalized gradient approximation (GGA). The elastic moduli for materials studied were determined and compared with experimental data. The influence of spin-orbit coupling on elastic properties of bismuth is demonstrated.

Electronic and magnetic properties of Fe on GaAs(100) surfaces

M. Košuth, H. Ebert
Department Chemie / Physikalische Chemie, Universität München, Butenandstr. 11, D-81377 München, Germany

Abstract

The electronic and magnetic properties of ferromagnet-semiconductor heterostructure multilayer systems have been studied by means of scalar-relativistic KKR-CPA band structure calculations. Concerning the resulting magnetisation profiles of Fe/(GaAs) and other related systems the most important features are that no magnetically dead layers occurred and an appreciable induced magnetisation was found in the semiconductor subsystem. By investigation of the hyperfine interaction more detailed information on the electronic structure could be obtained.

Treatment of actinide $6p$ states on $p_{1/2}$ local orbital extended scalar-relativistic basis

J. Kuneš[1], P. Novák[1], R. Schmid[2], P. Blaha[3] and K. Schwarz[3]
[1]*Institute of Physics, Academy of Sciences, Cukrovarnická 10, CZ-162 53 Prague, Czech Republic*
[2]*Institut für Theoretische Physik, Johann Wolfgang Goethe-Universität Robert-Mayer-Str. 8, D-60054 Frankfurt am Main, Germany*
[3]*Institute of Physical and Theoretical Chemistry, TU Vienna, Getreidemarkt 9, A-1060 Vienna, Austria*

Abstract

Description of the relativistic effects in $6p$ states of actinides on the scalar-relativistic (SR) basis, which is used in many ab-initio codes, is known to be inadequate. As a consequence some physical quantities turn out to be rather sensitive to the computational parameters. We present a method, which eliminates this 'unpleasant' feature while keeping the 'nice' properties of the SR basis. In particular local orbitals with the $6p_{1/2}$ radial function are used to extend the SR basis in the second-variational-step. The method is applied to fcc-Th and US and the results compared to those obtained with the conventional SR basis.

Electronic and Magnetic Properties of Fe Adatoms and Small Clusters on Ag(100) Surface

Bence Lazarovits, László Szunyogh, Peter Weinberger
Center for Materials Science, TU Vienna

Abstract

The *embedded cluster method* as based on the fully relativistic spin-polarized Screened Korringa-Kohn-Rostoker method is used to calculate the electronic and magnetic properties of magnetic nanostructures embedded in a two-dimensional translation invariant host. A careful analysis with respect to the self-consistently treated portion of the host is presented. The calculations show strongly enhanced spin and orbital moments of an Fe adatom and in small clusters of Fe on a Ag(001) surface. In particular, the interaction energy between two Fe adatoms is self-consistently calculated and an unusual, non-oscillating behavior as a function of their distance is observed.

The APW+lo method and application to periodic arrays of sodalite supported F-centers

Georg K. H. Madsen, Peter Blaha, Karlheinz Schwarz
TU Wien, Inst.f.Physical and Theoretical Chemistry A-1060 Vienna, Austria

Abstract

The newly implemented APW+lo method[1] is presented. The present APW basis set consists of energy-independent augmented plane-wave functions in contrast to Slater's APW. As opposed to the LAPW basis set the radial part of the APW basis functions does not contain an energy derivative term. This means that the APW's are less constrained and thus basis set convergence is reached faster (i.e. with fewer plane waves) than with the LAPW basis. The energy dependence is provided by adding local orbitals (lo), which are constructed by a radial function at the same energy as the APW plus its energy derivative. Furthermore additional LO's can be included at different energies to improve the description of semi-core states. The APW + lo method will be a part of the WIEN2k code[2] and has

been implemented in a flexible manner that allows different orbitals on the same atom to be treated with different types of basis functions.

The Alkali-Electro-Sodalites are a unique group of materials where the sodalite lattice supports a BBC array of anti-ferromagnetically coupled A_4^{3+} clusters.[3] APW+lo calculations reproduce the anti-ferromagnetic ground state and show that the magnitism is caused by non-atom centered electrons. Calculations of forces in that very large saving in computing time can be achieved when applying the APW+lo basis set to such open systems. This opens the possibility of predicting the equation of state and the critical pressure for metallization of these unique materials.

References

[1] E. Sjöstedt, L. Nordström, and D. J. Singh, Solid state comm. **114**, 15 (2000).

[2] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2k, A Full Potential Linearized Augmented Plane Wave Package for Calculating Crystal Properties.*, Tech. Universität Wien, Austria, 1999.

[3] V. I. Srdanov, G. D. Stucky, E. Lippmaa, and G. Engelhardt, Phys. Rev. Lett. **80**, 2449 (1998).

Magnon spectra of bulk and layered materials by means of fully relativistic KKR method

Krisztián Palotás, László Udvardi

Department of Theoretical Physics, TU Budapest

Abstract

The magnon spectra can be calculated in two ways within the LSD approximation: we can determine the transverse dynamic spin susceptibility using linear response theory, or the parameters appearing in the Heisenberg Hamiltonian.

In our treatment we found the spin–wave solutions of the Landau–Lifshitz equation by expanding the free energy up to second order. The Force Theorem was applied in order to find the free energy of the system and analytical expressions were derived for the second derivatives of the band energy in the framework of the fully relativistic KKR method.

The magnon spectrum was determined for bulk bcc Fe and a monolayer of Fe on Cu(001) surface.

Calculations of magnetic moments and hyperfine fields on gamma-Fe/Cu(001) monolayers by first principles method

J.A. Gomez and D. Guenzburger

Abstract

Abstract available in PDF at http://195.113.32.128/EGSCM/abstracts/gomez.pdf

---

Intermixing at interfaces of Fe/W multilayers

Y.Chushkin, E.Majkova, S.Luby, M.Jergel, A.Anopchenko, R.Senderak
Institute of Physics SAS, 842 28 Bratislava, Slovak Republic

Abstract

The interface reactions in (1nmFe/xnmW) and (2nmFe/xnmW) multilayers (x=1,2,4,5 and 7) with 5 or 10 periods in as deposited state and under KrF laser irradiation with fluencies F=0.05-0.25 Jcm^{-2} and 1 or 10 pulses were studied by X-ray scattering techniques and TEM. Structurally coherent layers along the [110] direction with bcc symmetry were found. This coherency is affected by the lateral waviness of the interfaces. The layered structure persists up to F=0.25 Jcm^{-2} and 10 pulses. Under the laser treatment both the interface roughness and mixing increase with increasing deposited energy and promoted bcc W grain growth is observed.

Density Functional Theory calculations for the UFe$_5$Al$_7$ compound

C. Cardoso[1], L. M. Sandratskii[2], T. Gasche[1,3], M. Godinho[1]
[1]*Departamento de Física, Faculdade de Ciências, Universidade de Lisboa, Portugal*
[2]*Institut für Festkörperphysic, Technische Hochsule, 64289 Darmstadt, Germany*
[3] *Laboratório de Física, Academia Militar, Amadora, Portugal*

Abstract

The magnetic structure of the UFe$_x$Al$_{12-x}$ compounds changes drastically with composition [1]. Thus, UFe4Al8 possesses a noncollinear magnetic structure with two almost orthogonal magnetic sublattices. An earlier theoretical study of UFe$_4$Al$_8$ [2] explained the origin of the unusual magnetism of this compound. We extend the theoretical study to the UFe$_5$Al$_7$ compound whose magnetic structure is cardinally different from the structure of 1-4-8. We present the results of the symmetry analysis that predicts a noncollinear configuration of the Fe moments. First-principles fully-relativistic calculations performed with the ASW method reproduce a drastic increase of the magnetization per formula unit in the transition from 1-4-8 to 1-5-7. The physical reasons for this transition and the role of the orbital polarization correction are discussed.

References

[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

Determination of the atomic configuration of Er-O complex in silicon by FLAPW method

M. Hashimoto, A. Yanase, H. Harima and H. Katayama-Yoshida
The Institute of Scientific and Industrial Research, Osaka Univ. Osaka, Japan

Abstract

Erbium (Er) doped semiconductors have strong interests because of their sharp and temperature stable luminescence of intra-$4f$ transition. Er impurities form complexes with oxygen atoms, which improves the low-solubility of Er in silicon. We studied the atomic configuration of Er-O complexes using the Full-potential linearized augmented plane wave method based on LDA. As a result, we proposed the existence of two different structures of Er-O6 complexes centers, one is stable and the other is meta-stable. Our proposed atomic configurations of Er-O6 complex can reasonably explain the result of EPR measurement, which reported the existence of several low-symmetry centers and similarity to the C_2 center of Er_2O_3.

Numerical simulation of magnetic multilayers

E. Kov'acs, F. Kusmartsev, R. T. Giles

Abstract

We study the dynamics of magnetic multilayers (MM) consisting of coupled magnetic layers. We have taken into account the linear and cubic force following to GinzburgLandau expansion. By solving the system of these non linear equations numerically we follow the development of the MM in time, and compute the Fourier spectra. A behavoiur of the potential domain wall has been studied in de tails, and highly different, sometimes chaotic regimes were observed in the case of slightly different initial conditions.

Spin-orbit coupling and higher-energy phases in W and Pb.

Dominik Legut

Abstract

Using full potential linearised augmented plane wave method we have performed total energy calculations for displacive transformation path in W and Pb. Each of these metals has a different ground-state structure, W has the body-centered cubic, Pb has the face-centered cubic structure, therefore their behavior along the trigonal deformation path vary. We have also studied the influence of spin-orbit coupling in these two materials, and in case of lead we have found significant effect on the curvature of total energy along the trigonal deformation path. Total energy calculations show that all higher-energy cubic structures studied are locally unstable with respect to trigonal deformations. Also the elastic constants of total energy were calculated, with or without the spin-orbit coupling, and compared with existing experimental data.

The optical, magnetooptical and magnetic properties of Fe/GaAs films: manifestation of interlayer exchange coupling

I.D.Lobov*, V.M.Maevskii*, L.V.Nomerovannaya*, M.M.Kirillova*, A.A.Makhnev* and F.A.Pudonin**
**Institute of Metal Physics, 18 Kovalevskaya St., 620219 Ekaterinburg, Russia*
***P.N.Lebedev Physical Institute, 53 Leninsky Prospectus, 117924 Moscow, Russia*

Abstract

Optical, magnetooptical and magnetic properties of layered Fe/GaAs system with a variable semiconducting spacer thickness t are investigated ($t_{\mathrm{GaAs}} = 6.4$–26.6 A). Three- and five-layer samples were prepared by magnetron sputtering on Si(100) substrates. The analysis of the obtained data allows us to make a conclusion about existence in Fe/GaAs structure of interlayer exchange coupling of AF type at $t_{\mathrm{GaAs}} \sim 20$ A. It is found, that the oscillation behaviour of equatorial Kerr effect is caused by change of the optical characteristics of Fe/GaAs films with growing of a semiconducting spacer thickness.

Uranium films prepared by dc sputtering

M.A. Rosa, A.P. Gonçalves, E. Alves, M.R. da Silva, M. Diego, O. Conde, M. Godinho,
M. Almeida

Abstract

Low-dimensionality systems containing uranium has been so far almost unexplored. With the aim of expanding the studies on this type of materials, thin films of uranium were prepared by dc magnetron sputtering. The depositions were performed onto silicon, glass and tungsten substrates between room temperature and $\sim 300^oC$. The structural characterization of the samples was done by RBS and GIXRD. For the microstructure analysis a SEM was used. Results show that there is a clear influence of the substrate and temperature on the the crystallographic structure of the films.

Magnetic behavior of $Mn_xZn_{1-x}F_2$ at strong fields

Andrés Rosales Rivera[1], José Marcilio C. Ferreira[2], Frederico C. Montenegro[2] and
Carlos A. Ramos[3]
[1]*Laboratorio de Magnetismo, Universidad Nacional de Colombia, A.A. 127, Manizales, Colombia*
2Departamento de Física, Universidade Federal de Pernambuco C.P. 50.670.901, Recife PE, Brasil
[3]*Centro Atómico Bariloche, 8400 S.C. de Bariloche, Río Negro, Argentina*

Abstract

The site-diluted antiferromagnet $Mn_xZn_{1-x}F_2$ in a uniform field has been largely studied as an experimental realization of the d = 3 random-field Ising model (RFIM). In this article we review recent DC magnetization and AC susceptibility studies, which yields the evolution of magnetic phase boundaries in the $Mn_xZn_{1-x}F_2$compound, at moderate magnetic dilution (0.30 ¡ x ¡ 0.50). At low DC fields (H), our results support a critical phase boundary, separating an ordered antiferromagnetic (AF) phase from the paramagnetic (P) one. For moderate fields, the AF ordering coexists with a spin-flop (SF) clustering. For strong H, a spin-flop phase dominates the upper part of the (H,T) phase diagram. We study the similarities and differences with recently reported results [1,2] for the isostructural, but more anisotropic compound $Fe_xZn_{1-x}F_2$, in the strong field regime.

[1] A. Rosales-Rivera, J. M. Ferreira, and F. C. Montenegro, Europhys. Lett. 50 (2000) 264.
[2] F.C. Montenegro, K. A. Lima, M. S. Torikachvili, and A. H. Lacerda, Sci. Forum 302-303 (1999) 371.

This work was supported by CNPq (Brazilian agency) and COLCIENCIAS (Colombia agency).

Electronic structure and ferromagnetism in ZnO-, ZnS-, ZnSe-, ZnTe-, GaAs- and GaN-based diluted magnetic Semiconductors

K. Sato

Abstract

The electronic structure and magnetism of 3d transition-metal-atom-doped ZnO-, ZnS-, ZnSe-, ZnTe-, GaAs- and GaN-based DMSs were investigated. The electronic structure calculations were performed using the KKR-CPA-LDA. The stability of the ferromagnetic state compared to that of the spin-glass state was systematically investigated as a function of carrier concentration. It is found that the magnetic states of DMSs shows a systematic behavior as a function of valence electron number and carrier concentration. Analyzing the calculated density of states, the origin of the ferromagnetism is discussed.

Substitutions in Finemet

Anna Zorkovska

Abstract

The outstanding magnetic properties of the nowadays so popular nanocrystalline soft magnetic materials follow from their typical structure. There are two important aspects of this relationship: i) the conversion of the structural elements from micro- to nanoscale that brings about a ***substantial enhancement of the surface-to-volume ratio***, and ii) the ***coincidence of the grain size scale with the typical magnetic length such as the exchange correlation length***, which allows ferromagnetic coupling between the grains.

My thesis represents a part of research project oriented on the study of physical properties of amorphous and nanocrystalline rapidly quenched ferromagnetic materials and focuses on the nanocrystalline soft magnetic alloy called Finemet ($Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$), invented by Yoshizawa, Oguma and Yamauchi in 1988. The tuning of magnetic properties of Finemet is usually achieved by i) modification of the processing conditions and ii) replacing some components by more or less similar elements. To modify the magnetic properties of Finemet by the latter approach, through affecting the microstructure, the crystallization process, and the alloy chemistry, to study the influence of substitutions on the magnetic properties of the crystalline grains and of the interconnecting matrix, are ***the main goals of my work***.

The influence of following elements was studied:
three rare earth elements, Gd, Pr and Nd replacing the Nb and partially the Fe. Since the rare-earth atoms have a considerable magnetic moment, we expected the modification of the magnetic properties because of the RE-Fe exchange interaction contribution.

Al replacing Fe. The reported positive influence of Al addition on the coercivity was the primary motivation for this substitution with the aim to obtain picture about the role of Al in the alloy.

Characterisation and oxidation of thin Co films with a Atomic Force Microscope

H. Loosvelt, G. Rens, K. Temst , C. Van Haesendonck and Y. Bruynseraede
Laboratory of Solid State Physics and Magnetism, K.U.Leuven, Celestijnenlaan 200 D, B3001 Heverlee, Belgium

Abstract

Thin Cofilms on amorphous SiO_2 substrates were prepared in a Riber MBE facility. The films were characterized by means of XRD and AFM measurements. The low angle XRD measurements confirm a thickness of 150 Åof the Cofilm; the high angle measurements show a textured film with a FCC cristal structure with a lattice constant a of 0.35447 nm. Detailed AFM measurements were carried out in order to investigate the selfaffine character of the Cofilm surface. The root mean square roughness s of the surface varies with length scale L. This is described by the scaling law $\sigma \propto L^H$ in which H is the scaling exponent. The scaling exponent was determined from the AFM data: H = 0.23 ± 0.03. We examined if it was possible to oxidize the Cofilm locally with the AFMtip by applying a voltage between the AFMtip and the sample [1]. This is important in order to use this oxidation as a lithographic technique. We succeeded in the local oxidation of the Cofilm and examined the influence of process parameters as scan speed and applied voltage on the height of the formed Cooxide. The typical scan speed that is used in an M5 AFM system is in the order of 1 Hz; typical applied voltage is 10 V. Further research is required to optimize these and other parameters (e.g. humidity) in order to 'write' oxidestructures on the Cofilm in a reproducible way.

[1] Vullers RJM, Ahlskog M, Cannaerts M, et al., Field induced local oxidation of Ti and Ti/Au structures by an atomic force microscope with diamond coated tips, J VAC SCI TECHNOL B 17: (6) 24172422 NOVDEC 1999

Acknowledgements
This work has been supported by the Fund for Scientific Research Flanders (FWO), the Belgian IUAP and Flemish GOA Programs. K Temst is a postdoctoral research fellow of the FWO.

Structural and magnetic properties of EuSPbS semiconductor multilayers.

Valentine V. Volobuev

Abstract

The EuSPbS semiconductor multilayers have been prepared in high vacuum by thermal evaporation of PbS and electronbeam evaporation of EuS. Their structure was investigated by TEM and XRD technique. The magnetic properties of the multilayers of ferromagnetic EuS intercalated with diamagnetic PbS were studied as function of EuS and PbS layer thickness. The critical temperature of the paramagnetferromagnet phase transition was determined from magnetization vs temperature measurements and was found to depend on

the underlying substrate (KCl (100) vs. BaF_2 (111) as well as the thickness of EuS layer). Antiferromagnetic coupling between feromagnetic layers was observed by neutron scattering for spacer PbS thickness from 4 to 90 Å. For thicker PbS layers (> 100 Å) ferromagnetic coupling was observed.

Interplay between superconductivity and magnetism in GdLa superlattices

Pascale Deen[1], J.P.Goff[1], R.C.C.Ward[2], M.R.Ward[2] ,S.Langridge[3] ,R.Dalgliesh [3],
S.Foster[3] , S.Gordeev[4]
[1]*Department of Physics, Oliver Lodge Laboratory, University of Liverpool,Liverpool,U.K*
[2]*Department of Physics, University of Oxford, Clarendon Laboratory, Oxford,UK.*
[3]*The ISIS Facility, Rutherford Appleton Laboratory, Didcot,UK.*
[4]*Department of Physics, Southampton University, Southampton,UK.*

Abstract

A $[Gd_{30}La_{10}]_60$ superlattice has been studied using SQUID magnetometry and Polarised Neutron Reflectivity. Zerofield cooling results in the coexistence of an antiferromagnetic alignment of the ferromagnetic Gd blocks and 3D superconductivity at low temperature. Field cooling from room temperature results in ferromagnetic coupling between the Gd blocks, and under these conditions the superconducting transition in the La is suppressed. The results will be discussed.

Structural Studies of Co/Cu (001) Multilayers

Victor Manuel Garcia Suarez, Jaime Ferrer.
Facultad de Ciencias. Universidad de Oviedo. Spain

Abstract

Using the molecular dynamics capabilities of the SIESTA code (Spanish Initiative for Electronic Simulations with Thousands of Atoms) we calculate the equilibrium configuration of a multilayer made of 6 atomic consecutive layers of Cu fcc and, subsequently, 6 atomic layers od Co fcc in the (001) direction. We study the equilibrium lattice constant of the unit cell of the multilayer and the distances among individual layers. We take into account cell pressures and energies and we conclude calculations when atomic forces are small enough.

Non-local Gilbert damping in the magnetic multilayers and two magnon scattering in ultrathin films

R. Urban, G. Woltersdorf, and B. Heinrich

Abstract

The recent FMR results will be presented. Two series of samples covered by Au were prepared to study resonance linewidth of a single Fe layer directly on GaAs(001) and its broadening in the presence of the second thick Fe film separated by gold spacer layer due to interaction between conducting electrons and spin-waves [L. Berger]. Increase in the linewidth is inversely proportional to the thickness of the Fe layer thickness as it was predicted by the theory. Two magnon scattering was studied using the Fe films covered by Cr in both in- and out-of-plane FMR measurement. In this experiment it was found that resonance linewidth becomes narrower in perpendicular configuration because two magnon scattering does not contribute to the relaxation [R. Arias, D. Mills].

First principles calculations of tunneling magnetoresistance

M. Zwierzycki[1,2] , K. Xia[2] , P.J. Kelly[2] , G. E. W. Bauer[1] , I. Turek[3]
[1] *Delft University of Technology, The Netherlands*
[2] *University of Twente, The Netherlands*
[3] *Academy of Sciences of the Czech Republic, Brno*

Abstract

Using a recently developed method for calculating transmission matrices from first principles, we study tunneling magnetoresistance focusing our attention on the influence of disorder on the conductance. The formalism based on the tightbinding linearmuffintin orbital surface Green's function method allows us to treat large lateral superlattices so that we can treat both specular and diffuse scattering on an equal footing. The systems under consideration are Fe—Vacuum—Fe and Fe—MgO—Fe tunnel junctions.

Effects of Interface States on Tunnelling Magnetoresistance

O. Wunnicke[1], N. Papanikolaou[1], R. Zeller[1], P.H. Dederichs[1], V. Drchal[2] and J. Kudrnovský[2]
[1]*Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany*
[2]*Institute of Physics, Academy of Sciences of the Czech Republic, CZ-18040 Praha 8, Czech Republic*

Abstract

We present a simple model and *ab-initio* Co|Vac|Co calculations to discuss the effects of resonant interface states on the tunnelling conductance. The model consists of two semiinfinite crystals separated by a constant potential barrier. It shows that the interface states form bonding and antibonding hybrids in the barrier. If the resonance condition is met, the electron tunnels through the barrier without attenuation. This leads to sharp peaks in the $\vec{q}_{||}$-resolved conductance. The model explains, why the interface resonances can dominate the conductance, although they occur only in a tiny fraction of the surface Brillouin zone.

Theory of the anomalous Hall effect

A. Crépieux, J. Wunderlich, V. Dugaev and P. Bruno

Abstract

The abstract is available in PDF at http://195.113.32.128/EGSCM/abstracts/crepieux.pdf.

Microscopic quantum theory of proximity effect in ferromagnet/superconductor/ferromagnet trilayers

A. Bagrets[1,3] , D. Bagrets[2,3] , C. Lacroix[1] , N. Ryzhanova[1,3] and A. Vedyayev[2,3]
[1] *Laboratoire Louis Néel, CNRS, BP 166, 38042 Grenoble, France*
[2] *CEA/Grenoble, DRFMC, SP2M/NM, 38054 Grenoble, France*
[3] *Department of Physics, Moscow State University, 119899 Moscow, Russia*

Abstract

We propose the consequent microscopic theory of proximity effect for the F/S/F trilayer structure [where S is low-T_c superconductor (Nb) and F is $3d$ ferromagnetic metal (Fe)] based on the direct analytical solution of Gorkov equations for the normal and anomalous Green functions, and on the self-consistent solution of the integral equation for the z-dependent order parameter in superconductor. It is assumed that the main mechanism of electron scattering in F-layer is $s-d$ one, in contrast to superconductor, where electron scattering is of the $s-s$ type. We found that, due to the presence of exchange field in ferromagnet, the Cooper pair wave function shows dumping oscillatory decay in the F-layer,and $T_c(d_F)$ dependence [here d_F is the width of F-layers] has also dumping oscillatory behavior. These results are in agreement with some experimental observations and with existing quasiclassical theory of proximity effect in $[\text{S/F}]_n$ multilayers based on Usadel equations. In contrast to quasiclassical approach, the consequent analysis shows that the effective length of damping of Cooper pair wave function oscillations is $\sim (1/l_\uparrow + 1/l_\downarrow)^{-1}$ [where $l_\uparrow$, $l_\downarrow$ are mean free

paths for spi-nup and spin-down electrons in ferromagnet], and the half of the period of oscillations is defined by the effective length $\xi_m^0 = \pi v_F/\varepsilon_{ex}$ [where v_F is Fermi velocity and ε_{ex} is exchange energy], meanwhile for simple solution of Usadel equations the effective lengths of damping and oscillations are the same and defined by the length $\xi_m = \sqrt{l v_F/\varepsilon_{ex}}$ [here l is the averaged electron mean free path in ferromagnet].

Magnetoresistance of epitaxially grown (110) multilayer films of $DyFe_2$ and YFe_2

J-M. L. Beaujour[1], S. Gordeev[1], G. J. Bowden[1], P. A. J. de Groot[1], B. D. Rainford[1], R. C. C. Ward[2], M. R. Wells[2] and A.G. M. Jansen[3]
[1]*Department of Physics and Astronomy, University of Southampton, S017 1BJ, UK*
[2]*Clarendon Laboratory, Oxford University OX1 3PU, UK*
[3]*Grenoble High Magnetic Field Laboratory, 38042 Grenoble, France*

Abstract

Magnetoresistance measurements have been performed on a (110) epitaxially grown 4000-Å $DyFe_2$ film, and two multilayer films [150-Å $DyFe_2$/150-Å YFe_2]×40 and [45-Å $DyFe_2$/55-Å YFe_2]×40, in applied fields of up to 23 T and temperatures from 10-300 K. The current in plane (CIP) method was used for current directions both perpendicular and parallel to the applied field. The results for the $DyFe_2$ film show a sharp maximum (minimum) in the perpendicular (parallel) resistivities, respectively, at the coercive field (B_c). In the multilayer samples, there is an additional contribution to the magnetoresistance from magnetic exchange springs set up in the magnetically soft YFe_2 layers. For both geometries, this contribution increases with magnetic field and is reversible above B_c. The magnetoresistance associated with the magnetic exchange springs was found to be of the order of a few percent.

Magnetic and transport properties of nanocomposite materials.

Oleksandr Chayka

Abstract

We studied magnetic and transport properties of the Fe-Ta-O and Fe-Hf-O films prepared by RF plasma jet technique. X-ray analysis and TEM observations revealed that the materials were composed of Fe-based metallic grains with nm size embedded in an insulating amorphous matrix consisting of Ta or Hf oxides mainly. Temperature dependence of resistance changes from metallic to tunneling type depending on material composition. Magnetoresistance (MR) up to 2.5% at 77.3K was observed in Fe-Hf-O film accompanying large resistivity of the order $10^5 \mu\Omega m$. MR can be explained by spin-dependent tunneling between the metal grains.

Perpendicular transport in Fe/InP/Fe heterostructures

H. C. Herper[1] , P. Weinberger[1] , L. Szunyogh[1] and C. Sommers[2]
[1]*Center for Computational Materials Science TU-Vienna, Gumperndorferstr. 1a, A-1060 Vienna, Austria*
[2]*Laboratoire de Physique des Solides, Universite de Paris-Sud, 91405 Orsay, France*

Abstract

The perpendicular electrical transport in Fe/InP/Fe heterostructures with different terminations is studied together with the electronic structure and the magnetic properties. The investigations are performed within the relativistic spin-polarized version of the screened Korringa-Kohn-Rostoker method and the Kubo-Greenwood formula. It is found that the sheet resistance becomes a constant with increasing spacer thickness. The absolute value of the constant depends on the magnetic orientation in the two leads. Furthermore, we can conclude that the termination of the spacer is mainly responsible for the magnetic structure at the interface and what is more important it causes a different magnetoesistance.

Magnetic and electronic structure of Fe/Cr superlattices with various Cr and Fe layer thicknesses

V.V.Ustinov, M.M.Kirillova, I.D.Lobov, L.N.Romashev, V.M.Maevskii, M.A.Milyaev, and O.N.Kiseleva
Institute of Metal Physics, Russian Academy of Sciences, Ekaterinburg, 620219, Russia

Abstract

The giant magnetoresistance, magnetic, optical, and magnetooptical properties of the MBE grown Fe/Cr superlattice series with various Fe and Cr layer thicknesses are studied. The angles θ_0 characterizing the noncollinear magnetic ordering in superlattices are defined and compared with theory. The nonmonotonic dependences on Fe and Cr layer thickness of properties investigated are discussed.

Appearance of inverse giant magnetorresistance in non-collinear magnetic systems

S. Di Napoli[1] , J. Milano[1,2] , A.M. LLois[1,2], H. Dreyssé[3].
[1]*Departamento de Física, UBA. Pab. I, Ciudad Universitaria - (1429) Buenos Aires, Argentina*
[2]*Lab. TANDAR, CAC, CNEA. Av. Gral. Paz 1499 - (1650) Partido de Gral. San Martín, Argentina*
[3]*Inst. de Phys. et de Chimie des Matériaux de Strasbourg, 23, rue du Loess, 67037 Strasbourg Cedex, France*

Abstract

Giant magnetoresistance (GMR) has been observed in a large variety of systems during the last decade. The most frequently observed type of GMR is the so called direct one (DGMR), that is, diminishing resistance in the presence of an applied magnetic field with respect to the situation in the absence of field . Less usual is the observation of inverse giant magnetoresistance (IGMR), increasing resistance in the presence of an applied magnetic field. We show on hand of a simple d-band hamiltonian that non-collinear magnetic configurations can contribute to large IGMR ratios. We make a systematic study as a function of band filling, magnetic moment and canting angle for some simple model examples.

Sensitivity of conductance oscillations in mesoscopic Andreev interferometers to the introduction of Ferromagnetism and spin orbit coupling

C.Newman and C.J.Lambert
School of Physics and Chemistry, Lancaster University, Lancaster LA1 4YB, UK

Abstract

A study of the sensitivity of the electrical conductance to the phase of the superconducting order parameters in mesoscopic Andreev interferometers is presented. Results are shown for the following ballistic systems in the zero temperature, zero bias limit: (1) A normal non-magnetic Andreev interferometer, (2) A mono-domanined ferromagnetic Andreev interferometer, and (3) a Normal Andreev interferometer in the presence of Spin orbit coupling. The 2-probe conductance is calculted within the multiple-scattering approach using an efiecient recursive Green's function technique to solve the Bogoliubov - de Gennes equation based on the tight binding model. It is shown that the well known oscillations in amplitude of conductance of the normal system are suppressed by the introduction of a magnetic exchange field and are killed when the magnetic length of the system is of order or less than the separation between the two superconducting islands. In a similar manner the introduction of Spin orbit coupling kills the oscillations when the spin mixing length is of order or less than the system width.

Influence of substrate temperature upon dislocation density in $YBa_2Cu_3O_{7-\delta}$ films

J. S. Park[1], V. G. Prokhorov[2], C. O. Kim[1],and Y. P. Lee[1]
[1]*Hanyang University, Seoul, Korea*
[2]*Institute of Metal Physics, Kiev, Ukraine*

Abstract

The substrate-temperature dependence of dislocations in the high-Tc superconducting $YBa_2Cu_3O_{7-\delta}$(YBCO) film has been examined by a qualitative analysis of the spatial distribution patterns of a high-intensity x-ray diffraction peak in the azimuthal plane near the (005) reciprocal lattice point. An increase in the substrate temperature from 720 ° up to 760 ° leads to an enhancement in the superconducting transition temperature Tc of the films deposited by the conventional laser ablation due to a crystallization. A further increase of the substrate temperature to 780 ° causes a decrease in Tc because of impurity phases. As the substrate temperature increases up to 780 ° for the laser ablation with improved characteristics of plasma plume, the dislocation content in the YBCO film is decreased. Therefore, a highly-textured YBCO film could be produced with the minimum surface resistance R_s and a high Q-factor at a substrate temperature of 780 ° by using this preparation method.

Magnetic after effect in manganite films.

M. Sirena[1], L. B. Steren[2], J. Guimpel[2]

Centro Atómico Bariloche and Insituto Balseiro. 8400 San Carlos de Bariloche - Río Negro - República Argentina

Abstract

We have investigated the time dependence of the magnetic and transport properties on magnetoresistant $La_{0.6}Sr_{0.4}MnO_3$ films and bulk samples. An important magnetic after-effect has been observed through magnetization and resistivity measurements in all the samples. The magnetization and resisitivity measured at low temperatures follows an "logarithmic-like" behavior. At higher temperatures, the magnetization decays essentially as an exponential function in the whole time scale while the logarithmic contribution is negligible. As function of the applied filed the viscosity presents a peak around the coercive field. When the film thickness is decreased the magnetic relaxation becomes more important and the magnetic viscosity increases.

Au_nCo_m clusters deposited on atomically flat silver films: a scanning tunneling microscopy study

N. Vandamme, S. Savinov, E. Janssens, S. Neukermans, P. Lievens, R.E. Silverans, and C. Van Haesendonck

Laboratorium voor Vaste-Stoffysica en Magnetisme, K.U.Leuven, 3001 Leuven (Belgium)

Abstract

Epitaxial Ag(111) films with different thickness (100, 130 and 200 nm) were deposited by molecular beam epitaxy on mica substrates held at 240 °C. The morphology of the Ag films was examined by atomic force microscopy (AFM) on micrometer scale, and by scanning tunnelling microscopy (STM) on nanometer scale.

On the atomically flat Ag surfaces $\mathrm{Au}_n\mathrm{Co}_m$ clusters were deposited at low energy. $\mathrm{Au}_n\mathrm{Co}_m$ cluster beams are produced with a laser vaporization source in a helium atmosphere. STM analysis of the deposited clusters yields information on the cluster shape and stability upon impact, as well as on cluster coagulation. We also studied the influence of the scanning STM tip on the cluster stability.

The influence of magnetic domain walls on the resistance of mesoscopic Co structures

Sofie Veldeman, Dieter Buntinx, Alexander Volodin, and Chris Van Haesendonck
Laboratorium voor VasteStoffysica en Magnetisme, K.U. Leuven, Celestijnenlaan 200 D, B3001 Leuven, Belgium

Abstract

We investigated the influence of the magnetic domain formation on the electrical resistance of mesoscopic ferromagnetic structures. Polycrystalline Co films (thickness 35 nm) are patterned by combining electron beam lithography and liftoff techniques. The magnetic properties are determined by magnetic force microscopy (MFM) and electrical resistance measurements in the presence of an inplane magnetic field. The magnetic domain configuration is also inferred from micromagnetic simulations. The simulations allow to properly interprete the MFM images. This has been checked for Co squares having a size of 1 x 1 $\mu\mathrm{m}^2$ and 2 x 2 $\mu\mathrm{m}^2$. Both the MFM measurements and the simulations reveal the presence of a closed domain structure at low magnetic fields. We measured in detail the magnetic properties of Wheatstone bridges where the four arms of the bridges consist of Co zigzag wires with segments having a width of 2 μm and a length of 6 μm. The Wheatstone bridges turn out to be very sensitive magnetic field sensors. The magnetoresistance strongly depends on both the direction and the amplitude of the applied magnetic field. Comparing the results of the magnetoresistance measurements to the magnetic domain structure, we conclude that there exists a close correlation between the specific domain structure and the magnetoresistance. Moreover, the mesoscopic dimensions of the bridges result in sample specific fluctuations of the magnetoresistance. Acknowledgements. This work has been supported by the Fund for Scientific Research Flanders (FWO) as well as by the Flemish Concerted Action (GOA) and the Belgian InterUniversity Attraction Poles (IUAP) research programs.

The Interdiffusion Lengths within Aluminium Bilayers

J.D.R. Buchanan[1], T.P.A.Hase[1], B.K.Tanner[1], W.F. Egelhoff, Jr.[2]
[1] *University of Durham, Department of Physics, South Road, Durham, DH1 3LE, U.K*
[2] *National Institute of Standards & Technology, Gaithersburg, Maryland 20899, U.S.A*

Abstract

In order to maximize the TMR effect in devices containing insulating barrier layers, the exact structure of the layers as well as the interfaces needs to be well characterized. Grazing incidence xray scattering is well suited to such an investigation as it is possible to distinguish between interface roughness and interdiffusion profiles across an interface. As a precursor to the growth of Al_2O_3 barrier layers, pure Al is normally deposited and then subjected to an oxidation process. We present a systematic study of the interdiffusion length and profile within sputtered samples of the form X/Al and Al/X where X is a metal from rows 4,5 and 6 of the periodic table.

Resonant Magnetic Xray Scattering in 3d Transition Metal Multilayers

T.P.A. Hase[1], B.D. Fulthorpe[1], S.B. Wilkins[1], B.K. Tanner[1], C.H. Marrows[2], B.J. Hickey[2] and M.D. Roper[3]
[1] *University of Durham, Department of Physics, South Road, Durham, DH1 3LE, U.K.*
[2] *University of Leeds, Department of Physics, Leeds, LS2 9JT, U.K.*
[3] *Daresbury Laboratory, Daresbury, Warrington, Cheshire, WA4 4AD, U.K.*

Abstract

The phenomenon of giant magnetoresistance (GMR) has been the driving force behind much research in transition metal multilayers over the last decade. Many studies have concentrated on the possible relationship between the structural and magnetotransport properties of the films. In particular, the role of interfacial roughness and/or crystalline perfection on the electron scattering has plagued researchers. The interfacial morphology is best elucidated using grazing incidence x ray scattering. In magnetic systems a key parameter that also needs to be measured is the morphology of the magnetic moment at the interfaces. Resonant magnetic xray scattering can be used to measure both the magnitude and direction of the moment within individual layers in thin magnetic films. In this poster we show how the technique can be used as an element and coupling specific magnetometer as well as a powerful technique to measure the magnetic disorder at the interfaces within the films.

Determination of the Valence band spin polarisation in the NiMnSb Heusler alloy

A. Tagliaferri, C. De Nadai, N.B Brookes, ESRF S. Andreiu, P. Tourban, F. Bertran, Nancy and LURE D. Ristoiu, J.P. Nozieres, CNRS Grenoble

Abstract

Materials with high spin polarisation at the Fermi level (EF) are considered the best candidates to enhance the performance of spin electronic device like spin valves and tunnelling junctions, where thin films of these materials can act as spin filters. NiMnSb and PtMnSb have been predicted to be half metallic ferromagnets and have a high Curie temperature, which attains the value of 730 K for NiMnSb and makes them particularly interesting for spinelectronic applications with respect to perovskites. We present new results obtained by Spinresolved Xray Photoemission Spectroscopy at the ID08 bealine of ESRF, which are the first experimental determination of the spin polarisation of the NiMnSb surface valence band.

Theoretical description of resonant magneto-optical properties in the X-ray regime

J. Minár and H. Ebert
Department Chemie / Physikalische Chemie, Universität München,
Butenandstr. 5-13, D-81377 München, Germany

Abstract

uring the last years the investigation of the magneto-optical effects in the X-ray regime has been used more and more for the investigation of magnetic and electronic structure of the magnetic materials. As for the optical regime of light, all magneto-optical properties in the X-ray regime are closely related to the optical conductivity. Our method for the calculation of the frequency dependent optical conductivity allows therefore a rather detailed discussion of all experimentally observable magneto-optical phenomena. It is based on the fully relativistic Green's function method (KKR-GF). Within our approach we are able to deal not only with ordered systems, but also with disordered ones, as well as multilayer and surface layer systems.

We present results of calculations for the Faraday effect for bulk Fe, as well as for disordered $Fe_{0.5}Ni_{0.5}$ and Co_xPt_{1-x} alloys.

The possible mechanisms of enhancement and suppression of TMR in magnetic tunnel junctions

A. Bagrets[1,3] , D. Bagrets[2,3] , B. Dieny[2] and A. Vedyayev[2,3]
[1]*Laboratoire Louis Néel, CNRS, BP 166, 38042 Grenoble, France*
[2]*CEA/Grenoble, DRFMC, SP2M/NM, 38054 Grenoble, France*
[3]*Department of Physics, Moscow State University, 119899 Moscow, Russia*

Abstract

The possible mechanisms of enhancement and suppression of TMR in magnetic tunnel junctions of the form $F_1/O/F_2$ (where F's are ferromagnetic layers, O is an oxide spacer) were investigated theoretically using generalized Kubo formalism and Green's function method. We predict that in the presence of magnetic impurities within the oxide barrier, due to resonant spin-dependent tunnelling, the TMR of the considered structure may be larger than TMR of the same structure without paramagnetic impurities. It is calculated that an increase in temperature leads to a decrease in the TMR amplitude due to excitation of spin-processes resulting in mixing of spin-up and down channels. It is shown that asymmetry in the location of the impurities within the barrier can lead to asymmetry in $I(V)$ characteristic of impurity assisted current. In the framework of $s-d$ model it was investigated the influence of impurity and magnon interfacial scatering on the TMR magnitude. Based on the previous band-structure calculations, we assume that the exchange split quasi free electrons with the density of states greater for majority spin sub-band give the main contribution to the TMR effect. We show that, due to the interfacial inter-band scattering, TMR can be substantially reduced even down to zero value. This is related to the fact that the delocalized quasi free electrons can scatter into strongly localized d sub-band, the density of states at Fermi level of which is larger for the minority spins compared to the majority spins. The presence of inelastic magnon scattering leads to a further decrease in the TMR magnitude at finite temperature.

Pulsed laser deposition and characterisation of high quality oxide thin films

C. Fitzgerald

Abstract

High quality superconducting ($YBa_2Cu_3O_{7d}$) and ferromagnetic (LaSrMnO and SrFeMoO) thin films were deposited on MgO and $SrTiO_3$ substrates using pulsed laser deposition. The quality of the thin films was investigated using xray diffraction (XRD) and atomic force microscopy (AFM). Electrical mea surements were made using standard fourpoint probe technique. 1/f noise measurements were also made in the 10^{-4} to 10^4 Hz regime in YBCO, LSMO, and SrFeMoO thin films.

The anomalous lineshapes at Ledge resonances of Nd/Pr superlattices

Pascale Deen[1] ,J.P.Goff[1] , R.C.C.Ward[2] ,M.R.Ward[2] ,A.Stunault[3]
[1]*Department of Physics, Oliver Lodge Laboratory, University of Liverpool, Liverpool, U.K.*
[2]*Department of Physics, University of Oxford, Clarendon Laboratory, Oxford, U.K.*
[3]*European Synchrotron Radiation Facility, BP 220, F38043, Grenoble Cedex, France*

Abstract

It was possible to study the magnetism of both the constituents of a superlattice, for the first time, using xray magnetic resonant scattering (XMRS) in Nd/Pr super lattices. However the lineshapes of the energy scans at the L absorption edge were found to be anomalous. The aim of the experiment, using the XMaS beamline at the ESRF, was to understand the origin of these lineshapes. The dominant features, a high energy peak at the absorption edge and a high energy shoulder were found to be due to dipolar transitions to a broad 5d band, directly probing the conduction electron spindensity wave responsible for the propagation of the magnetic order through superlattices. In contrast to the lineshapes at the L_{II} edge the lineshapes at the L_{III} edge reveal a quadrupolar peak in conjunction with a dipolar peak thereby allowing us to quantify the extent of the localised induced ordering of the Pr 4f moments in the Nd/Pr superlattice.

Spin sensitive UHV low temperature scanning tunnelling microscopy in high magnetic fields

P. Messina, A.Schneider, L.Vitali, G.Wittich and K.Kern
Max Plank Institute for solid state research, Heisemberg str.1 Stuttgart, Germany

Abstract

Magnetism is one of the most fascinating fields of physics and it is being investigated for more than 200 years now. Nevertheless there are still phenomena such as High Tc superconductivity and magnetism on an atomic scale whose explanation is expected be related to unknown magnetic effects. It is therefore necessary to develop a technique which can detect magnetism with high spatial resolution. This requirement suggests to use a scanning probe technique such as an STM in a configuration sensitive to the electron spin. Such a configuration is achieved by using the spatial precision of STM movements along with a magnetic sensitive tip and is expected to lead to a lateral resolution of the local magnetic moment of less than 10 nm. To our knowledge only one method so far has been proven to be capable to resolve magnetic moments on this scale. It makes use of a metal tip coated with a ferromagnetic material capable of spin selective tunnelling [1]. However we would like to use two different physical principles which may turn out to be more suited to combine the magnetic sensitivity with atomic manipulation. We want to use a superconducting tip made up of Nb or Ta. We may use two different properties of the superconducting state to resolve magnetism on the atomic scale. The first phenomena is the so called Andreev reflection. It

uses the fact that if an electron travels from a normal metal to a SC with an energy inferior to the SC gap it will be reflected at the interface unless another electron with an inverse spin can follow the first one into the SC and form a new Cooper pair. This will not be possible if , due to spin polarization in the normal metal, this second state is not available. Therefore if the STMtip is superconducting the tunneling current will be dependent on the local magnetic polarization of the sample provided the bias applied is less than the SC gap [2]. The second property we may use, is the breaking up of Cooper pairs in the presence of magnetic impurities. The strength of the cooper pair bonding is in general sensitive to the presence of local magnetic impurities. In the vicinity of such an impurity one of the electrons of the pair is scattered differently from the other one. This scattering process leads to two polarized states whose energy lays inside the SC gap. We will try to pick up a magnetic cluster with the tip so that spin polarized tunnelling can be achieved due to the breaking up of Cooper pairs[3]. Both techniques considered therefore require cryogenic conditions in an UHV environment. The requirement of having an STM capable of atomic manipulation is matched only if an adequate STM design and appropriate electronics are provided together with an high stability of the microscope. The combination of these 5 technical requirements is being addressed in the construction of a new instruments (still under construction) of which we outline the main features. Some proposals for possible experiments are also presented.

[1] M. Bode et al. Phys.Rev.Lett 81, 4256 (1998)
[2] R.J. Soulen et al. Science 282, 85 (1998)
[3] L.Brgi PhD thesis EPFL (1999)

List of Lecturers

Rolf Allenspach	IBM Zurich	ral@zurich.ibm.com
Stefan Bluegel	IFF, FZ Juelich	S.Bluegel@fz-juelich.de
Patrick Bruno	MPI Halle	bruno@mpi-halle.de
Carlo Carbone	IFF, FZ Juelich	C.Carbone@fz-juelich.de
Peter Dederichs	IFF, FZ Juelich	p.h.dederichs@fz-juelich.de
Hubert Ebert	LMU Munich	he@gaia.phys.chemie.uni-muenchen.de
Helmut Eschrig	IFW, Dresden	h.eschrig@ifw-dresden.de
Albert Fert	Universite Paris-Sud, Orsay	fert@lcr.thomson-csf.com
Peter Gruenberg	IFF, FZ Juelich	p.gruenberg@fz-juelich.de
Balazs Gyorffy	University of Bristol	b.gyorffy@bristol.ac.uk
Jürgen Hafner	University of Vienna	Juergen.Hafner@univie.ac.at
Břetislav Heinrich	S. Fraser Univ., Burnaby, BC	bheinric@sfu.ca
Jürgen Henk	Max Planck Institut Halle	henk@mpi-halle.de
Werner Hofer	University College London	w.hofer@ucl.ac.uk
Xiaofeng Jin	Fudan Univ., Shanghai	xfjin@fudan.ac.cn
Paul Kelly	University of Twente	p.j.kelly@tn.utwente.nl
Juergen Kirschner	Max Planck Institut Halle	kirschner@mpi-halle.de
Colin Lambert	Lancaster University	c.lambert@lancaster.ac.uk
Peter Levy	New York University	levy@nyu.edu
Alexander Lichtenstein	University of Nijmegen	A.Lichtenstein@sci.kun.nl
JiříMathon	City University London	J.Mathon@city.ac.uk
Ingrid Mertig	TU Dresden	mertig@theory.phy.tu-dresden.de
David Rafaja	Charles Univ. Prague	rafaja@karlov.mff.cuni.cz
Georg Schmidt	University Wuerzburg	georg.schmidt@physik.uni-wuerzburg.de
Ilja Turek	ASCR, IPM Brno	turek@ipm.cz
Gerrit van der Laan	CLRC Laboratory Daresbury	g.vanderlaan@dl.ac.uk
Peter Varga	TU Vienna	varga@iap.tuwien.ac.at
Bedřich Velický	Charles Univ. Prague	velicky@karlov.mff.cuni.cz
Peter Weinberger	TU Vienna	pw@cms.tuwien.ac.at

List of Participants

Rolf Allenspach	IBM Zurich	ral@zurich.ibm.com
Zdeněk Arnold	ASCR, Inst. of Physics Prague	arnold@fzu.cz
Alexei Bagrets	Laboratoire Louis Neel, CNRS Grenoble	bagrets@labs.polycnrs-gre.fr
Grzegorz Banach	ILTSR Polish Acad. Sci. Wroclaw	banach@int.pan.wroc.pl
Jean-Marc Laurent Beajour	University of Southampton	jmlb@phys.soton.ac.uk
Peter Bencok	ESRF Grenoble	bencok@esrf.fr
Stefan Bluegel	IFF, FZ Juelich	S.Bluegel@fz-juelich.de
Georges Bouzerar	MPI Halle	bouzerar@mpi-halle.de
Patrick Bruno	MPI Halle	bruno@mpi-halle.de
James Buchanan	Durham University	j.d.r.buchanan@dur.ac.uk
Carlo Carbone	IFF, FZ Juelich	C.Carbone@fz-juelich.de
Claudia Cardoso	Universidade de Lisboa	m19908@cc.fc.ul.pt
Miroslav Černý	IPM, ASCR Brno	mcerny@ipm.cz
Oscar Cespedes Boldoba	Trinity College, University of Dublin	cespius@yahoo.com
Oleksandr Chayka	Institute of Physics, AS CR Prague	chayka@fzu.cz
Liviu Ionut Chelaru	MPI Halle	chelaru@tango.exp.bessy.de
S. P. Chen	National Taiwan University Taipei	d89222002@ms89.ntu.edu.tw
Olexandr Chernyavski	Charles Univ. Prague	chernyavski@apollo.karlov.mff.cuni.cz
Yuriy Chushkin	Institute of Physics, SAS Bratislava	fyzijura@savba.sk
Morrel Cohen	Rutgers Univ. New Jersey	marcohen@rci.rutgers.edu
Adeline Crepieux	MPI Halle	crepieux@mpi-halle.mpg.de
Peter Dederichs	IFF, FZ Juelich	h.dederichs@fz-juelich.de
Pascale Deen	University of Liverpool	pascale@liv.ac.uk
Augustin del Moral	Univ. Zaragoza	delmoral@posta.unizar.es
Martin Diviš	Charles Univ. Prague	divis@mag.mff.cuni.cz
Václav Drchal	ASCR, Inst. of Physics Prague	drchal@fzu.cz
Alexey Drovosekov	P.L. Kapitza Institute Moscow	drovosek@kapitza.ras.ru
Joerg Ebert	Darmstadt University of Technology	jebert@hrzpub.tu-darmstadt.de
Hubert Ebert	LMU Munich	he@gaia.phys.chemie.uni-muenchen.de
Axel Enders	MPI Stuttgart	a.enders@fkf.mpg.de
Jussi Enkovaara	Helsinki University of Technology	jen@fyslab.hut.fi
Helmut Eschrig	IFW, Dresden	h.eschrig@ifw-dresden.de
Francesca Federici	City University London	F.Federici@city.ac.uk
Paolo Ferriani	University of Modena	ferriani@unimo.it
Albert Fert	Universite Paris-Sud, Orsay	fert@lcr.thomson-csf.com
Ciara Bridget Fitzgerald	Trinity College Dublin	perri@maths.tcd.ie
Samantha Foster	ISIS, Rutherford Appleton Laboratory	S.Foster@rl.ac.uk
Martin Friak	IPM, ASCR Brno	mafri@ipm.cz
Iosif Galanakis	IFF, FZ Juelich	I.Galanakis@fz-juelich.de
Javier Antonio Gómez Romero	CBPS Rio de Janeiro	gomez@cbpf.br
Peter Gruenberg	IFF, FZ Juelich	p.gruenberg@fz-juelich.de
Ruben Guerrero Sanchez	Universidad Autonoma de Madrid,	Cubeleg@hotmail.com
Balazs Gyorffy	University of Bristol	b.gyorffy@bristol.ac.uk
Jürgen Hafner	University of Vienna	Juergen.Hafner@univie.ac.at
Thomas Hase	University of Durham	t.p.a.hase@dur.ac.uk
Masahiko Hashimoto	Osaka Univ.	hashimot@cmp.sanken.osaka-u.ac.jp
Ladislav Havela	Charles Univ. Prague	havela@apollo.karlov.mff.cuni.cz
Marcus Heide	FZ Juelich	m.heide@fz-juelich.de
Břetislav Heinrich	S. Fraser Univ., Burnaby	bheinric@sfu.ca
Jürgen Henk	MPI Halle	henk@mpi-halle.de

Heike Christine Herper	CMS TU Vienna	hh@cms.tuwien.ac.at
Werner Hofer	University College London	w.hofer@ucl.ac.uk
Václav Janiš	Inst. of Physics Prague	janis@fzu.cz
Blanka Janoušová	Charles Univ. Prague	blanka@mag.mff.cuni.cz
Pavel Javorský	Charles Univ. Prague	javor@mag.mff.cuni.cz
Xiaofeng Jin	Fudan University Shanghai	xfjin@fudan.ac.cn
Jií Kamarád	Inst. of Physics Prague	kamarad@fzu.cz
Paul Kelly	University of Twente	p.j.kelly@tn.utwente.nl
Juergen Kirschner	MPI Halle	kirschner@mpi-halle.de
Olexandr Kolomiets	Charles Univ. Prague	kolomiet@mag.mff.cuni.cz
Michal Košuth	LMU Muenchen	Michal.Kosuth@cup.uni-muenchen.de
Masato Kotsugi	MPI Berlin	kotsugi@spring8.or.jp
Endre Kovacs	University of Debrecen	kendre@dtp.atomki.hu
Josef Kudrnovský	ASCR, Inst. of Physics Prague	kudrnov@fzu.cz
Jan Kuneš	Institute of Physics, AS CR Prague	kunes@fzu.cz
Colin Lambert	Lancaster University	c.lambert@lancaster.ac.uk
Petr Lazar	Institute of Physics of Materials, ASCR Brno	lazar@physics.muni.cz
Bence Lazarovits	Vienna University of Technology	bl@cms.tuwien.ac.at
Y. R. Lee	Nat. Taiwan Univ. Taipei	b0326abc@ms26.hinet.net
Dominik Legut	IPM, ASCR Brno	Legut@ipm.cz
Peter Levy	New York University	peter.levy@nyu.edu
Alexander Lichtenstein	University of Nijmegen	A.Lichtenstein@sci.kun.nl
Yuntao Liu	HMI Berlin	yuntao.liu@hmi.de
Ivan Lobov	IMP Ekaterinburg	i_lobov@imp.uran.ru
Hugo Loosvelt	LSPM (VSM) Leuven	Hugo.Loosvelt@fys.kuleuven.ac.be
František Máca	ASCR, Inst. of Physics Prague	maca@fzu.cz
Georg Madsen	TU Vienna	gmadsen@theochem.tuwien.ac.at
Natalyia Makedonska	Nat. Ac. of Science of Ukraine Kharkov	makedonskaya@ilt.kharkov.ua
Ivan Marri	Universita di Modena	marri@unimo.it
Jan Mašek	ASCR, Inst. of Physics Prague	masekj@fzu.cz
Jiří Mathon	City University London	J.Mathon@city.ac.uk
Frank Matthes	IFW Dresden	f.matthes@ifw-dresden.de
Phivos Mavropoulos	IFF, FZ Juelich	ph.mavropoulos@fz-juelich.de
David Ménard	Colorado State University	menard@lamar.colostate.edu
Ingrid Mertig	TU Dresden	mertig@theory.phy.tu-dresden.de
Paolo Messina	MPI Stuttgart	Paolo.Messina@fkf.mpg.de
Julian Milano	Lab. Tandar, CAC, Buenos Aires	milano@cnea.gov.ar
Jan Minar	LMU Muenchen	jm@eeb02.cup.uni-muenchen.de
Thomas Mühl	IFW Dresden	t.muehl@ifw-dresden.de
Vladimír Nekvasil	ASCR, Inst. of Physics Prague	nekvasil@fzu.cz
Chris Newman	Lancaster University	c.newman@lancaster.ac.uk
Pavel Novák	ASCR, Inst. of Physics Prague	novakp@fzu.cz
Krisztian Palotas	TU Budapest, Dept. of Theor. Phys.	palotas@born.phy.bme.hu
Jeong Soo Park	Hanyang University Seoul	jspark651010@hananet.net
Neil Pattinson	Lancaster University	n.pattinson@lancaster.ac.uk
J. Milton Pereira	University of Western Ontario London	jpereira@julian.uwo.ca
Jiří Prchal	Charles Univ. Prague	zizik@email.cz
David Rafaja	Charles Univ. Prague	rafaja@karlov.mff.cuni.cz
Silke Roether	Institut fur Theoretische Physik Dresden	silke@die-physiken.de
M. Alexandra Rosa	Universidade de Lisboa	marosa@fc.ul.pt

Andrés Rosales Rivera	Univ. Nac. de Colombia, Sede Manizales	arosales@emtelsa.multi.net.co
Ján Rusz	University of P. J. Šafárik Košice	rusz@apollo.karlov.mff.cuni.cz
Kazunori Sato	Osaka Univ.	ksato@cmp.sanken.osaka-u.ac.jp
Georg Schmidt	University Wuerzburg	georg.schmidt@physik.uni-wuerzburg.de
Vladimír Sechovský	Charles Univ. Prague	sech@mag.mff.cuni.cz
Gianluca Selvaggi	University of Physics of Modena	gselvaggi@unimo.it
Yuliya Shabakaeva	Nat. Ac. of Science of Ukraine Kharkov	SHABAKAYEVA@ilt.kharkov.ua
Daniel Šimek	Charles Univ. Prague	simek@fzu.cz
Ondej Šipr	Institute of Physics, AV CR Prague	sipr@fzu.cz
Martin Sirena	Centro Atomico Bariloche.	sirenam@ib.cnea.gov.ar
Victor Manuel Garcia Suarez	Universidad de Oviedo Asturias	victor@condmat.uniovi.es
Pavel Svoboda	Charles Univ. Prague	svoboda@mag.mff.cuni.cz
Olexandr Syshchenko	Charles Univ. Prague	syshchen@mag.mff.cuni.cz
Alberto Tagliaferri	ESRF Grenoble	Alberto.Tagliaferri@esrf.fr
Mohand Talanana	University of Twente Enschede	M.Talanana@tn.utwente.nl
Ilja Turek	ASCR, IPM Brno	turek@ipm.cz
Andrey Umerski	Dept. of Applied Math. Milton Keynes	A.Umerski@open.ac.uk
Radovan Urban	Simon-Fraser-University Burnaby, BC	rurban@sfu.ca
Gerrit van der Laan	CLRC Laboratory Daresbury	G.van_der_Laan@dl.ac.uk
Nele Vandamme	Katholieke Universiteit Leuven,	nele.vandamme@fys.kuleuven.ac.be
Peter Varga	TU Vienna	varga@iap.tuwien.ac.at
Denys Vasilyev	Charles Univ. Prague	vasilyev@apollo.karlov.mff.cuni.cz
Jana Vejpravová	Charles Univ. Prague	jana@mag.mff.cuni.cz
Sofie Veldeman	Katholieke Universiteit Leuven	Sofie.Veldeman@fys.kuleuven.ac.be
Bedich Velický	Charles Univ. Prague	velicky@karlov.mff.cuni.cz
Valentine Volobuev	Kharkov State Polytechnic University	volobuev@kpi.kharkov.ua
Yu-Jen Wang	National Tsing-Hua University Hsinchu	d873581@oz.nthu.edu.tw
Yung-Hung Wang	National Tsing-Hua University Hsinchu	d887510@oz.nthu.edu.tw
Peter Weinberger	TU Vienna	pw@cms.tuwien.ac.at
Olaf Wunnicke	IFF FZ Juelich	O.Wunnicke@fz-juelich.de
Jan Zabloudil	TU-Vienna (CMS)	jz@cms.tuwien.ac.at
Anna Zorkovska	P.J.Safarik Univ. Kosice	zorkov@kosice.upjs.sk
Maciej Zwierzycki	Uniwersity of Twente, Enschede	M.Zwierzycki@tn.utwente.nl
Andela Kalvova	Charles Univ. Prague	
Agung Nugroho	Univ. of Amsterdam	
Milan Dopita	Charles Univ. Prague	dopita@apollo.karlov.mff.cuni.cz

4 News from the ESF Programme

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

4.1 News about the Proposal for a New ESF Programme 'Psi-k2'

The present Programme (= mega-network) 'Psi-k' of the European Science Foundation (ESF) will end in December 2002, and the Committee is now preparing a follow-on proposal 'Psi-k2'. It would again be an 'a la carte' Programme which the national research councils of different European countries would have to pay real money to join. Once a country has joined, anyone in that country can partake fully in the Programme activities. So if you want to go to the workshops etc., you will have to press your national research council to pay and join. We will alert you through the email list when the time comes to do that, and who the right official in your research council is. It will be in the late autumn or winter.

In the meantime this is to keep you informed about the plans. The activities will be broadly as in the present Psi-k Programme, with one or two additions.

One feature will certainly be about a dozen Working Groups focusing on particular areas of research, and of course anyone will be free to collaborate in those; in fact they are encouraged to do so, to get into a new field or to pick up new ideas or tools or to find a new partner for collaboration. IF YOU HAVE AN IDEA FOR A PARTICULAR WORKING GROUP THAT YOU WOULD LIKE TO PROPOSE AND ORGANISE, THEN PLEASE LET ME KNOW, AND WE WILL SEE WHETHER WE CAN INCLUDE IT.

A second new project may or may not get included. Everyone is in favour of the idea, but there are currently intense discussions about whether it is feasible in practice. The idea is this. Everywhere there are being developed new applications or extensions of the standard codes, eg for calculating phonons or non-collinear magnetism or NMR shifts or tunnelling in an STM or ..., and everyone wants to have these for the particular code that they use. The project which we call 'the toolbox' would work on making these available as widely as possible. Nice idea, but with problems in practice.

Volker Heine, Psi-k chairman
(vh200@phy.cam.ac.uk)

4.2 Reports on Workshops/Conferences

4.2.1 Report on Symposium A – 2001 E-MRS Spring Meeting

"Computational Materials Science Across Time and Length Scales"

Strasbourg, June 5-8, 2001

Between the atomic and the macroscopic scale of materials science lies a length scale gap of about 9 orders of magnitude and a time scale gap of about 12 orders of magnitude. Yet to understand the macroscopic implications of the atomic structure and to simulate materials in a convincing way, methods need to be found to bridge this chasm.

Bridging the micro- and macroscales is a very topical area as was witnessed in a lively symposium with 11 invited talks, 33 oral contributions, and 21 posters. If one consensus emerged at the meeting it is that the problems are more pressing than ever before, but also that much progress has already been made, with a great deal more within reach. Although a completely automatic procedure to cross time and length scales still eludes scientists, and may very well not exist, tantalizing hints were given as to how such a procedure might operate. On the microscopic scale, many talks were devoted to first-principles electronic structure calculations on an unprecedented scale and with a very high level of accuracy. To scale these results up in time and space, the kinetic Monte Carlo (KMC) method and the finite element method (FEM) seem the most promising candidates. In certain cases, the molecular dynamics (MD) technique may also be applicable, although the size of systems is still somewhat small, even with today's supercomputers, and the time scale can be problematic in systems with large energy barriers. Ways to embed the microscopic into the macroscopic in a mathematically rigorous manner are still being developed and refined. When this embedding is performed in the most naive way, problems arise due to ghost forces, but several schemes are now available to eliminate these unphysical phenomena.

The meeting revolved around a number of topical areas. Fundamental issues were discussed in the opening session, with numerous example applications, such as the behavior of liquid crystals, the evolution of defects in semiconductors, and the aging of steels. Clearly, a wide range of materials and problems were addressed in these talks, with a general emphasis on the universal features shared by these various systems, rather than on their differences. Thin film growth, for metals as well as semiconductors, was addressed in two sessions. The KMC approach is very well suited to this kind of phenomena, although the recently developed level set method seems to be very promising as well and deserves further study. The session on elastic properties centered mainly around dislocation motion and fracture. Here the KMC and the MD methods (the latter if necessary supplemented by Voter's acceleration technique) are able to provide good results. One afternoon was devoted to magnetic systems, including microscopic studies as well as micromagnetic simulations. Some very impressive computer animations were shown to demonstrate the evolution of a magnetic system under the influence of a time-dependent magnetic field. Linking this well-established theory to microscopic parameters is clearly a priority. The final morning focused on technological applications. It included talks on semiconductor devices, quantum dots, oxidation, and creep strenghtened oxides, to name just a few, which clearly demonstrate the wide range of shared challenges.

All in all, the symposium gave a good overview of the state-of-the-art. It was evident that considerable progress has been made in this area in the last year and that much more can be expected in the near future. A great deal of cross-fertilization has already occurred and scientists have shown an appreciation for the shared challenges and their common resolution, rather than being blinded by the differences between various materials. Visualization and animation emerged as powerful tools to understand and elucidate the phenomena that were observed. The coming years promise to be very exciting in this rapidly evolving field.

List of invited speakers

F. Cleri (Rome, Italy),
K. W. Jacobsen (Lyngby, Denmark),
P. Jensen (Villeurbanne, France),
L. P. Kubin (ONERA, France),
B. I. Lundqvist (Gothenburg, Sweden),
J. Neugebauer (Berlin, Germany),
P. Vogl (Muenchen, Germany),
S. Schmauder (Stuttgart, Germany),
A. La Magna (Catania, Italy),
R.E. Rudd (Livermore, USA),
J. Fidler (Vienna, Austria).

Publication

A special issue of Computational Material Science, edited by Elsevier, will be published with a selection of the accepted papers. The volume should have around 300 pages.

Programme

The programme can be found on the WEB:

http://www-emrs.c-strasbourg.fr

Acknowledgements

Financial assistance for the symposium was provided by the European Science Fundation through the program Ψ_k (Electronic Structure Calculations for Elucidating the Complex Atomistic Behaviour of Solids and Surfaces), Université Louis Pasteur from Strasbourg and Institut de Physique et Chimie de Strasbourg. The support from these organizations and particularly from the Ψ_k was es sential and is gratefully acknowledged.

Hugues Dreyssé, Risto Nieminem and Luc T. Wille

The organizers of the symposium

4.2.2 Report on the DFT School and Workshop

SCHOOL AND WORKSHOP
"DFT for the Study of Complex Oxides"
The Royal Institution of Great Britain, May 14-18, 2001

The workshop has been supported by:

European Science Foundation – Research Programme STRUC-Ψ_k

Institute of Physics – Thin Film and Surfaces Group

Organisers:

M. Alfredsson, F. Corà, A. Sokol, J. Gale, N. Harrison

Our aim in organising this Workshop was that of providing a forum to discuss and review the current progress in Density Functional Theory for the study of solid-state systems, with an emphasis to the properties of oxides.
The invited speakers provided a wide range of expertise, from the formulation of DFT to the software implementation of the theory and its applications to the solid state.

INNOVATIVE COMPONENTS IN THE PROGRAMME

In defining the programme, we have introduced three contributions which are not often included in the schedule of scientific meetings, which we comment on below.

1) School

The increased demand of expertise in molecular modelling, both in academia and in industry, requires us to train young researchers in this rapidly expanding discipline. For this reason, the Workshop was coupled with a 2-day School on DFT, in which the students have been given a broad account of the theory and applications from scientists that have personally contributed to the development of the field.
Thanks to the commitment and quality of the lecturers, the School combined the tutorial aspect with an exciting presentation of current developments. This has been beneficial not only for the students but also for senior scientists, as the broad range of topics presented has improved their knowledge of each other's work.
According to the comments we have received from the participants, the lecturers at the School communicated to the students not only new knowledge, but also a scientific curiosity on DFT which, if sustained, will have a beneficial effect in their curricula.

2) Code demonstrations

During the first day of the Workshop, we dedicated two hours to the presentation of codes which enable the application of DFT to solids. Representatives of 12 major European codes gave short presentations, complemented by practical demonstrations during the two poster sessions. The code demonstration was a great success with the participants, and it has been very informative to learn how many advanced options are now allowed by one or the other code. This information is often difficult to obtain without a session explicitly dedicated to the codes.

3) Homework studies

We defined two systems to be studied as "homework" by the participants prior to the Workshop. These were a spin polarised defect in α-quartz and the metal-insulator phase transition in V_2O_3. Despite being structurally simple, correctly describing the electronic behaviour of these systems is still a challenge for DFT calculations. This choice helped us in focussing the discussion during the workshop; in particular, the comparison of results on V_2O_3 obtained with standard DFT, LDA+U and hybrid HF-DFT Hamiltonians was very useful in highlighting the features, advantages and limitations of the different techniques.

Such a combination of tutorial and research meetings, complemented by a selection of homework-style topics to focus the discussions, is a format that we would highly recommend for future workshops.

SCIENTIFIC CONTENT

The Workshop programme was comprised of 28 oral presentations, partitioned into six sessions, each dedicated to a different topic in either the theoretical aspects of DFT or its application to oxides.

The arguments presented can be broadly classified as: the Formulation of Functionals, Surface Science and Catalysis, Electronic Properties, Magnetic Systems, Free Energy Calculations, and the Computational Methods beyond DFT in the solid state.

Each session was initiated by a keynote speaker focussing on the "applications and limits" of DFT in his field of research, followed by a selection of invited and contributed talks on different, and less widely used, theoretical approaches applicable to the same problems. This format encouraged extensive discussions, which were initiated during the talks and continued in the two "general discussion" sessions at the end of the first and second day of the Workshop.

We now try to highlight a few developments which, from our point of view, are important new contributions to the field. We would like to emphasise, however, that all lecturers gave excellent presentations of their area of research, which makes it difficult to single-out individual contributions to the Workshop.

1) Formulation of Functionals

This session included wide-ranging reviews by Levy and Perdew, while Becke contributed a related tutorial to the School. The distinction between the "first-principle" derivation and the empirical fitting of functionals, has been given a new direction by Tozer. He proposed a new empirical functional fitted to the true Kohn-Sham potential, calculated for molecular systems with Coupled Cluster methods, rather than to the experimentally available geometric and energetic data for small molecules as it has normally been performed in past years.

The general worsening of calculated results on increasing the atomic number of the constituent atoms was also discussed. This was attributed to the selection of reference compounds in the fitting of functionals, which is biased towards organic molecules and hence lighter elements.

2) Surface Science and Catalysis

An important aspect of modelling work in this area relies on the models employed to represent the solids, and in particular the active sites on the surface. A comprehensive review of embedding methods was presented by Sherwood, while Sauer, Catlow, Payne and Ugliengo described the study of heterogeneous processes at surfaces.

The usefulness of combining high-level QM calculations with simpler Hamiltonians,either as an initial stage of the study, or as a means to provide adequate embedding fields in embedded-cluster approaches, was also discussed in depth.

In a related topic, free energy calculations were presented by Scheffler and Kresse. These studies included the evaluation of the chemical potential in open systems, a crucial component for the application of DFT to model important cases such as crystal growth mechanisms.

3) Calculations of electronic and magnetic properties

3a) Dielectric properties: Three complementary approaches for the calculation of the dielectric properties of oxides were presented by Resta (Berry phase), Gonze (Density Functional Perturbation Theory) and De Boeij (Time-Dependent Current DFT). While the first two formulations are now well established, and have systematic applications, TD-CDFT is a more recent development, and provides an alternative route to evaluate the dielectric properties of oxides. Particular emphasis in the results was given to the calculation of the frequency-dependent dielectric constants and of the ferroelectric polarisation of insulating oxides.

3b) Magnetic properties and Charge Localisation: This is a critical application area, where DFT studies often fail to reproduce experimental results. Several lecturers in the Workshop have highlighted possible improvements to the theory: these include Temmerman (SIC), Lichtenstein, Blaha and Kresse (LDA+U), Dovesi and Gavartin (hybrid HF-DFT functionals), while Daul introduced the Density Matrix Renormalisation Group formalism, applied with success to describe the magnetic states of molecular systems.

4) The scientific presentations have been complemented by a selection of invited talks aimed at highlighting the **directions of future development** for the computational study of solids. In this category we include both the mathematical tools that enable a more efficient description of complex systems within standard DFT Hamiltonians, but also the definition of more accurate Hamiltonians that go beyond the mean-field one-electron approximation.

In the former case, order-N methods were described by Sanchez-Portal and Gillan, while the latter was treated by Needs and Godby who described their recent work in developing Quantum Monte Carlo and GW methods for solids.

DISCUSSION SESSIONS

Some of the topics introduced in the lectures have been discussed more in depth in the "General discussion" sessions: the first discussion concentrated on the treatment in the framework of DFT of degenerate and nearly degenerate states, with particular interest in a correct definition of the atomic energies and multiplets. The problem of charge localisation in DFT, along with the on-site correlation effects, was in the centre of the second discussion, which extended to the definition of charges in QM methods.

A question often inferred, but never formulated explicitly during the meeting, relates to the necessity of defining a set of reference and well characterised problems in crystalline compounds. The definition of similar reference sets for molecular systems has been crucial for the development of the "empirical" functionals, and also to evaluate the accuracy of new Hamiltonians and functionals. Such a reference has not yet been defined for crystalline materials; achieving this goal requires a combined effort from the solid-state community, including experimental as well as computational investigations. We believe, however, that once defined, this reference set would have a widely beneficial effect for the field; for instance it could be used to develop a new empirical functional explicitly designed for solid-state applications. We would like to leave open the question concerning the feasibility of such a project, and suggest this topic as a possible subject for future discussion meetings, as well as of proposals for further work.

POSTER SESSIONS

The scientific programme was complemented by 40 poster presentations, divided between two sessions. The main topic during the first poster session was the study of surfaces, while the second session was mostly dedicated to the study of bulk properties. As with the oral presentations, posters were of high quality, which encouraged discussions and future collaborations. During the poster sessions, the code representatives presented posters and gave practical demonstrations of their computer codes.

ATTENDANCE

During the meeting we had a total of 101 attendees, representing 18 countries, partitioned as follows: 51 participants from the UK, 7 from Germany, 6 from the USA, 4 each from Italy, France, Spain and the Netherlands, 3 from Sweden, Switzerland and South Africa, 2 from Austria, Russia, Poland and Finland, and 1 from Canada, Ireland, Belgium and Croatia. Of them, 73 person attended the School and 96 the Workshop.

We offered 26 student bursaries (with the following geographical partition: 11 to UK students, 6 each to students from Western and Eastern European countries, 3 to students from outside Europe). Unfortunately, 5 representatives from African Countries have been unable to attend the meeting because of delays in obtaining their Visa. In addition, we were able to support 27 invited speakers.

Programme and Abstracts

Programme of the DFT school (14-15 May 2001)

14/5/2001

Session Chair: M. Alfredsson

9.00	-	10.00	N. Handy	Introduction: from a many-particle system to 1-particle equations
10.00	-	11.00	M. Levy	On degeneracies in DFT through constrained search theory
11.00	-	11.30		Coffee break
11.30	-	12.30	P. Blaha	The 1-particle potential
12.30	-	14.00		Lunch

Session Chair: N. Harrison

14.00	-	15.00	R. Catlow	Models of the Solid: periodic boundary conditions, clusters and embedding
15.00	-	16.00	A. Sokol	Examples/Demonstrations
16.00	-	16.30		Coffee break
16.30	-	17.30	A. Becke	Approximations to Vxc
17.30	-	18.30	A. Wander	Derivation and performance of basis sets and pseudopotentials

15/5/2001

Session Chair: J. Gale

9.00	-	10.00	R. Dovesi	Practical implementations
10.00	-	11.00	P. Ugliengo	Performance of functionals: a comparison of calculated properties - I Structural properties and energetics
11.00	-	11.30		Coffee break
11.30	-	12.30	F. Corà	Examples/demonstrations
12.30	-	14.00		Lunch

Session Chair: A. Sokol

14.00	-	15.00	X. Gonze	Performance of functionals: a comparison of calculated properties - II response properties of the charge-density
15.00	-	16.00	C. Daul	Performance of functionals: a comparison of calculated properties - III Magnetic properties and open-shell systems
16.00	-	16.30		Coffee break
16.30	-	17.30	M. Payne	*Ab-initio* molecular dynamics
18.00	-	20.00		Wine reception

Programme of the DFT workshop(16-18 May 2001)

16/5/2001

General Introduction.

Session Chair: F. Corà

9.00 - 9.05	F. Corà	Welcome and introductory notes
9.05 - 9.50	R. Catlow	Recent applications of DFT in solid-state and materials science
9.50 - 10.05	F. Corà	Overview and introduction to the code presentation
10.05 - 10.45		Code presentations (part 1)
10.45 - 11.15		Coffee break

Session Chair: P.Ugliengo

11.15 - 12.15	J. Sauer	Applications and limits of DFT in surface chemistry and catalysis
12.15 - 13.00		Code presentations (part 2)
13.00 - 14.00		Lunch

Foundations and perspectives of DFT.

Session Chair: A. Becke

14.00 - 15.00	J. Perdew	Beyond the Generalized Gradient Approximation
15.00 - 15.30	M. Levy	On excited states in DFT
15.30 - 16.00	E. Bylaska	Comparing the efficiency and accuracy of the projector-augmented wave DFT method (PAW) against Gaussian based DFT methods
16.00 - 16.30		Coffee break

Session Chair: P. Blaha

16.30 - 17.00	R. Dovesi	The performance of hybrid functionals in the solid state
17.00 - 17.30	D. Tozer	The performance of semi-empirical molecular functionals in solid-state system
17.30 - 18.30	General discussion	Discussion Chairs: I. Abarenkov and R. Catlow
18.30		Poster session 1, including demonstrations of the following codes: AB-INIT, CASTEP, CHEMSHELL, CRYSTAL, SIESTA, WIEN

17/5/2001

Surface Chemistry and Catalysis.

Session Chair: J. Sauer

9.00	-	10.00	M. Scheffler	The effect of temperature and pressure (beyond the 0K-0Pa treatment of solids)
10.00	-	10.30	P. Ugliengo	Modelling the Broensted acidity of H-faujasite, H-chabazite and H-edingtonite with CRYSTAL-98 periodic code
10.30	-	11.00	G. Kresse	First-principles calculations for V_xO_y grown on Pd(111)
11.00	-	11.30		Coffee break

Session Chair: I. Abarenkov

11.30	-	12.00	P. Sherwood	Embedded cluster models - a flexible modular implementation for enzymes, zeolites and oxides
12.00	-	12.30	J. F'dez Sanz	DFT calculations and MD classical simulations of transition metal deposition on metal oxide surfaces
12.30	-	13:00	M. Payne	Quantum Molecular Dynamics
13.00	-	14:00		Lunch

Application of oxides in electronics.

Session Chair: W. Temmerman

14.00	-	15:00	R. Resta	Dielectric polarization of insulating solids within DFT
15.00	-	15.30	X. Gonze	Zirconium and lead in SiO_2: dielectric and dynamical properties
15.30	-	16.00		Coffee break

Session Chair: C. Daul

16.00	-	16.30	P. de Boeij	Time dependent current density functional theory and the macroscopic polarisation of nonmetallic crystals
16.30	-	17.00	T. Saha	Using MTOs to extract the physics/chemistry
17.00	-	18.00	General discussion	Discussion Chairs: R. Resta and M. Scheffler
18.00	-	19.00		Poster session 2, including demonstrations of the following codes: ADF-BAND, CPMD, DMOL, FHIMD, VASP
19.00	-	19.30	F. James	Michael Faraday, and the early history of scientific discovery at the Royal Institution
19.30				Sherry reception and Conference dinner

18/5/2001

Open-shell systems and magnetic properties.

Session Chair: J. Perdew

9.00	-	10.00	C. Daul	Applications and limits of DFT in the calculation of magnetic properties
10.00	-	10.30	P. Blaha	Charge distribution and EFGs in cuprates using LDA+U within the LAPW method
10.30	-	11.00	A. Lichtenstein	Electronic structure of magnetic oxide: LDA+U
11.00	-	11.30		Coffee break

Session Chair: R. Dovesi

11.30	-	12.00	W. Temmerman	Cu valency change induced by O doping in YBCO
12.00	-	12.30	M. Koudriachova	First principles predictions of Li intercalation in titania
12.30	-	13.00	J. Gavartin	Charge trapping in cubic alkali halides and oxides: The charge localisation problem in the DFT calculations
13.00	-	14.00		Lunch

Pressure, temperature and system size.

Session Chair: R. Catlow

14:00	-	14.30	A. Oganov	Quantum mechanics of the Earth's mantle minerals
14.30	-	15.00	D. Sanchez-Portal	Software solutions: towards linear scaling?
15.00	-	15.30		Coffee break

Session Chair: N. Harrison

15.30	-	16.00	R. Needs	Quantum Monte Carlo study of oxides
16.00	-	16.30	R. Godby	Excited states and total energies from *ab initio* many-body theory
16.30				Concluding remarks

Beyond the Generalized Gradient Approximation

John P. Perdew
Department of Physics, Tulane University, New Orleans, LA 70118, USA

The local density and generalized gradient approximations for the exchange-correlation energy of a many-electron system are now standardly and widely used in solid state physics and quantum chemistry. This talk discusses the non-empirical construction of these functionals, and the advantages of the non-empirical approach. It then discusses similar constructions of density functionals beyond the GGA, including (a) meta-generalized gradient approximations, which use not only the local density and its gradient but also its Laplacian and/or orbital kinetic energy density, and (b) hyper-generalized gradient approximations for the correlation energy, which are designed to be compatible with exact exchange.

Variational Density Functional Theory for Excited States

Mel Levy
Tulane University, Department of Chemistry, New Orleans, Louisiana 70118, US

It is shown that there exists a variational Kohn-Sham density-functional theory, with a minimum principle, for the self-consistent determination of an individual excited-state energy and density. Exact properties of the required functional are ascertained, including a Koopmans theorem. This knowledge allows the employment of an effective potential that gives encouraging numerical results, and also helps to explain the success of a recent perturbation theory and its time-dependent counterpart.

1. M. Levy and A. Nagy, Phys. Rev. Lett., 83, 4361 (1999).
2. M. Levy and J. P. Perdew, in Density Functional Methods in Physics, edited by R.M. Dreizler and J. da Providencia (Plenum, New York, 1985).

Comparing the efficiency and accuracy of the projector-augmented wave DFT method (PAW) against Gaussian based DFT methods

Eric J. Bylaska (PNNL), Marat Valiev (UCSD), John H. Weare (UCSD), and James R. Rustad (PNNL)
William R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest Na-

tional Laboratory, P.O. Box 999, Richland, WA 99352 USA
eric.bylaska@pnl.gov

Density Functional Theory (DFT) has proven to be a useful tool for studying many chemically important systems and many numerical methods have been developed to solve DFT equations. Three of the more popular methods include Gaussian basis set methods [1], linear-augmented-plane-wave (LAPW) methods, and pseudopotential plane-wave (PSPW) methods[2]. All three methods can be made very accurate, and have been capable of predicting structures, frequencies, and energetics for a wide class of compounds. However, with rare exceptions, PSPW methods are not used in DFT studies of 3d transition metal (TM) clusters. The lack of PSPW based calculations of these systems is mainly due to the presence of localized 3d states that actively participate in the bond formation. First, the nodeless nature of these states prevents an efficient application of the norm-conserving pseudopotential approximation resulting in the extremely large size of the plane wave basis set. Second, because of the significant overlap between the valence and core density, the latter cannot be simply discarded as it is usually done in pseudopotential methods. In the recent years new techniques have been developed to address these problems and PSPW methods are slowly finding their way into the transition metal cluster chemistry. It would be beneficial for PSPW methods to work well, because Gaussian basis set and LAPW methods lack capabilities. In particular, PSPW methods can perform *ab initio* molecular dynamics extremely efficiently, and treat unit cells up to a few hundred atoms. Another advantage of PSPW methods is that they are transferable from molecules to surfaces to solids. In contrast, Gaussian-based methods have very different basis set requirements for gas and solid phase applications, complicating the transferability of these methods.

The PSPW method used in this study is based on the Projector Augmented Wave (PAW) approach by Blochl[3]. Its parallel implementation and its application to several transition metal complexes is presented. A unique aspect of our PAW code[4] is that it can treat both charged and neutral cluster systems. We discuss how this can be achieved via accurate numerical treatment of Coulomb Greens function with free space boundary conditions. The strategy for parallelizing of the PAW code is based on distributing the plane wave basis across the processors. This is a most versatile approach and is easily implemented using a parallel three-dimensional Fast Fourier Transformation (FFT). We report parallel performance analysis of our program as well as three-dimensional FFT's and discuss large-scale parallelization issues of the PAW code. Using a series of transition metal dimers, monoxides, and dioxides, as well as large transition metal-oxide and aqueous complexes, it is shown that a free space PAW code can give structural parameters and energies in good agreement with more traditional Gaussian based methods[5].

1. D. R. Salahub, Ab Initio Methods in Quantum Chemistry-II, K. P. Lawley (John Wiley and Sons Ltd., New York, 1987), p. 447.
2. R. Car and M. Parrinello, Phys. Rev. Lett. 55, 2471 (1985).

3. P. E. Blochl, Phys. Rev. B 50, 17953 (1994).
4. E.J. Bylaska, M. Valiev, R. Kawai, and J.H. Weare, in preparation
5. R. J. Harrison, J. A. Nichols, T. P. Straatsma, M. Dupuis, E. J. Bylaska, G. I. Fann, T. L. Windus, E. Apra, J. Anchell, D. Bernholdt, P. Borowski, T. Clark, D. Clerc, H. Dachsel, B. de Jong, M. Deegan, K. Dyall, D. Elwood, H. Fruchtl, E. Glendenning, M. Gutowski, A. Hess, J. Jaffe, B. Johnson, J. Ju, R. Kendall, R. Kobayashi, R, Kutteh, Z. lin, R. Littlefield, X. Long, B. Meng, J. Nieplocha, S. Niu, M. Rosing, G. Sandrone, M. Stave, H. Taylor, G. Thomas, J. van Lenthe, K. Wolinski, A. Wong, and Z. Zhang, NWChem, A Computational Chemistry Package for Parallel Computers, Version 4.0" (2000), Pacific Northwest National Laboratory, Richland, Washington 99352-0999, USA.

The description of unpaired electrons in solid state systems

Roberto Dovesi
Theoretical Chemistry Group, V. P. Giuria 5, University of Turin, Italy

The performance of four hamiltonians (LDA, GGA, B3LYP, HF) in ionic and covalent systems.
The cases of the F centers in alkali halides (where the electron is in a very diffuse s type state), of the trapped hole centers in MgO (quite localized p-type state), of the vacancy in diamond (sp hybrid) and of NiO (very localized d type state).

The performance of semi-empirical molecular functionals in solid-state systems

P P Rushton$^{(1,2)}$*, S J Clark*$^{(2)}$*, and D J Tozer*$^{(1)}$
(1) Department of Chemistry University of Durham;
(2) Department of Physics, University of Durham
South Road, DURHAM, DH1 3LE, UK

A recent tendency in functional development has been to choose a flexible functional form, and optimize its parameters by fitting to molecular data. It is important to assess how well these semi-empirical functionals perform for solid state systems, particularly those containing atoms that are absent from the fitting data.

We have used the semi-empirical Hamprecht-Cohen-Tozer-Handy (HCTH) functional to determine lattice constants, cohesive energies, bulk moduli and electronic band gaps for a series of zinc-blende semiconductors. The results degrade significantly as the periodic table is descended, reflecting the predominance of low-atomic-number atoms in the fitting data used to determine HCTH. We investigate whether the results can be improved by choosing more appropriate fitting data.

The HCTH functional does not satisfy the uniform gas limit. We examine how the calculated results change when this condition is imposed; the corresponding changes in molecular properties are also considered.

Modelling the Brønsted acidity of H-faujasite, H-chabazite and H-edingtonite with CRYSTAL-98 periodic code

P. Ugliengo$^{(1)}$*, B. Civalleri*$^{(1)}$*, R. Dovesi*$^{(1)}$ *and N.M. Harrison*$^{(2)}$
(1) Dip. Chimica IFM, University of Torino, Via P. Giuria 7, I-10125 Torino, ITALY
(2) CLRC Daresbury Laboratory, Daresbury, WA4 4AD Warrington; and
Dep. of Chemistry, Imperial College, SW7 2AY London

The Brønsted acidity of Al-substituted faujasite, chabazite and edingtonite is studied with the periodic approach based on gaussian basis set expansion of the crystalline orbitals as coded in CRYSTAL-98 programme. For all considered zeolites, the geometries have been fully optimized by using a semiclassical shell model ion-pair potential method as coded in the GULP programme. For faujasite and edingtonite, the focus has been on the relative stabilities of structures differing in the location of the acidic proton at the highest Si/Al ratio. For chabazite, four different Si/Al ratios have been studied by setting the proton on the most stable position. The B3-LYP hamiltonian, coupled with a 6-31G(d,p) basis set, has then been used to compute the relative stabilities of the resulting structures, the OH stretching frequency and the electric field gradient at the acidic proton nucleus.

For chabazite, the OH stretching frequency does correlate with the Si/Al ratio, in that the higher the Si/Al ratio the lower the OH stretching frequency. For faujasite, the four classical proton locations have been analyzed and the order of stability resulted as O1H(0) > O3H(4) > O2H(8) > O4H(9) in agreement with the experimental observed site occupancy but at variance with the recent results based on QM-Pot methodology (M. Sierka and J. Sauer, JPC B in press) and the full periodic DF/GGA calculation (J.-R. Hill et al., JPC A, 103 (1999) 3772), which both predict the O4H position definitely more stable than the O2H one. The corresponding OH harmonic frequencies has been computed for each H position and compared with the available experimental data as well as with the quoted periodic calculations. Comparison with the results computed with the ONIOM method on large clusters is also addressed.

First-principles calculations for V_xO_y grown on Pd(111)

G. Kresse, S. Surnev, M.G. Ramsey, F.P. Netzer

Institut für Materialphysik, Universität Wien, Sensengasse 8, A-1090 Wien, Austria

An approach to access the stability of oxides growing on top of a metal support is presented. In combination with first-principles calculations, it allows to predict the stable structures as a function of the thickness of the evaporated metal ad-layer and as a function of the oxygen pressure. The ideas are applied to thin vanadium oxide films growing on Pd(111). To investigate the stability of these oxide films, first-principles calculations for more than 50 thin films of V_xO_y on Pd were performed at varying stoichiometry and coverage. The general principles determining the growth of thin vanadium oxide films on Pd(111) are discussed, and the experimental results are interpreted in the light of the first-principles calculations. At 1 ML vanadium coverage, a complicated succession of structures is predicted by the calculations. At high oxygen pressure bulk like V_2O_3 phases are stable.

At lower oxygen pressure, however, a surface stabilised (2 x 2) reconstruction with a formal stoichiometry of V_2O_3 is predicted, and rectangular and hexagonal vanadium-dioxide phases are expected to grow. At very low oxygen pressures, first the vanadium-dioxide phases and then the surface V_2O_3 phase decompose and the liberated V atoms move subsurface. These predictions are in good general agreement with experiment. An important result of the study is that the metal surface stabilises thin films which have no equivalent bulk phases.

Embedded cluster models - a flexible modular implementation for enzymes, zeolites and oxides.

Paul Sherwood
CLRC Daresbury Laboratory, Warrington, WA4 4AD, UK

We will describe our approach to QM/MM calculations using a variety of QM and MM codes and a range of QM..MM coupling paradigms. We will discuss the implementation of the ChemShell package, a Tcl-based scripting language which provides the framework for integration and management of the QM/MM coupling terms. A number of sample applications from the European collaboration QUASI (Quantum Simulation in Industry) will be used to illustrate the use of different packages and approaches to embedding. Some consideration will be given to the technical issues raised by the need to maintain modularity while allowing the exploitation of massively parallel computer systems.

DFT calculations and MD classical simulations of transition metal deposition on metal oxide surfaces

Javier Fernandez Sanz and N. Cruz Hernandez
Universidad de Sevilla , Dpto. Química Física, Facultad de Química, E-41012 Sevilla (SPAIN)

Metal deposition constitutes one of the most appealing methods for the preparation of new materials of technological interest (catalysis, gas sensors, Å). Addition of metal atoms to a surface can in principle look for different targets. Thus, a given relatively inert surface can be promoted by adding an alkali metal like Na. In another direction, specific catalysts are prepared by supporting transition metal atoms on inert surfaces. In these materials several questions are relevant from a microscopic point of view. First we are interested by the properties of the metal surface interface: the nature of the bond, the extension of the surface reduction, etc. Secondly, we would like to know the detailed structure of the particles adsorbed at the surface. This information could help for both a better understanding of the interface and a suitable description of the active sites in a given surface reaction. In this contribution we report on theoretical work aimed to analyze these two aspects in a series of metal-support systems. As inert support we have considered metal oxides such as TiO_2, Al_2O_3, and MgO. On these surfaces, both promoting metals (Na) and transition metals (Pd, Cu, Ag) have been deposited. The nature of the metal-surface interaction has been analyzed by means of *ab initio* quantum mechanical DFT calculations using embedded cluster and periodic slab models. On the other hand, the structure of the supported particles has been analyzed through classical molecular dynamics (MD) simulations using potential functions determined from *ab initio* DFT calculations.

Some recent references:
M. A. San Miguel, C. J. Calzado and J. F. Sanz. Surf. Sci. 1998, 409, 92-100.
C. J. Calzado, M. A. San Miguel and J. F. Sanz. J. Phys. Chem. B 1999, 103, 480-86.
M. A. San Miguel, J. F. Sanz, L. J. Alvarez and J. A. Odriozola, Phys. Rev. B, 1998, 58, 6057-6062.
J. F. Sanz and C. M. Zicovich-Wilson. Chem. Phys. Letters, 1999, 303, 111.

Quantum Molecular Dynamics

M.C. Payne
TCM Group, Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK

Dynamical simulations can be used to perform an unbiased exploration of the phase space of a system. Given their very high computational cost, *ab initio* dynamical simulations can only achieve a very limited exploration of this phase space. Nevertheless, such simulations have had a profound impact on our understanding of some complex systems. I shall illustrate the power of this approach by describing applications of this technique to study catalytic reactions in zeolites [1] and to study surface diffusion [2].

1. I. Stich, J.D. Gale, K. Terakura and M.C. Payne, Chem.Phys.Lett. 283, 402 (1998).
2. N. Marzari, D. Vanderbilt, A. De Vita and M.C. Payne, Phys.Rev.Lett. 82, 3296 (1999).

Dielectric Polarization of Insulating Solids within DFT

Raffaele Resta
Max-Planck Institut für Festköperforschung, D-70506 Stuttgart, Germany;
Permanent address: INFM - Dipartimento di Fisica Teorica, Università di Trieste, I-34014, Italy.
resta@ts.infn.it

The macroscopic polarization of an insulating solid is formally defined as the dipole of a finite sample, divided by the sample volume: such dipole is dominated by surface effects. Typically, one gets rid of surface effects by dealing with extended systems within Born-von Kármán (BvK) periodic boundary conditions, but this does not solve the polarization problem: the dipole is in fact the expectation value of the position operator, which in its usual form is an ill defined operator within BvK.

This long-standing problem has been solved since 1992. At the root of the modern theory is a Berry phase [1]: polarization crucially depends on the phase of the KS orbitals, and cannot be retrieved from their moduli only, i.e. from the charge density. Berry-phase calculations of macroscopic polarization in a vanishing electric field- as needed for studies of piezoelectricity, ferroelectricity, and lattice dynamics- are now routinely performed within DFT. The related, though different, problem of evaluating the polarization induced by a macroscopic field is addressed in a rather different way, namely, by means of linear response (density-functional perturbation theory).

The modern theory even affects the very foundations of DFT. Contrary to a naive expectation, the macroscopic polarization of a correlated system is in principle different from the one of the corresponding KS noninteracting system, as evaluated from the phases of the KS orbitals [2]. An open question is how much does this feature affect practical calculations.

DFT studies, based on the modern theory, have shed new light about the behaviour of oxygen ions in oxides. An observable and very fundamental quantity is the dynamical charge (also called infrared charge) of oxygen in a given solid: by definition it measures the coupling between electric fields and ionic displacements, ergo it measures the macroscopic polarization induced by sublattice displacements when dealing with lattice dynamics, piezoelectricity, and ferroelectricity. While in the extreme ionic limit the oxygen dynamical charge is obviously -2, actual values are highly notrivial, particularly in oxides having a mixed ionic/covalent character. DFT calculations have proved that values as large as -6 are common in ferroelectric oxides; the physical mechanisms responsible for this and other interesting phenomena have been elucidated [3].

1. R. Resta, J. Phys.: Condens. Matter 12, R107 (2000).
2. X. Gonze, Ph. Ghosez, and R.W. Godby, Phys. Rev. Lett. 74, 4035 (1995); R. Resta, Int. J. Quantum. Chem. 75, 599 (1999).
3. R. Resta, M. Posternak, and A. Baldereschi, Phys. Rev. Lett. 70, 1010 (1993); M. Posternak, R. Resta, and A. Baldereschi, Phys. Rev. B 50, 8911 (1994); Ph. Ghosez, J. -P. Michenaud, and X. Gonze, Phys. Rev. B 58, 6224 (1998).

Zirconium and lead in SiO_2: dielectric and dynamical properties

X. Gonze, Fr. Detraux and G.-M. Rignanese
Unité de physico-chimie et de physique des matériaux, Université Catholique de Louvain, Boltzmann, Pl. Croix du sud 1, 1348 - Louvain-la-neuve, Belgium

The dielectric properties of silicas are considerably modified by the presence of foreign atoms, including lead or zirconium. Incorporation of the latter in the silica framework gives an interesting high-k dielectrics for microelectronics applications, while the former is used in houseware industry. Within density-functional theory, we first computed structural properties of mineral alamosite ($PbSiO_3$) and zircon ($ZrSiO_4$), then determined the formation energy associated with different sites for zirconium and lead impurities in quartz. We also focused on the response of these materials to homogeneous electric fields and atomic displacements, in order to determine dielectric and dynamical properties, using density-functional perturbation theory. Based on thermodynamical grounds, we find that a lead atom prefers to substitute silicon, to be associated with an oxygen vacancy, or to be an interstitial (despite its size). The experimental change of index of refraction is correctly reproduced. We discuss the change of static dielectric constant associated with different models for the zirconium impurity, and compare it with experimental data.

Time Dependent Current Density Functional Theory and the Macroscopic Polarisation of Nonmetallic Crystals

P.L. de Boeij, F. Kootstra, R. van Leeuwen and J.G. Snijders
Theoretical Chemistry, Rijksuniversiteit Groningen, Nijenborgh 4, 9746 AG Groningen, The Netherlands
p.l.de.boeij@chem.rug.nl, http://theochem.chem.rug.nl

It is well established by now that macroscopic polarisation of (nonmetallic) crystals is not a property that can be derived from the periodic charge density in the bulk of the crystal. In particular, surface charges have dominant contributions. Nevertheless one can show that the bulk intrinsic part of this macroscopic polarisation, which can be probed through the dielectric function in optical experiments, is a well defined property of the current density in the bulk.

The Kohn-Sham system of independent particles that is capable of describing this macroscopic polarisation correctly and that uses the common periodic boundary condition, has to be determined by effective scalar and vector potentials. (see e.g. [1])

We show that the extension of time dependent DFT which, for the first time, includes current dependent functionals [2] is quite succesful in describing this dynamic polarisation, and we obtain good results for several semiconductors [3]. In this description exchange and correlation effects contribute to both the lattice periodic potential and to the macroscopic effective electric field.

1. F. Kootstra, P.L. de Boeij and J.G. Snijders, J. Chem. Phys. 112, 6517 (2000), Phys. Rev. B 62, 7071 (2000).
2. G. Vignale and W. Kohn, Phys. Rev. Lett. 77, 2037 (1996).
3. P.L. de Boeij, F. Kootstra, R. van Leeuwen and J.G. Snijders, submitted.

Using MTOs to extract the physics/chemistry

Tanusri Saha and Ole Krogh Andersen
Max-Planck-Institut für Festkörperforschung, Postfach 800665, DE-70506 Stuttgart

Muffin tin orbitals constitute an accurate and flexible local-orbital basis set which may be chosen as minimal (e.g. sp3 for diamond). This is important not only for the economy of DF calculations, but also for the interpretation of results and for the construction of model Hamiltonians. The latter may for instance include electronic correlations or enable one to do molecular dynamics for large systems. Examples for high-temperature superconducting cuprates, ladder compounds and colossal magneto-resistive double perovskites will be given.

Applications and limits of DFT in the calculation of magnetic properties

Ilaria Ciofini and Claude A. Daul
Department of Chemistry, University of Fribourg, Pérolles, CH 1700 Fribourg, Switzerland

An overview of computational techniques based on the Density Functional Theory for the calculation of the magnetic properties of molecular and supramolecular assemblies is presented. Three different approaches to compute the exchange coupling constant (J) are reviewed, i.e. the Broken Symmetry (BS) Technique, the Single Determinant (SD) Approach, and the Spin Projection Method. The BS approach has been widely applied to clusters containing several paramagnetic metal centres or to paramagnetic organic radical species. The SD approach has been originally developed to compute the multiplet structure and electronic spectra of transition metal complexes, but has recently been applied successfully to compute the splitting of spin manifolds of molecular magnets. The latter method, is mainly an extension of the HF concept of spin de-contamination to DFT. In the field of molecular magnetism DFT is becoming a convenient alternative to more sophisticated and time consuming post-HF, Dedicated CI methods and many applications appeared in the last years. Here we present a short review of recent DFT calculations of the magnetic structure of transition metal binuclear systems and complexes containing one paramagnetic transition metal ion coupled to organic radicals. Some applications to systems where electron delocalisation or localisation extends over two or more metallic centres, e.g. in mixed valence compounds, are also presented. Finally, the importance and the limits of cluster based calculations in order to elucidate local properties of extended systems, i.e. for solids, will be underlined.

Charge distribution and EFGs in Cuprates using LDA+U within the LAPW method

P. Blaha
Inst. F. Physical and Theoretical Chemistry, TU Vienna, Austria

It is well known that conventional bandstructure calculations based on LSDA fail to predict the correct magnetic and/or insulating ground state of many late transition metal oxides. This is in particular true for the non-superconducting parents of the high Tc cuprates, which are antiferromagnetic (AF) insulators, whereas band theory predicts them as non-magnetic metals. Various schemes for improvements with more or less empirical character have been put forward and the LDA+U method is one of them. Of course, LDA+U calculations do get the proper ground state for these AF cuprates, but here we investigate whether LDAU+U also leads to correct charge densities in these systems.

The electric field gradient (EFG) depends sensitively on the non-sphererical charge distribution around an atom. It can be measured very accurately and thus provides a sensitive

test of the quality of a calculation. Previously we have found, that the EFGs in both, doped and undoped cuprates, is well described by conventional LDA calculations for all atomic sites except the Cu-site (Cu2) in the CuO_2 planes, that is crucial for superconductivity. For these Cu2-sites the theoretical Cu-EFG is too small by a factor of two.

Application of the LDA+U method in general gives a significant improvement of this situation. For all AF cuprates the anisotropy of the charge density around the planar Cu site is enlarged, the Cu d-hole gets solely $d_{x^2-y^2}$ character and the resulting EFG increases and agrees well with experiment. The EFGs at the other sites are almost uneffected and remain in good agreement with experiment too.

Unfortunately, for the superconducting (nonmagnetic) cuprates the improvement is not so clear. For $YBa_2Cu_3O_7$ various magnetic solutions are possible and could be interpreted as “frozen” spin-fluctuations. For AF order the EFG is in agreement with experiment, while for the nonmagnetic solution it is still too small.

Electronic structure of magnetic oxide: LDA+U

A.I. Lichtenstein
University of Nijmegen, 6525 ED Nijmegen, The Netherlands

Density functional scheme have been highly successful for the electronic structure calculations of different non-correlated systems. We discuss some failure of the local density approximation (LDA) for the charge, spin and orbital ordering in transition metal compounds. General formulation of LDA+U method which takes into account local Coulomb correlations for d-shell of transition metals in the crystal within the mean-field approximation is present [1]. This approach describe well the antiferromagnetic Mott insulators and rare-earth systems. Electronic structure, spin and orbital ordering of transition-metal (TM) oxides are investigated in framework of rotationally invariant LDA+U method. We analyzed the magnetic interactions in MnO and NiO and made comparison with the LDA results. Mechanism of the orbital polarization is also related to the screened Coulomb interactions in 3d-shell. Numerical calculations successfully explain spin and orbital magnetic ordering in FeO and CoO [2] as well as the origin of surface electronic states in NiO [3].

1. V.I. Anisimov, F. Aryasetiawan, and A.I. Liechtenstein. J. Phys.: Condens. Matter. 9, 767 (1997). The full-potential LMTO-version of LDA+U code: http://www.physics.rutgers.edu/ savrasov
2. I. V. Solovyev, A. I. Liechtenstein, and K. Terakura, Phys. Rev. Lett., 80, 5758 (1998).
3. S.L.Dudarev, A.I. Liechtenstein, M.R. Castell, G.A.D. Briggs, and A.P. Sutton, Phys. Rev. B. 56, 4900, (1997).

Cu valency change induced by O doping in YBCO

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

An *ab initio* local spin density study of $YBa_2Cu_3O_6$, $YBa_2Cu_3O_{6.5}$, and $YBa_2Cu_3O_7$ is presented. The method includes self-interaction corrections for the Cu d states, which enables a description of various valency configurations of both planar and chain Cu atoms. For $YBa_2Cu_3O_6$ the antiferromagnetic and insulating state is described with planar (chain) Cu occurring in a divalent (trivalent) state. The evolution in the CuO_2 plane from insulating to metallic behaviour upon oxygenation is accomplished by the delocalisation of the majority Cu $d_{x^2-y^2}$-O2 p_x-O3 p_y band.

First principles predictions of Li intercalation in titania.

Marina V. Koudriachova $*^{(1)}$, *Nicholas M. Harrison*$^{(2)}$ *and Simon W. de Leeuw*$^{(1)}$
(1) Computational Physics, TU Delft, Lorentzweg 1, 2628 CJ Delft, the Netherlands
(2) Department of Chemistry, Imperial College of Science, Technology and Medicine, London, SW7 2AY, U.K.

Lithium-rechargeable batteries have attracted widespread attention due to their high energy densities and high open circuit voltage (OCV). The performance of the battery is controlled by the electrochemical properties of electrodes, which determine the shape of OCV. The design of new battery materials requires a microscopic understanding of the stable sites and diffusion pathways which is very difficult to obtain from experiment. Therefore, first principles simulation, which provides accurate and reliable energy surfaces, has a key role to play in identifying and characterising prospective electrode materials. Here we present a new model of Li-intercalation into rutile and anatase structured titania developed from first principles calculations [1]. The model includes both thermodynamic and kinetic effects and explains the observed differences in intercalation behaviour and their temperature dependence. The important role of strong local deformations of the lattice and elastic screening of inter-lithium interactions is demonstrated. This screening mechanism leads to interactions which vary strongly with concentration making the parametrisation of the Monte Carlo calculations of OCV not feasible. Instead the OCV was obtained through numerical differentiation of the energy which approximates the free energy at low temperatures. The mechanisms which underly the thermodynamics and kinetics of Li intercalation are dominated by the strong coupling between the charge, structural and spin degrees of freedom. The details of charge and spin distributions are examined and the associated electronic structure discussed. The charge and spin densities donated to the lattice were found to be not homogeneously distributed.The majority of

the charge localises on Ti-sites neighbouring the Li-ion but the spin is localised on the second nearest neighbour Ti-ions.To the authors knowledge this is the first observation of, so called, spin charge separation in first principles calculations although the concept has become an important component of recent work on high-T_c superconductivity.

In addition a new phase of $LiTiO_2$ is reported. It was observed in electrochemical experiments, but the structure was not resolved [2]. The model of diffusion limited intercalation developed here has a number of consequences for the design of new battery materials and extends the class of prospective systems. For instance, ageing in anatase can be avoided by restricting the insertion fraction and efficient insertion is much more likely to be achieved along the tetragonal *c*-direction than the *a*-direction as in current devices.

1. M.V.Koudriachova, N.M. Harrison, S.W. de Leeuw. Phys.Rev.Lett. **86** (2001) 1275
2. W.J.Macklin and R.J.Neat, Solid State Ionics 53-56, 694-700 (1992)

Charge trapping in cubic Alkali Halides and Oxides: The charge localisation problem in the DFT calculations.

J.L. Gavartin and A.L. Shluger
Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK
j.gavartin@ucl.ac.uk

Untill recently the problems of charge (spin) localisation in disordered crystals have been considered either phenomenologically, or using semiquantitative tight-binding Hamiltonians. Recent advances in density functional theory suggest this approach to be a method of choice for the quantitative analysis of any adiabatic many-electron problem. However, there is a growing body of evidence, that the density functional predictions are biased towards delocalised solutions.

We report the applications of the Spin Density Functional Theory to several problems in crystals, where both localised and extended electron states are possible. In such situation any bias of the theory towards one type of solutions can be critical and might ultimately lead to qualitatively wrong predictions. One example is a localisation of charge (or spin) arising from a strong electron-phonon coupling.

We review the application of the density functional theory to three practical problems:
i) Peierls instability in the 1D metallic chains;
ii) Exciton and hole self-trapping in Sodium Chloride; and
iii) Weak electron localisation in thermally disordered Magnesium Oxide.

Our results demonstrate that in all three cases, the DFT calculations clearly underestimate a tendency for localisation in favour of extended electronic states. Moreover, our calculations predict no self-trapping for either an exciton or a hole in alkali-halides, which contradicts the existing experimental evidence.

We discuss the effects of the energy functionals, boundary conditions and basis sets (plane-wave and atomic), and compare where available the DFT results with the unrestricted Hartree-Fock and post Hartree-Fock calculations.

Quantum mechanics of the Earth's mantle minerals

Artem R. Oganov, John P. Brodholt, G. David Price
University College London, Gower St., London WC1E 6BT

All our present knowledge of the structure and composition of the Earth's interior is obtained by a combination of seismological observations, cosmochemical constraints, and the knowledge of physical properties of minerals. Unfortunately, the relevant properties and behaviour of minerals at extreme temperature-pressure conditions of the Earth's interior are usually known very poorly from experiment. State-of-the-art *ab initio* simulations are capable of giving the desired information. Using quantum-mechanical calculations, we resolve some of the outstanding geological problems related to the lower mantle of the Earth.

Our static and molecular dynamics simulations were performed within the generalised gradient approximations (Perdew-Wang 1991) using a plane wave basis set and ultrasoft pseudopotentials as implemented in the VASP code (Kresse, Furthmuller, 1991). I shall discuss the following several case studies and their global geological implications.

The Al_2SiO_5 polymorphs (kyanite, andalusite, sillimanite) have a phase diagram, which proved to be difficult to study experimentally because of very small energy difference between the phases; for the same reason this diagram is a challenge for theory. It was suggested (Ahmed-Zaid and Madon, 1991) that a close-packed high-pressure phase with the V_3O_5-like structure is stable and can be the main mineral of Al in the lower mantle. Our simulations (Oganov and Brodholt, 2000) successfully reproduce the experimental phase diagram, and show that at high pressures Al_2SiO_5 breaks down into a mixture of oxides instead of transforming into a new phase.

As metastable phases, the Al_2SiO_5 minerals can persist well beyond their stability fields, until at 40 GPa andalusite and sillimanite spontaneously transform: andalusite into an amorphous phase, and sillimanite into a phase with the same space group (isosymmetric polymorphism) (Oganov et al., 2001a). Mechanism of these transitions is analysed in detail, and new general insights into chemical bonding are obtained.

$MgSiO_3$ perovskite, the major Earth-forming mineral (70mantle, or 40(24-136 GPa, 1500-4000 K) using *ab initio* molecular dynamics. The calculations yield accurate equation of state, thermoelastic properties, and elastic constants (Oganov et al. 2001b,c). With these properties for the first time we were able to quantitatively analyse seismic tomography data. These results substantially extend our understanding of the Earth's dynamics, plate tectonics, and generation of earthquakes and volcanism.

Other potentially important mantle phases (MgO, FeO, etc.) are the subject of our current research.

Ahmed-Zaid I., Madon M. (1991). Nature, 353, 426-428.
Kresse G., Furthmuller J. (1996). Comput. Mater. Sci., 6, 15-50.
Oganov A.R., and Brodholt J.P. (2000). Phys. Chem. Minerals, 27, 430-439.
Oganov A.R., Price G.D., Brodholt J.P. (2001a). Acta Crystallographica, Ser. A. Submitted.
Oganov A.R., Brodholt J.P., Price G.D. (2001b). Earth Planet. Sci. Lett., 184, 555-560.
Oganov A.R., Brodholt J.P., Price G.D. (2001c). Nature (under review).

First-principles electronic structure simulations for very large systems

Daniel Sánchez-Portal,[1] *Emilio Artacho*[2]*, Alberto García*[3]*, Julian Gale*[4]*, Javier Junquera*[2]*, Pablo Ordejón*[5]*, and José M. Soler*[2]
(1) Departamento de Física de Materiales, Facultad de Química, Universidad del País Vasco, Apt.1072, 20080 San Sebastián, Spain
(2) Departamento de Física de la Materia Condensada, C-III, Universidad Autónoma, 28049 Madrid, Spain
(3) Departamento de Física de la Materia Condensada, Universidad del País Vasco, Apdo. 644, E-48080 Bilbao, Spain
(4) Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, SW7 2AY, U.K.
(5) Institut de Ciència de Materials de Barcelona, CSIC, Campus de la UAB, Bellaterra 08193, Barcelona, Spain

We have developed a very optimized method to perform first-principles electronic structure simulations in very large and complex systems. Our scheme utilizes some of the most standard approximations for electronic calculations in condensed systems such as, pseudopotentials to replace the core electrons, DFT in its local or gradient corrected versions, or the use of real space grids to perform some the operations. One of the key differences is, however, the election of the basis set. Our basis set is a linear combination of numerical orbitals (NAOs), which are constructed from the solutions of the atomic pseudopotentials, being constrained to be zero beyond a given radius. Most of the efficiency of the method relies on this basis. This is not just because the NAOs provide a much smaller basis than other common choices (like plane-waves) but because, by exploiting their locality, the computational cost for the construction and storage of the Hamiltonian and the electronic density is made to scale linearly with the system size. Due to this central role, a considerable effort has been devoted to obtain orbital bases that meet the standards of precision of conventional first-principles calculations, while keeping as short a range as possible. Simple schemes to generate transferable bases that satisfy both requirements will be presented.

The order-N construction of the self-consistent Hamiltonian is already a great advantage. For insulating systems we can go further, and the whole calculation can be made to scale linearly. This is achived in two steps: i) The wave functions are not explicitly orthogonalized. Instead, we use a modified energy functional, whose minimization produces orthogonal wave functions and the same energy and density as the Kohn-Sham functional. ii) The use of localized Wannier-like wave functions.

Forces and stresses are efficiently and accurately calculated, allowing for structural relaxations and molecular dynamics simulations.

The result of this effort has been implemented in the SIESTA code, which has been applied with success to very different systems, such as nanotubes, biomolecules, adsorbates in surfaces, amorphous and liquid semiconductors, etc. I will review briefly some of these applications.

Quantum Monte Carlo study of oxides

R.J. Needs and M.D. Towler
TCM Group, Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK

An accurate treatment of electron correlation in real materials presents a formidable challenge to condensed matter theorists and quantum chemists alike. We use the fixed-node diffusion quantum Monte Carlo (DMC) method, which is one of the most accurate methods known for calculating the energies of many-electron systems. In this talk I will describe DMC calculations on oxide materials such as NiO. The trial wave function is of central importance in the DMC method, and I will discuss the relative merits of different trial wave functions for these systems.

Excited States and Total Energies from Ab Initio Many-Body Theory

Rex Godby
Department of Physics, University of York, York YO10 5DD, United Kingdom

Ab initio many-body perturbation theory based on Green's functions has become a standard computational technique for calculating quasiparticle and optical excitation energies of atoms, molecules and solids, especially at the level of the GW approximation. In the first part of my talk I will review this theory and the associated computational techniques, presenting examples of its successes and limitations [1-5].

In the second part of the talk I will turn to the ground-state total energy. Progress has become slow in constructing ever better approximations to the exact Kohn-Sham total-energy functional of density-functional theory that are applicable in a wide range of situations. In my view this reflects the extreme complexity of the exact functional, including, for example, its ultra-non-local dependence on the electron density in certain situations.

These non-analyticities in the exchange-correlation energy functional may be circumvented by reformulating the total energy using Green's-function many-body perturbation theory, starting from a Kohn-Sham non-interacting system as the "zeroth-order" approximation, as a practical alternative to DFT. A real-space-imaginary-time representation [1,4,5] offers an efficient framework for implementing a fully self-consistent GW approximation, which is a conserving approximation. We show very promising results for total energies of homogeneous and inhomogeneous systems within such an approximation [6]. We shall also demonstrate promising results using an related, very inexpensive, approach [7] which uses a very simple model self-energy within the framework of generalised Kohn-Sham theory, and costs barely more than a LDA calculation.

1. H.N. Rojas, R.W. Godby and R.J. Needs, Phys. Rev. Lett. 74 1827 (1995).
2. I.D. White, R.W. Godby, M.M. Rieger and R.J. Needs, Phys. Rev. Lett. 80 4265-8 (1998).
3. Martin M. Rieger and R.W. Godby, Phys. Rev. B 58 1343 (1998).
4. Martin M. Rieger, L. Steinbeck, I.D. White, H.N. Rojas and R.W. Godby, Computer Physics Communications 117 211-228 (1999).
5. L. Steinbeck, A. Rubio, L. Reining, M. Torrent, I. D. White and R.W. Godby, Computer Physics Communications 125 105-118 (2000).
6. P. García-González and R.W. Godby, Phys. Rev. B 63 075112 (2001).
7. P. Sánchez-Friera and R.W. Godby, Phys. Rev. Lett. 85 5611 (2000).

Further references and links available at http://www-users.york.ac.uk/ rwg3/talks.html

List of participants and email addresses

I.V. Abarenkov	aiv@iva.usr.pu.ru
M. Alfredsson	mariaa@ri.ac.uk
H. Aourag	haourag@hotmail.com
X. Aupi	aupixv@sbu.ac.uk
A. A. Bagatur'yants	sasha@photonics.ru
F. Bawa	bawa@arrhenius.che.chalmers.se
A. Becke	becke@chem.queensu.ca
B. Biehler	biehler@libertysurf.fr
P. Blaha	blaha@theochem.tuwien.ac.at
P. de Boeij	p.l.de.boeij@chem.rug.nl
S. Braithwaite	spencer@ri.ac.uk
E.J. Bylaska	eric.bylaska@pnl.gov
R. Catlow	richard@ri.ac.uk
I. Ciofini	ilaria.ciofini@unifr.ch
S. Clark	s.j.clark@durham.ac.uk
D. Coombes	davidc@ri.ac.uk
C. Cooper	saccac@cardiff.ac.uk
F. Corà	furio@ri.ac.uk
S. Cristol	sylvain@ri.ac.uk
N. Cruz-Hernandez	norge@cica.es
I. Czekaj	ncczekaj@kinga.cyf-kr.edu.pl
C. Daul	Claude.Daul@unifr.ch
A. Davies	A.Davies@surrey.ac.uk
B. Delley	bernard.delley@psi.ch
R. Dovesi	dovesi@ch.unito.it
S. Elliott	Simon.Elliott@tcd.ie
A. Ferrari	aferrari@ch.unito.it
A. Foster	asf@fyslab.hut.fi
M. Foster	martinf@ri.ac.uk
I. Franklin	ilona@ri.ac.uk
S. French	sam@ri.ac.uk
J.D. Gale	j.gale@ic.ac.uk
J.L. Gavartin	j.gavartin@ucl.ac.uk
M. Gillan	ucapmjg@ucl.ac.uk
R. Godby	rwg3@york.ac.uk
X. Gonze	gonze@pcpm.ucl.ac.be
R. Grybos	ncgrybos@cyf-kr.edu.pl
N. Handy	nch1@hermes.cam.ac.uk
N.M. Harrison	n.m.harrison@dl.ac.uk
N. Henson	neil.henson@lanl.gov
S. Islam	M.Islam@surrey.ac.uk
T. Johnson	Tobias.Johnson@inoc.chalmers.se
K. Johnston	karen.johnston@qub.ac.uk
M.V. Koudriachova	marina@barium.tn.tudelft.nl

G. Kresse	Georg.Kresse@univie.ac.at
N. de Leeuw	n.h.deleeuw@reading.ac.uk
C. Lennartz	Christian.Lennartz@basf-ag.de
M. Letz	Ltz@schott.de
M. Levy	mlevy@mailhost.tcs.tulane.edu
A. Lichtenstein	A.Lichtenstein@sci.kun.nl
P.E. Lippens	lippens@univ-montp2.fr
F. Lopez-Geijo	f.lopez-gejo@ucl.ac.uk
S. Mangwejane	ngoepep@unin.unorth.ac.za
A. Markman	a.markmann@ucl.ac.uk
D. Middlemiss	dsm3@st-and.ac.uk
M. Mistry	manisha@ri.ac.uk
D. Mkhonto	ngoepep@unin.unorth.ac.za
B. Montanari	b.montanari@ic.ac.uk
D. Munoz-Ramos	d.munoz@qf.ub.es
R. Needs	rn11@phy.cam.ac.uk
C. Nelson	chrisn@ri.ac.uk
J. Neville	jonathanneville@hotmail.com
C. Niederhalt	christoph.niederalt.cn@bayer-ag.de
D. Ntoahae	ngoepep@unin.unorth.ac.za
A.R. Oganov	a.oganov@ucl.ac.uk
L. Ojamäe	lars@physc.su.se
E. Orhan	emmanuelle.orhan@univ-rennes1.fr
E. Patino	ejp@fyslab.hut.fi
M. Payne	mcp1@phy.cam.ac.uk
J. Perdew	perdew@mailhost.tcs.tulane.edu
B. Peric	bperic@rudjer.irb.hr
L. Pollack	lpollack@xula.edu
A. Ramirez-Cuesta	a.j.ramirez-cuesta@rdg.ac.uk
N. Ramsahye	naseem@ri.ac.uk
M. Reinhold	m.reinhold@rocketmail.com
R. Resta	R.Resta@fkf.mpg.de
F. Rogemond	Francois.Rogemond@univ-st-etienne.fr
P. Rushton	p.p.rushton@durham.ac.uk
I. Saadoune	iman@ri.ac.uk
T. Saha	T.Dasgupta@fkf.mpg.de
D. Sanchez-Portal	sqbsapod@scsx03.sc.ehu.es
J.F. Sanz	sanz@cica.es
J. Sauer	js@qc.ag-berlin.mpg.de
A. Sayede	sayede_adlane@hotmail.com
M. Scheffler	scheffler@FHI-Berlin.MPG.DE
C. Schelle	schelle@mrl.ucsb.edu
D. Schoemaker	schmaker@uia.ua.ac.be
A. Seitsonen	aps@prr.mpi-stuttgart.mpg.de
P. Sherwood	P.Sherwood@dl.ac.uk
G. Silly	gilles.silly@univ-lemans.fr
A. Simperler	alex@ri.ac.uk

A.A. Sokol	alexei@ri.ac.uk
M. Szymanski	m.szymanski@ucl.ac.uk
W. Temmerman	W.M.Temmerman@dl.ac.uk
D.J. Tozer	d.j.tozer@durham.ac.uk
P. Ugliengo	ugliengo@ch.unito.it
J. Wakelin	jon.wakelin@ceram.co.uk
A. Wander	A.Wander@dl.ac.uk
M. Warren	Michele.C.Warren@man.ac.uk
D. Willock	willockdj@cardiff.ac.uk
K. Wright	kate@ri.ac.uk

4.3 ESF Workshop/Conference Announcements

4.3.1 CECAM/PSIK Workshop on Oxide-Metal Interfaces

Progress and Challenges

Lyon, 4-6 October, 2001

Christian Elsaesser and I are organising a two day workshop on this theme, which will take place in Lyon from 4 to 6 October this year, financially supported by the STRUC-PSIK network and CECAM. The idea is to look at the state of the art in PSI-k style theory, and confront it with some real problems and challenges; for this reason a number of experimentalists and at least three or four representatives from industry will be taking part. We welcome further participants from the Psi-k community who could obtain some financial support from the network. A programme of speakers and further details may be found on the website:

`http://titus.phy.qub.ac.uk/Oxide_Metal_2001/announcement.html`

Professor Mike Finnis
Atomistic Simulation Group
School of Mathematics and Physics
The Queen's University of Belfast
Belfast BT7 1NN, Northern Ireland

5 News from UK's CCP9

UK's Collaborative Computational Project 9 on "Computational Studies of the Electronic Structure of Solids"

Collaborative Computational Project 9 (or CCP9) is the main national network for computational electronic structure. in the UK. It includes 33 different research groups, working in 11 main subject areas. The group web pages at: http://psi-k.dl.ac.uk/CCP9/ include up to date details of all the CCP9 collborative projects, the working group membership, workshops and training courses which we organise.

It is with great sadness that we report the death of Professor David Bullett. David has been a long standing member of CCP9 and has been a leading member of the UK electronic structure community. In Cambridge in the mid 1970's he developed, with PW Anderson, the concept of the chemical pseudopotential. This explains why hopping matrix elements between local atomic orbital basis functions are short ranged, and hence plays an important part in the foundation of tight-binding theories of electronic structure. These ideas were central to the development of real-space electronic structure methods at Cambridge and elsewhere, and provide the foundations for several of the modern approaches to order N electronic structure calculation. David Bullett moved to the University of Bath where he continued to work on tight binding methods, and he also became a very successful department head. Unfortunately he became ill with a brain tumor, from which he died on 13 July.

In other news, the CCP9 renewal proposal "Linear Scaling Methods for nanoscience materials and chemistry" has been submitted to the research council EPSRC. The project PI is Prof M Gillan of University College London, and the flagship project collaboration involves groups in Cambdridge (Artacho), Oxford (Briggs), and Imperial College London (Gale). The proposal also includes support for international visitors to UK groups, and workshops and hands on tranining courses relating to several CCP9 related projects.

James F. Annett
Chairman, CCP9

6 General Workshop/Conference Announcements

6.1 Summer School on DFT

3rd circular

2nd Summer School on Computational Physics: Density Functional Theory

The Centre for Computational Physics (http://cfc.fis.uc.pt/) is organizing its 2nd Summer School on Computational Physics: Density Functional Theory. It will take place at Caramulo, a mountain resort in central Portugal, between August 28, 2001 and September 1, 2001.

The school will start with some introductory lectures on Density Functional Theory, and will cover its computational aspects, modern developments, difficulties and future prospects. There will be both theoretical lectures and practical sessions.

The school webpage is at http://cfc.fis.uc.pt/events/DFT2001/.

We only have five places to fill, so hurry if you are interested!

Please forward this message to anyone you think might be interested.

Fernando Nogueira

7 General Job Announcements

Post-Doctoral Positions at the EPFL (Lausanne) Institute for Numerical Research in the Physics of Materials (IRRMA)

There are currently post-doctoral positions available for talented and motivated individuals at the Institute for Numerical Research in the Physics of Materials (IRRMA) of the EPFL in Lausanne. The positions are for one year and could be extended for a second one. These individuals will join research projects in computational condensed matter physics or chemistry.

Research topics are:

(i) disordered network forming materials (vitreous materials, thin dielectric films on silicon, aqueous systems)

and

(ii) heterogeneous catalysis on oxide surfaces.

Previous experience with computational techniques based on density functional theory is requested.

The interested candidates should send their

(1) curriculum vitae,
(2) publication list,
(3) preference for research topic,
(4) one or two reprints representative of previous research,
(5) confidential letters of recommendation to:

Alfredo Pasquarello
IRRMA-EPFL
PPH-Ecublens
CH-1015 Lausanne
Switzerland

Tel : +41 21 693 44 16
Fax : +41 21 693 66 55
E-mail : Alfredo.Pasquarello@epfl.ch

Postdoctoral Position(s) in Computational Materials Science

Forschungszentrum Jülich, Germany

One (and possibly two) post-doctoral positions are available in the Institute of Solid State Research (IFF) of the Forschungszentrum Jülich. This position is in addition to that held by Dr Jaakko Akola, and all are within the framework of a "Transfer Project" funded by the Federal German Ministry for Education and Research (BMBF) and industrial partners. Other groups involved in the project are those of: K. Binder (Universität Mainz), D. Heermann (Universität Heidelberg), K. Kremer (Max-Planck-Institut für Polymerforschung, Mainz), and M. Parrinello (now at CSCS, Manno, Switzerland).

The goal of the project is to develop, extend, and apply modern methods of computer simulation to problems of current interest, including those of our industrial partners. A long-term aim is to extend the applicability of density functional (DF) methods to larger systems, and to provide more reliable force fields for use in classical simulations of very large systems. In addition to basic problems in DF theory, our group will focus on simulations involving structure and reactions of organic molecules and polymers, and the structure and properties of silicates and other minerals. Prof. P. Ballone (University of Messina) is actively involved in the project. We have generous access to the computing facilities in Jülich, one of the largest supercomputer centers in Europe.

The applicant should have experience in the area of density functional theory and its applications; experience with Car-Parrinello techniques would be an advantage. Molecular dynamics and Monte Carlo calculations using classical force fields are also being carried out. The salary, which depend on marital status and number of dependents, will be based on German tarifs, such as BAT. There is no restriction to citizens of the European Union, but this would have benefits to both sides.

Requests for further information and applications should be addressed to:

R. O. Jones
Forschungszentrum Jülich
I F F
D-52425 Jülich, Germany
e-mail : `r.jones@fz-juelich.de`
Tel. : (+49) 2461-614202
Fax : (+49) 2461-612850

Information about recent work of the group and access to recent publications can be obtained under the URL:

http://www.fz-juelich.de/iff/personen/R.Jones

Postdoctoral Fellowships

Tsukuba, Japan

The Japan Society for the Promotion of Science (JSPS) is offering a number of postdoctoral fellowships for two years starting between 1 April and 30 September 2002. The basic requirements for the fellowships are:

1. The candidate must be a citizen of a country which has diplomatic relations with Japan.
2. The candidate must possess a PhD obtained within six years prior to 1 April 2002 (not earlier than 2 April 1996).

The stipend will be 320,000 Yen per month. Accomodation is provided free of charge. Some financial support for travelling and research expenses is available. Air ticket to Japan will be covered.

More details of the fellowships may be found in

http://www.jsps.go.jp

under Program (English version).

The successful candidate will be working in the newly founded Research Institute for Computational Sciences in Tsukuba, Japan, headed by Prof. K. Terakura. S/he is expected to work in one of the following fields:

- Excited-state theories (GW approximation, Time-Dependent Density Functional Theory) and their applications.
- Development of total energy method for molecules and solids
- Other areas such as transport in nanomaterials are also possible.

A background in electronic structure theory is expected and knowledge of many-body theory is desirable but not necessary.

Candidates wishing to apply for the fellowships are requested to send a letter of recommendation and a CV containing a short description of past and present research activities and a list of published articles to the address below, by ordinary mail or e-mail.

The deadline is 6 August 2001.

Ferdi Aryasetiawan
Research Institute for Computational Sciences (RICS),
National Institute of Advanced Industrial Science and Technology,
AIST Tsukuba Central 2, 1-1-1, Umezono, Tsukuba, Ibaraki,
305-8568, Japan

E-mail: f-aryasetiawan@aist.go.jp
Tel: +81-298-61-3419
Fax: +81-298-61-3171

PROJECT STUDENTSHIP IN COMPUTATIONAL MATERIALS SCIENCE

University of Exeter, UK

An EPSRC funded three year project studentship is available from October 1 for theoretical work on interstitial clusters created by ion-implantation in silicon. The work will be linked with experimental work being carried out in the UK and Europe.There are considerable opportunities for travel.

The researcher will join a large and active group working on defects in a range of semiconductors. The group has access to national supercomputers and is part of a consortium which has recently acquired a large machine. The applicant will be registered for a PhD degree.

Applicants should possess a first or upper second class degree in Physics or a relevant discipline.

Normal EPSRC rates apply.

The historical city of Exeter is situated in the attractive South Western part of the UK close to two National Parks. It is in easy drive of a number of surfing beaches.

Applicants should send a CV and arrange for three references to be sent, preferably by e-mail, by 17 September.

R. Jones
Professor of Computational Physics,
School of Physics,
University of Exeter,
Exeter EX4 4QL

Tel +0044 (0) 1392 264134
Fax +0044 (0) 1392 264111

email: r.jones@exeter.ac.uk

Information on the group's activities can be found on

http://newton.ex.ac.uk/research/semiconductors/theory/jones/

POSTDOCTORAL POSITION

IN NATIONAL ENERGY RESEARCH SCIENTIFIC COMPUTING CENTER (NERSC)

LAWRENCE BERKELEY NATIONAL LABORATORY

The scientific computing group at NERSC has one immediate postdoctoral opening in nanoscale electronic structure calculations. The hired person is going to work with Dr. Lin-Wang Wang in (1) electronic structure calculations of various nanostructures (e.g., CdSe colloidal quantum dots, rods, arrays); (2) methodology developments for nanoscale electronic structure calculations. This position is a result of a recent DOE funded nanoscience initiative project. Close collaborations with experimental groups at lawrence Berkeley Lab and UC Berkeley Campus (e.g., Prof. A. P. Alivisatos's group) is expected. A Ph.D degree in physics or related fields is required and experience in electronic structure calculation is preferred. The position is initially for one year with the posibility of renewal for up to three years. Highly competitive salary will be offered. NERSC (http://www.nersc.gov) is the largest civilian research computer center in the United States with its recently installed 2,528 processor IBM SP computer being the second fastest in the world (http://www.top500.org). The scientific computing group (`http://www.nersc.gov/research/SCG`) is a diverse group working on various aspects of scientific computation. A few group members with close collaborations are in the field of material science simulation (Drs. A. Canning, N. Jensen, D. Raczkowski, and L.W. Wang). The lab is situated at the culturally diverse Berkeley and San Francisco Area. More information about our research activities can be found at `http://www.nersc.gov/~linwang`, and about the position at `http://www.lbl.gov/CS/Careers/OpenPositions/index.html`.

Interested person should send curriculum vitae and recommendation letters to:

Dr. Lin-Wang Wang
Lawrence Berkeley Lab
1 Cyclotron Road
Mail stop 50F
Berkeley, CA 94720

E-mail:lwwang@lbl.gov

LBNL is an equal opportunity/affirmative action employer.

Post-doc Positions

Department of Physics, University of Ioannina, Greece

Job Description : Two post-doctoral positions (one of 24 months and another one of 12 months), working as part of a EU Research Training Network, are available at the Department of Physics of the University of Ioannina, Greece, starting immediately. These are "young researcher" posts, open primarily to nationals of EU Member or Associated States (other than GR) aged under 35. Researchers resident in the Community for over 5 years may also apply. The aim of the project is to use molecular dynamics simulations for the study of the structural, dynamic and diffusive properties of the nanostructured Al alloys under development. (See http://www.materials.ox.ac.uk/nano-al).

Letters of application, including a full CV, list of publications and the names and addresses of three referees should be sent to Prof. G.A. Evangelakis, Department of Physics, University of Ioannina, Ioannina, Greece, 45110, from whom further particulars are available. e-mail: gevagel@uoi.cc.gr.

The closing date for applications is 31 August 2001.

Salary: 2100 euro per month.

Scientific Discipline: MAT, PHY

Start date: immediately.

Contact:

Prof. G.A. Evangelakis,
Department of Physics,
University of Ioannina,
Ioannina, Greece, 45110

Tel: +30 651 98590
Fax: +30 651 98675
E-mail: gevagel@uoi.cc.gr

Postdoctoral Research Fellow (experimentalist)

based at Daresbury Laboratory, Daresbury, Warrington, Cheshire, UK

”Magnetic X-Ray Dichroism of Magnetic Multilayers and Thin Films”

Applications are invited for a postdoctoral research fellowship in the Magnetic Spectroscopy Group to maintain, enhance and use the Magnetic X-ray Dichroism facilities at the UK national synchrotron at Daresbury. The work centers around soft x-ray absorption, scattering and photoemission using polarized x-rays and high-resolution low-energy electron diffraction (HRLEED) to characterise novel magnetic materials and nanostructures, see http://srs.dl.ac.uk/msg.

You should have research experience in one or more of the following fields: synchrotron radiation physics, magnetism or surface science.

The post is available for one year with a salary within the range GBP 17,278 to GBP 25,969 per annum.

Informal enquiries to Prof G van der Laan, tel: 01925 603448, fax: 01925 603124, email: `g.van_der_laan@dl.ac.uk`.

For further particulars and details of how to apply please write to the Personnel Office, University of York, Heslington, York YO10 5DD (e-mail: jobs@york.ac.uk), quoting reference number /6065 or see:

http://www.york.ac.uk/admin/persnl/jobs/6065.htm.

The closing date for applications is 2 August 2001.

To appear in the following publications

Nature Thursday 12 July 2001
University’s Job Vacancies page on WWW Jobs in the Academic Community: Jobs.ac.uk.

Theoretical Postdoctoral Position

Materials Modelling Laboratory

University of Oxford, UK

Salary range: GBP 16,775 - 25,213 p.a.

Applications are invited for a 3-year postdoctoral position to model electronic spin-dependent transport in magnetic thin-film structures. The research is funded by the EPSRC and will be performed jointly with Dr Evgeny Tsymbal and Professor David Pettifor, FRS. First-principle and tight- binding band structure methods will be used to investigate magnetoresistive phenomena in systems relevant to magnetic memory and storage applications. Expertise in ab- initio electronic structure calculations is essential. The post is available from 15 September 2001.

Applications including a full CV, list of publications and the names and addresses of three referees should be sent to The Deputy Administrator (Teaching), Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, UK, from whom further particulars are available. Please quote Ref. DJ01/020. The closing date for applications is 1 September 2001.

THEORY POSITION

The University of Illinois

A post-doctoral research position in theory is available with Duane D. Johnson, Professor in the Department of Materials Science & Engineering, The University of Illinois Urbana-Champaign. Salary range is US$28,000 - 32,000.

Applications are invited from those with Ph.D. for a one year (or more) postdoctoral position to model effects of chemical and structural defects in alloys, including mechanics and thermodynamics. Expertise in first-principles,electronic-structure calculations is essential, background with Green's function multiple-scattering theory preferred. The position is available from 15 September 2001.

Please send a letter of application, resume with list of publications, along with names, addresses and e-mail of three references, and a statement of research interests to: Mrs. Judy Brewer at mse@uiuc.edu (with reference to Johnson/PD01). The closing date for applications is 1 September 2001.

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

Duane D. Johnson, Professor
Department of Materials Science & Engineering
The University of Illinois
312E MatSE Bldg. C-246
1304 W. Green Street, Urbana, IL 61801
e-mail: duanej@uiuc.edu

Ph. D. Graduate Positions

NEW JERSEY INSTITUTE OF TECHNOLOGY

Several graduate positions (for Ph. D candidates) are available immediately for students to work with Prof. Sergej Savrasov in Department of Physics, New Jersey Institute of Technology, on electronic structure calculations of strongly correlated electronic systems. The project involves extensive development of methods, algorithms and computer programs for integrating the dynamical-mean-field based many-body methods into the electronic structure framework as well as their applications to materials with strong correlations. Financial support will be provided via teaching assistants (TA) for the students with good GRE scores. The New Jersey Institute of Technology is located in downtown Newark with access to the Manhattan area. We have strong collaborations with Bell Laboratories, Rutgers University, Princeton University and Columbia University. The assistantships are expected to start on September 1, 2001. To secure TA positions and to allow for student visa paperwork, interested candidates should contact S. Savrasov at savrasov@physics.rutgers.edu as soon as possible. Please also supply the names and addresses (e-mails) of two references. For additional information, please visit our web site http://www.njit.edu.

Sergej Savrasov
Department of Physics
New Jersey Institute of Technology
161 Warren Street
University Heights
Newark, New Jersey 07102-1982
Tel: (732) 445-4381
FAX: (732) 445-4381

savrasov@@physics.rutgers.edu (preferred)
savrasov@princeton-tech.com

Postdoc in Computational Materials Science

Computational Materials Physics Group

University of Montreal

Applications are invited for one or two POSTDOCTORAL POSITIONS, available IMMEDIATELY, in the computational materials physics group (”groFNUM”) at the Université de Montréal, which consists of professors Michel Côté, Laurent J. Lewis and Normand Mousseau. The group research interests are varied and include: semiconductor structure, dynamics and relaxation; glass structure and glass transition; diffusion and growth; radiation-matter interactions; properties of novel materials such as organic molecular crystals and polymers; clusters; superlattices; surface physics; algorithmic development; etc. Information on the group's activities can be found on web site http://www.esi.umontreal.ca/ grofnum/ . groFNUM is part of the GCM (Thin Film Group – Groupe de recherche en physique et technologie des couches minces), which includes strong experimental and theoretical components. EXTENSIVE experience with various numerical methods in materials physics – such as first-principles electronic structure calculations, ab-initio (Car-Parrinello), tight-binding, and semi-empirical (e.g., EAM, EMT) molecular dynamics, atomistic Monte-Carlo, ART – is essential and prerequisite.

IMPORTANT NOTE: In conformity with the university's policy, this position is open to RECENT Ph.D.'s, i.e., no more than two or three years after graduation. Individuals who expect to receive their Ph.D. within the next few months are encouraged to apply. Only suitable candidates will receive a reply and will be invited to provide letters of reference; there is no need to provide such letters at this time. The appointment is for two years: an initial one-year appointment, renewable for a second year upon mutual agreement.

Interested individuals should send their curriculum vitae as soon as possible, preferably by e-mail, to either Prof. Michel Côté (Michel.Cote@umontreal.ca), Prof. Laurent J. Lewis (Laurent.Lewis@umontreal.ca) or Prof. Normand Mousseau (mousseau@physcn.umontreal.ca), or by regular mail at:

Département de physique,
Université de Montréal,
C.P. 6128, Succursale Centre-Ville,
Montréal, Québec, Canada H3C 3J7.

Postdoctoral Position

Department of Chemistry
University of California, Berkeley

A postdoctoral opening is available for theoretical work at Berkeley in the area of electronic structure of semiconductor nanostructures, focusing on calculation and analysis of spin coherences and non-linear magneto-optical phenomena. Suitable candidates should have experience in one or more of the following areas: solid-state physics, large scale numerical calculations, many-body theory, condensed phase simulations, nanoscience and nanotechnology. Close collaboration with experimental groups in Berkeley and Santa Barbara will be involved, as well as investigation of applications to solid state quantum computation.

Interested candidates should contact Professor K. B. Whaley, Department of Chemistry, University of California, Berkeley, CA 94720 with e-mail to whaley@socrates.berkeley.edu. Please send a curriculum vitae, list of publications, and a list of at least three references with phone/fax numbers and e-mail addresses. Review of applications will begin immediately and continue until the position is filled.

Professor K. Birgitta Whaley
Department of Chemistry
University of California, Berkeley
CA 94720-1460

Tel: (510) 643-6820
Fax: (510) 642-7732
Email: whaley@socrates.berkeley.edu

PhD and Postdoctoral Positions in Nanoscale Science

Modeling and Simulation of Nanostructures assembled from Molecules

Institute of Physics, University of Basel, Switzerland

Applications are invited for the following positions within an interdisciplinary initiative in Nanoscience funded by the Swiss National Science Foundation and coordinated from our Institute.

1. One PhD position, the aim of the research leading to a doctoral thesis being to understand the controlled attachment and ordering of molecules on patterned substrates. This appointment is for 3 years with a starting salary near 32 000 Swiss Francs (rising to 37 000 Swiss Francs in the 3rd year). The candidate should have a university degree in physics or physical chemistry with a strong background in theory and experience in Fortran or C programming. Knowledge of condensed matter physics or chemistry, numerical methods and a good command of the english and/or german languages are desirable.

2. One postdoctoral position focused on understanding the properties of molecules attached between closely spaced electrodes and subject to applied electric potentials. The idea is to adapt semi-empirical or first-principles electronic structure and to combine them with computations of transport characteristics. The initial appointment is for one year, renewable upon mutual agreement, with a starting salary near 63 000 Swiss Francs for a candidate in the first year after a PhD degree in physics, chemistry or materials science. He/she should have a strong background in theoretical and computational methods in electronic structure or transport, and experience in applying them to problems motivated by experiments.

The groups involved have expertise in transport theory, mesoscopic physics, electronic structure and molecular dynamics calculations, modeling of scanning probe microscopy and manipulation, and have contacts with other leading groups in those disciplines. Collaboration is expected with parallel experimental projects ultimately aimed at assembling and characterizing "molecular machines" and molecule-based electronic devices, which are coordinated by Dr. Thomas Jung (Paul Scherrer Institute, Villigen) and Prof. Christian Schnenberger (University of Basel).

Requests for further information and applications for either position (including curriculum vitae, list of publications, names and coordinates of three persons who could supply recommendations) should be sent to

Dr. Alexis Baratoff
Departement of Physics and Astronomy
University of Basel
Klingelbergstr. 82, 4056 Basel
Switzerland
Tel.: +41 (0)61267 3726
Fax: +41 (0)61 267 3784
Email: alexis.baratoff@unibas.ch

or to

Prof. Christoph Bruder
Departement of Physics and Astronomy
University of Basel
Klingelbergstr. 82, 4056 Basel
Switzerland
Tel.: +41 (0) 61 267 3692
Fax: +41 (0) 61 267 1349
Email: christoph.bruder@unibas.ch

http://theorie5.physik.unibas.ch/
http://www.nanoscience.unibas.ch

A Postdoctoral Position

University of Nebraska

We have an opening for a theoretical postdoctoral associate preferably with experience in noncollinear magnetism to be filled immediately. The initial appointment will be for one year. The renewal depends on the satisfactory performance and the renewal of the grant. The salary is expected to be around 32,000 U.S. dollars per year. Anyone interested in this position is requested to send a copy of his/her resume and have two reference letters sent directly to the address given below. Transmittal of this material by fax will be very helpful.

Sitaram Jaswal
266 Behlen Laboratory
University of Nebraska
Lincoln,NE 68588-0111
U.S.A.
Email: sjaswal1@unl.edu
Tel: 402 472 2787
Fax: 402 472 2879

Job Vacancies in the Queen's University of Belfast

Please note that we have studentships in the Atomistic Simulation Group for a number of projects leading to a PhD; full details are on our website:

http://titus.phy.qub.ac.uk

Professor M. W. Finnis
Atomistic Simulation Group
School of Mathematics and Physics
The Queen's University of Belfast
Belfast BT7 1NN, Northern Ireland

tel.:+44 (0) 2890 335330
fax.:+44 (0) 2890 241958
email: m.finnis@qub.ac.uk

PhD Studentship in Computational Methods
Department of Chemistry, University of Edinburgh, UK

A PhD studentship in Computational Methods to work with Dr. Carole Morrison, Department of Chemistry, University of Edinburgh is currently available.

The project will involve the application of plane-wave density functional theory to study a number of novel molecular crystal systems. More details available at:

`http:/www.ed.ac.uk/~cam01`

8 Abstracts

Study of mechanical behavior of bcc transition metals using bond-order potentials

M. Mrověc[1], V. Vitek[1], D. Nguyen-Manh[2], D. Pettifor[2], L.G. Wang[3], M. Šob[3],
[1] *Department of Materials Science nad Engineering, University of Pennsylvania,*
3231 Walnut St., Philadelphia, PA 19104-6272, U.S.A.
[2] *Department of Materials, University of Oxford, Parks Road,*
Oxford OX1 3PH, U.K.
[3] *Institute of Physics of Materials, Academy of Sciences of the Czech Republic,*
Žižkova 22, CZ-616 62 Brno, Czech Republic

Abstract

Deformation properties of body-centered cubic transition metals are controlled by the core structure of screw dislocations and their studies involve extensive computer simulations. In this paper we present the recently constructed bond-order potentials (BOP) that are based on the real-space parametrized tight-binding method. In order to examine the applicability of the potentials we have evaluated the energy differences of alternative structures, investigated several transformation paths leading to large distortions and calculated phonon dispersions. Using these potentials we have calculated γ-surfaces that relate to the dislocation core structures and discuss then the importance of directional bonding in studies of dislocations in transition metals.

(Published in *Multiscale Phenomena in Materials – Experiment and Modelling*, edited by D.H. Lasilla, I.M. Robertson, R. Phillips, B. Devincre, Mater. Res. Soc. Symp. Proc. vol. **578**, Materials Reseach Society, Warrendale, PA, 2000, pp. 199-204.)

Contact person: Mojmír Šob (mojmir@ipm.cz)

Ab initio simulation of a tensile test in $MoSi_2$ and WSi_2

M. Friák[1,2], M. Šob[1], V. Vitek[3]
[1] *Institute of Physics of Materials, Academy of Sciences of the Czech Republic,*
Žižkova 22, CZ-616 62 Brno, Czech Republic
[2] *Institute of Condensed Matter Physics, Faculty of Science, Masaryk University,*
Kotlářská 2, CZ-611 37 Brno, Czech Republic
[3] *Department of Materials Science nad Engineering, University of Pennsylvania,*
3231 Walnut St., Philadelphia, PA 19104-6272, U.S.A.

Abstract

The tensile test in transition metal disilicides with $C11_b$ structure is simulated by *ab initio* electronic structure calculations using full potential linearized augmented plane wave method (FLAPW). Full relaxation of both external and internal parameters is performed. The theoretical tensile strength of $MoSi_2$ and WSi_2 for [001] loading is determined and compared with those of other materials.

(Accepted for publication in *High-Temperature Ordered Intermetallic Alloys IX*, Mater. Res. Soc. Symp. Proc. vol. **646**, Materials Reseach Society, Warrendale, PA 2001.)

Contact person: Mojmír Šob (mojmir@ipm.cz)

Ab initio calculation of phase boundaries in iron along the bcc-fcc transformation path and magnetism of iron overlayers

M. Friák[1,2], M. Šob[1], V. Vitek[3]
[1] *Institute of Physics of Materials, Academy of Sciences of the Czech Republic,*
Žižkova 22, CZ-616 62 Brno, Czech Republic
[2] *Institute of Condensed Matter Physics, Faculty of Science, Masaryk University,*
Kotlářská 2, CZ-611 37 Brno, Czech Republic
[3] *Department of Materials Science nad Engineering, University of Pennsylvania,*
3231 Walnut St., Philadelphia, PA 19104-6272, U.S.A.

Abstract

A detailed theoretical study of magnetic behavior of iron along the bcc-fcc (Bain's) transformation paths at various atomic volumes, using both the local spin density approximation (LSDA) and the generalized gradient approximation (GGA), is presented. The total energies are calculated by spin-polarized full-potential LAPW method and are displayed in contour plots as functions of tetragonal distortion c/a and volume; borderlines between various magnetic phases are shown. Stability of tetragonal magnetic phases of γ-Fe is discussed. The topology of phase boundaries between the ferromagnetic and antiferromagnetic phase is somewhat similar in LSDA and GGA, however, the LSDA fails to reproduce correctly the ferromagnetic bcc ground state and yields the ferromagnetic and antiferromagnetic tetragonal states at too low volume. The calculated phase boundaries are used to predict the lattice parameters and magnetic states of iron overlayers on various (001) substrates.

(Published in Phys. Rev. B 63 2001, 052405)
Contact person: Mojmír Šob (mojmir@ipm.cz)

Ab initio analysis of energetics of σ-phase formation in Cr-based systems

J. Havránková[1], J. Vřešťál[1], L.G. Wang[2] and M. Šob[2]

[1] *Institute of Theoretical and Physical Chemistry, Faculty of Science,*
Masaryk University, Kotlářská 2, CZ-611 37 Brno, Czech Republic

[2] *Institute of Physics of Materials, Academy of Sciences of the Czech Republic,*
Žižkova 22, CZ-616 62 Brno, Czech Republic

Abstract

A new theoretical approach to the explanation of experimentally determined positive enthalpy of formation in Cr-based σ-phases is presented. It turns out that the energy of formation of σ-phases in Cr-Co and Cr-Fe systems is found negative taking the pure components in σ-phase structure as standard states. Our treatment represents the first step to a new model of explanation of the stability of the σ-phase.

(Published in Phys. Rev. B 63 2001, 174104)

Contact person: Mojmír Šob (mojmir@ipm.cz)

Ab Initio Simulation of Three-Axial Deformation of Perfect Iron Crystal

M. Černý[1,2], P. Šandera[1], J. Pokluda[1], M. Friák[2,3] , M. Šob[2]

[1] *Institute of Engineering Physics, Faculty of Mechanical Engineering,*
Brno University of Technology, Technická 2, 616 69 Brno, Czech Republic.
[2] *Institute of Physics of Materials, Academy of Sciences of the Czech Republic,*
Žižkova 22, CZ-616 62 Brno, Czech Republic
[3] *Institute of Condensed Matter Physics, Faculty of Science, Masaryk University,*
Kotlářská 2, CZ-611 37 Brno, Czech Republic

Abstract

Ab initio electronic structure calculations of ideal strength, bulk modulus and equilibrium lattice parameter of iron in the body-centered-cubic lattice under three-axial tension are performed using the linear muffin-tin orbitals method in atomic sphere approximation (LMTO-ASA) and the full-potential linearized augmented plane waves method (FLAP-W). Magnetic ordering is taken into account by means of spin-polarized calculation. Two exchange-correlation energy approximations are employed, namely the local (spin) density approximation (LDA) and the generalized gradient approximation (GGA). Computed values are compared with experimental data.

(Accepted for publication in Proceedings of the 3rd Int. Conf. on Materials Structure and Micromechanics of Fracture, Brno, June 27-29, 2001)

Contact person: Mojmír Šob (mojmir@ipm.cz)

Ab initio Modelling of Deformation of Perfect Cubic Crystals under Triaxial Tension

M. Černý[1,2], P. Šandera[1], J. Pokluda[1]
[1] *Institute of Engineering Physics, Faculty of Mechanical Engineering,*
Brno University of Technology, Technická 2, 616 69 Brno, Czech Republic.
[2] *Institute of Physics of Materials, Academy of Sciences of the Czech Republic,*
Žižkova 22, CZ-616 62 Brno, Czech Republic

Abstract

Ab initio calculations of ideal strength of cubic crystals under three-axial tension are performed using the LMTO-ASA method. Two exchange-correlation term approximations (LDA, GGA) are applied. Computed values are compared with those obtained previously by means of semi-empirical approach. Values of equilibrium lattice parameter obtained in the framework of ab-initio method are well comparable with experimental data whereas a less satisfactory agreement was achieved in case of bulk moduli and cohesive energy.

(Accepted for publication in Proceedings of the 3rd Int. Conf. on Materials Structure and Micromechanics of Fracture, Brno, June 27-29, 2001)

Contact person: Miroslav Černý (mcerny@ipm.cz)

Sensitivity of electron and electron-positron momentum densities to various electron and positron crystal potentials

H. Sormann[1], M. Šob[2]

[1] *Institut für Theoretische Physik, Technische Universität Graz,*
Petersgasse 16, A-8010 Graz, Austria

[2] *Institute of Physics of Materials, Academy of Sciences of the Czech Republic,*
Žižkova 22, CZ-616 62 Brno, Czech Republic

Abstract

This paper presents a comprehensive survey on the influence of various crystal potentials used for the calculation of electron and positron Bloch states on electron and electron-positron momentum densities. Our investigation deals with alkali metals and the complete series of $4sp$ and $3d$ metals, and it covers both the behavior of valence and core electrons as well as the central momentum region and some Umklapp regions. The main results of this paper are: (i) the sensitivity of the electron-positron momentum density with respect to various crystal potentials is significantly higher for $4sp$ and $3d$ metals than for the alkali metals, (ii) for all metals of the $3d$ series, the electron-positron momentum densities are generally more sensitive to the potentials than the corresponding electron momentum densities. Possible complications regarding the comparison of theoretical and experimental electron-positron momentum profiles and extracting information on electron-positron interaction are also discussed.

(Accepted for publication in Phys. Rev. B 2001)

Contact person: Heinz Sormann (sormann@ifk.tu-graz.ac.at)

Application of ab initio electronic structure calculations to grain boundary structure

M. Šob[1], I. Turek[1], L.G. Wang[1], V. Vitek[2]
[1] *Institute of Physics of Materials, Academy of Sciences of the Czech Republic,*
Žižkova 22, CZ-616 62 Brno, Czech Republic
[2] *Department of Materials Science nad Engineering, University of Pennsylvania,*
3231 Walnut St., Philadelphia, PA 19104-6272, U.S.A.

Abstract

State-of-the-art electronic structure methods are briefly characterized and their application to electronic structure of the (=5(210)/[001] tilt grain boundary in tungsten, magnetic moments at the (=5(310)/[001] tilt grain boundary in iron, and magnetic behaviour of Ru and Rh overlayers at the Ag(001) substrate is shown.

(Accepted for publication in *Proc. 10th International Metalurgical and Materials Conference METAL 2001*, TANGER, Ostrava 2001, pp. 1-9 (CD-ROM).

Contact person: Mojmír Šob (mojmir@ipm.cz)

Giant enhancement of orbital moments and perpendicular anisotropy in epitaxial Fe/GaAs(100)

Y.B. Xu, M. Tselepi, C.M. Guertler, C.A.F. Vaz, G. Wastlbauer, J.A.C. Bland
Cavendish Laboratory, University of cambridge, Cambridge CB3 0HE, UK
E. Dudzik and G. van der Laan
Magnetic Spectroscopy Group, Daresbury Laboratory, Warrington WA4 4AD, UK

Abstract

The spin and orbital magnetic moments and the perpendicular magnetic anisotropy of 8 and 33 monolayer epitaxial bcc Fe films grown on GaAs(100)-4×6 have been measured using x-ray magnetic circular dichroism and polar magneto-optical Kerr effect. Both the films have approximately the same spin moments of about 2.0 μ_B close to that of the bulk value. The ultrathin film shows a giant orbital moment enhancement of about 300% with respect to the bulk value and a perpendicular interface anisotropy field $H_s^{\mathrm{Fe-GaAs}}$ of the order of -5×10^4 Oe. This may be partially due to an increased degree of localization of electronic states at the Fe/GaAs interface associated with atomic scale interface structure.

(Published in J. Appl. Phys. **89**, 7156 (2001))
Contact person: G.VanDerLaan@dl.ac.uk

Complex Magnetism in Ultra-Thin Films: Atomic-Scale Spin Structures and Resolution by the Spin-Polarized Scanning Tunneling Microscope

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

Abstract

In this paper we present a density functional theory investigation of complex magnetic structures in ultra-thin films. The focus is on magnetically frustrated antiferromagnetic Cr and Mn monolayers deposited on a triangular lattice provided by a Ag(111) substrate. This involves noncollinear magnetic structures which we treat by first-principles calculations on the basis of the vector spin-density formulation of the density functional theory. We find for Cr/Ag(111) a coplanar noncollinear periodic 120° Néel structure, for Mn/Ag(111) a row-wise antiferromagnetic structure and for Fe/Ag(111) a ferromagnetic structure as magnetic ground states. The spin-polarized 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. We discuss a recent application to this operation mode of the SP-STM on Mn/W(110) which led to the first observation of a two-dimensional antiferromagnet on a nonmagnetic metal. The future potential of this approach is demonstrated by calculating SP-STM images for different magnetic structures of Cr/Ag(111). The results show, that the predicted noncollinear magnetic ground state structure can clearly be discriminated from competing magnetic structures. A general discussion of the application of different operation modes of the SP-STM is presented on the basis of the model of Tersoff and Hamann.

(Accepted by Appl. Phys. A)

Contact person: s.bluegel@fz-juelich.de

Hop, skip or jump? Proton transport in the CaZrO3 perovskite oxide.

M. Saiful Islam, R. Andrew Davies, Julian D. Gale
Department of Chemistry, University of Surrey,
Guildford GU2 7XH, UK

Abstract

http://www.rsc.org/CFmuscat/intermediate.cfm?FURL=/ej/CC/2001/b100960p.PDF

(Chem. Comm., 2001, 661)
Contact person: m.islam@surrey.ac.uk:

Resolving noncollinear magnetism by spin-polarized scanning tunneling microscopy: Mn/Cu(111)

D. Wortmann[†], Ph. Kurz[†], S. Heinze[†,¶], K. Hirai[‡], G. Bihlmayer[†],
and S. Blügel[†,+]
[†] *Institut für Festkörperforschung, Forschungszentrum Jülich,*
D-52425 Jülich, Germany
[+] *Fachbereich Physik, Universität Osnabrück,D-49069 Osnabrück, Germany*
[¶] *Zentrum für Mikrostrukturforschung, Universität Hamburg,*
D-20355 Hamburg, Germany
[‡] *Department of Physics, Nara Medical University, Kashihara,*
Nara 634-8521, Japan

Abstract

We present a density functional theory (DFT) investigation of magnetically frustrated Mn monolayers deposited on the triangular lattice of the Cu(111) surface. Noncollinear magnetic structures are treated on the basis of the vector spin-density formulation of the DFT. The spin-polarized scanning tunneling microscope operated in the constant-current mode is proposed as a powerful tool to investigate these complex magnetic structures.

(Submitted to J. Magn. Magn. Mater.)
Contact person: s.bluegel@fz-juelich.de

First-Principles Interpretation of Scanning Tunneling Microscopy applied to Transition-Metal Surfaces: Buried CuIr/Cu(100) Surface Alloys

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

Abstract

For the example of scanning tunneling microscopy (STM) experiments carried out for Ir impurities and chains buried in the sub-surface layer of Cu(001), we represent the present status of analyzing STM experiments of transitions-metal surfaces using first-principles calculations based on the density functional theory to describe the electronic structure of the sample in combination with the model of Tersoff and Hamann to evaluate the tunneling current between tip and sample. We show that transition-metal defect structures below the Cu(100) surface can be detected by STM and the detection should not be restricted to Ir defects nor limited to defects in the sub-surface layer.

(Submitted to Phys. Stat. Sol.)
Contact person: s.bluegel@fz-juelich.de

The electronic and optical properties of InGaAs/InP and InAlAs/InP superlattices

Chiara Ghidoni, Rita Magri, and Stefano Ossicini
Istituto Nazionale per la Fisica della Materia (INFM)
and Dipartimento di Fisica, Università di Modena e Reggio Emilia,
Via Campi 213/A, I-41100 Modena, Italy

Abstract

We study using first-principle calculations the electronic and optical properties of $In_{0.5}Ga_{0.5}As/InP$ and $In_{0.5}Al_{0.5}As/InP$ superlattices, where the InGaAs and InAlAs alloys are described through an appropriate ordered ternary structure. The calculated electronic properties show that the substitution of Ga with Al originate an opening of the band gap from the infrared to the near-visible and a transformation of the band alignment from type I to type II. Through the analysis of the optical properties we discuss successfully the giant polarization anisotropy observed in these systems.

(Surface Science, in press)

Contact person: ossicini.stefano@unimo.it

ORBITAL DEGENERACY AND MAGNETISM OF PEROVSKITE MANGANESE OXIDES

I. V. Solovyev
JRCAT-Angstrom Technology Partnership, AIST, Central 4, 1-1-1 Higashi,
Tsukuba 305-0046, Japan
and
Institute of Metal Physics, 18, Kovalevskaya St., Ekaterinburg 620219, Russia
K. Terakura
JRCAT-National Institute of Advanced Industrial Science and Technology, AIST,
Central 4, 1-1-1 Higashi, Tsukuba 305-8562, Japan
and
Research Institute for Computational Sciences, AIST,
Central 2, 1-1-1 Umezono, Tsukuba 305-8568, Japan

Abstract

A rich variety of phases observed in doped manganites, including complex spin-charge-orbital ordered structures, are reviewed from the viewpoint of their magnetic stability, using both the first-principles electronic structure calculations and the model tight-binding approach. It is argued that the microscopic mechanism underlying the low-temperature phase diagram is the spin double exchange incorporated with the realistic orbital degeneracy for the itinerant e_g electrons. This provides a unique opportunity for the phase control. On the one hand, the spin alignment controls the dimensionality of the double-exchange system. An anisotropic antiferromagnetic ordering lifts the orbital degeneracy and results in the orbital ordering. On the other hand, the orbital state can be changed by external lattice distortions. This may cause the change of the magnetic ground state as well. Two examples illustrating this idea, the Jahn-Teller distortion in $\mathrm{LaMnO_3}$ and the tetragonal strain in $\mathrm{La_{1-x}Sr_xMnO_3}$, are discussed. The antiferromagnetic states built of the one-dimensional zigzag ferromagnetic chains present a very special class of magnetic solutions. The ferromagnetic chains behave as band insulator, that explains the magnetic stability and electronic properties of these states, which are typically refereed to the charge and orbital ordering concomitant the antiferromagnetic spin ordering. Finally, characteristic features of the optical conductivity for different magnetic structures are discussed.

(To be published in Springer-Verlag, ed. by D. J. Singh)
Manuscripts available from: igor@jrcat.or.jp

Collective excitations in alkali metals on Al(111)

S. R. Barman, C. Stampfl, Y. Q. Cai, K. Horn
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6,
14195 Berlin-Dahlem, Germany
P. Häberle, W. Ibañez
Universidad Técnica Federico Santa María, Casilla, Valparaíso, Chile

Abstract

The photon-excited multipole plasmon and the bulk-like plasmon modes have been studied in Na/Al(111) and K/Al(111). These collective modes appear for a coverage of $\geq$2 monolayers. Both the multipole and the bulk-like plasmon modes exhibit interesting variations in frequency, line shape and relative intensity with adlayer coverage. The reasons for such behaviour are discussed on the basis of existing theoretical results. The substrate Al multipole plasmon is found to attenuated by smooth adlayer growth. Deposition of K on 2 ML Na/Al(111) results in the growth of K related collective excitation at the expense of the Na modes. For complicated surface structures like Al(111)-($\sqrt{3} \times \sqrt{3}$)$R30°$:K or the Al(111)-(2×2):Na surface alloy, electron charge density profiles at the surface are calculated based on *ab initio* DFT-LDA method to explain the photoyield data. The importance of the shape of the charge density profile in determining the collective excitations is demonstrated. For Al(111)-($\sqrt{3} \times \sqrt{3}$)$R30°$:K, a strong increase in intensity in the energy region of the K plasmons is observed in the on-top structure which is attributed to a 'mixed plasmon' mode. While the experimental observations for smooth alkali metal adlayers are in good agreement with existing theory, more theoretical work, especially for the complicated surface structures, is desirable.

(submitted to: Phys. Rev. B)
Contact person: C. Stampfl (stampflc@fhi-berlin.mpg.de)

Composition, structure and stability of $RuO_2(110)$ as a function of oxygen pressure

Karsten Reuter and Matthias Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6,
14195 Berlin-Dahlem, Germany

Abstract

Using density-functional theory (DFT) we calculate the Gibbs free energy to determine the lowest-energy structure of a $RuO_2(110)$ surface in thermodynamic equilibrium with an oxygen-rich environment. The traditionally assumed stoichiometric termination is only found to be favorable at low oxygen chemical potentials, i.e. low pressures and/or high temperatures. At realistic O pressure, the surface is predicted to contain additional terminal O atoms. Although this O excess defines a so-called polar surface, we show that the prevalent ionic model, that dismisses such terminations on electrostatic grounds, is of little validity for $RuO_2(110)$. Together with analogous results obtained previously at the (0001) surface of corundum-structured oxides, these findings on (110) rutile indicate that the stability of non-stoichiometric terminations is a more general phenomenon on transition metal oxide surfaces.

(submitted to: Phys. Rev. B)

Contact person: Karsten Reuter (reuter@fhi-berlin.mpg.de)

Island Nucleation in Metal Thin-Film Growth

Kristen Fichthorn, Michael Merrick
The Pennsylvania State University, University Park, PA, USA
Rossitza Pentcheva, Matthias Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6,
14195 Berlin-Dahlem, Germany

Abstract

Island nucleation and growth during thin-film epitaxy is typically described using mean-field rate equations. Assuming that interactions between adatoms do not extend beyond the short range and that deposited atoms remain on top of the substrate, among other things, these equations can be solved to yield a scaling relationship that predicts the density of stable islands as a function of the deposition rate and the diffusivity of an isolated adatom Recent theoretical and experimental studies indicate that the assumptions behind this "s-tandard" nucleation theory are not always upheld. Medium- and long-range interactions between adatoms may change the picture that nucleation theory provides. Also, intermixing of deposited atoms into the substrate can occur in heteroepitaxy. We review our recent theoretical studies, in which we have used density-functional theory calculations and kinetic Monte Carlo simulations to probe the initial stages of thin-film epitaxy for: (i) the growth of Ag on a strained Ag(111) surface and (ii) the growth of Co on Cu(001). We discuss the "novel" growth modes in these systems and related experimental work.

(submitted to: Proc. NATO ARW on Atomistic Aspects of Epitaxial Growth (Corfu, Greece), Kluwer Academic Publ., Dordrecht)

Contact person: Kristen Fichthorn (fichthorn@psu.edu)

MODELLING ELECTRON ENERGY-LOSS SPECTRA OF DISLOCATIONS IN SILICON AND DIAMOND

C. J. Fall, J. P. G. Goss, R. Jones
School of Physics, University of Exeter,
Exeter EX4 4QL, UK
A. T. Blumenau
Physics Department, University of Paderborn,
D-33095 Paderborn, Germany
P. R. Briddon
Department of Physics, University of Newcastle,
Newcastle upon Tyne NE1 7RU, UK

Abstract

The presence of dislocations in semiconductor crystals can strongly influence the electrical and optical properties of the material. Electron energy-loss spectroscopy (EELS) performed near dislocation cores is one of the few experimental techniques that can yield valuable information about the electronic levels associated with dislocations, both within and above the band gap. Recent EELS spectra measured near dislocations in silicon have shown differences from bulk regions [1], but there are still issues regarding their interpretation. In this study, using self-consistent ab initio calculations, we model and predict EELS spectra acquired on dislocation cores of various partial dislocations in silicon and diamond, and compare the results with bulk spectra. In particular, we consider various core structures of the 30° and 90° partial glide dislocations. In diamond, we find evidence of empty states localised on the dislocation core below the bulk band edge, in agreement with experimental evidence [2]. In silicon, we reproduce the peak splitting in the conduction band seen experimentally at the 30° partial dislocation [1]. This information could prove crucial to help resolve whether any electrical or optical activity is associated with undecorated dislocations in these materials.

[1] Batson, P. E. (1999) Physical Review Letters 83, 4409
[2] Bruley, J. and Batson, P. E. (1989) Physical Review B40, 9888

Presented at ICDS XXI July 16-20 Gießen (Germany)
Contact person: Caspar Fall (C.J.Fall@exeter.ac.uk).
Reprints available on request

Isotopic effects on vibrational modes of thermal double donors in Si and Ge

L. I. Murin
Institute of Solid State and Semiconductor Physics, Minsk 220072, Belarus
J. L. Lindström
Department of Physics, Lund University, S-221 00 Lund, Sweden
V. P. Markevich
Centre for Electronic Materials, UMIST, M601QD Manchester, UK
T. Hallberg
Defence Research Establishment, P.O. Box 1165, SE-58111 Linköping, Sweden
V. V. Litvinov
Belarusian State University, F. Scornia av. 4, 220050 Minsk, Belarus
J. Coutinho, R. Jones
School of Physics, University of Exeter, EX4 4QL Exeter, UK P. R. Briddon
Department of Physics, University of Newcastle, NE1 7RU Newcastle, UK
S. Öberg
Department of Mathematics, Luleå University of Technology, S-97187 Luleå, Sweden

Abstract

The local vibrational modes of thermal double donors in Si and Ge are investigated by FTIR and *ab-initio* modelling. At most two oxygen modes are detected from each donor, which exhibit regular shifts with increasing donor number. By using mixtures of ^{16}O and ^{18}O, it is found that in Si the upper band does not yield any new modes suggesting that any oxygen atom is decoupled from any other. However, the lower frequency bands exhibit unique mixed modes proving for the first time that oxygen atoms are coupled together and in close spatial proximity. *Ab-initio* calculations demonstrate that the modes and their isotopic shifts are consistent with a model involving two parallel chains of oxygen atoms linking second neighbour Si atoms, terminated by O-atoms close to the normal position for interstitial O.

Presented at ICDS XXI July 16-20 Gießen (Germany)

Contact person: José Coutinho (J.P.A.Coutinho@exeter.ac.uk).

Reprints available on request

Thermal double donors in Si and Ge

R. Jones, J. Coutinho
School of Physics, University of Exeter, EX4 4QL Exeter, UK
S. Öberg
Department of Mathematics, Luleå University of Technology, S-97187 Luleå, Sweden
P. R. Briddon
Department of Physics, University of Newcastle, NE1 7RU Newcastle, UK

Abstract

Three experiments appear to cast doubt on self-interstitial-free models of the family of thermal donors, based on oxygen defects of increasing size. These are a) the rapid transformation of TDD(N) into TDD(N+1) with activation energies considerably lower than that of oxygen diffusion, b) the lack of any appreciable spin-density on oxygen in TDD(N)$^+$, and c) the observation of only *two* oxygen related vibrational modes associated with each donor. However, we show that the oxygen only model of the donors is compatible with experiment for a structure involving an insulating core with normal oxygen coordination, surrounded by over-coordinated oxygen atoms which are responsible for the donor activity. It is also shown that the calculated stress-energy tensors for the early donors are in good agreement with the measurements.

Presented at ICDS XXI July 16-20 Gießen (Germany)
Contact person: José Coutinho (J.P.A.Coutinho@exeter.ac.uk).
Reprints available on request

Over-coordinated oxygen in the interstitial carbon-oxygen complex

J. Coutinho, R. Jones
School of Physics, University of Exeter, EX4 4QL Exeter, UK
P. R. Briddon
Department of Physics, University of Newcastle, NE1 7RU Newcastle, UK
S. Öberg
Department of Mathematics, Luleå University of Technology, S-97187 Luleå, Sweden
L. I. Murin
Institute of Solid Sate and Semiconductor Physics, Minsk 220072, Belarus
V. P. Markevich
Centre for Electronic Materials, UMIST, Sackville Street, Manchester M601QD, UK
J. L. Lindström
Department of Physics, University of Lund, S-221 00 Lund, Sweden

Abstract

The interstitial carbon-oxygen complex is one of the most prominent defects formed in e-irradiated Cz-Si containing carbon. Stress alignment investigations have shown that the oxygen atom only perturb the carbon interstitial but the lack of a high frequency oxygen mode has been taken to imply that the the oxygen atom is over-coordinated. Local vibrational mode spectroscopy and *ab-initio* modeling are used to investigate the defect. We find new modes whose oxygen isotopic shifts, along with the piezoscopic stress-energy tensor support the trivalent model, thus providing evidence for oxygen over-coordination.

Presented at ICDS XXI July 16-20 Gießen (Germany)
Contact person: José Coutinho (J.P.A.Coutinho@exeter.ac.uk).
Reprints available on request

Evidence for H_2^* trapped by carbon impurities in silicon

B. Hourahine, R. Jones
School of Physics, University of Exeter,
Exeter EX4 4QL, UK
S. Öberg
Department of Mathematics, Luleå University of Technology, S-97187 Luleå, Sweden
P. R. Briddon
Department of Physics, University of Newcastle, NE1 7RU Newcastle, UK
V. P. Markevich
Centre for Electronic Materials, UMIST, M601QD Manchester, UK
R. C. Newman
Centre For Electronic Materials Devices, The Blacket Laboratory,
The Department of Physics, Imperial College, London SW7 2BZ, UK
J. Hermansson, M. Kleverman, J. L. Lindström
Department of Physics, Lund University, S-221 00 Lund, Sweden
L. I. Murin
Institute of Solid State and Semiconductor Physics, Minsk 220072, Belarus
N. Fukata, M. Suezawa
Institute of Materials Research, Tohoku University, Sendai 980-8577, Japan

Abstract

Local mode spectroscopy and *ab initio* modelling are used to investigate two trigonal defects found in carbon rich Si into which H had been in-diffused. Isotopic shifts with D and ^{13}C are reported along with the effect of uniaxial stress. Ab-initio modelling studies suggest that the two defects are two forms of the CH_2^* complex where one of the two hydrogen atoms lies at an anti-bonding site attached to C or Si respectively. The two structures are nearly degenerate and possess vibrational modes in good agreement with those observed.

Presented at ICDS XXI July 16-20 Gießen (Germany)
Contact person: Ben Hourahine (B.Hourahine@exeter.ac.uk).
Reprints available on request

Piezospectroscopic analysis of the hydrogen - carbon comp lexes in silicon

O. Andersen, L. Dobaczewski, A. R. Peaker
Centre for Electronic Materials, University of Manchester Institute of Science and Technology, P.O.Box 88, Manchester M60 1QD, UK
K. Bonde Nielsen
Institute of Physics and Astronomy, University of Aarhus, Aarhus, Denmark
B. Hourahine, R. Jones
School of Physics, University of Exeter,
Exeter EX4 4QL, UK
P. R. Briddon
Department of Physics, University of Newcastle, NE1 7RU Newcastle, UK
S. Öberg
Department of Mathematics, Luleå University of Technology, S-97187 Luleå, Sweden

Abstract

We have observed the donor ($E_c - 0.22$ eV) and acceptor ($E_c - 0.16$ eV) levels related to hydrogen-carbon complexes in silicon. The donor level is only detected at low temperatures after proton implantation. This hydrogen-carbon complex irreversibly reconfigures at temperatures above 225 K to a configuration characterized by the acceptor level, which is stable up to room temperature. The same acceptor level is also observed after atomic hydrogen diffusion. We have used Laplace transform deep level transient spectroscopy (DLTS) to show the influence of uniaxial stress on the electron emission process and the effect of the stress-induced alignment for the acceptor state. The pattern of the Laplace DLTS peak splittings indicate a trigonal symmetry of the defect. First principles calculations were carried out on the hydrogen-carbon defects with a view to determining their electrical levels and stress response for comparison with the experimental results.

Presented at ICDS XXI July 16-20 Gießen (Germany)
Contact person: Ben Hourahine (B.Hourahine@exeter.ac.uk).
Reprints available on request

Second generation wave-function thermostat for ab-initio molecular dynamics

Peter E. Blöchl
Clausthal University of Technology, Institute for Theoretical Physics,
Leibnizstr.10, D-38678 Clausthal-Zellerfeld, Germany

Abstract

A rigorous two-thermostat formulation for ab-initio molecular dynamics using the fictitious Lagrangian approach is presented. It integrates the concepts of mass renormalization and temperature control for the wave functions. The new thermostat adapts to the instantaneous kinetic energy of the nuclei and thus minimizes its influence on the dynamics. Deviations from the canonical ensemble, which are possible in the previous two-thermostat formulation, are avoided. The method uses a model for the effective mass of the wave functions, which is open to systematic improvement.

(submitted to: Physical Review B on July 20th, 2001)
Latex-file available from
http://www.pt.tu-clausthal.de/atp/publist.shtml
or from http://www.arxiv.org/ as cond-mat/0107435

Interatomic electron transport by semi-empirical and ab initio tight-binding approaches

I. Turek,[a,d,e] J. Kudrnovský,[b,d] V. Drchal,[b,d] L. Szunyogh,[c,d] and P. Weinberger [d]
[a] *Institute of Physics of Materials, AS CR, CZ-61662 Brno, Czech Republic*
[b] *Institute of Physics, AS CR, CZ-18221 Prague 8, Czech Republic*
[c] *Institute of Physics, TU Budapest, H-1521 Budapest, Hungary*
[d] *Center for Comput. Materials Science, TU Vienna, A-1060 Vienna, Austria*
[e] *Dept. Electronic Structures, Charles Univ., CZ-12116 Prague 2, Czech Republic*

Abstract

A unified approach to the interatomic electron transport within the Kubo linear response theory is sketched that is applicable both in semi-empirical (matrix-element based) and ab initio (wave-function based) tight-binding (TB) techniques. This approach is based on a systematic neglect of the electron motion inside the atomic (Wigner-Seitz) cells leading thus to velocity operators describing pure intersite hopping. This is achieved by using piecewise constant coordinates, i.e., coordinates that are constant inside the cells. The formalism is presented within the simple semi-empirical TB method, the TB linear muffin-tin orbital (LMTO) method, and the screened Korringa-Kohn-Rostoker (KKR) method with emphasis put on the formal analogy of the derived formulae. The results provide a justification of current assumptions used in semi-empirical TB schemes, an assessment of properties of recent TB-LMTO approaches, and an alternative formulation of electron transport within the screened KKR method. The formalism is illustrated by a calculation of residual resistivity of substitutionally disordered fcc Ag-Pd alloys.

(Submitted to Physical Review B)
Contact person: Ilja Turek (turek@ipm.cz).
Postscript file available on request.

Ab initio theory of transport in FeRh-based natural magnetic multilayers

I. Turek,[a,b,d] J. Kudrnovský,[c,d] V. Drchal,[c,d] P. Weinberger,[d] and P.H. Dederichs[e]
[a] *Institute of Physics of Materials, AS CR, CZ-61662 Brno, Czech Republic*
[b] *Dept. Electronic Structures, Charles Univ., CZ-12116 Prague 2, Czech Republic*
[c] *Institute of Physics, AS CR, CZ-18221 Prague 8, Czech Republic*
[d] *Center for Comput. Materials Science, TU Vienna, A-1060 Vienna, Austria*
[e] *Institut für Festkörperforschung, FZ Jülich, D-52425 Jülich, Germany*

Abstract

The electronic structure and the residual resistivity of random FeRh-based alloys in the CsCl structure are calculated for different spin configurations using the tight-binding linear muffin-tin orbital method. The effect of substitutional impurities (Pd, Rh) is described by means of the coherent potential approximation. It is shown that impurity scattering leads to giant magnetoresistance effects in qualitative agreement with experiment.

(Submitted to J. Magn. Magn. Mater.)
Contact person: Ilja Turek (turek@ipm.cz).
Postscript file available on request.

Correlation effects and satellite intensities in photoemission from ferromagnetic interfaces; Co, fe, Cr on Cu(1 1 13)

G. Panaccione
INFM, TASC Laboratory, Basovizza, Trieste, Italy
H.A. Dürr
Inst. Festkoerperforschung, Juelich, Germany
J. Vogel
Lab. Louis Neel, CNRS, Grenoble, France
N.B. Brookes
ESRF, Grenoble, France
G. van der Laan
Magnetic Spectroscopy Group, Daresbury Laboratory, Warrington WA4 4AD, UK

Abstract

We present magnetic dichroism in photoemission (MCD) results obtained at the $2p$ core level of Co, Fe and Cr grown on Cu(1 1 13). By performing measurements under both magnetization and polarization reversal we obtain the true MCD signal as well as the small CDAD and MLDAD signals, which can always be present in these experiments. The $2p$ MCD spectra display strong magnetic signals at the main edges accompanied by satellite features.

(Published in J. Magn. Magn. Mat. **233**, 57 (2001))
Contact person: G. van der Laan (G.VanDerLaan@dl.ac.uk)

Even-harmonic generation due to beyond-Born-Oppenheimer dynamics

Thomas Kreibich,[1] Manfred Lein,[1,2] Volker Engel,[2] and E. K. U. Gross[1]
[1]*Institut für Theoretische Physik,*
Am Hubland, 97074 Würzburg, Germany
[2]*Institut für Physikalische Chemie,*
Am Hubland, 97074 Würzburg, Germany

Abstract

We calculate the harmonic spectrum generated by a model HD molecule in a strong laser pulse. The unequal nuclear masses lead to the emission of even harmonics, i.e., photon frequencies which are even multiples of the laser frequency. The effect does not occur within the Born-Oppenheimer approximation. In the high-frequency region, the even harmonics are almost of the same order of magnitude as the odd ones.

(Submitted to Phys. Rev. Lett.)
Contact E.K.U. Gross: gross@physik.uni-wuerzburg.de

Ghost-interaction correction in the ensemble-Kohn-Sham scheme for excited states

N.I. Gidopoulos*, P.G. Papaconstantinou†, E.K.U. Gross*

*Institut für Theoretische Physik, Universität Würzburg,
Am Hubland, D-97074 Würzburg, Germany

†Institute of Materials Science,
National Centre for Scientific Research "Demokritos",
GR153 10 Ag. Paraskevi Attikis, Greece

Abstract

We observe that the direct Coulomb (Hartree) term appearing in the ensemble-density-functional theory for excited states contains an unphysical ("ghost") interaction which has to be corrected by the ensemble exchange and correlation functional. We propose a simple additive correction to the conventional ensemble exchange energy in the form of an orbital functional. Treating this corrected exchange energy functional self-consistently within the optimized effective potential method one finds a significant improvement of atomic excitation energies.

(Submitted to Phys. Rev. Lett.)

Contact E.K.U. Gross: gross@physik.uni-wuerzburg.de

Towards time-dependent density-functional theory for molecules in strong laser pulses

T. Kreibich, N.I. Gidopoulos, R. van Leeuwen, and E.K.U. Gross
Institut für Theoretische Physik, Universität Würzburg,
Am Hubland, D-97074 Würzburg, Germany

Abstract

To describe the dynamical interplay of electronic and nuclear degrees of freedom in molecules exposed to strong laser pulses, we present two different variational approaches based on the statonary-action principle: A mean-field treatment of the electron-nuclear interaction and an explicitly correlated ansatz. The two methods are tested on a one-dimensional model of H_2^+ which can be solved exactly. The correlated approach significantly improves upon the mean-field treatment, especially in the case of laser fields strong enough to cause substantial dissociation.

(Submitted to Phys. Rev. Lett.)
Contact E.K.U. Gross: gross@physik.uni-wuerzburg.de

Quasiparticles in $d-$wave superconductors within DFT

Z. Szotek(1), B.L. Gyorffy(2), W.M. Temmerman(1),
O.K. Andersen(3), and O. Jepsen(3)
(1) *Daresbury Laboratory, Daresbury, Warrington, WA4 4AD, U. K.*
(2) *H H Wills Physics Laboratory, University of Bristol,*
Tyndall Avenue, Bristol, BS8 1TL, U. K.
(3) *Max-Planck-Institut für Festkörperforschung,*
Postfach 800665, D-70506, Stuttgart, Germany

Abstract

We present a semiphenomenological approach to calculating the quasiparticle spectra of high temperature superconductors. It is based on a particularly efficient parametrization of the effective electron-electron interaction afforded by the density functional theory for superconductors and a tight-binding-linearized-muffin-tin-orbital scheme for solving the corresponding Kohn-Sham-Bogoliubov-de Gennes equations. We apply this methodology to $YBa_2Cu_3O_{7-\delta}$ (YBCO) and illustrate its potential by investigating a number of site and orbital specific, but otherwise phenomenological, models of pairing in quantitative detail. We compare our results for the anisotropy of the gap function on the Fermi surface with those deduced from photoemission experiments on single crystals of YBCO. Also, the low temperature specific heat and penetration depth are calculated and compared with measurements. We investigate the doping dependence of the superconducting gap, transition temperature, T_c, and penetration depth. We present new evidence that the Van Hove-like scenario is an essential feature of superconductivity in the cuprate superconductors. Since our description of pairing is phenomenological, we shed new light on the physical mechanism of pairing only indirectly and conclude, provisionally, that the dominant pairing interaction operates between electrons of opposite spins, on nearest neighbour Cu sites in $d_{x^2-y^2}$ orbitals.

(Accepted, J. Phys. CM)
Contact person: Z. Szotek (Z.Szotek@dl.ac.uk)

Simple rules for determining 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, United Kingdom*
[4] *INFP, Forschungszentrum Karlsruhe, Postfach 3640, Karlsruhe D-76021 Germany*

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.

(Accepted, J. Phys. CM)

Contact person: W.M. Temmerman (W.M.Temmerman@dl.ac.uk)

Ab initio angle-resolved photoemission in multiple scattering formulation

M. Lüders[1], A. Ernst[1,2], W. M. Temmerman[1], Z. Szotek[1],
P. J. Durham[1]
[1] *Daresbury Laboratory, Daresbury,*
Warrington, WA4 4AD, Cheshire, U.K.
[2] *Max Planck Institut für Mikrostrukturphysik, Halle, Germany*

Abstract

The theory of *ab initio* semi-relativistic angle-resolved photoemission calculations is formulated within the real-space multiple scattering theory and the single-particle approximation. It has the flexibility and simplicity to study systems with layered structures and more general complex geometries. For layered structures the layer-resolved potentials are obtained self-consistently with the Korringa-Kohn-Rostoker (KKR) method. The advantage of the present approach is that both the self-consistent potential and the photocurrent are treated on the same footing and calculated within the same formalism. The approach is illustrated through a study of the angle-resolved photoemission for real space, layered systems with two-dimensional periodicity, with the specific application to Cu.

(Accepted, J. Phys. CM)
Contact person: W.M. Temmerman (W.M.Temmerman@dl.ac.uk)

9 SCIENTIFIC HIGHLIGHT OF THE MONTH

First principles simulations of hemeproteins: From the active center to the full protein

Carme Rovira[1] and Michele Parrinello [2]

[1] Departament de Química Física. Facultat de Química
Universitat de Barcelona.Martí i Franquès 1, 08028 Barcelona, Spain.
[2] CSCS- Swiss Center for Scientific Computing. ETH Zürich.
Via Cantonale, Galleria 2. CH-6928 Manno (TI), Switzerland.

Abstract

We present a computational study of the interplay between the structure, energy and dynamics of the active center of hemeproteins. Our calculations are based on density functional theory (DFT) combined with molecular dynamics (MD), within the Car- Parrinello scheme. Starting from the optimized structures of models for the active center, we quantify the trends in their ligand binding properties and their intrinsic dynamics at room temperature, helping to clarify experimental results for hemeproteins and biomimetics. The influence of the rest of the protein in the active center is investigated by means of hybrid QM/MM calculations based on density functional theory combined with a classical force field. It is shown that while the heme-CO bond in carbonmonoxy myoglobin (Mb-CO) is quite robust, both the CO stretch frequency and the strength of the CO$\cdots$His64 interaction are very dependent on the orientation and tautomerization state of the distal histidine residue (His64). Further aspects of these interactions and its biological implications are discussed.

1. Introduction

Hemeproteins are proteins having a heme molecule as active center (Figure 1). They perform vital roles in cellular catalysis, transport and storage [1]. For example, hemoglobin (Hb) transports oxygen in the blood (from the lungs to the muscles) and transfers the oxygen to myoglobin (Mb) which stores it in muscles. The specificity of the protein continues to fascinate chemists, as it depends on many structural and dynamic features of not only the active center but also the surrounding polypeptide framework. These features are routinely studied by crystallographic methods, which traditionally represent a protein as a static molecule with a unique structure. However, today it is widely accepted that proteins are not static but complex dynamic systems which are characterized as "screaming and kicking" [2] and undergoing "proteinquakes" [3].

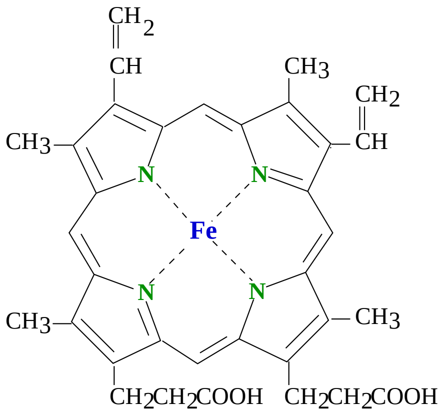


Figure 1. Molecular structure of heme b (also called protoporphyrin IX), the active center of myoglobin, hemoglobin and other hemeproteins. The substituent groups of the iron-porphyrin vary from one hemeprotein to another. In the case of myoglobin, they are two propionates, two vinyls and four methyl substituents.

Classical molecular dynamics simulations have revealed many dynamical features of these proteins, complementing the information obtained with structural techniques [4]. For instance, the most likely pathways for the ligand entry and exit from the active center of myoglobin have been identified with MD simulations [5]. However, subtle electronic/structural/spin changes (and chemical reactions) taking place at the active center cannot be described with the currently available force fields. Instead, these processes are traditionally studied by means of quantum chemistry methods using simplified models of the active center, often changed to make them as symmetric as possible. These type of computations are commonly performed at a fixed structure [6]. During the last few years, the fast development of efficient first principles methods based on Density Functional Theory (DFT) has allowed to model the reactivity of the active center beyond the "frozen structure approximation", thus capturing most of the chemistry of these systems [7]. In this respect, the first steps towards the modelling of the protein dynamics without relying on empirical parameters, have been performed [8]. In this article we will summarize our work in the modeling of myoglobin (Mb), a small globular hemeprotein that stores oxygen in muscles until it is released in the respiration process. Related works of us on hemoglobin biomimetics, as well as other hemeproteins can be found in reference [9].

The structure of Mb is known from X-ray and neutron diffraction studies [4]. In addition, several features in the dynamics and electronic structure have been investigated by infrared, Raman, Mössbauer, and ESR spectroscopy [12]. Another important source of information is provided by experiments on synthetic models (biomimetics) such as the picket-fence-oxygen molecule and its derivatives [10], for which dynamic information in the femtosecond time scale is now available [11]. Despite all this studies, many essential aspects of this function, such as the way the protein controls the binding of ligands (O_2, CO and NO), the precise structure of the Fe- ligand bonds or the structure-spin-energy relations at the active center, are a topic of debate [1e].

Structural studies (neutron and X-ray diffraction [4]) show that the active center of myoglobin (the heme) is located on one side of the protein. The heme is attached to the polypeptide framework through a covalent bond between the nitrogen atom of one of the protein residues (His93, named as proximal histidine) and the iron atom. The opposite face of the iron-porphyrin (Figure 2) is free to bind oxygen. The oxygenated protein exhibits a bent end-on geometry of the Fe-O_2 fragment both in MbO_2 [14] and HbO_2 [13], as it is also found in isolated hemes [10]. Neutron and X-ray diffraction measurements have found that the O_2 is hydrogen-bonded with the N-H of His64 in MbO_2 and α-Hb [14] [13]. However, there is no evidence of a hydrogen bond in β-HbO_2, where free rotation of the ligand around its equilibrium position is expected [13]. Recent EPR measurements in cobalt substituted Hb have also found evidence of O_2 rotation [15]. In addition, the four-fold disorder found in the crystal structure of picket-fence-oxygen systems [10]. has been interpreted as a dynamic O_2 motion by both Mössbauer and NMR experiments [16].

The FeCO fragment is bent in all available X-ray and neutron diffraction analysis of carbonmonoxy myoglobin (MbCO). This distortion was early thought to be responsible for the well known protein discrimination against CO (the affinity ratio CO/O_2 is lower in the protein than in biomimetic systems). However, a surprising wide range of FeCO angles (7^o - 60^o) have been reported in different X-ray studies (two recent high resolution MbCO structures [4] still give discrepant Fe-C-O angles). Thus, the precise quantification of the heme-CO structure seems to require X-ray resolution higher than it is presently available. On the other hand, spectroscopic studies [17] have predicted just a small distortion ($<$FeCO angle $\geq 173^o$) which, according to recent theoretical investigations, has a negligible energetic cost [6g, 7e]. As a consequence, the functional role of the FeCO distortion is nowadays very questioned [18].

There is less structural information available for nitrogenmonoxy myoglobin (MbNO) [19] than for MbCO and MbO_2. Nevertheless, a few biomimetic systems with a NO ligand have been characterized. Thermodynamic measurements show that the NO ligand exhibits a unique effect upon binding to an iron-porphyrin derivative: it has a tendency to weaken the axial trans ligand bond [20]. This has been observed in MbNO and its biomimetics, as well as in other heme proteins such as Guanylate cyclase. In this case, the effect is so strong that the binding of NO to the heme induces the release of the trans axial histidine [20b].

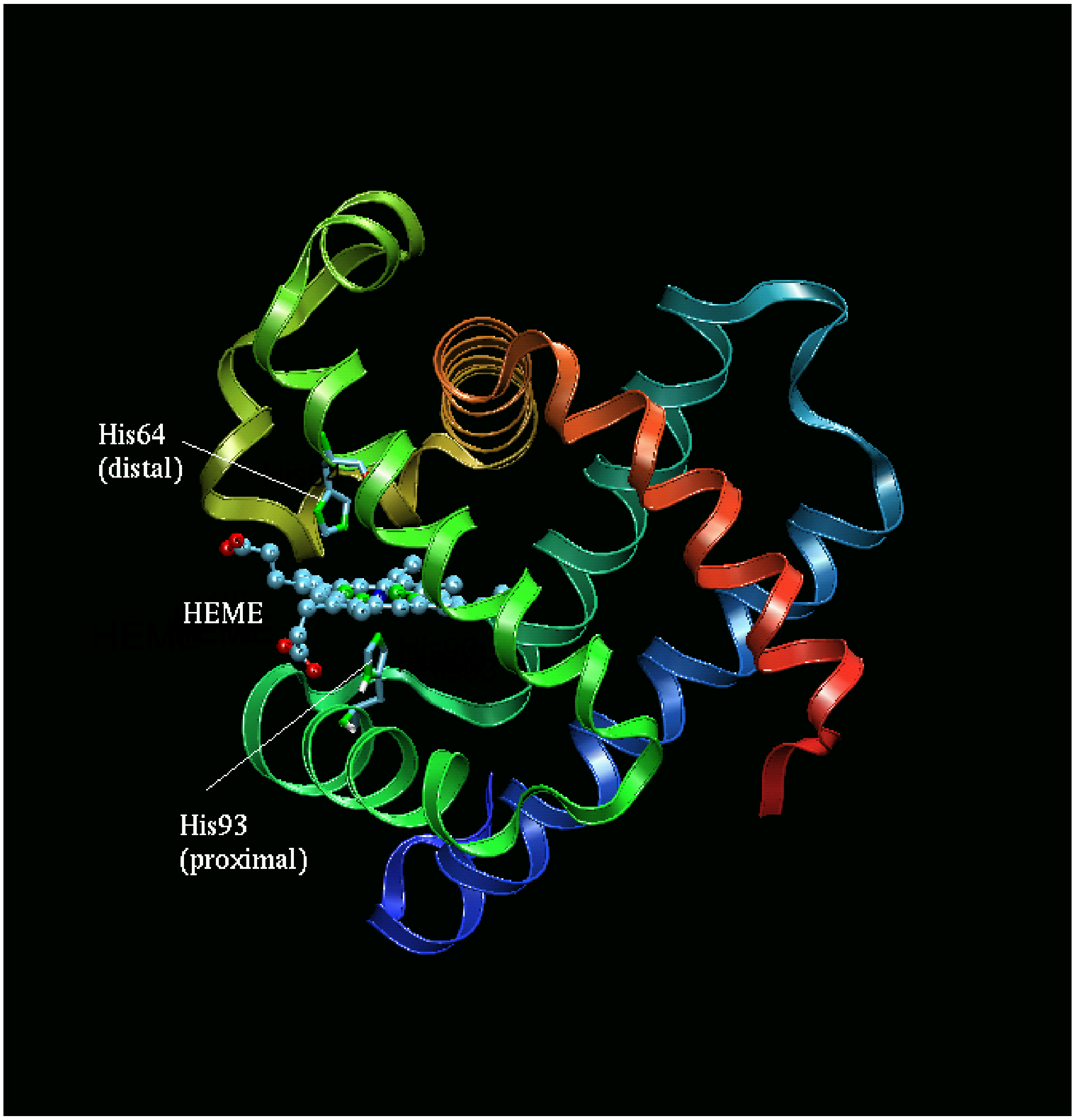


Figure 2. Structure of myoglobin (deoxy form). The heme active center is highlighted, as well as the proximal and distal histidines.

In order to understand all these issues, a precise knowledge of the intrinsic structural and dynamical properties of the heme-ligand bonds becomes of great interest. Theoretical studies could be very valuable in providing these data. It would also be extremely interesting to transcend a purely static point of view and examine fully the influence of thermal fluctuations. This is what motivated us to start a first principles study of the ligand binding properties of myoglobin. In a first step, we analyzed the interplay between the structure, energy and dynamics of the binding of O_2, CO and NO to the heme active center. The models we used for our study, shown in Figure 3, are of the type FeP-AB (FeP = iron- porphyrin, AB = CO, NO, O_2), Fe(Heme)-O_2 and FeP(Im)-AB (Im = imidazole). The imidazole molecule mimics the effect of the proximal histidine aminoacid (Figure 2). In a second step, we analyzed the interaction between the active center and the rest of the protein, by means of hybrid QM/MM simulations.

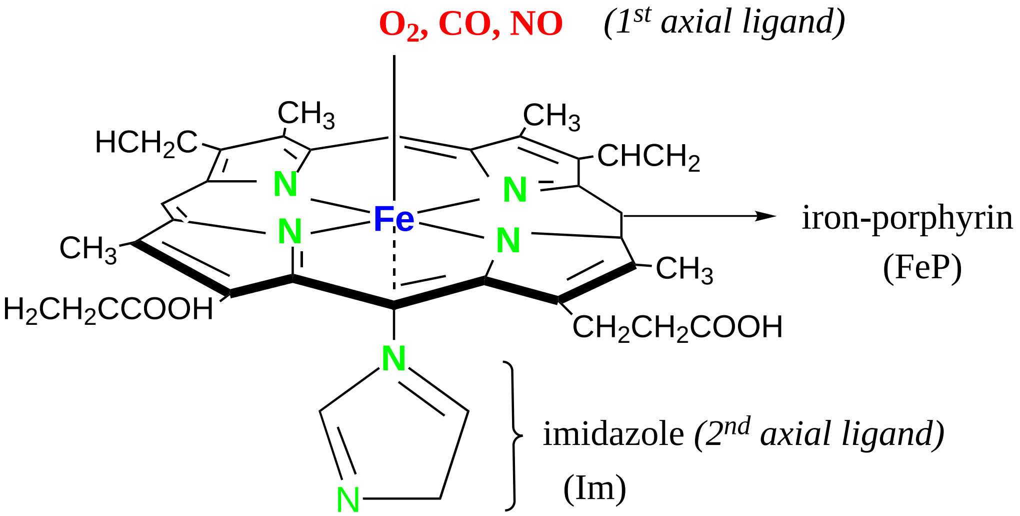


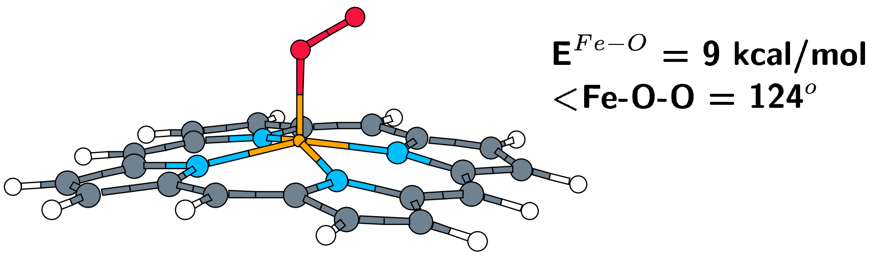
Figure 3. Active center models used in the calculations.

2. Myoglobin active center

2.1. Structure, energy and electronic state

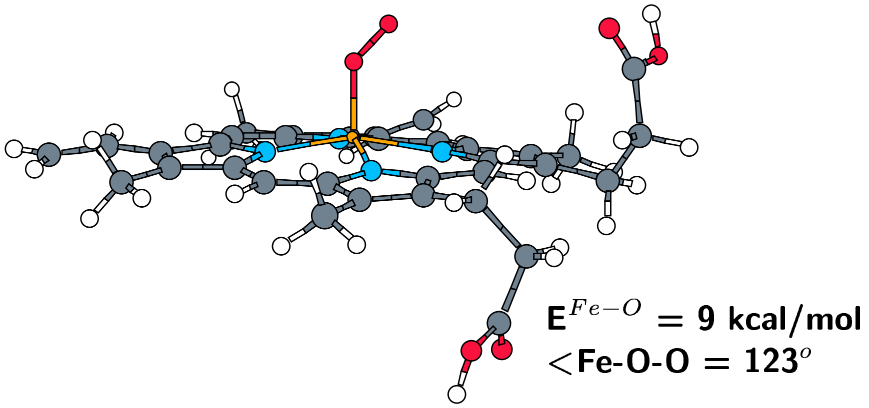
The structures of iron-porphyrin (FeP), FeP-AB (AB = O_2, CO, NO) and FeP(Im)AB (Im = imidazole) were optimized, without symmetry constraints, for the lowest energy spin state of each system. This was found to be a triplet for FeP, singlet for FeP- CO, FeP-O_2, FeP(Im)CO and FeP(Im)-O_2, and doublet for FeP-NO and FeP(Im)-NO, which is in agreement with experiments. As shown in Figure 4 (top), all pentacoordinated FeP-AB complexes are characterized by having a curved porphyrin. This type of distortion reinforces the bonding between the Fe(d_{z2}) orbital and the $3\sigma_g$ orbital of the diatomic molecule (the d_{z2} orbital becomes hybridized by mixing some s and z character). The binding energy with respect to dissociation of the diatomic ligand amounts to 9 kcal/mol (FeP-O_2), 26 kcal/mol (FeP-CO) and 35 kcal/mol (FeP-NO). The enhanced binding of CO and NO compared to O_2 can be understood in terms of the variation of the Fe(d_{z2})- AB($3\sigma_g$) interaction. In the case of CO and NO, the $3\sigma_g$ orbital is more polarized towards the C and N atoms (the ones binding to Fe), while for O_2 it is shared among both oxygen atoms. It is also worth mentioning that the energy of these systems changes little upon rotation of the AB ligand with respect to the Fe-A bond (less than 2 kcal/mol), which indicates that a rotational motion of the ligand at room temperature is likely to occur. A side-on type of Fe-O_2 binding, where both oxygens are coordinated to the metal atom, was found to be unstable. The structure evolved towards the end-on global minimum in all attempts. Nevertheless, this type of structure has been unambiguously detected in the low temperature infrared (IR) and resonant Raman (RR) spectra on the co- condensation of irontetraphenyl-porphyrin (FeTPP) and O_2 [21]. The effect of the porphyrin tetraphenyl substituents, not present in the computed model, could be the reason of the stabilization of the side-on isomer. In fact, in our early study we found [9a] that the porphyrin tetrapivalaminophenyl substituents enhance substantially the O_2 binding to the picket-fence experimental model.

iron-porphyrin-oxygen (FeP-O_2)



E^{Fe-O} = 9 kcal/mol
<Fe-O-O = 124°

heme-oxygen (FeH-O_2)



E^{Fe-O} = 9 kcal/mol
<Fe-O-O = 123°

Figure 4. Top: Optimized structure of the iron-porphyrin-O_2 model. Bottom: Optimized structure of the same system considering the full heme b molecule FeH-O_2 (H = heme).

In order to relate these structure/energy changes with the properties of the protein, it is necessary to exclude any possible influence from the chemical groups which are closest to the iron-porphyrin (the porphyrin -$(CH_2)_3COOH$, -CH=CH_2, and -CH_3 substituents, as well as the proximal histidine residue). Thus, additional calculations including the porphyrin substituent groups (see Figure 4). Our calculations showed [9d] that the local structure of the FeO_2 bond in the FeH-O_2 complexes (H = heme b or protoporphyrin IX) is the same that in FeP-O_2. Most importantly, the binding energy of the ligand does not change. Similar results were obtained for the CO and NO complexes. Therefore, the porphyrin substituents present in the myoglobin active center do not change the main ligand binding properties of the iron-porphyrin.

In contrast, addition of an imidazole (Im) axial ligand (Figure 3) does introduce major changes on the binding of ligands. These changes are schematized in Figure 5. Variations in the internal porphyrin structure have not been detailed since these are minor. The only structural change due to Im is the lose of porphyrin out-of-planarity. However, the binding energy of the Fe-O_2

and Fe-CO bonds is substantially enhanced (left center in Figure 5). This can be understood in terms of the increase of the σ- donor character of the imidazole orbital that interacts with the Fe(d_{z2}) orbital. In contrast to CO and O_2, the energy of the Fe-NO bond shows practically no variation with the addition of the imidazole, even though a similar enhancement of the σ-donor character of the imidazole should be expected. However, in this case a competing effect appears, which is related to the occupation of the Fe(d_{z2}) orbital. This orbital (the HOMO one) is antibonding with respect to the Fe-NO interaction, and thus contributes to the weakening of the Fe-NO bond. The balance between both effects results in the insensitivity of the Fe-NO bond with respect to trans axial ligation.

Similar trends were found upon attaching the diatomic molecule to the FeP-Im system (right→center in Figure 5). The binding energy of the Fe-N_ϵ bond increases upon binding of CO or O_2, but changes little (it even weakens) upon NO binding. This type of changes are consistent with the well-known trans repulsive effect of the NO when binding to iron-porphyrin derivatives. Studies of reactions of heme models with imidazole, CO, O_2 and NO [20] (a) show that the addition of NO to an imidazole-bound iron- porphyrin weakens the Fe-Im bond, while the reverse is found for CO and O_2.

It is worth noting that the binding energy values obtained for O_2 are in agreement with thermodynamic measurements of oxygen binding to myoglobin and biomimetic heme models, for which Ho values in the range of 10-19 kcal/mol are reported [22]. The large imbalance between the binding energies of CO and O_2 in the gas phase underlines the fact that the protein environment plays a major role in modulating the relative binding between both ligands. Recent experiments on $FeT_{pyr}PH_2$-NO have reported values a binding enthalpy of 29 kcal/mol [23], a value very similar to the one we computed for FeP-NO.

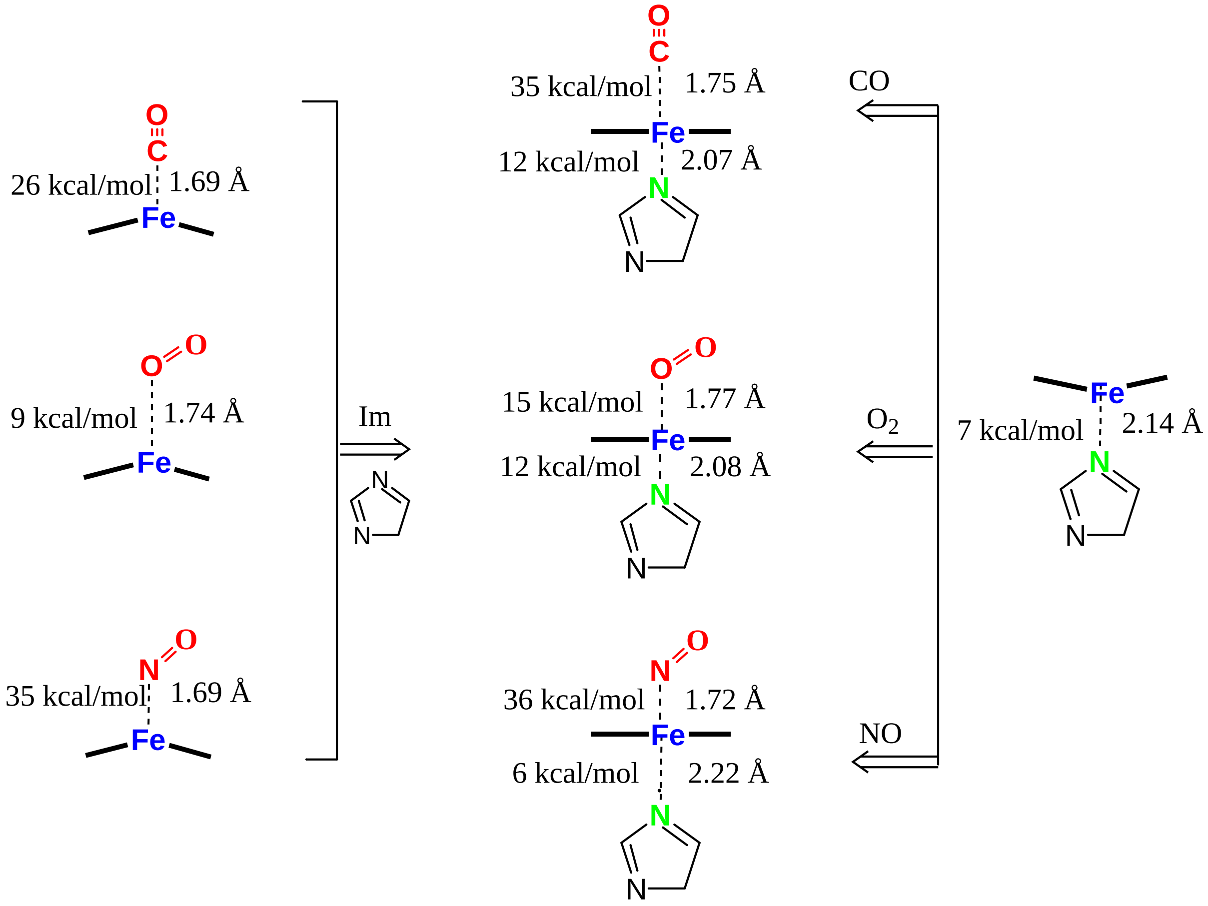


Figure 5. Scheme of the structure/energy changes upon addition of an imidazole axial ligand to the FeP(AB) systems (left to right) or addition of a diatomic AB molecule to the FeP(Im) system (right to left), with AB = CO, O_2, NO.

2.2. Heme-ligand dynamics

The dynamics of the CO ligand at room temperature was investigated in the FeP(Im)- CO model. Our simulations show that the CO ligand undergoes a fast motion around its equilibrium position: the projection of the oxygen atom on the porphyrin plane samples all porphyrin quadrants in less than 0.5 ps. An interesting property that can be extracted from the simulation is the allowed distortion of the Fe-C-O fragment. We quantified this distortion by using the tilt (δ) and bend (θ) angles, which have been often related to the protein discrimination against CO. Figure 6 shows the probability distribution of the δ and θ angles obtained from the dynamics. Small fluctuations ($\delta \leq 8^o$, $\theta \leq 13^o$) have a sizable probability to take place, but larger deformations do not occur. Therefore, for a FeCO not perturbed by the environment, small δ - θ deviations (similar to those reported by spectroscopic studies [17]) can occur just due to the thermal motion and not as a consequence of steric hindrance by the protein. This is consistent with the conclusions of recent DFT calculations [6g, 7e] which have predicted that small δ - θ variations do not have a significant energetic cost. It should also be noted that, given the complex motion of the ligand, the instantaneous structure of the FeCO unit cannot be easily defined just in terms of the δ and θ angles; the problem should be best regarded as that of a highly dynamic FeCO moiety, sampling many different conformations with different probability in a short time.

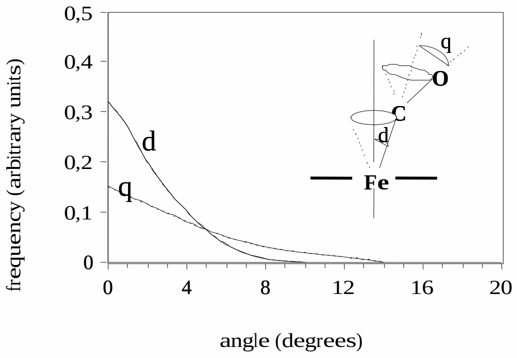
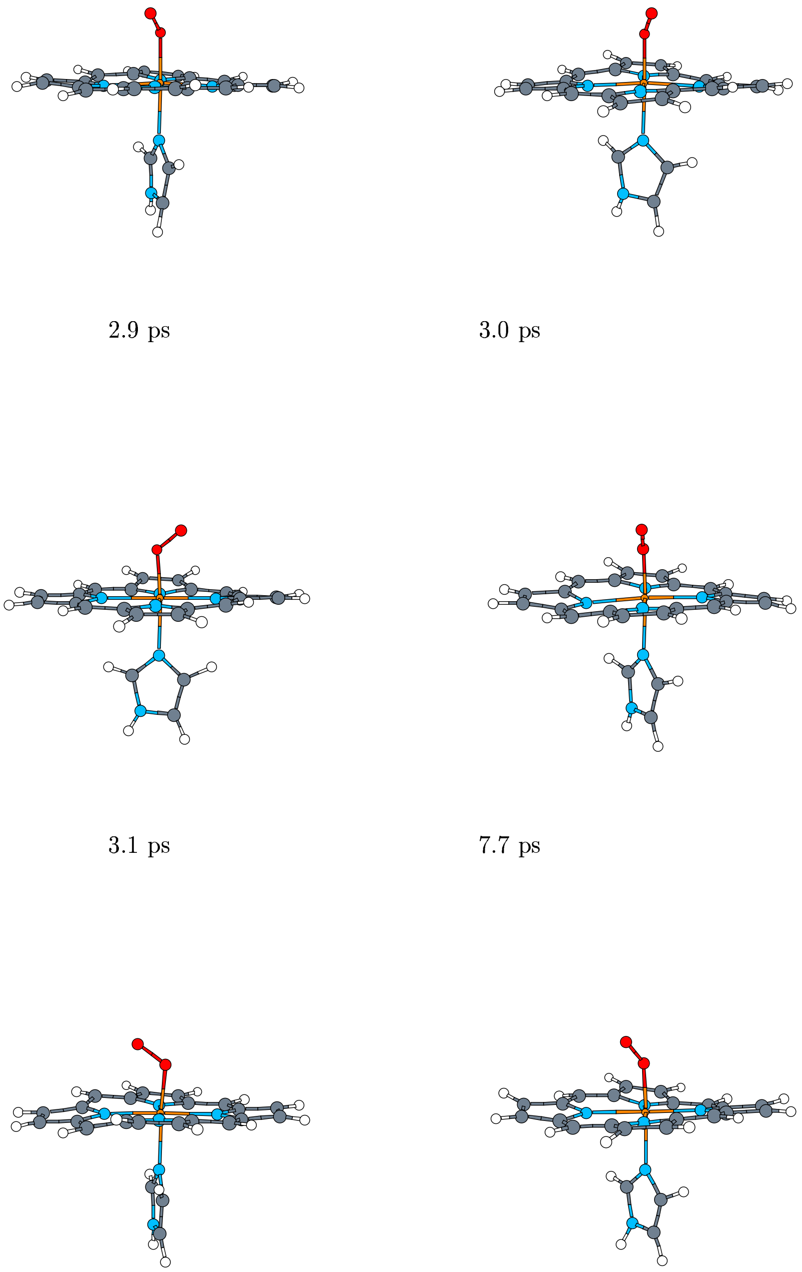


Figure 6. Frequency distribution corresponding to the two angles commonly used to describe the distortion of the FeCO fragment (θ = bending angle, δ = tilting angle).

A MD simulation for the oxyheme model, FeP(Im)(O_2), was performed for a total time of 15.5 ps. The dynamics of the bent FeO_2 unit was found to be more complex than in the case of the CO system. Selected snapshots of this simulation are shown in Figure 7. During the first period of the simulation the O-O axis projection on the porphyrin plane lies on one of the porphyrin quadrants, although it undergoes large oscillations between the two closest Fe-N_p bonds (N_p = porphyrin nitrogen atom). However, after 2.2 ps the O_2 jumps over one Fe-N_p bond towards the next porphyrin quadrant. We observed five of these jumps during the whole simulation, with an average time interval of 4 - 6 ps. All transitions take place via rotation of O_2 around the Fe-O axis and involve a conformation with a more open Fe-O-O angle (124^o - 129^o) and the Fe-O bond slightly tilted (3-5^o) with respect to the heme perpendicular (i.e., the perpendicular direction with respect to the average plane defined by the four N_p atoms). This confirms the fact that the OO/Fe-N overlaping configuration is the transition state for the dynamic motion of O_2 between the porphyrin quadrants, something not obvious from experiments [24].



2.9 ps

3.0 ps

3.1 ps

7.7 ps

7.8 ps

10.4 ps

Figure 7. Snapshots of the dynamics of the FeP(Im)O_2 active center model.

The average structure of the FeO_2 fragment that we obtain from the simulation is very similar to the equilibrium structure of the FeP(Im)-O_2 system: Fe-O = 1.75 Å, <FeOO = 122^o, O-O = 1.30 Å. The average FeOO angle is though slightly more open (124^o) and the Fe-O distance is larger (1.86 Å) due to the anharmonicity of the corresponding vibrational modes. This structure is however very different from the experimental values of its closely related picket-fence myoglobin biomimetic: Fe-O = 1.75 Å, <FeOO = 129^o, 133^o; O-O = 1.15 Å, 1.17 Å. This could be due to the fact that X-ray do not measure distances and angles directly, but rather the positions of maximum probability, from which the other structural properties are deduced. We can prove this point from our MD trajectory. If we take the position of maximum probability and then extract distances and angles we find: Fe-O = 1.72 Å, <FeOO = 139^o, O-O = 1.19 Å. Although this is in better agreement with experiment, these values are irrealistic (the O-O distance, for instance, is shorter than the gas phase value of 1.23 Å). Therefore, although this reconciles theory and experiment, it also illustrates the risk of assigning a static structure to a highly dynamical moiety such as the FeO_2 unit. Similar considerations hold for the reported data on the proteins. In particular, the Fe-O-O angles reported by neutron and X-ray structures of oxymyoglobin [14] and oxyhemoglobin [13] are very discrepant (115^o for MbO_2, 153^o for α-Hb and 159^o for β-Hb) and not even sampled in our simulation. On the other hand, a recent X-ray structure [4g], reports a <FeOO angle very close to our computed value (122^o). It could be argued that the <FeOO angle in the protein is affected by H-bond to the His64 residue. However, it has been very recently shown [7e] that such a hydrogen bond does not modify significantly the structure of the FeO_2 unit.

Overall, our simulation reveals a highly anharmonic dynamics for the O_2 ligand: it undergoes large amplitude oscillations within one porphyrin quadrant and jumps from one to the other within 4-6 ps. This is consistent with the highly dynamic nature of O_2 bound to heme proposed by several experiments in proteins and biomimetics [10] [24] especially those which lack a hydrogen bond at the terminal oxygen. Ligand rotation in these models has been shown to occur by NMR experiments [24b,c] on the basis of the equivalence of the pyrrole proton resonances. Our results suggest that, for non-hydrogen bonded O_2, precise determination of the rate of rotation would require picosecond time resolution.

3. Interaction of the heme with the protein

The above results show that most of the properties of the Heme-Ligand bonds (Ligand = CO, O_2, NO), namely its spin state, structure and dynamics, are well reproduced by modeling only the active center. This leads to an obvious question, which is what is the role of the rest of the protein on the binding of ligands. The surrounding protein has in fact a major role, for instance, in controlling the entry and release of the ligands. Protein fluctuations open channels in the interior of the protein that allow the ligands to entry and reach the active center. Recent classical MD simulations have been able to identify some of these channels [5]. Another role, whose origin has not yet been elucidated, is the control of the binding affinity of different ligands. In fact, the values we compute for the binding energies have the right trends (NO $>$ CO $>>$ O_2) but not the right absolute values. The bond of the CO is far too strong to justify the experimental CO/O_2 ratio in the equilibrium constants for the ligand binding reaction. This is however not surprising. It is known since the 70's that the relative binding CO/O_2 is controlled by the polypeptide framework [25]. A sensitive probe of this influence are the different CO stretch frequencies that appear in the IR spectrum of Mb-CO [26]. These peaks evidence that there are protein substates that interact differently with the ligand. Nevertheless, the relation between each CO stretch frequency and specific protein conformations has not yet been clarified [27].

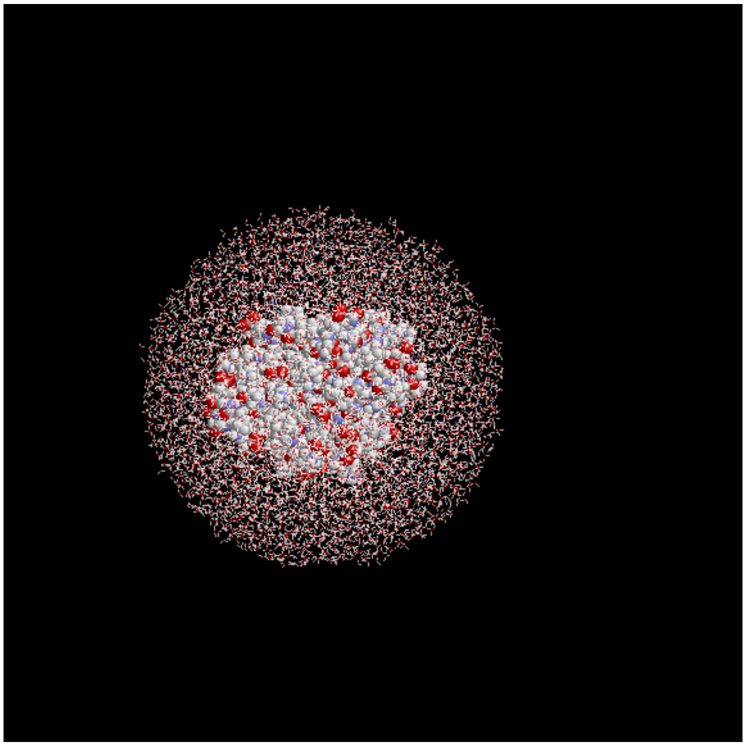
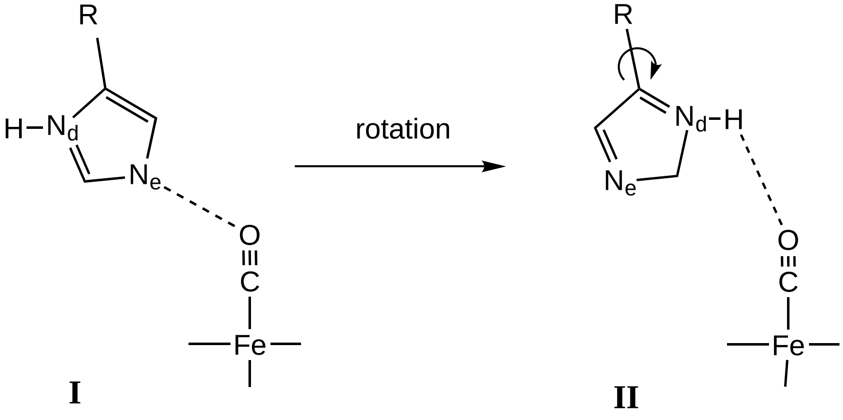


Figure 8. Protein embeeded in the water shell.

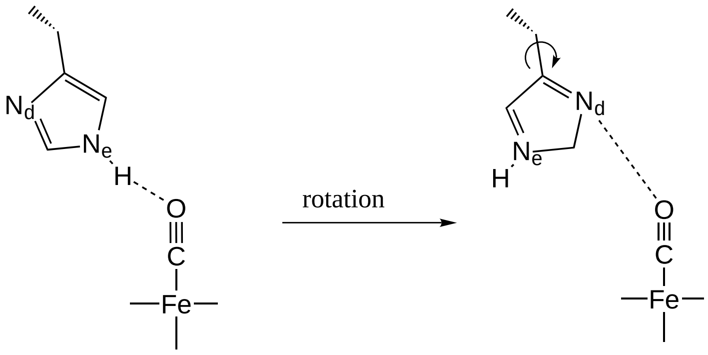
In an attempt to help the interpretation of the IR spectrum of Mb-CO, we decided to model the full protein at the QM/MM level and to evaluate the changes in the CO stretching frequency for different protein conformations. The QM/MM method we used combines the same first principles description of the active center that we have used up to now with a force-field treatment (using the CHARMM force field) of the rest of the protein. The QM- MM boundary is modeled with the use of link atoms (we refer to reference [28] for details on the QM/MM implementation). As QM region (the part that we will treat with DFT) we chose the CO ligand, the porphyrin, and the axial imidazole (see Figure 2). The porphyrin substituents were not included, since we previously found that they do not affect the properties of the Fe-ligand bonds. On the other hand including the Im of the proximal His (directly bonded to the heme) is crucial since it has an effect on strengthening the Fe-CO bond (section 2.1). With this QM-MM partition we can be confident that the energy/spin/structure relations of the heme will be well described. The protein was additionally enveloped in a 37 Å sphere of equilibrated TIP3P water molecules (see Figure 8) so as to take into account solvation effects. The number of QM and MM atoms treated in the calculation are 63 and 20000, respectively.

Before starting the calculations, it is crucial to decide what is the initial structure of the protein that we take for the calculation. Although one could just take the crystal structure directly, this is not very convenient since X-ray structures are an average among many different instantaneous protein conformations. Instead, it is physically more meaningful to consider snapshots of previous MD simulations done with the same force field used in the QM/MM calculations.

Classical simulations of MbCO using the CHARMM force field [29] were done considering different tautomerization states of the distal histidine residue (His64). These simulations evidenced that when His64 is protonated at N_δ (named N_δ-tautomer) it often rotates such that it can expose either the N_δ-H bond or the unprotonated N_ϵ atom towards the CO.

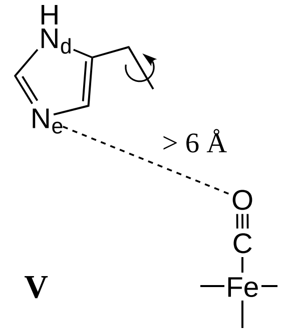


Thus, we took snapshots corresponding to these two distal His conformations. We also took another snapshot (**III**) from a simulation started with the His64 proton placed on the N_ϵ atom (N_ϵ-tautomer). As rotation of His64 did not occur in the time scale of the classical simulation (1 ns) we forced it by inducing a 180 rotation around the C1-C2 bond of His64 (**IV**).



III **IV**

Finally, we took a fifth snapshot in which the distal His moved away from the CO (this occurred after 600 ps of the simulation).



V

These protein configurations, denoted **I**-**V**, are representative of the dynamics of the heme pocket. The results obtained in the structural relaxation for each of these protein conformations are summarized in the next table.

Table 1. Main parameters defining the optimized heme-CO structure of each protein conformation **I-V**. The last row corresponds to the results obtained for the heme-CO isolated model (section 2.1).

structure	interaction type	O···X	C-O	Fe-C	<FeCO	Fe-N$_p$
exp.	$CO^{\cdots}N_\epsilon$	4.0-2.60	1.09-1.21	1.73-2.21	120 - 172	2.01-2.06
I	$CO^{\cdots}N_\epsilon$	3.39	1.16	1.76	177.3	2.00-2.02
II	$CO^{\cdots}N_\delta$	3.47	1.16	1.75	179.3	1.98-2.03
III	$CO^{\cdots}H-N_\epsilon$	2.69	1.17	1.74	176.1	1.99-2.02
IV	$CO^{\cdots}N_\delta$	3.90	1.16	1.74	175.7	1.99-2.02
	$CO^{\cdots}H-C$	2.18				
V	$CO^{\cdots}N_\epsilon$	6.03	1.16	1.75	177.6	1.99-2.03
	$CO^{\cdots}H-C$	4.03				
heme-CO	–	-	1.17	1.72	180.0	2.02

As expected, the heme-ligand structure is not very sensitive to the protein conformation. All of them have similar Fe-ligand bonds (also similar from the gas phase values we obtained previously) and, most importantly: the Fe-CO angle is essentially linear in all cases, even when the proton of the distal His is close to the CO. This suggests that the FeCO fragment should be regarded as a linear bond. The fact that X-ray structures give a distorted FeCO bond is likely to be related to the limited resolution at region of the active center.

Concerning to the CO stretch frequency, we indeed obtain significant changes depending upon the protein conformation, as we can see in the following table.

Table 2. Shift of the C-O and Fe-C stretch frequencies with respect to the isolated heme-CO system for each of the protein conformations **I - V**. Hydrogen bond energies are also listed. Distances are given in Å, frequencies in cm^{-1} and energies in kcal/mol.

structure	interaction type	O···X	$\Delta\nu_{CO}$	$\Delta\nu_{FeC}$	$\Delta E_{O...X}$
I	$CO^{\cdots}N_\epsilon$	3.39	+14	-62	+2
II	$CO^{\cdots}N_\delta$	3.47	-14	18	-2.5
III	$CO^{\cdots}H-N_\epsilon$	2.69	-23	61	-3.4
IV	$CO^{\cdots}N_\delta$	3.90	-4	10	-0.9
	$CO^{\cdots}H-C$	2.18			
V	$CO^{\cdots}N_\epsilon$	6.03	-1	10	-0.1
	$CO^{\cdots}H-C$	4.03			
heme-CO	–	–	0	0	–

Whenever the proton of the distal His is close to the CO (**II**, **III**), the CO frequency decreases (the shift is negative). Instead, the shift is positive when the unprotonated nitrogen comes close to CO (**I**). The largest downshift (-23 cm-1) is given by the CO···H-N interaction in the N_ϵ-tautomer (**III**). In this case, the possible N-H···OC hydrogen bond is geometrically more favored than in the other configurations. The configuration with the distal His far from the ligand (**V**) practically does not shift the CO frequency . This is in agreement with mutagenesis experiments showing an enhancement of the highest CO frequency peak in the IR spectrum when His64 is replaced for an apolar residue [30]. Configuration **IV** practically does not shift significantly the CO frequency either. This could be due to the opposite effect of both the protonated and the unprotonated N at intermediate distances. Our calculations also evidence the inverse correlation between the $\Delta\nu_{CO}$ and $\Delta\nu_{FeC}$ values ($\Delta\nu_{CO}$ increases as $\Delta\nu_{FeC}$ decreases). This general trend has been observed across a wide range of heme proteins and biomimetic systems [31].

The frequency changes of Table 2 can be rationalized in terms of variations in the Fe- CO back bonding (i.e. the interaction of the d-Fe levels with the empty σ^* CO orbitals). When a positive charge approaches the CO (such as the proton of His64), the orbitals are energetically stabilized. As they get closer in energy to the Fe-d orbitals, the back bonding increases and, as a consequence, the CO frequency decreases. Thus, a downshifted ν_{CO} is observed for the CO···H-N interactions (**II**, **III**). In contrast, a negative charge approaching the CO (such as a nitrogen lone pair) would decrease the back bonding and increase νCO. In agreement with this argument, an upshift of ν_{CO} is obtained for the arrangement I.

Similar changes in CO frequency have been observed experimentally. As mentioned above, the IR spectrum of carbonmonoxy myoglobin shows three main CO stretching bands. The origin of all these bands is still unclear but is often assumed that they correspond to different orientations and/or protonation state of the distal His [31]. The shifts in the CO frequency that we obtain give further support to this interpretation. Further details about this study including the interpretation of the IR spectrum in terms of our calculated shifts can be found in ref. [32].

As in the case of vibrational frequencies, the interaction energy of the ligand with the distal residue (last column in Table 2) is very dependent on the conformation and protonation state of the distal His. Configuration **I** lead to a repulsive interaction (2 kcal/mol), while the interaction is favorable when the protonated nitrogen is close to the CO. We find the largest stabilization for the N_ϵ tautomer, as in this case the H-bond is more favored. This is at variance from the common assumption [31a] that only O_2 could be hydrogen bonded to His64. However, our calculations support recent RR measurements [33] that show spectroscopic evidence of a hydrogen bond between CO and His64.

For the sake of comparison, we did a calculation replacing the CO by O_2 (just to estimate the strength of the analogous O_2···His64 interaction). It is commonly accepted that His64 is protonated at N_ϵ in MbO_2. Hence, we did the calculation on arrangement **III** where the proton of N_ϵ is pointing towards the ligand (Figure 9). The H-bond in that case amounts to about -5.1 kcal/mol. Therefore our calculations find the O_2 more stabilized by H-bond than the CO, although H-bond takes place in both cases.

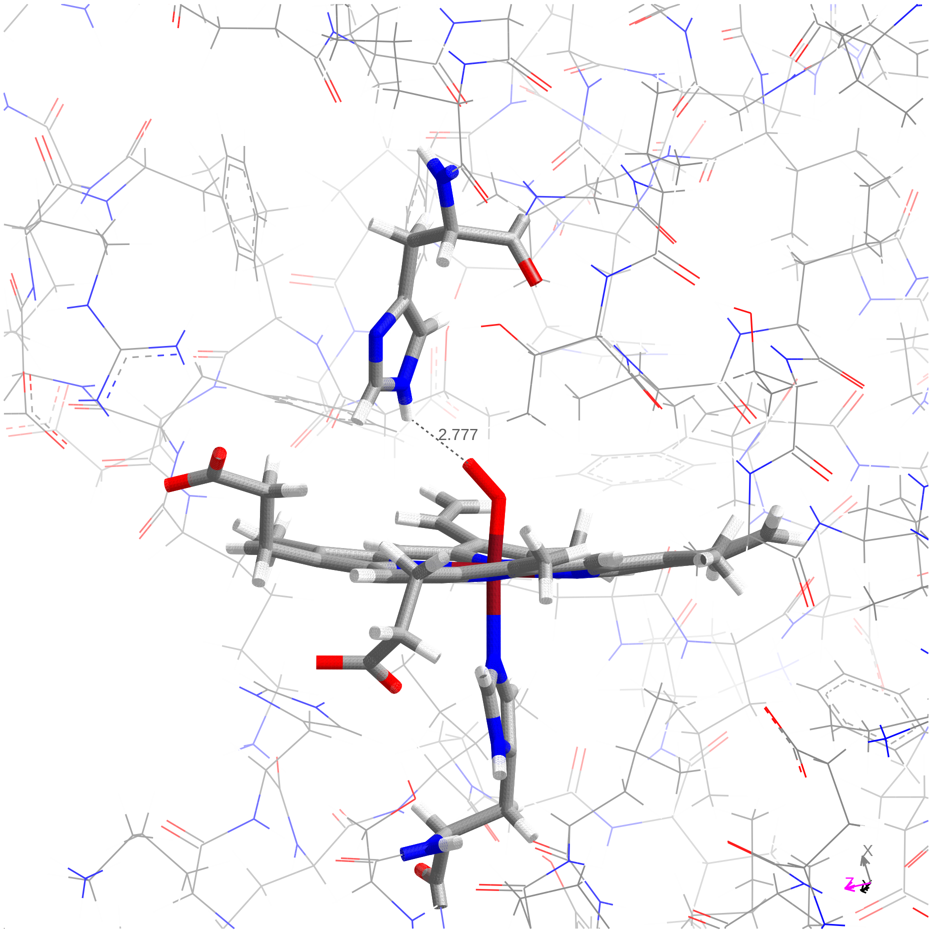


Figure 9. Optimized structure of oxymyoglobin (MbO_2) in the region around the heme active center.

4. Conclusions

In this study we have quantified the binding of CO, NO and O_2 to myoglobin. All three ligands induce a significant curvature of the heme active center when binding to the iron, although the porphyrin planarity is restored by the trans binding of an imidazole ligand. Unlike the imidazole axial ligand, the heme substituents do not influence the structure and the binding energy of the Fe-Ligand bonds (Ligand = CO, O_2, NO).

Significant differences in the binding properties of the three ligands are observed. *The Fe-O_2 bond is much weaker than Fe-CO and Fe-NO, and the binding angle increases on going from O_2 to CO.* Most of these changes can be traced back to differences in the electronic structure. In the case of the six-coordinated complexes, occupation of the Fe(d_{z^2}) orbital in the NO complex leads to the elongation and weakening of the bond with the trans axial ligand, while for O_2 and CO the imidazole reinforces the iron-diatomic bond. Rotation of the oxygen around the Fe-O bond involves a small energy barrier ($<$ 2 kcal/mol), which indicates that several rotational conformations could be available at room temperature. Indeed, our MD simulations show *the O_2 ligand undergoing large amplitude oscillations within one porphyrin quadrant and jumping to another quadrant in the picosecond time scale.* In contrast, just a fast motion of the ligand around its equilibrium position characterizes the dynamics of the FeCO unit, with a maximum distortion 13^o in the <FeCO angle.

Hybrid QM/MM calculations based on density functional theory combined with the CHARMM force field highlight the effect of the distal pocket conformation on the properties of the Fe-CO bond in MbCO and help the interpretation of the CO absorption bands in the IR spectrum. Our calculations, performed on selected snapshots from a classical MD trajectory, show that the local structure around the Fe atom practically recovers that of the gas-phase heme-CO system, where the FeCO is linear. Therefore, *the heme-CO structure seems to be quite robust and not influenced by the protein environment.* Instead, both the CO stretch frequency and the strength of the CO$\cdots$His64 interaction appear to be very dependent on the orientation and tautomerization state of His64. This can be rationalized in terms of the changes in the Fe-CO back bonding when a positive/negative charged group approaches the CO ligand. Our calculations show that, *in contrast with the common assumption that only the binding of O_2 is stabilized by interaction with the distal histidine residue, a significantly stabilization also occurs for the CO ligand.* Nevertheless, the CO$\cdots$His64 interaction is smaller than $O_2\cdots$His64 one.

In summary, our calculations have quantified the interplay between the structure, energy and dynamics of the heme active center and its interaction with the protein. This helps to understand some of the unknown questions in hemeprotein research such as the precise structure of the Fe-ligand bonds, their intrinsic dynamics, the role of the proximal and distal histidines and the origin of the CO stretch bands of the IR spectrum of MbCO. Of course, many relevant biological processes, like ligand migration into the solvent and the folding of the proteins, occur in long time scales and thus cannot be treated currently by ab initio molecular dynamics (AIMD). However, we believe that the present study illustrates how AIMD simulations can provide useful hints in order to understand the mechanism of short time scale processes in proteins.

Acknowledgments

We thank the Garching Computer Center (Garching, Germany) for computing support. C. Rovira acknowledges the financial support of the "Incorporacin de doctores y tecnólogos" program of the Spanish Ministry of Science and Technology. C.R thanks useful discussions with many friends and colleagues during the years "in der Klinik": Jürg Hutter, Pietro Ballone, Karel Kunc, Mauro Boero, Roger Rousseau, Carla Molteni and Irmgard Frank.

Appendix: computational details

All calculations presented here are based on the density functional theory within the LDA and LSD approximations. The Kohn-Sham orbitals are expanded in a plane wave (PW) basis set, with a kinetic energy cutoff of 70 Ry. The Ceperley-Alder expression for correlation and gradient corrections of the Becke-Perdew type are used [34]. We employ ab initio pseudopotentials, generated using the Troullier-Martins scheme [35]. The following core-radii, in a.u., were used: 1.23 for the s, p atomic orbitals of carbon, 1.12 for s, p of N, 0.5 for the s of H, and 1.9, 2.0, 1.5, 1.97, respectively, for the s, p, d, f atomic orbitals of Fe. The non-linear core-correction [36] was used (with core- charge radius of 1.2 a.u.). We employed the Car-Parrinello molecular dynamics method [37] for optimization of the atomic structures. A successive use of quenching and annealing performed for about one picosecond was necessary to reach a final convergence of 10-5 and 5.10-4 a.u. for electronic and ionic gradients, respectively. Structure optimizations were performed with no constraints starting from non-symmetric structures. The convergence of our results with the energy cutoff in the PW expansion was investigated for an iron-porphyrin. The ordering of spin states was found to be insensitive to the PW cutoff value, and the energy differences changed only very slightly (within 0.5 kcal/mol) [9]e. Structural parameters were found to be even less sensitive than energy differences to the PW cutoff. Molecular dynamics simulations at room temperature were performed using a time step of 0.12 fs, with the fictitious mass of the Car-Parrinello Lagrangian set to 700 au. The deuterium mass for the hydrogen atoms was used. The systems, enclosed in supercells of 16 Å x 16 Å x 20 Å periodically repeated in space, were allowed to evolve during 2 ps in order to achieve vibrational equilibration. The MD was performed for a total period of 18 ps and 15.5 ps for FeP(Im)-CO and FeP(Im)-O_2, respectively. The hybrid QM/MM calculations have been done using the EGO-CPMD code [28]., which is an interface between the EGO classical code, based on the CHARMM force field, with the CPMD code of Stuttgart. Harmonic ligand stretch frequencies were computed from the diagonalization of the Hessian matrix obtained by numerical energy derivatives.

References

[1] See for instance: (a) M. F. Perutz, G. Fermi, B. Luisi, B. Shaanan, R. C. Liddington, R. C.; *Acc. Chem. Res.* **20**, 309, 1987. (b) B. A. Springer, S. G. Sligar, J. S. Olson, G. N.

Phillips, *Chem. Rev.* **94**, 669, 1994. (c) M. Momenteau, C. A. Reed, *Chem. Rev.* **94**, 659, 1994. (d) J. S. Olson, G. N. Phillips, *J. Biol. Chem.* **271**, 17593, 1996. (e) J. T. Sage, P. M. Champion, in "Small substrate recognition in heme proteins", *Comprehensive Supramolecular Chemistry*, vol 5, 171-213, 1996. (f) S. Hirota, L. Tiansheng, G. N. Phillips, J. S. Olson, M. Mukai, T. Kitagawa, *J. Am. Chem. Soc.*, **118**, 7845, 1996.

[2] (a) G. Weber. *Adv. Prot. Sci.*, **29**, 1, 1975. (b) H. Frauenfelder, S. G. Sligar, P. G. Wolynes. Science. **254**, 1598, 1991.

[3] A. Ansari, J. Berendsen, S. F. Bowne, H. Frauenfelder, I. E. T. Iben, T. B. Sauke, E. Shyamsunder, R. D. Young. *Proc. Natl. Acad. Sci. USA*, **82**, 5000, 1985.

[4] (a) I. Schlichting, J. Berendzen, G. N. Phillips, R. M. Sweet, *Nature* **371**, 808, 1994. (b) F. Yang, G. N. Phillips *J. Mol. Biol.* **256**, 762, 1996. (c) J. Kuriyan, S. Wilz, M. Karplus, G. Petsko, *J. Mol. Biol.* **192**, 133, 1986. (d) X. Cheng, B. P. Schoenborn, *J. Mol. Biol.* **220**, 381, 1991. (e) F. Yang, G. N. Phillips, *J. Mol. Biol.* **256**, 762, 1996. (f) A. N. Kachalova, H. Popov, D. Bartunik, *Science* **284**, 473, 1999. (g) J. Vojtechovsky, K. Chu, J. Berendzen, R. M. Sweet, I. Schlichting, *Biophys. J.* **77**, 2153, 1999.

[5] B. Schulze, H. Grubmller, J. D. Evanseck. *J. Am. Chem. Soc.*, **122**, 8700, 2000.

[6] See for instance: (a) A. Dedieu, M.-M. Rohmer, A. Veillard, *Chem. Phys.* **97**, 10964, 1983. (b) A. Waleh, N. Ho, L. Chantranupong, G. H. Loew, *J. Am. Chem. Soc.* **111**, 2767, 1989. (c) W. D. Edwards, B. Weiner, M. C. Zerner, *J. Am. Chem. Soc.*, **108**, 2196, 1986. (d) P. Jewsbury, S. Yamamoto, T. Minato, M. Saito, T. Kitagawa, *J. Am. Chem. Soc.*, **116**, 11586, 1994. (e) H. Nakatsuji, J. Hasegawa, H. Ueda, M. Hada, *Chem. Phys. Lett.* **250**, 379, 1996 (f) R. H. Havlin, N. Godbout, R. Salzmann, M. Wojdelski, W. Arnold, C. E. Schulz, and E. Oldfield. *J. Am. Chem. Soc.* **120**, 3144, 1998. (g) Vangberg, T.; Bocian, D. F.; Ghosh, A. *J. Biol. Inorg. Chem.* **2**, 526, 1997.

[7] (a) T. G. Spiro, P. M. Kozlowsli, *J. Am. Chem. Soc.* **120**, 4524, 1998. (b) F. Maseras, *N. J. Chem.* **22**, 327, 1998. (c) C. Rovira, P. Ballone, M. Parrinello. *Chem. Phys. Lett.* **271**, 140, 1997. (d) C. Rovira, K. Kunc, J. Hutter, P. Ballone, M. Parrinello, *J. Phys. Chem. A* **101**, 8914, 1997. (e) E. Sigfridson, U. Ryde, *J. Biol. Inorg. Chem.* **4**, 99, 1999. (f) M. D. Segall, M. C. Payne, S. W. Ellis, G. T. Tucker, R. N. Boyes, *Phys. Rev. E* , 4618, 1998. (g) D. A. Scherlis, C. B. Cymeryng, D. A. Estrin, *Inorg. Chem.* **39**, 2352 (2000).

[8] (a) F.Alber, O.Kuonen, L.Scapozza, G.Folkers, P. Carloni, *Protens: Struc. Func. Gen.* **31**, 453, 1998. (b) D. E. Sagnella, K Laasonen, M. L. Klein, *Biophys. J.* **71**, 1172, 1996. (c) C. Rovira, M. Parrinello. *Biophys. J.* **78**, 93, 2000.

[9] (a) C. Rovira, M. Parrinello. *Chem. Eur. J.*, **5**, 250, 1999. (b) C. Rovira, P. Carloni, M. Parrinello. *J. Phys. Chem. B* **103**, 7031, 1999. (c) M. Kaupp, C. Rovira, M. Parrinello. *J. Phys. Chem. B* **104**, 5200, 2000. (d) C. Rovira, M. Parrinello. *Int. J. Quant. Chem.* **80**, 1172, 2000. (e) C. Rovira, K. Kunc, J. Hutter, M. Parrinello. *Inorg. Chem.* **40**, 11, 2001.

[10] (a) G. B. Jameson, G. A. Rodley, W. T. Robinson, R. R. Gagne, C. A. Reed, J. P. Collman, *Inorg. Chem.* **17**, 850, 1978. (b) B. Jameson, F. Molinaro, J. A. Ibers, J. P. Collman, J. I. Brauman, E. Rose, K. S. Suslick, *J. Am. Chem. Soc.* **102**, 3224, 1980.

[11] B. Steiger, J. S. Baskin, F. C. Anson, A. H. Zewail, *Angew. Chem. Int. Ed.* **39**, 257, 2000.

[12] A. X. Trautwein, E. Bill, E. L. Bominaar, H. Winkler, in *Bioinorganic Chemistry*, Vol. 78 (Springer-Verlag, Berlin, 1991), p. 1.

[13] B. Shaanan, *J. Mol. Biol.* **171**, 31, 1983.

[14] (a) S. E. V. Phillips, and B. P. Schoenborn, *Nature* **292**, 81, 1981. (b) S. E. V. Phillips, *J. Mol. Biol.* **142**, 531, 1980.

[15] J. H. Bowen, N. V. Shokhirev, A. M. Raitsimring, D. H. Buttlaire, F. A. Walker *J. Am. Chem. Soc.* **101**, 8683, 1997.

[16] (b) J. Mispelter, M. Momenteau, D. Lavalette, J.-M. Lhoste, *J. Am. Chem. Soc.* **105**, 5165, 1983. (c) E. Oldfield, H. C. Lee, C. Coretsopoulos, F. Adebodum, K. D. Park, S. Yang, J. Chung, B. Phillips, *J. Am. Chem. Soc.* **113**, 8680, 1991.

[17] (a) J. T. Sage, W. Jee, *J. Mol. Biol.* **274**, 21, 1997. (b) M. Lim, T. A. Jackson, P. A. Anfinrud, *Science* **269** 962, 1995.

[18] (a) C. Slebodnick, J. A. Ibers, *J. Biol. Inorg. Chem.* **2**, 521, 1997.

[19] (a) W. R. Scheidt, M. E. Frisse, *J. Am. Chem. Soc.* **97**, 17, 1975. (b) W. R. Scheidt, P. Piciulo, *J. Am. Chem. Soc.* **98**, 1913, 1976. (c) E. Allen Brucker, J. S. Olson, M. Ikeda-Saito, G. N. Phillips, *Prot. Str. Func. Gen.* **30**, 352, 1998.

[20] (a) T. G. Traylor, V. S. Sharma, *Biochemistry* **31**, 2847, 1992. (b) E. J. Rose, B. M. Hoffman, *J. Am. Chem. Soc.* **105**, 2866, 1983.

[21] (a) T. Watanabe, T. Ama, K. Nakamoto, *J. Phys. Chem.* **88**, 440, 1994. (b) L. M. Proniewicz, I. R. Paeng, K. Nakamoto, *J. Am. Chem. Soc.* **113**, 3294, 1991. (c) K. Nakamoto, *Coord. Chem. Rev.* **100**, 363, 1990.

[22] M. Momenteau, C. A. Reed, *Chem. Rev.* **94**, 659, 1994.

[23] O. Chem, S. Broh, A. Liechty, D. P. Ridge, *J. Am. Chem. Soc.* **121**, 11910, 1999.

[24] (a) K. Spartalian, G. Lang, J. P. Collman, R. R. Gagne, C. A. Reed, *J. Chem. Phys.* **63**, 5375, 1975. (b) J. Mispelter, M. Momenteau, D. Lavalette, J.-M. Lhoste, *J. Am. Chem. Soc.* **105**, 5165, 1983. (c) E. Oldfield, H. C. Lee, C. Coretsopoulos, F. Adebodum, K. D. Park, S. Yang, J. Chung, B. Phillips, *J. Am. Chem. Soc.* **113**, 8680, 1991.

[25] L. Stryer, *Biochemistry*, Fourth Edition, Freeman, New York, 1995.

[26] J. B. Johnson, D. C. Lamb, H. Frauenfelder, J. D. Mller, B. McMahon, G. U. Nienhaus, R. D. Young. *Biophys. J.* **71**, 1563, 1996.

[27] T. Li, M. L. Quillin, G. N. Phillips, J. S. Olson. *Biochemistry* **33**, 1433, 1994.

[28] M. Eichinger, P. Tavan, J. Hutter, M. Parrinello, *J. Chem. Phys.* **110**, 10452, 1999.

[29] Schulze, B. and J. D. Evanseck. *J. Am. Chem. Soc.* **121**, 6444, 1999..

[30] (a) D. P. Braunstein, K. Chu, K. D. Egeberg, H. Frauenfelder, J. R. Mourant, G. U. Nienhaus, P. Ormos, S. G. Sligar, B. A. Springer, R. D. Young, *Biophys. J.* **65**, 2447, 1993. (b) T. Li, M. L. Quillin, G. N. Phillips, J. S. Olson. *Biochemistry*, **33**, 1433, 1994.

[31] (a) G. B. Ray, X.-Y. Li, J. A. Ibers, J. L. Sessler, T. G. Spiro. *J. Am. Chem. Soc.* **116**, 162, 1994. (b) G. N. Phillips, M. L. Teodoro, T. LI, B. Smith, J. S. Olson. *J. Phys. Chem. B* **103**, 8817, 1999.

[32] C. Rovira, B. Schulze, M. Eichinger, J. D. Evanseck, M. Parrinello. *Biophys. J.* **81**, 435, 2001.

[33] M. Unno, J. F. Christian, J. S. Olson, J. T. Sage, P. M.Champion *J. Am. Chem. Soc.* **120**, 2670, 1998.

[34] (a) A. D. Becke, *J. Chem. Phys.* **84**, 4524, 1986. (b) J. P. Perdew, *Phys. Rev. B* **33**, 8822, 1986.

[35] N. Troullier, J. L. Martins, *Phys. Rev. B* **43**, 1993, 1991.

[36] S. G. Louie, S. Froyen, M. L. Cohen, *Phys. Rev. B* **26**, 1738, 1982.

[37] (a) Car, R; Parrinello M. *Phys. Rev. Lett.* **55**, 2471, 1985. (b) G. Galli, M. Parrinello, *Computer Simulation in Materials Science*, Edited by V. Pontikis and M. Meyer, Kluwer, Dordrecht, 1991, and references therein.