Ψ_k Newsletter

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

Number 62   April 2004

Contents

1 Editorial

This newsletter is in principle dominated by workshop/conference announcements that can be found in the RTN3-, ESF- and general announcements-sections. In the ESF section there are also two reports on recent meetings. One is the Joint ICTP-DEMOCRITOS International School on "Continuum Quantum Monte Carlo Methods", and the other the "KKR-Workshop: New developments, applications, and collaborations". The latter contains abstracts of presented papers. The available position announcements can be found in the usual section, followed by the section of the abstracts of newly submitted papers. The newsletter is finished with the scientific highlight of the month by Jacek Goniakowski (Marseille and Paris), Christine Mottet (Marseille), and Claudine Noguera (Paris) on **"Non-reactive metal-oxide interfaces: from model calculations towards realistic simulations"**. Please check 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 2004 workshops and hands-on courses (subject to funding). 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-network@daresbury.ac.uk	**messages to the whole Ψ_k community**

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

2 News from the RTN3 "Exciting"

"Ab initio methods for calculation of optical properties of matter"

2.1 Third Meeting Announcement

The third network meeting in the EU RTN network EXCITING (ab initio methods for calculation of optical properties of matter) will be held in Aarhus (Denmark) 13-15 April 2004. The meeting will also be open to participants who are not directly associated with a node of this network.

For further information :

`http://www.phys.au.dk/~nec/excaar.htm`

Niels E. Christensen
Professor (Theor. Solid St. Physics)
Institute of Physics and Astronomy
Aarhus University
DK-8000 Aarhus C
Denmark

Tel.: (+45) 8942 3666
Fax : (+45) 8612 0740

3 News from the ESF Programme

"Towards Atomistic Materials Design"

3.1 ESF Workshop/Conference Announcements

3.1.1 Workshop on "Electronic structure beyond density functional theory"

12-16 July 2004, Leiden, The Netherlands

Organizers: Claudia Filippi, Matthew Foulkes, Shiwei Zhang

The workshop is funded by the Lorentz Center and the Psi-k ESF programme

This workshop will focus mainly on quantum Monte Carlo (QMC) methods, which are among the most successful post-DFT approaches. QMC methods have yielded accurate results for the correlated properties of large molecules and solids where conventional quantum chemistry techniques are extremely difficult to apply. They provide a unique tool for exploring electronic correlations in systems of interest to materials science, and for obtaining conclusive answers in cases where DFT is inadequate.

The goal of this workshop is to reach out to researchers interested in the development and application of QMC methods. It will bring together scientists from different communities (QMC, DFT, quantum chemistry, lattice models, GW, dynamical mean-field theory, etc.) with a common interest in ab-initio many-body calculations, and will include focused discussions on outstanding issues. We welcome researchers who are not yet QMC practitioners but who are interested in acquiring the expertise. We hope that the synergy brought by the diversity of participants will spawn new ideas and lead to rapid growth of the field.

The workshop will have a combination of invited talks and discussion sessions with ample time for close iteractions. Limited funds are available to cover lodging expenses of participants and contribute towards travel costs.

Tentative list of invited participants includes: Giovanni Bachelet, Stefano Baroni, Dario Bressanini, Michel Caffarel, David Ceperley, Michael Dolg, Stephen Fahy, Rex Godby, Jeffrey Grossman, Mal Kalos, Alexander Lichtenstein, Arne Luchow, Lubos Mitas, Saverio Moroni, Richard Needs, Andrew Rappe, Kevin Schmidt, Martin Schutz, Sandro Sorella, Matthias Troyer, Cyrus Umrigar, and more.

For further information and registration, see

`http://www.lc.leidenuniv.nl/lc/web/2004/20040712/info.php3?wsid=107`

The deadline for registration is 30 April 2004.

3.1.2 Joint CECAM-Psi-k Network Workshop

The Nature of Hydrogen Bonding and Density Functional Theory
at CECAM, Lyon, France, 2-5, June 2004
Organizers: Joel Ireta, Martin Fuchs and Matthias Scheffler

http://w3.rz-berlin.mpg.de/~ireta/member/lyon.htm

MOTIVATION

The aim of this joint CECAM-Psi-k Network workshop is to bring together the key theoreticians who have analyzed the nature of hydrogen bonding and the quality of xc-functionals for describing them. The main objective is to discuss the accuracy of different exchange correlation functionals for predicting interactions in hydrogen bonded systems.

TOPICS

-Ability of xc-functionals for describing hydrogen bonding (benchmarking xc functionals with respect to MP2, CI, CC, Quantum Monte Carlo)

-The nature of the hydrogen bonding interaction

-Hydrogen bonding cooperativity

-Dynamical properties of hydrogen bonded systems (vibrational properties, proton-transfer barriers)

INVITED SPEAKERS

E. J. Baerends (Vrije Universiteit, Amsterdam, The Netherlands)
D. A. Dixon (University of Alabama, Tuscaloosa, USA)
M. Elstner (Universitt Paderborn, Paderborn, Germany)
M. Fuchs (Fritz-Haber-Institut, Berlin, Germany)
H. Guo (University of Tennessee, Knoxville, USA)
P. Hobza (Academy of Sciences of the Czech Republic, Prague, Czech Republic)
K. J. Jalkanen (Technical University of Denmark, Lyngby, Denmark)
M. Klein (University of Pennsylvania, Philadelphia, USA)
W. Kohn* (University of California, Santa Barbara, USA)
K. Laasonen (University of Oulu, Oulu, Finland)
D. Marx (Ruhr-Universitt, Bochum, Germany)
K. Mller-Dethlefs (University of York, York, U. K.)
S. Raugei (SISSA, Trieste, Italy)
D. R. Salahub (University of Calgary, Calgary, Canada)
A. Savin (CNRS et Universit Paris VI, Paris, France)

J. Sauer (Humboldt-Universitt, Berlin, Germany)

K. Sen (University of Hyderabad, Hyderabad, India)

G. Scuseria (Rice University, Houston, USA)

W. Yang (Duke University, Durham, USA)

* To be confirmed

PARTICIPATING IN THE WORKSHOP

If you would like to participate in this workshop, please send a title and abstract for your proposed contribution (poster session) to Joel Ireta (ireta@fhi-berlin.mpg.de). Places are limited, but we plan to invite as many participants as possible. We will confirm places for participants in April.

For further information please check the workshop webpage

`http://w3.rz-berlin.mpg.de/~ireta/member/lyon.htm`

ELECTRONIC STRUCTURE SIMULATIONS OF NANOSTRUCTURES (ESSN-2004): TOWARDS AN UNDERSTANDING OF PHYSICAL, CHEMICAL AND BIOLOGICAL PROCESSES

UNIVERSITY OF JYVÄSKYLÄ, FINLAND

JUNE 18-21, 2004

http://www.phys.jyu.fi/essn04

FINAL REMINDER - DEADLINE FOR REGISTRATION: MARCH 31ST!

SCOPE OF THE WORKSHOP

The scope of this workshop is to explore the current status of the research in the broad area of electronic structure simulations of nanoclusters, nanoparticles and nanostructures in various fields of physics, chemistry and biology. A number of experimental talks are added in the program to promote exchange of ideas and interdisciplinary collaborative efforts between simulations and experiments. The program will consists of invited lectures, short "hot topic" oral presentations (selected from contributed abstracts), poster sessions, and tutorial sessions on modern electronic structure theory, which are included for the benefit of the attending students and young researchers. This workshop is partially supported by the Psi-K network.

Speakers include: W. Andreoni, T. Bernhardt, J. Eloranta, T. Frauenheim, R. Gebauer, B. Hammer, U. Heiz, O. Ikkala, U. Landman, M. Moseler, A. Nakajima, G. Pacchioni, J.-Y. Raty, K. Reuter, A. Rubio, G. Scoles, A. Selloni, M. Di Ventra, R. Wolkow, L. Wöste

The titles of the invited talks are now shown on the workshop website

http://www.phys.jyu.fi/essn04

Organizing committee: H. Hakkinen, U. Heiz, M. Manninen, G. Pacchioni, A. Selloni

Deadlines: Registration, accommodation and abstracts by March 31, 2004.

For more information, see

http://www.phys.jyu.fi/essn04

Contact: essn2004@phys.jyu.fi

3.1.4 Psi-k Working Group 7 (Semiconductors and Nanotechnology) Meeting

Jyväskylä, Finland
June 18-21, 2004

This is the announcement for the Psi-k Working Group 7 (Semiconductors and Nanotechnology) meeting in Jyväskylä, Finland, during June 18-21, 2004. The meeting will coincide with the symposium Electronic Structure Simulations of Nanostructures (ESSN-2004).

The home page of the event is

http://www.phys.jyu.fi/research/clusters/essn04/

There will be additional speakers from among the WG-7 participants, including Peter Kratzer, Adam Foster, Yuchen Ma, Martti Puska, and others.

Please register and book accommodation through the website above, and inform also me (rni@fyslab.hut.fi) about your attendance.

I would also appreciate for spreading this information further.

Travel support will be available to Ph.D. students and post-docs interested in attending. Requests, possibly accompanied by recommendations from senior colleagues, should be sent to me via e-mail.

Looking forward to active participation.

Risto Nieminen
Spokesperson for WG-7 (Semiconductors and Nanotechnology)

3.1.5 NANOEXC2004 Workshop

Workshop on

Theory and Modeling of Electronic Excitations in Nanoscience

19-23 September 2004

Hotel Villa del Mare
85041 Acquafredda di Maratea (Italy)

E-Mail: nanoexc2004@roma2.infn.it
http://www.fisica.uniroma2.it/ palummo/conferenza.html

This three-day conference is devoted to the theory and modeling of electronic excitations in nanostructured materials, in order to assess the latest achievements and the perspectives for first-principles theoretical methods in this field. The workshop will offer the opportunity to discuss open questions, to compare the drawbacks and advantages of different approaches, and to present pioneering applications to real materials of current experimental interest. In particular, we plan to give emphasis to recent successful simulations in the field of nanoscience (nanotubes, quantum dots/wells, superlattices, surfaces, molecular electronics, bio-electronics and interdisciplinary fields like medical applications) as well as to theoretical advances related, for instance, to the efficient and accurate solution of the Bethe-Salpeter equation for optical spectra.

Further details about the programme and the registration procedure are available on the workshop homepage

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http://www.fisica.uniroma2.it/~palummo/conferenza.html
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The deadline for registration and abstract submission is 25 June 2004.

Organisers:

Pablo García-González

Maurizia Palummo

Olivia Pulci

Arno Schindlmayr

Nathalie Vast

3.2 Reports on ESF Workshops/Conferences

3.2.1 Report on Joint ICTP-DEMOCRITOS International School on "CONTINUUM QUANTUM MONTE CARLO METHODS"

ICTP, Trieste, Italy

11-23 January 2003

Co-sponsored by Psi-k (ESF) and MCC (NSF)

Organizers: S. Baroni, D. M. Ceperley and S. Moroni

**http://www.democritos.it/events/montecarlo.php
or http://agenda.ictp.trieste.it/agenda/current/fullAgenda.php?ida=a0332**

Quantum Monte Carlo (QMC) indicates a set of stochastic computational methods to calculate properties of many–body systems to a high level of accuracy (say recovering 50 to 100% of the correlation energy, depending on the algorithm and the system), with a favorable scaling with respect to the number of particles.

In the context of continuum systems, typical applications have been quantum fluids and solids (electron gas and Wigner crystals, condensed phases of Helium, trapped gases, both at zero and finite temperature) and electronic structure problems (from atoms and molecules to clusters and solids).

This two-weeks school has presented theory and applications of a variety of QMC methods, namely variational Monte Carlo, several implementations of projection Monte Carlo (diffusion, auxiliary field, reptation), and path integral Monte Carlo.

The School was organized in lectures during the morning, and computer sessions in the afternoon. The discussion of each technique included the basic formalism, technical information on the implementation when relevant, and illustrative results on physically significant problems. The computer sessions were based in part on simple codes, specifically written for this school to familiarize with concepts and algorithms, and in part on state-of-the-art codes with applications to systems representative of real research subjects. The lecture notes, as well as most of the codes used in the computer labs are available at http://www.democritos.it/events/montecarlo.php or http://agenda.ictp.trieste.it/agenda/current/fullAgenda.php?ida=a0332

Most of the topics covered at the school are well established techniques.

The Variational Monte Carlo method has been discussed in conjunction with optimization strategies for atomic and molecular wave functions and correlated sampling for interatomic potential energy surfaces.

Diffusion Monte Carlo, based on imaginary time projection to the exact ground state, is the most popular zero-temperature QMC method. Its application to the electron gas problem has been

illustrated using the TAS code, which includes non-standard features and recent developments such as the fixed-phase approximation and the twist-average boundary conditions. Atomic, molecular and solid-state DMC calculations have been presented using the CASINO code, a comprehensive package including pseudopotential solid-state simulations and interfaces with several popular electronic structure codes. An alternative projection method, Reptation QMC, has also been covered, together with its practical application to doped helium clusters.

The Path Integral Monte Carlo method has been discussed in the discretized-path implementation, using the pair-product action and the multilevel Metropolis sampling. This is the only finite-temperature QMC scheme in which particle exchange has been systematically and efficiently incorporated, and Fermion statistic has been treated (in the "restricted path" approximation). A tutorial on the UPI code has been given, featuring the simulation of normal and superfluid helium.

The case of auxiliary field Monte Carlo is somewhat different. AFMC is a method borrowed from lattice simulations with appealing potential advantages in applying QMC to continuum systems with non-local pseudopotentials and in general within the well-developed machinery of standard (one-body) electronic structure calculations. The novelty of the AFMC method presented at the School concerns the implementation of importance sampling and the control of the sign (or phase) problem. Its general accuracy and efficiency is still under investigation, but the first results are encouraging, and the method could have a significant impact.

This School was mainly intended for graduate students and young post-doctoral scientists, and we originally planned to have about 40 students. Thanks to the facilities made available by the ICTP, however, it has been possible to extend the audience to more than 80 people (still, we could only accept about 50with scientific interests ranging from quantum chemistry to nuclear physics and previous expertise on QMC ranging from none to excellent. Many lectures were also attended by several faculty members of local institutions.

We are confident that among the abundant amount of information conveyed during the School each participant had the opportunity to find enough interesting and accessible material, depending on his scientific interests and prior knowledge of the subject. Indeed, most of the students have been following both the lectures and the computer labs up to the last day of these very busy weeks, and the available personal feedback from the participants was generally very positive.

We believe that our School will have a non negligible impact on the community of QMC practitioners. A first positive outcome of the School is the number of participants and applications, well beyond the expectation of the organizers. This witnesses widespread interest for QMC and will presumably lead to an increase in the scientific activity based on these methods. A second point is that the format of a School is probably more efficient than that of a Workshop in spreading technical innovation between research groups with expertise in QMC. Finally, we hope that events of this kind will contribute, in the long term, to produce standard and relatively "black–box" QMC tools, in analogy with what happened for Density Functional electronic structure calculations in the last decade.

<div align="center">**FINAL PROGRAM**</div>

12 January 2004

08:30 - 09:30	REGISTRATION
08:30 - 09:30	OPENING
10:00 - 11:00	D.M. CEPERLEY
	INTRODUCTION TO MONTE CARLO
11:00 - 11:30	— Break —
11:30 - 12:30	D.M. CEPERLEY
	INTRODUCTION TO MONTE CARLO
	continued
12:30 - 15:00	— Lunch break —
15:00 - 18:00	S. MORONI
	COMPUTER LABORATORY SESSION

13 January 2004

09:00 - 11:00	C. FILIPPI
	VARIATIONAL MONTE CARLO FOR MOLECULAR SYSTEMS
11:00 - 11:30	— Break —
11:30 - 12:30	C. FILIPPI
	VARIATIONAL MONTE CARLO FOR MOLECULAR SYSTEMS
	continued
12:30 - 15:00	— Lunch break —
15:00 - 18:00	F. SCHAUTZ / C. FILIPPI
	COMPUTER LABORATORY SESSION

14 January 2004

09:00 - 11:00	D.M. CEPERLEY
	DIFFUSION MONTE CARLO
11:00 - 11:30	— Break —
11:30 - 12:30	D.M. CEPERLEY
	DIFFUSION MONTE CARLO
	continued
12:30 - 15:00	— Lunch break —
15:00 - 18:00	F. SCHAUTZ / S. MORONI
	COMPUTER LABORATORY SESSION

15 January 2004

09:00 - 11:00   D.M. CEPERLEY
                     PERIODIC SYSTEMS AND ELECTRON GAS
11:00 - 11:30   — Break —
11:30 - 12:30   S. DE GIRONCOLI
                     TUTORIAL ON PSEUDOPOTENTIALS
12:30 - 15:00   — Lunch break —
15:00 - 18:00   M. HOLZMANN / C. PIERLEONI
                     COMPUTER LABORATORY SESSION

16 January 2004

09:00 - 11:00   M.D. TOWLER
                     SOLID STATE APPLICATIONS
11:00 - 11:30   — Break —
11:30 - 12:30   M.D. TOWLER
                     SOLID STATE APPLICATIONS
                     continued
12:30 - 15:00   — Lunch break —
15:00 - 18:00   N.D. DRUMMOND / M.D. TOWLER
                     COMPUTER LABORATORY SESSION

19 January 2004

09:00 - 11:00   S. ZHANG
                     AUXILIARY FIELD QUANTUM MONTE CARLO
11:00 - 11:30   — Break —
11:30 - 12:30   S. ZHANG
                     AUXILIARY FIELD QUANTUM MONTE CARLO
                     continued
12:30 - 15:00   — Lunch break —
15:00 - 18:00   W. PURWANTO
                     COMPUTER LABORATORY SESSION

20 January 2004

09:00 - 11:00   D.M. CEPERLEY
                    PATH INTEGRAL MONTE CARLO
11:00 - 11:30   — Break —
11:30 - 12:30   D.M. CEPERLEY
                    PATH INTEGRAL MONTE CARLO
                    continued
12:30 - 15:00   — Lunch break —
15:00 - 18:00   M. HOLZMANN / C. PIERLEONI
                    COMPUTER LABORATORY SESSION

21 January 2004

09:00 - 11:00   D.M. CEPERLEY
                    PATH INTEGRAL MONTE CARLO
                    continued
11:00 - 11:30   — Break —
11:30 - 12:30   D.M. CEPERLEY
                    PATH INTEGRAL MONTE CARLO
                    continued
12:30 - 15:00   — Lunch break —
15:00 - 18:00   M. HOLZMANN / C. PIERLEONI
                    COMPUTER LABORATORY SESSION

22 January 2004

09:00 - 11:00   S. MORONI
                    REPTATION MONTE CARLO
11:00 - 11:30   — Break —
11:30 - 12:30   D.M. CEPERLEY
                    RESPONSE FUNCTIONS, EXCITED STATES,
                    MAXIMUM ENTROPY METHOD
12:30 - 15:00   — Lunch break —
15:00 - 18:00   S. MORONI
                    COMPUTER LABORATORY SESSION

23 January 2004

09:00 - 11:00   D.M. CEPERLEY
                    RESTRICTED FERMION PATH INTEGRALS
11:00 - 11:30   — Break —
11:30 - 12:30   D.M. CEPERLEY
                    EXCHANGE IN QUANTUM CRYSTALS
12:30 - 12:45   CLOSING REMARKS

LIST OF PARTICIPANTS

A BECCARA Silvio   Cornell Theory Center, Ithaca, NY, USA
AICHINGER Michael Otto   Johannes Kepler Universitat Linz, AUSTRIA
AKRAMOV Farrukh R.   Samarkand State University, UZBEKISTAN
AL-SAIDI Wissam Abdo   College of William & Mary, Williamsburg, VA, USA
AMOVILLI Claudio   Universita' degli Studi di Pisa, ITALY
ASPURU-GUZIK Alan   University of California at Berkeley, CA, USA
ATTACCALITE Claudio   SISSA, Trieste, ITALY
BARONI Stefano   SISSA, Trieste, ITALY
BAJDICH Michal   North Carolina State, Raleigh, NC, USA
BERGLI Elise   University of Oslo, NORWAY
BRAIDA Benoit   Universite' de Paris VI, FRANCE
CASULA Michele   SISSA, Trieste, ITALY
CAZORLA Claudio   Universitat Politecnica de Catalunya, Barcelona
CEPERLEY David M.   University of Illinois At Urbana-Champaign, IL, USA
CHIOFALO Maria Luisa   Universita' degli Studi di Pisa, ITALY
CHUNG Myung-Hoon   Hong-Ik University, Choongnam, REPUBLIC OF KOREA
COSLOVICH Daniele   Universita' degli Studi di Trieste, ITALY
DE GIRONCOLI Stefano   SISSA, Trieste, ITALY
DOMIN Dominik   University of California at Berkeley, CA, USA
DRUMMOND Neil David   Cambridge University, UNITED KINGDOM
DUAN Xiangmei   Universita' degli Studi di Trieste, ITALY
DUFF Andrew   University of Bristol, UNITED KINGDOM
ESFARJANI Keivan   Sharif University of Technology, Tehran, IRAN
FILIPPI Claudia   Universiteit Leiden, NETHERLANDS
FLORIS Franca Maria   Universita' degli Studi di Pisa, ITALY
FRATESI Guido   SISSA, Trieste, ITALY
GALEK Peter Tadeusz   University of Cambridge, UNITED KINGDOM
GEIST Wolfgang   Georgia Institute of Technology, Atlanta, GA, USA
GHULGHAZARYAN Ruben   Yerevan Physics Institute, ARMENIA
GIOVANNETTI Gianluca   Universita degli Studi 'La Sapienza', Roma, ITALY
GRIBOVA Nadejda   Academy of Sciences of Russia, Troitsk, RUSSIA

GRODA Yaroslav	State Technological University, Minsk, BELARUS
GUCLU Alev Devrim	Cornell Theory Center, Ithaca, NY, USA
HAZZARD Kaden Richard Alan	Ohio State University, Columbus, OH, USA
HOLZMANN Markus	Universite de Paris VI, FRANCE
ILORI Olusoji Olusola	Obafemi Awolowo University, Ile-Ife, NIGERIA
LEINO Markku Olavi	Tampere University of Technology, Tampere, FINLAND
LOPEZ RIOS Pablo	Cambridge University, UNITED KINGDOM
MA Andrea Tak Yue	Cambridge University, UNITED KINGDOM
MARCHETTI Riccardo	Universita' degli Studi di Perugia, ITALY
MARCHI Mariapia	Universita' degli Studi di Trieste, ITALY
MARCONI Veronica	Centro Atomico Bariloche, San Carlos, ARGENTINA
MARLO Meri Sari	Helsinki University of Technology, FINLAND
MENENDEZ PROUPIN Ariel	Universidad Catolica, Santiago, CHILE
MIKOSZ Aleksandra Anna	Utah State University, Logan, USA
MILITZER Burkhard	Carnegie Institution of Washington, Washington D.C., USA
MIRANDA Caetano Rodrigues	Universidade Estadual de Campinas, BRAZIL
MONTOYA MARTINEZ Javier	Universidad del Valle, Cali, COLOMBIA
MORONI Saverio	Universita degli Studi 'La Sapienza', Roma, ITALY
MOTAPON Ousmanou	Universite de Douala, CAMEROON
OWUSU Alfred	University of Cape Coast, GHANA
PAOLINI Stefano	SISSA, Trieste, ITALY
PARKER William David	Ohio State University, Columbus, OH, USA
PAYAMI Mahmoud	Atomic Energy Organization, Teheran, IRAN
PIERLEONI Carlo	Universita' degli Studi di L'Aquila, ITALY
POPSUEVA Victoria	University of Oslo, NORWAY
PURWANTO Wirawan	College of William & Mary, Williamsburg, VA, USA
RADNAI Zoltan	Cambridge University, UNITED KINGDOM
RASANEN Esa Heikki	Helsinki University of Technology, FINLAND
RECINE Gregory	Stevens Institute of Technology, Hoboken, NJ, USA
REINE Simen Sommerfelt	University of Oslo, NORWAY
REINHARDT Peter	Universite' Pierre et Marie Curie, Paris, FRANCE
ROSSI Maurizio	Universita' degli Studi di Milano, ITALY
ROSTAD Mateusz Marek	University of Oslo, NORWAY
SALOMON FERRER Romelia	University of California at Berkeley, CA, USA
SAVKIN Vladimir	Katholieke Universiteit, Nijmegen, NETHERLANDS
SCEMAMA Anthony	Universite' Pierre et Marie Curie, Paris, FRANCE
SCHAUTZ Friedemann	Universiteit Leiden, NETHERLANDS
SHULENBURGER Luke Nathan	University of Illinois At Urbana-Champaign, IL, USA
SINITSYN Valentine	Ural State University, Ekaterinburg, RUSSIA
SOLA Ester	Universitat Politecnica de Catalunya, Barcelona, SPAIN
SORKIN Viacheslav	Israel Institute of Technology, Haifa, ISRAEL
SRIVASTAVA Vipul	Barkatullah University, Bhopal, INDIA
STELLA Lorenzo	SISSA, Trieste, ITALY

SUBASI Ahmet Levent	Bilkent University, Ankara, TURKEY
SUEWATTANA Malliga	College of William & Mary, Williamsburg, VA, USA
TARASCO Silvia	Universita' degli Studi dell'Insubria, Como, ITALY
TAYLANOV Nizam	National University of Uzbekistan, Tashkent, UZBEKISTAN
THOM Alexander J. William	Cambridge University, UNITED KINGDOM
TOSIC Tatjana	University of Novi Sad, SERBIA AND MONTENEGRO
TOWLER Michael David	Cambridge University, UNITED KINGDOM
UMARI Paolo	Ecole Polytechnique Federal de Lausanne, SWITZERLAND
VRANJES Leandra	University of Split, CROATIA
WAGNER Lucas Kyle	North Carolina State University, Raleigh, NC, USA
WHITLEY Heather Dawn	University of California, Berkeley, CA, USA
WIERZBOWSKA Malgorzata	University of Dublin, IRELAND
ZACCHEDDU Maurizio	Universiteit Leiden, NETHERLANDS
ZENG Lang	Georgia Institute of Technology, Atlanta, GA, USA
ZHANG Shiwei	College of William & Mary, Williamsburg, VA, USA

3.2.2 Report on the KKR Workshop in Munich

"KKR-Workshop: New developments, applications, and collaborations"

Organized by

Hubert Ebert (University Munich, Germany) and
Duane D. Johnson (University of Illinois, Urbana-Champaign, USA)

Sponsored by

Ψ_k**-network of the European Science Foundation (ESF)**
and
Materials Computation Center at the Frederick Seitz Material Research
Laboratory (University of Illinois, Urbana-Champaign, USA)
in collaboration with
EU-network Computational Magnetoelectronics
CCP9 - Collaborative Computational Project for the Study of the Electronic
Structure of Condensed Matter

The goal of the workshop, held from 13th until 15th February 2004 at the University of Munich, was to bring together European and United States researchers developing and applying KKR electronic structure methods; especially to share recent advances and to enhance international collaborations on method and software development. The various contributions (23 oral and 24 poster presentations; 54 participants - see below) indeed reflected the many recent developments and their applications in a number of different fields.

The combination of the KKR-method with various many-body techniques have been discussed and demonstrated by several contributions. This included the dynamical mean field theory (DMFT) techniques (Chioncel, Minar), the Self-interaction Corrections (SIC) approach (Lders, Daene), the Optimized Potential Method (OPM) (Akai) and – as a very new approach – the use of the dynamical CPA (Gyorffy).

Closely connected with an improved treatment of many-body effects are corresponding developments and applications in the field of electron spectroscopy. Contributions in this field dealt with photo emission (Minar, Szajek, Winter), X-ray absorption (Giorgetti, Sipr), Appearance Potential Spectroscopy (Braun), optical properties (Perlov), positron annihilation (Benea), and magnetic Compton-scattering (Major).

A very appealing property of the KKR method is its applicability to systems without three dimensional periodicity. This feature has been exploited in contributions dealing with thin films (Udvardi), surfaces (Winter), intefaces (Yavorsky), nanowires (Lazarovits, Ujfalussy), nanocontacts (Mertig, Szunyogh), impurities (Jezierski), and inclusions (Eisenbach) in bulk systems, supported clusters and nanostructures (Stepanyuk, Niebergall) and free clusters (Sipr, Bornemann).

Concerning the treatment of disordered alloys the combination of the KKR-method with the Coherent Potential Approximation (KKR-CPA) has been very successful in the past. This was demonstrated by work presented on electronic and thermodynamic properties of alloys (Johnson) and ordering phenomena in metallic alloys (Bruno). Another application of the KKR-CPA was devoted to the investigation of magnetic properties at finite temperature within the disordered local moment (DLM) model (Staunton). This contribution in particular dealt with the influence of spin-orbit coupling. Another new technical development concerning the treatment of disorder is the non-local CPA (Rowlands), that allows to go in a systematic way beyond the single-site CPA.

The great flexibility of the KKR-method stems from the fact that it gives directly access to the electronic Green's function. This feature is exploited in particular when dealing with the transport properties of nanostructures (Mavropoulos, Szunyogh, Papanikolaou, Bagrets, Mertig, Popescu). Another example for this is a recently developed description for the magnetic high-field susceptibility of magnetic alloys (Mankovskyy).

A rather large number of contributions (including applications of other band structure methods) were dealing with materials interesting for applications in magneto-electronics. Besides the magnetic-nano-structure mentioned above, most interest was on diluted magnetic semiconductors (Akai, Dederichs, Sanyal) and half-metallic systems (Temmerman, Szotek).

According to the primary aim of the workshop some few contributions were selected as key lectures that deal with technical developments, as the implementation of the Lloyd formula (Zeller) and the data exchange between different program packages making use of XML (Schulthess), and also to review the activities of the non-European participating groups (USA: Stocks; Japan: Akai). In line with this, an adequate amount of time had been devoted to discussions on common future developments and collaborations. One of the resulting arrangements of these discussions is to have the next KKR-workshop in Bristol in 2006.

Hubert Ebert
Duane D. Johnson

Workshop program

Time	Friday	Saturday	Sunday
9		Staunton 30	Mavropoulos 30
		Rowlands 30	Szunyogh 30
10		Braun 30	Lueders 30
		Coffee 30	Coffee 30
11		Ujfalussy 30	Akai 40
		Stepanyuk 30	Chioncel 30
12		Sipr 30	Popescu 30
	Lunch	Lunch 90	Lunch 80
13			
	Welcome		
14	Johnson 30	Schulthess 40	
	Bruno 30	Mertig 30	
15	Sanyal 30	Coffee + Poster 90	
	Dederichs 30		
16	Coffee 30		
	Gyorffy 30	Stocks 40	
17	Perlov 30	Zeller 40	
	Minar 30	Discussions 20	
18	Discussions I3 40		
19		Dinner (Erdinger)	

List of oral talks

KKR in Osaka

H. Akai

Department of Physics, Faculty of Science, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560-0043, Japan, akai@phys.sci.osaka-u.ac.jp

Electronic structure versus spin polarization in complex Heusler alloys

J. Braun

Physikalisches Institut, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm Str. 10, 48149 Münster, jbraun@uni-muenster.de

Half-metallic semi Heusler alloys like NiMnSb have been ascribed promising materials for spintronic devices, because of theoretically predicted high spin polarization at the Fermi level. An unexpected low spin polarisation is found from Spin-resolved Appearance Potential Spectroscopy (SRAPS) measurements. A quantitative theoretical analysis of the experimental SRAPS-data reveals that variations in the morphology take the responsibility for this discrepancy. The calculations are based on a fully relativistic theory of SRAPS, which describes the measured spectra as the self-convolution of the matrix-element weighted, unoccupied density of states.

Charge distributions and ordering phenomena in metallic alloys: a Charge Excess Functional (CEF) theory

E. Bruno

Physics Department University of Messina, Salita Sperone, Contrada Papardo, ebruno@unime.it

Ab-initio electronic structure of correlated systems

L. Chioncel

University of Nijmegen, Toernooiveld 1, 6500 GL, Netherlands, chioncel@sci.kun.nl

We propose a self-consistent method for electronic structure calculations of correlated systems that combines the local density approximation (LSDA) and the dynamical mean field theory (DMFT). The LSDA part is based on the exact muffin-tin orbitals (EMTO) approach, meanwhile the DMFT uses a perturbation scheme that includes the T-matrix with fluctuation exchange (FLEX) approximation. The current LSDA+DMFT implementation fulfills both self-energy and charge self-consistency requirements. We present results on the electronic structure calculations for bulk $3d$ transition metals (Cr, Fe and Ni) and the half metallic ferromagnet NiMnSb.

Exchange Interactions and Curie Temperatures in Diluted Magnetic Semiconductors

P. Dederichs

Institut für Festkörperforschung, Forschungszentrum Jülich, D52425 Jülich, p.h.dederichs@fz-juelich.de

Dynamical KKR-CPA

B. Gyorffy

CMS TUWien, Technische Universität Wien, Getreidemarkt 9/134, A-1060 Wien, Oestereich, b.gyorffy@bristol.ac.uk

Importance of Partial Order for Predicting Electronic and Thermodynamic Properties of Alloys for Comparison to Characterization Experiments

D. Johnson

University of Illinois, Dept. of Materials Science and Engineering 202 Met. & Mining Bldg. C-246 1304 West Green Street, IL 61801, Urbana, USA, duanej@uiuc.edu

Self-interaction correction in multiple scattering theory

M. Lüders

Daresbury Laboratory, Daresbury, UK, m.lueders@dl.ac.uk

Some problems of the local spin-density (LSD) approximation when applied to d- or f- electron systems are related to the spurious self-interaction of the LSD. It has already been demonstrated that these shortcomings can be largely remedied by applying the so called self-interaction correction (SIC) to the LSD. However, traditional LSD-SIC calculations are computationally very demanding, and applications to alloys, for instance, are very difficult.

Here we will propose a simplified version of LSD-SIC, based on the multiple scattering formalism, which uses a local self-interaction correction, and show how it can be implemented in the KKR method. The multiple-scattering aspect of this new SIC method allows an implementation of the coherent potential approximation (CPA) in a straight-forward manner. This facilitates applications of the SIC to alloys and pseudo alloys which could describe intermediate valences. This provides a first step towards a dynamical SIC, which will allow for dynamical valence fluctuations.

As a demonstration of the method, we study the well-known α-γ transition of Ce, where we also show how the SIC operates in terms of multiple scattering theory.

A KKR Green function formalism for ballistic transport

P. Mavropoulos

FF, Forschungszentrum Juelich IFF, Forschungszentrum Juelich, D-52425 Juelich, Germany, Ph.Mavropoulos@fz-juelich.de

Transport in metallic nanocontacts

I. Mertig

MLU Halle, D-06099 Halle, mertig@physik.uni-halle.de

Influence of correlation effects on the spin-resolved VB-XPS

J. Minar[1], H. Ebert[1], L. Chioncel[2], A. Lichtenstein[2], C. Nadai[3], N. Brookes[3]

[1]Department Chemie/ Physikalische Chemie, University of Munich, Butenandtstr. 5-13, D-81377 Munchen, Germany, jan.minar@cup.uni-muenchen.de,
[2]University of Nijmegen, Toernooiveld 1, 6500 GL, Netherlands
[3] ESRF, Boite Postale 220, 38043 Grenoble Cedex, France

Calculations of valence band photoemission spectra on the basis of the local approximation to density functional theory have been very succesfully in the past for many transition metal systems. However it is well known that correlation effects play for some materials a rather crucial role. Fortunately, it is often well justified to represent these by a local, i.e. site-diagonal self-energy. In this case correlation effects can straightforwdly be incorporated within calculations based on the one-step model of photoemission. This applies in particular for its spin-polarised relativistic version that allows to deal with the Fano-effect and magnetic dichroism.

Corresponding results will be presented for ferromagnetic Ni, for which the pure Fano-effect, that means the spin-polarisation of the photo-current due to spin-orbit coupling has been investigated. Results of investigations on the spontanous spin-polarisation in the ground-state by means of spin-resolved VB-XPS will be presented for the half-metallic ferromagnet NiMnSb. Within these investigations correlation effects are accounted for via the electronic self-energy calculated by recently proposed LDA+DMFT scheme (DMFT: dynamical mean field theory). As it turn out, taking correlation effects into account the agreement between theory and experiment is significantly improved.

Accounting for many-body effects in the calculations of the optical and magnetooptical properties of moderatly correlated solids

A. Perlov[1], S. Chadov[1], H. Ebert[1], L. Chioncel[2], A. Lichtenstein[2]

[1]Department Chemie/ Physikalische Chemie, University of Munich, Butenandtstr. 5-13, D-81377 München, Germany, alexander.perlov@cup.uni-muenchen.de
[2] University of Nijmegen, Toernooiveld 1, 6500 GL, Netherlands

The optical and magnetooptical properties of 3d metals are theoretically investigated taking into account dynamical correlation effects. Various schemes to approximate the effective self-energy, including Second Order Perturbation Theory and Dynamic Mean Theory+Fluctuation Exchange methods have been implemented and investigated. It is shown that accounting for many-body correlation effects is very important for 3d metals to get a quantitative agreement with experimental results. While LSDA-based calculations of optical and magnetooptical properties in general lead to a satisfying qualitative agreement with experimental spectra, inclusion of correlation effects in particular give the correct position of prominent spectral features.

Relativistic Effects on the Transport Properties of Ferromagnetic-Semiconductor-Ferromagnetic Trilayer Systems

V. Popescu[1], H. Ebert[1], N. Papanikolaou[2], R. Zeller[3], P. H. Dederichs[3]

[1]Department Chemie/ Physikalische Chemie, University of Munich, Butenandtstr. 5-13, D-81377 München, Germany, voicu.popescu@cup.uni-muenchen.de
[2]Institute of Microelectronics, NCSR "Demokritos", Athens, Greece,
[3]Inst. für Festkörperforschung, Forschungszentrum Jülich, Postfach 1913, D-52425 Jülich, Germany

Spin-dependent transport between two ferromagnetic electrodes separated by either an insulator or a semiconductor has received a lot of interest in the last years due to its potential technological applications. The impressive theoretical work done in this field, however, still lacks a fair quantitative agreement with the experimental results.

Some possible sources leading to the existing discrepancies have been investigated and will be presented and discussed. For this we have applied a Tight-Binding Spin-Polarised Relativistic Multiple Scattering Theory (TB-SPR-KKR) method in calculating the electronic structure of an Fe/GaAs/Fe magnetic tunnel junction. Interface relaxation, interface inderdiffusion by means of a Coherent Potential Approximation (CPA) and Spin-Orbit Coupling (SOC) have been accounted for.

The transport properties are calculated according to the Landauer-Büttiker formalism on a relativistic level. Model calculations allowed us to investigate in detail the spin-flip contribution to the conductance, at the Fe/GaAs interface and/or within the semiconductor spacer.

Korringa-Kohn-Rostoker nonlocal coherent-potential approximation

D. Rowlands

University of Warwick, England, 26 Trearddur Road,Trearddur Bay, Anglesey LL65 2WB, d.a.rowlands@warwick.ac.uk

First principles study of diluted magnetic semiconductors

B. Sanyal

Theoretical Magnetism Group,Department of Physics, Uppsala University, Angstromlaboretoriet, Box 534, 75121 Uppsala, Sweden, biplab@fysik.uu.se

Towards a common i/o system for electronic structure codes

T. Schulthess

Oak Ridge National Laboratory, Metals and Ceramics Division, P.O. Box X, TN 37830, Oak Ridge, USA, schulthesstc@ornl.gov

Magnetic and spectroscopic properties of free iron clusters

O. Šipr

Institute of Physics, AS CR, Cukrovarnicka 10, 162 53 Praha 6, sipr@fzu.cz

Local spin and orbital magnetic moments at atoms in free iron clusters containing 9–89 atoms and at iron crystal surfaces are theoretically investigated within a fully relativistic framework based on the local density approximation. The site- and size-dependence of these properties is quite complex in free clusters and distinctly differs from a simple average between the properties of bulk and surface systems. The depth-profiles of the clusters and of the crystal surfaces exhibit different behaviour. The convergence of local magnetic properties towards the bulk values is significantly faster for planar surfaces than for free clusters. The local spin magnetic moments depend linearly on the effective coordination number of given atom. Theoretical x-ray magnetic circular dichroism (XMCD) spectra of free clusters differ from their bulk counterpart mainly through smaller widths and sharper maxima of the main peaks. A small yet distinct feature just above the main L_3 edge peak appears for all the investigated clusters and could thus serve as a marker of clusterization.

The Disordered Local Moment Picture of Magnetism and the KKR-NLCPA

J. Staunton

University of Warwick, Dept. of Physics, University of Warwick, Coventry CV4 7AL, U.K., j.b.staunton@warwick.ac.uk

Magnetic nanostructures stabilized by surface-state electrons

V. Stepanyuk

MPI Halle, Weinberg 2, D-06120 Halle, stepanyu@mpi-halle.de

Spin dynamics studies of the magnetic structure of alloys and interfaces

M. Stocks

Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6114, stocksgm@ornl.gov

Effect of impurities on the transport through a gold point contact

L. Szunyogh

Dept. Theor. Physics, Budapest Univ. of Technology and Economics, H-1111 Budapest, Budafoki u. 8., Hungary, szunyogh@heisenberg.phy.bme.hu

Atomic–sized nanocontacts are of considerable interest for basic research as they exhibit transport properties remarkably different from the classical behavior. One of those particular features is that, at sufficiently low temperatures, the conductance of the contact gets quantized. In this talk we present how the Kubo-Greenwood formalism as implemented within the Korringa-Kohn-Rostoker Embedded Cluster Method can be applied to calculate the conductance of metallic contacts. Rigorous numerical tests demonstrate the reliability of the method. The conductance of model nanocontacts between two semi-infinite Au leads are calculated for different thicknesses of the constriction. Motivated by recent experiments on AuPd alloy contacts we investigate effects of Pd as well as Co and Fe impurities placed at different positions in the contact. We observe that Pd and Fe impurities do not in fact influence the conductance. On the other hand, Co impurities, in particular, when placed along the central axis of the contact seem to assist the transport through the constriction. Resolving the local densities of states of the Co atom with respect to orbital-like components we are able to correlate this observation with a sharp $d_{3z^2-r^2}$-like peak in the vicinity of the Fermi energy.

Ab-initio spin-dynamics of small nanoparticles on surfaces

B. Ujfalussy

University of Tennessee, Nielsen Physics Bldg, Knoxville, TN, USA, ujfalussyb@ornl.gov

On the calculation of Lloyd's formula

R. Zeller

Institut für Festkörperforschung, Forschungszentrum Jülich, D52425 Jülich, Ru.Zeller@fz-juelich.de

Transport and magnetoresistance properties of atomic-sized contacts

A. Bagrets

Martin-Lüther-Universität Halle-Wittenberg, Fachbereich Physik, Fachgruppe Teoretische Physik, 06099 Halle (Saale), Germany, bagrets@physik.uni-halle.de

A relativistic description for the positron annihilation in solids

D. Benea[1], Zs. Major[2] and H. Ebert[1],

[1]Department Chemie / Physikalische Chemie, Universität München, Butenandstr. 5-13, D-81377 München, Germany, diana.benea@cup.uni-muenchen.de,
[2] H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, BS8 1TL Bristol, UK

A fully relativistic formulation for the of spin resolved momentum density is presented together with a corresponding scheme to determine the two dimensional projection of the electron-positron momentum density for metals. This formalism is set up within the framework of spin-polarised relativistic Korringa-Kohn-Rostoker (SPR-KKR) method of bandstructure calculations. The resulting two dimensional projection of the electron-positron momentum density is usually identified with the two-dimensional angular correlation of the annihilation radiation (2D-ACAR) experimental spectra. Various two dimensional projections of the electron-positron momentum density of vanadium are presented and compared with nonrelativistic LMTO calculation and experimental data.

Magnetic and Spectroscopic Properties of Iron Platinum Clusters

S. Bornemann, H. Ebert

Department Chemie / Physikalische Chemie, Universität München, Butenandstr. 5-13, D-81377 München, Germany, sven.bornemann@a-city.de

The SPR-KKR method was applied to the calculation of ordered FePt Clusters up to a size of 177 atoms. The Calculations showed, that the DOS and magnetic moments of inner cluster atoms become quickly bulk like, while the corresponding averaged values over all cluster atoms

approach the bulk value much slower, as one would expect. The obtained results are in line with experiment, but a direct comparism with the much larger nano-particles is still not possible.

Electronic structure of 3d transition metal oxides: Implementation of SIC in KKR

M. Däne[1], W. Hergert[1], D. Koedderitzsch[2]

[1]Martin-Lüther Untversität Halle-Wittenberg, FG Theorie, FB Physik, Uni Halle, D-06099 Halle (Postfach), daene@physik.uni-halle.de
[2]Daresbury Laboratory, Daresbury,UK, D.Koedderitzsch@physik.uni-halle.de

Strong correlation effects which underline the electronic structure of transition metal oxides or lanthanide and actinide metals and their compounds cannot be adequately described in the framework of the local spin density approximation (LSDA) in the density functional theory (DFT). This can be partly be attributed to the substantial self-interaction included in the LDA. To go beyond LSDA-DFT self interaction corrections (SIC) can be implemented in the band-picture. Such an approach has been used to describe, e.g. the magnetic properties of NiO or the $\gamma \rightarrow \alpha$ phase transition of Ce.
We will present a simplified local rotationally invariant SIC scheme which can be efficiently implemented in the multiple scattering theory. The SIC within the Green's function Korringa-Kohn-Rostoker (KKR) method can be used together with the coherent potential approximation (CPA) to treat alloy problems for correlated systems. The method is illustrated on the electronic structure study of NiO.

Magnetic Structure of Iron Inclusions in Copper

M. Eisenbach

Oak Ridge National Laboratory, Bethel Valley Road, Oak Ridge, TN 37831, USA, eisenbachm@ornl.gov

XMCD at LII,III edges of Er and K-edge of Fe and Co in $Er(Fe_xCo_{1-x})_2$ compounds

C. Giorgetti

LURE, bat 209 d Centre Universitaire Paris Sud BP 34 F-91898 ORSAY CEDEX, Christine.Giorgetti@lure.u-psud.fr

Influence of impurities on the electronic and magnetic properties of FeTiSn

A. Jezierski[1], A. Slebarski[2]

[1]Institute of Molecular Physics PAS, MN.Smoluchowskiego 17, jeziersk@ifmpan.poznan.pl,
[2]Institute of Physics, University of Silesia, Katowice, Poland

We present an effect of local atomic disorder on the electronic and magnetic properties of

Fe_2TiSn, $Fe_{2-x}Ni_xTiSn$, $Fe_{2-x}Co_xTiSn$ Heusler type alloys. The band structures are calculated by ab-inito methods (LMTO [1], SPR KKR-CPA [2], FPLMTO [3-4], VASP [5-8]). Ab-intio electronic structure calculations are in good agreement with measured x-ray photoemission valence-band spectra. In Fe_2TiSn we observe a pseudogap located at the Fermi level. The pseudogap is strongly reduced by local disordering and the substitution of Fe by Ni or Co atoms [9-11]. We also study the change of the electronic structure of Fe_xTiSn (2 ¡x ¡ 1).

The calculations have been performed using the ab-initio total-energy and molecular-dynamics program VASP (Vienna ab-initio simulation program) developed at the Institut fûr Materialphysik of the Universität Wien [5-8],

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KKR approach for relaxation of nanostructures

A. Klavsyuk

Martin-Lüther-Universität, Fachbereich Physik, Martin-Lüther-Universität, Halle-Wittenberg, Friedemann-Bach-Platz 6, 06108 Halle, Germany, klavsjuk@physik.uni-halle.de

Magnetism of thin Fe films on GaAs

M. Košuth, V. Popescu, H. Ebert

Department Chemie / Physikalische Chemie,
Universität München, Butenandstr. 5-13, D-81377 München, Germany,
michal.kosuth@cup.uni-muenchen.de

The electronic and magnetic properties of thin Fe layers on GaAs have been studied using the fully-relativistic TB-KKR band structure method. The most important features observed in the magnetisation profiles are that no magnetically dead layers occur and there is an appreciable induced magnetisation in the semiconductor subsystem. An increase of the orbital moment in the Fe layers both at the surface as well as at the Fe/semiconductor interface has been observed.

Calculations of the magnetocrystalline anisotropy energy for thin layers of Fe on a semiconductor substrate confirm the preferable in-plane magnetisation with a noticeable uniaxial character in accordance with experiments.

In the experiments the Fe surface of the GaAs/Fe system is covered by protective layers of Au to prevent the Fe-corrosion. The quantitative and qualitative effects of additional Au layers on top of GaAs/Fe to the magnetic anisotropy will be presented and discussed.

Magnetic Properties of Finite Chains

B. Lazarovits[1], L. Szunyogh[1,2] and P. Weinberger[1]

[1]Center of Computational Materials Science, Vienna University of Technology, Gumpendorferstr. 1A, A-1060, Vienna, Austria, bl@cms.tuwien.ac.at

[2]Department of Theoretical Physics and Center for Applied Mathematics and Computational Physics, Budapest University of Technology and Economics, Budafoki út 8, H-1521, Budapest, Hungary

We present calculated magnetic properties of finite linear chains of Co and Fe deposited on or embedded into Pt and Cu substrates. The calculations are performed fully relativistically using the embedding technique within the Korringa–Kohn–Rostoker method.

For Co chains on Pt(111) we found independently from the length of the chains that the easy axis is perpendicular to the surface. The size of the calculated magnetic anisotropy energy and of the anisotropy of the orbital moment fits very well to available experimental values for monoatomic Co chains deposited on a Pt(997) surface.

For Fe wires deposited on Cu(100) and Cu(111) surfaces we obtained an off-plane easy axis while for chains embedded into the substrate the direction of magnetization depends on the distance from the surface. We also found a relatively large magnetic anisotropy between two in-plane magnetic orientations, namely, the one along the chain and the other perpendicular to the chain. The calculated value of the in-plane magnetic anisotropy energy for the Fe chains on top of the Cu(111) surface compares well to available experimental values.

Superconductivity and Magnetism of $ZrZn_2$

Zs. Major[1], S. B. Dugdale[1], R. J. Watts, G. Santi, M. A. Alam, S. M. Hayden, J. A. Duffy, J. W. Taylor, T. Jarlborg, E. Bruno[2], D. Benea[3], H. Ebert[3]

[1]H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, United Kingdom, zs.major@bristol.ac.uk,
[2]Physics Department University of Messina, Salita Sperone, Contrada Papardo,
[3]Department Chemie/ Physikalische Chemie, University of Munich, Butenandtstr. 5-13, D-81377 München, Germany

The discovery of the ferromagnetism co-existing with superconductivity in the compound UGe_2, followed by similar discoveries in $ZrZn_2$ and URhGe, has re-opened the debate about the relationship between magnetism and superconductivity. At the centre of this debate is the question of the pairing mechanism for the superconductivity, with the speculation that it is magnetically rather than phonon-mediated. Knowledge of the topology of the Fermi surface (FS) is vital to an understanding of the superconductivity. Furthermore, such measurements are a stringent test of electronic structure calculations, on which the models for the superconductivity rely.

The existence of large, flat areas of Fermi surface (FS) is reported in the paramagnetic phase of $ZrZn_2$ from positron annihilation experiments. Such features have previously been predicted by electronic structure calculations, and their presence used in models of both magnetically mediated superconductivity and the phonon-mediated Fulde-Ferrell-Larkin-Ovchinnikov superconducting state. Moreover, the most strongly mass-renormalized FS sheet, which dominates the Fermi level density-of-states, is seen for the first time. Comparison between measured and calculated spin-densities in momentum space shows that the significant delocalization of the magnetic moment in real space is well accounted for by *ab initio* calculations.

Magnetic response functions of para- and ferromagnetic alloys

S. Man'kovsky, H. Ebert

Dept. Chemie/Phys. Chemie, Universität München, Butenandtstr. 5-13,
D-81377 München, Germany, sm@nike.cup.uni-muenchen.de

The results of a theoretical study of the magnetic susceptibility as well as field-induced magnetic circular X-ray dichroism (MCXD) of para- and ferromagnetic metals and alloys are presented. The theoretical description of the magnetic susceptibility is based on a combination of a linear response approach and the fully relativistic Green's function formalism. Additional contributions to the magnetic susceptibility (e.g. spin-charge response function, contribution related to a Fermi level shift) become important in the ferromagnetic state if compared with the paramagnetic one. Illustrating examples are presented for various 3d transition metal systems. In particular, the high-field magnetic susceptibilities have been calculated for pure bcc Fe and fcc Ni as well as for ferromagnetic $Fe_{1-x}Co_x$ alloy. The results obtained are in a reasonable agreement with experimental ones. It is demonstrated also that the field-induced MCXD method allows to study in detail the partial susceptibilities of the alloy partners, that cannot be supplied by any other experimental technique.

Adatoms and small clusters in 2D electron gas: KKR approach

L. Niebergall

MPI Halle, Weinberg 2, D-06120 Halle, lnieber@mpi-halle.de

Ab initio core-level and Auger kinetic energy shifts

W. Olovsson[1], I. A. Abrikosov[2], B. Johansson[1,3], A. Newton[4], R. J. Cole[5] and P. Weightman[4]

[1]Department of Physics, Uppsala University, Box 530, SE-751 21 Uppsala, weine.olovsson@fysik.uu.se,
[2]Department of Physics and Measurement Technology, Linköpings University, SE-581 83 Linköping, Sweden,
[3]Applied Materials Physics, Department of Materials Science and Engineering, Royal Institute of Technology, SE-100 44 Stockholm, Sweden
[4]Department of Physics and Surface Science Research Center, University of Liverpool, Liverpool L69 3BX, United Kingdom
5Department of Physics and Astronomy, Centre for Materials Science and Engineering, University of Edinburgh, EH9 3JZ, United Kingdom

By studying alloy-to-metal energy shifts obtained from photoelectron spectroscopy it is possible to gain a better understanding of the electronic structure and chemical bonding in a solid, as the shift depends on the atoms local chemical environment. A first-principles theoretical study is made for the $3d$ core-level binding energy shift and kinetic energy shift for the $L_3M_{4,5}M_{4,5}$ (core-core-core) Auger transition over the concentration range of fcc random AgPd alloys. The calculations are based in the density functional theory with KKR-ASA and the coherent potential approximation and use the complete screening picture, which includes both initial (core-electron energy eigenvalue) and final state effects (due to screening of the core-hole) in the same scheme. The results are found to be in excellent agreement with experiment.

Conductance through single atoms: an ab-initio approach

N. Papanikolaou

Institute of Microelectronics, NCRS Demokritos, NCSR Demokritos, GR-153 10, Athens, Greece, N.Papanikolaou@imel.demokritos.gr

Monte Carlo simulation of magnetic properties of small metal clusters

S. Polesya, S. Bornemann, H. Ebert, S. Man'kovsky and J. Minar

Dept. Chemie/Phys. Chemie, Universität München, Butenandtstr. 5-13, D-81377 München, Germany, svitlana.polesya@cup.uni-muenchen.de

Temperature dependent magnetic properties of small clusters of 3d-elements and their compounds both unsupported and deposited on metallic surfaces have been studied using MC simulations together with the extended Heisenberg model. The exchange parameters of the systems under consideration have been obtained from ab initio spin-polarized KKR calculations of electronic structure. It is shown that the temperature T_C of a transition from magnetically ordered to a disordered state for clusters consisting of few atoms is strongly determined by the exchange interaction between spins. The dependence of T_C on the cluster size is analyzed and compared to the value obtained for an infinite crystal. The effect of an external magnetic field on the cluster magnetic properties is investigated for small Co clusters on the Pt(111) surface. Due to the cluster anisotropy at low temperatures the strong deviation from Langevin-like behavior is observed.

KKR-CPA study of induced magnetic moment in $Fe_{1-x}M_x$ disordered alloys and Fe/M (001) superlattices with M = V, Nb, Ta, Mo

M. Shelyapina

Dept. of Quantum Magnetic Phenomena, St.Petersburg State University, Ulyanovskaya 1, Petrodvorets, 198904, St.Petersburg, Russia, marina@ms4828.spb.edu

In this work we report on a theoretical study of the magnetic couplings in $Fe_{1-x}M_x$ disordered bulk alloys and in Fe/M (001) superlattices (with M = V, Nb, Ta and Mo). The calculations were curried out using the charge and spin self-consistent Korringa-Kohn-Rostoker method combined with coherent-potential-approximation (KKR-CPA). To study the origin of the magnetic moment in $Fe_{1-x}V_x$ the hyperfine fields were calculated within the full relativistic approach.

For the considered transition metal M an antiferromagnetic coupling between the Fe and the M magnetic moments in $Fe_{1-x}M_x$ disordered alloys was obtained. In Fe_5/M_1 and Fe_4/M_2 superlattices for all cases an antiferromagnetic coupling between Fe and M layers was derived which decreases from V to Mo atoms. The impact of the interface interdiffusion on the induced M and reduced Fe magnetic moments in Fe_5/M_1 and Fe_4/M_2 is also considered. The atom interdiffusion leads to increase the total and average iron magnetic moments, while the induced magnetic moment increases for M = V and does not change for the other atoms.

The hyperfine field calculations carried out in $Fe_{1-x}V_x$ showed that s-contribution to the spin magnetic moment $\mu_{spin,s}$ stems from B_{hf}^{val} of s-electrons, while $\mu_{spin,d}$ is caused by the core contribution to the hyperfine field (s-like and non-s as well). The concentration dependency of B_{hf} stems from the valence contribution, essentially from s-electrons.

Electronic structure and X-ray photoemission spectra of APtSn (A = Th, U or Ti, Zr, Hf)

A. Szajek[1], A. Bajorek[2], G. Chełkowska[2], J.A. Morkowski[2], R. Troć[3]

[1]Inst. of Molecular Physics, Polish Academy of Sciences, ul. M. Smoluchowskiego 17, 60-179 Poznan, Poland, szajek@ifmpan.poznan.pl
[2]A. Chełkowski Institute of Physics, Silesian University, Uniwersytecka 4, 40-007 Katowice, Poland
[3]W. Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 1410, 50-950 Wrocław, Poland

The APtSn (A= Th, U or Ti, Zr, Hf) compounds crystallize in the cubic MgAgAs-type structure (space group no. 216; $F(-4)3m$). UPtSn is known as a semimetal with band gap in the electronic density of states, similar behavior was observed in isostructural compounds ThPtSn and ZrPtSn [1]. In this paper we present electronic structure of APtSn compounds studied by X-ray photoemission spectroscopy and *ab-initio* calculations. The band calculations were performed based on the tight binding version of the linear muffin-tin orbitals (TB LMTO) method in the atomic sphere approximation (ASA). The gaps in the densities of states are formed: 11 meV for UPtSn, 34 meV for ThPtSn, 298 meV for ZrPtSn, 192 meV for HfPtSn, and 369 meV for TiPtSn.

1. R. Troć et al., Phil. Mag. vol.83, no.10, 1 April 2003, pp.1235-53

Half-Metallic Transition Metal Oxides

Z. Szotek

Daresbury Laboratory, Daresbury, UK, Z.Szotek@dl.ac.uk

We discuss an application of the self-interaction corrected local spin density approximation (SIC-LSD) to half-metallic transition metal oxides, and among them double perovskites and magnetite (Fe_3O_4). We show that also such simple transition metal monoxides as NiO and MnO can acquire half-metallic characteristics when doped with vacancies. We concentrate on the electronic and magnetic properties of these compounds and in magnetite, in addition, issues of charge order are also thoroughly investigated.

Study of Half-Metallicity in LSMO

W. Temmerman

Daresbury Laboratory, Daresbury, UK, w.m.temmerman@dl.ac.uk

One-electron calculations were performed for $La_{1-x}Sr_xMnO_3$ (LSMO) (x=0.7) and $SrTiO_3$ (STO), and for the surfaces of these materials, as well as the interface of LSMO/STO. TB-LMTO-LSDA and SIC-LSDA LMTO-ASA methods were used. The calculations for nonstochiometric perovskites were based on a stochiometric supercell model ($[La_2SrMnO3]_n$, where n=1, 2, 3) and a rigid band model. From SIC-LSDA calculations a half-metallic state was obtained for LSMO with manganese in the configuration Mn^{+3}, where the localised electrons are the $3t_{2g}$ and one e_g. The supercell method was used to model LSMO and STO surfaces and to study the influence of the terminating layer on the electronic structure. Calculations for the junction LSMO/STO/LSMO were carried out for interfaces MnO_2/SrO and LaO/TiO_2. The results show a pronounced dependence on the terminating layers both for the surface and the interface.

Magnetic structures of thin films from first principles

L. Udvardi

Department of Theoretical Physics, Budapest Univ. of Technology and Economics, Budafoki út 8, H-1111, Budapest, Hungary, udvardi@bolyai.phy.bme.hu

Electronic structure and ARPES spectra of vicinal Cu(111) surfaces

H. Winter, R. Eder

Inst. für nukleare Festkörperphysik, Kernforschungszentrum Karlsruhe, 7500 Karlsruhe, Germany, winter@infp.fzk.de

The electronic structure of the Cu(332) and Cu(221) surfaces is obtained by the self-consistent screened KKR method. ARPES spectra for the Shockley-type surface states at binding energies near 0.5 eV are calculated within the one-step formalism and found to be in good agreement with experimental data. There is a parabolic band, asymmetrically displaced to the boundary of the surface Brillouin zone. We show that the asymmetry occurs only in the ARPES spectra, wheras the underlying surface band structure is symmetric and explain the asymmetry of the ARPES spectra by analyzing the surface state wave function.

Ab initio study of noncollinear magnetic structures. Application to fcc Fe grown on Cu substrate

B. Yavorsky, I.Mertig

MLU Halle, Friedemann-Bach-Platz 6, 06108 Halle(Saale), yavorsky@physik.uni-halle.de

Thin films of fcc Fe stabilized by epitaxial growth on a Cu(100) substrate have been a subject of great interest for both experimentalists and theoreticians. The question of magnetic ground state of fcc Fe, however, is still open. In the recent experimental study (D.Qian *et al.* Phys.Rev.Lett **87**, 227204, (2001)) a non-collinear magnetic order in Cu(100)/Fe is discussed.

We present results of *ab initio* electronic structure calculations for the 6Fe/8Cu/6Fe slab made by means of a TB-KKR method modified for non-collinear magnets. Self-consistent potentials were used for the calculations of the densities of states and the total energies for different magnetic configurations of the Fe film.

List of participants

Akai, H.
Department of Physics, Faculty of Science, Osaka University 1-1 Machikaneyama, Toyonaka, Osaka 560-0043, Japan

Bagrets, Alexej
Martin-Luther-Universitaet Halle-Wittenberg, Fachbereich Physik, Fachgruppe Teoretische Physik, 06099 Halle (Saale), Germany

Benea, Diana
Ludwig-Maximilians-University of Munich, Department Chemistry / Physical Chemistry Butenandtstr. 11, 81377 Munich, Germany

Biava, Dominic
UIUC 316 W. John St. Champaign, IL, USA

Bornemann, Sven
Ludwig-Maximilians-University of Munich, Department Chemistry / Physical Chemistry Butenandtstr. 11, 81377 Munich, Germany

Braun, Jürgen
Physikalisches Institut Universitt Mnster, Wilhelm-Klemm Str. 10, D-48149 Münster, Germany

Bruno, Ezio
Physics Department -University of Messina Salita Sperone - Contrada Papardo

Chadov, Stanislav
Ludwig-Maximilians-University of Munich, Department Chemistry / Physical Chemistry Butenandtstr. 11, 81377 Munich, Germany

Chioncel, Liviu
University of Nijmegen Toernooiveld 1, 6500 GL

Daene, Markus
Martin-Luther Untversität Halle-Wittenberg FG Theorie, FB Physik, Uni Halle, D-06099 Halle (Postfach)

Dederichs, Peter
Institut fuer Festkoerperforschung Forschungszentrum Juelich, D52425 Juelich

Ebert, Hubert
Ludwig-Maximilians-University of Munich, Department Chemistry / Physical Chemistry Butenandtstr. 11, 81377 Munich, Germany

Eisenbach, Markus
Oak Ridge National Laboratory Bethel Valley Road, Oak Ridge, TN 37831, USA

GIORGETTI, Christine
LURE bat 209 d Centre Universitaire Paris Sud BP 34 F-91898 ORSAY CEDEX

Ginatempo, Beniamino
Dip. di Fisica -University of Messina Salita Sperone 31- 98166 Messina (Italy)

Gyorffy, Balazs
CMS,TUWien CMS,Technische Universitat Wien, Getreidemarkt 9/134,A-1060 Wien, Oestereich

HLIL, El kébir
CNRS Grenoble 25,Av des Martyrs 38042 Grenoble, France

Hergert, Wolfram
Martin-Luther Untversität Halle-Wittenberg FG Theorie, FB Physik, Uni Halle, D-06099 Halle (Postfach)

Jezierski, Andrzej
Institute of Molecular Physics PAS MN.Smoluchowskiego 17, Poland

Johnson, D. D.
University of Illinois, Dept. of Materials Science and Engineering 202 Met. & Mining Bldg. C-246, 1304 West Green Street, IL 61801, Urbana, USA

Klavsyuk, Andriy
Martin-Luther-Universität Fachbereich Physik, Halle-Wittenberg, Friedemann-Bach-Platz 6,06108 Halle, Germany

Koedderitzsch, Diemo
Daresbury Laboratory Daresbury, UK

Košuth, Michal
Ludwig-Maximilians-University of Munich, Department Chemistry / Physical Chemistry Butenandtstr. 11, 81377 Munich, Germany

Lounis, Samir
IFF, Forschungszentrum Juelich. D-52425 Juelich, Germany

Lazarovits, Bence
Center fof Computational Materials Science, Vienna University of Technology, Vienna, Austria Gumpendorferstr. 1A,, A-1060 Vienna, Austria

Lueders, Martin
Daresbury Laboratory Daresbury, UK

Major, Zsuzsanna
H H Wills Physics Laboratory, University of Bristol Tyndall Avenue, Bristol, BS8 1TL, United Kingdom

Man'kovsky, Sergey
Ludwig-Maximilians-University of Munich, Department Chemistry / Physical Chemistry Butenandtstr. 11, 81377 Munich, Germany

Mavropoulos, Phivos
IFF, Forschungszentrum Juelich IFF, Forschungszentrum Juelich, D-52425 Juelich, Germany

Mertig, Ingrid
MLU Halle D-06099 Halle, Germany

Minár, Ján

Ludwig-Maximilians-University of Munich, Department Chemistry / Physical Chemistry Butenandtstr. 11, 81377 Munich, Germany

Niebergall, Larissa
MPI Halle Weinberg 2, D-06120, Halle, Germany

Olovsson, Weine
Department of physics, Uppsala university Box 530, SE-751 21 Uppsala

Papanikolaou, Nikos
Institute of Microelectronics, NCRS Demokritos NCSR Demokritos, GR-153 10, Athens, Greece

Perlov, Alexander
Ludwig-Maximilians-University of Munich, Department Chemistry / Physical Chemistry Butenandtstr. 11, 81377 Munich, Germany

Polesya, Svetlana
Ludwig-Maximilians-University of Munich, Department Chemistry / Physical Chemistry Butenandtstr. 11, 81377 Munich, Germany

Popescu, Voicu
Ludwig-Maximilians-University of Munich, Department Chemistry / Physical Chemistry Butenandtstr. 11, 81377 Munich, Germany

Rowlands, Derwyn
University of Warwick, England 26 Trearddur Road, Trearddur Bay, Anglesey LL65 2WB

Sanyal, Biplab
Uppsala University Theoretical Magnetism Group,Department of Physics, Angstromlaboretoriet, Box 534, 75121 Uppsala, Sweden

Schulthess, Thomas
Oak Ridge National Laboratory, Metals and Ceramics Division P.O. Box X, TN 37830, Oak Ridge, USA

Shelyapina, Marina
Dept. of Quantum Magnetic Phenomena, St.Petersburg State University 1,Ulyanovskaya, Petrodvorets, 198904, St.Petersburg, Russia

Sipr, Ondrej
Institute of Physics, AS CR Cukrovarnicka 10, 162 53 Praha 6, Czech Republic

Staunton, Julie
University of Warwick Dept. of Physics, Coventry CV4 7AL, U.K.

Stepanyuk, Valeri
MPI Halle Weinberg 2, D-06120, Halle, Germany

Stocks, Malcolm
Oak Ridge National Laboratory P.O. Box 2008, Oak Ridge, TN 37831-6114

Szajek, Andrzej
Inst. of Molecular Physics, Polish Academy of Sciences ul. M. Smoluchowskiego 17, 60-179 Poznan, Poland

Szotek, Zdzislawa
Daresbury Laboratory Daresbury, UK

Szunyogh, Laszlo
Dept Theor Physics, Budapest Univ of Technology and Economics H-1111 Budapest, Budafoki
u. 8., Hungary

Temmerman, Walter
Daresbury Laboratory Daresbury, UK

Udvardi, Laszlo
Department of Theoretical Physics,Budapest Univ. of Technology and Economics Budafoki ut
8, H-1111, Budapest, Hungary

Ujfalussy, Balazs
University of Tennessee Nielsen Physics Bldg, Knoxville, TN, USA

Winter, H.
Inst. für nukleare Festkörperphysik,Kernforschungszentrum Karlsruhe 7500,Karlsruhe

Yavorsky, Bogdan,
MLU Halle Friedemann-Bach-Platz 6, 06108 Halle(Saale), Germany

Zeller, Rudolf
Institut fuer Festkoerperforschung Forschungszentrum Juelich, D52425 Juelich

4 General Workshop/Conference Announcements

4.1 Workshop Hands-on WIEN2k

WIEN2k Workshop

Electronic Structure Calculations of Solids with the WIEN2k Code

July 12-15, 2004

Penn State University, State College, USA

Chairman: Jorge Sofo

Email: sofo@psu.edu

First Announcement

The program package WIEN2k allows to perform electronic structure calculations using density functional theory (DFT). This workshop is aimed at anyone who wants to learn how DFT calculations can be done using the full-potential (Linearized) Augmented Plane Wave + local orbitals (FP-APW+lo) method as embodied in the WIEN2k code (or related topics). Presently this code is used worldwide by more than 600 groups from academic and industrial reserach institutions to solve many material science problems.

The workshop will include lectures from the code developers, P. Blaha, K. Schwarz, G. H. K. Madsen J.Luitz, C. Ambrosch-Draxl and J.Sofo. In addition there will be hands-on exercies and presentation of results.

- Preliminray Program:
  - A short introduction into density functional theory and the (L)APW (+lo) method
  - Introduction to the use of the WIEN2k program package
  - Hands-on experience (on LINUX clusters)
  - Features of WIEN2k (structure optimization, optical properties, LDA+U, magnetism)
  - New features (non-linear optics, non-collinear magnetism, phonons, etc.)
  - Posters, results obtained with WIEN and related topics
  - Discussions and exchange of experience between users and developers

Conference site:

The conference will take place at Pennsylvania State University in State College PA, USA)

Contact:

For further details see one of the WWW-pages

http://msu.psu.edu/events/ or http://www.wien2k.at/

or send an email to sofo@psu.edu

4.2 Workshop 'Hands-on-FPLO'

Final Announcement

UC Davis, California, June 18-22, 2004

This is the final announcement for the Workshop 'Hands-on-FPLO', to be held at UC Davis, California, June 18-22, 2004.

The FPLO package is an efficient and accurate method to solve the Kohn-Sham equations of DFT.

Features:

local (optimized) basis
no shape restriction to potential and spin density
scalar/fully relativistic (4-component)
fixed spin moment method
coherent potential approximation
LSDA+U
up to 100 atoms per unit cell

There is no workshop fee, only travel and accomodation have to be covered by the participants.

Dr. Manuel Richter
Dept. of Theoretical Solid State Physics
IFW Dresden e.V.
P.O. Box 270016
D-01171 Dresden, Germany

Tel.: +49-351-4659-360
Fax.: +49-351-4659-490
Email: m.richter@ifw-dresden.de
WWW: `http://www.ifw-dresden.de/~manuel/`

4.3   Symposium on "Crystallography of Planetary Interiors"

26-31 August, 2004, Budapest, Hungary

This is to inform you of the symposium "Crystallography of Planetary Interiors" that will be part of the 22nd European Crystallographic Meeting (ECM-22) in Budapest, Hungary, from 26 to 31 August 2004. The scope of the symposium will include theoretical and experimental aspects of the structure, properties, and stability of planet-forming materials (from alloys and silicates of the Earth to molecular fluids of the giant planets) at extreme conditions, focussing on the latest advances in this field. We anticipate an exciting scientific programme of this symposium and would like to encourage to attend as many people working in this field as possible. All the necessary information about ECM-22 (scientific programme, details of registration, abstract submission, accomodation, bursaries, social programme, etc.) can be found on the official ECM-22 website:

http://www.ecm22.mtesz.hu/

Please note the major deadlines: 1 March for bursaries and abstract submission, 1 May for registration and accomodation payment.

We look forward to meeting you in Budapest.

Artem R. Oganov and Leonid S. Dubrovinsky

Chairmen of symposium "Crystallography of Planetary Interiors"

4.4   Joint European Magnetic Symposia (JEMS04)

The forthcoming Joint European Magnetic Symposia (JEMS04,

http://www.ifw-dresden.de/imw/jems04/),

Dresden, Germany, September 5-10, 2004, will include a Symposium on

"Electronic Structure of Magnetic Materials".

We would like to encourage you to submit abstracts for this symposium. The deadline for abstract submission has been extended till March 7. Abstract submission after February 19 is possible via the follwing URL:

http://www.ifw-dresden.de/imw/jems04/late

Please take this chance to establish closer contact to applied research on magnetic materials.

Susanne Mirbt and Manuel Richter.

4.5 Third Windsor School on Condensed Matter Theory

"Field Theory of Quantum Coherence, Correlations and Mesoscopics"

Windsor (UK), 9-22 August 2004

We have the pleasure to announce the Third Windsor School on Condensed Matter Theory "Field Theory of Quantum Coherence, Correlations and Mesoscopics", which will be held at Windsor (UK), 9-22 August 2004 with support of EU. We would be very grateful if you distributed this information to interested parties.

This Summer School will present a comprehensive course in field-theoretical applications to correlation effects in disordered and mesoscopic systems and degenerate ultra-cold atomic gases. The course will provide an introduction into these topics and an overview of standard and recently emerged non-perturbative techniques used in studies of interaction effects in low-dimensional systems, nanostructures, and also pattern formation in statistics problems. Lectures in theoretical methods will be complemented by reviews of advanced experiments on mesoscopic electron systems and BEC, and focused research seminars. Core courses will be given by B. Altshuler (Princeton), I. Aleiner (Columbia University), A. Aspect (Orsay), J. Chalker (Oxford), P. le Doussal (Paris), J. von Delft (Munchen), L. Glazman (Minneapolis), T. Giamarchi (Geneve), L. Kadanoff (Chicago), I. Lerner (Birmingham), L. Levitov (MIT), J. Mooij * (Delft) , J. Pendry (Imperial College), B. Simons * (Cambridge), V. Vapnik (NEC-Princeton), and P. Wiegmann (Chicago).

The Organizing Committee will offer a limited number of travel and accommodation grants to eligible participants under 35 years old.

Deadline for application is 1 May 2004.

Further Information and Applications Forms are available from the WWW at:

http://www.lancs.ac.uk/users/esqn/windsor04

Organisers:

Vladimir I. Falko (Director)
Thierry Giamarchi
Igor Lerner
Jan van Delft

4.6 Workshop on "Local correlation methods: From molecules to crystals"

Torino, Italy

September 9-11, 2004

Local Correlation techniques permit the accurate and efficient evaluation of post-HF correlation corrections in large molecules. Their adaptation for the solution of the same problem in non-conducting periodic systems is straightforward in principle but technically demanding. Implementation of local-MP2, the simplest form of post-HF ab initio scheme, in connection with the CRYSTAL program (CRYSCOR project) is currently at an advanced stage, as the result of the collaboration between the Theoretical Chemistry Group of the Torino University and scientists from different Institutions (M. Schuetz, C. Zicovich).

In order to analyze the present stage of CRYSCOR, to discuss computational strategies, to suggest new developments, to propose applications and to promote new collaborations in this area of research, the Torino group is organizing a 3-day workshop with the participation, on invitation, of some eminent scientists.

More detailed information, and a "Declaration of interest form" are found at

http://www.theochem.unito.it/workshop04

4.7 Swedish Summer School on 'Magnetism and Transport in Solids'

14th-18th June 2004

Uppsala, Sweden

Organizers: Biplab Sanyal & Olle Eriksson
Theoretical Magnetism Group, Department of Physics,
Uppsala University, Sweden

Venue: Angstromlaboratoriet, Uppsala University

A summer school on the theoretical and experimental aspects of magnetism and transport in solids will be held during 14th-18th June 2004 at the Angstrom Laboratory, Uppsala University, Sweden. Leading experts in this research field will be invited to present their overviews on current research topics. This summer school is intended mainly for PhD students, postdocs and young researchers and is expected to have 60 participants in total. The conference fee is 100 Euros (materials, refreshments and conference dinner excluding accommodation). Further enquiries can be made by sending email to Biplab.Sanyal@fysik.uu.se or Olle.Eriksson@fysik.uu.se. Information about the school can also be found at

http://www.fysik.uu.se/theomag/summerschool2004.html.

Tentative list of invited speakers:

P. J. Kelly, University of Twente, The Netherlands

P. Weinberger, Center for Computational Materials Science, Vienna, Austria

K. Baberschke, Freie Universität, Berlin, Germany

I. Mertig, Martin-Luther-Universität, Halle, Germany

J. A. C. Bland, Cavendish Laboratory, University of Cambridge, England

T. Dietl, Institute of Physics, Polish Academy of Sciences, Warszawa, Poland

J. M. D. Coey, SFI Laboratory, Trinity College, Dublin, Ireland

O. Heinonen, Seagate Technology, USA

P. H. Dederichs, Institut für Festkörperforschung, Jülich, Germany

J. Kudronovsky, Institute of Physics,Academy of Sciences,Praha, Czech Republik

J. Kirshner, Max-Planck-Institut für Mikrostrukturphysik, Halle, Germany

N. Garcia, Laboratorio de Fisica de Sistemas Pequenos y Nanotechnologia, Madrid, Spain

S. A. Wolf, DARPA/DSO, VA, USA

D. Awschalom, University of California, Santa Barbara, CA, USA

G. Mathon, Department of Mathematics, City University, London, U.K.

D. Loss, University of Basel, Switzerland

H. Zabel, Ruhr-Universität Bochum, Germany

S. Bluegel, Institut für Festkörperforschung, Jülich, Germany

H. Ebert, Ludwig-Maximilians-Universität München, Germany

N. Marzari, MIT, USA

A. Fert, CNRS-Thales, France

B. Barbara, CNRS, France

C. Binns, University of Leicester, UK

P. Ravindran, University of Oslo, Norway

4.8　3rd International Conference "Computational Modeling and Simulation of Materials"

May 30 - June 4, 2004

Acireale (CT), Sisily, Italy

The provisional programme of the 3rd International Conference "Computational Modeling and Simulation of Materials" is now on the web. The Conference features more than 450 scientific presentations covering emerging advances of modeling and simulation of materials, from fundamental issues throughout applications in devices and industrial problems. Hot posters are encouraged. To submit please go to:

http://www.technagroup.it/modeling.htm

Dr. Pietro Vincenzini
Conference Chairman

4.9 Second Conference of the Asian Consortium for Computational Materials Science (ACCMS-2)

July 14-16, 2004, Novosibirsk, Russia

All the information on the above conference can be found at

http://www-lab.imr.edu/ accms/.

Dr. Hiroshi Mizuseki
Institute for Materials Research
Tohoku University
URL: http://www-lab.imr.edu/ mizuseki/

4.10 One-day Symposium on Atomistic Simulation

Queen's University Belfast

Friday 21 May 2004

Prof. Ruth Lynden-Bell retired recently from Queen's University. To honour her contributions to science and bring together some of her many succesful collaborators, friends and admirers, Ali Alavi and Mike Finnis are organising a one day Symposium on Atomistic Simulation followed by a reception and dinner at Queen's. We would like to welcome you here. There will be no fee and coffee and tea will be provided. To register simply email Mike Finnis (m.finnis@qub.ac.uk). You can book a place at the reception and dinner (on a first-come-first-served basis until mid-April) by sending a cheque for 35 GBP to Mike Finnis, made payable to Queen's University Belfast. Places are limited, so don't delay!

Time of Symposium: Friday 21 May 2004, 9am-5pm.

Place: Emeleus Lecture Theatre, Department of Pure and Applied Physics, Queen's University Belfast, Northern Ireland, UK.

Speakers:

Charusita Chakravarty (Delhi)
David Coker (Boston)
Daan Frenkel (Amsterdam)
Lev Gelb (St. Louis)
Peijun Hu (Belfast)
Paul Madden (Oxford) (tbc)
Sally Price (London)
Jay Rasaiah (Maine)
Michiel Sprik (Cambridge)
S. Yashonath (Bangalore) (tbc)

5 General Job Announcements

40th Anniversary Readerships
Department of Physics, University of York, U.K.

The University has recently announced the creation of up to ten new Readerships to mark its 40th anniversary and to complement the eleven 40th Anniversary Professors recently appointed. The Department of Physics strongly encourages applications for these Readerships, which may be held in the Department solely, or jointly between two Departments at York. Those appointed to these Readerships will already be recognised as making a major contribution to their discipline, with the ability to progress to even more senior positions of intellectual and research leadership.

The Department particularly encourages applications (whether for Physics-only or interdepartmental appointments) which are consistent with its strategy for research development. The immediate priority is to build on strengths to achieve critical mass in its four main research groups Nanophysics (formed from our Magnetic Materials and Surface Physics groups), Condensed Matter Theory, Laser-Plasma Physics and Nuclear Physics, which is reflected in 7 new academic posts in these groups in 2003 and 2004, and a 1 million pounds University investment in equipment (a new Centre for Nanolithography and Analysis, joint with the Department of Electronics, and a Detector Development Laboratory in Nuclear Physics), with plans for further expansion.

The Department has 23 academic staff members, 29 research fellows and visitors and 22 support staff. The student population comprises 300 undergraduates and 50 postgraduates, and both have increased by over 80% in the last 6 years, accompanied by an ongoing rise in research funding.

Informal enquiries to Professor Rex Godby, Head of Department (432231, rwg3@york.ac.uk). Further particulars and details of how to apply are available under "Job Vacancies" at

http://www.york.ac.uk/physics.

Applications must be submitted by post to arrive by 15 April 2004.

The University of York is committed to diversity and has policies and developmental programmes in place to promote equality of opportunity. It particularly welcomes applications from ethnic minority candidates.

Lectureship in Condensed Matter Theory
Department of Physics, University of York, U.K.

As part of a major investment in new academic posts in 2003 and 2004 we intend to appoint a Lecturer in the Condensed Matter Theory group. We seek a person who will rapidly establish their own research programme in theoretical condensed-matter physics, including grant funding and studentships. Some overlap with existing research (electronic structure, nanostructures, molecular dynamics, quantum/atom optics and micromagnetics) is desirable. The person appointed will contribute to our teaching programme.

The Department has 23 academic staff members, 29 research fellows and visitors and 22 support staff. The student population comprises 300 undergraduates and 50 postgraduates, and both have increased by over 80% in the last 6 years, accompanied by an ongoing rise in research funding.

Informal enquiries to Professor Mohamed Babiker (Tel. +44 (0)1904 432287, e-mail meb6@york.ac.uk); Professor Rex Godby, Head of Department (432231, rwg3@york.ac.uk); or any member of the group. Salary in the range GBP 23,296-33,679 p.a. (pay award pending). A PhD or equivalent is required for this post.

Further particulars and details of how to apply are available under "Job Vacancies" at

http://www.york.ac.uk/physics.

Applications must be submitted by post to arrive by 5 May 2004.

The University of York is committed to diversity and has policies and developmental programmes in place to promote equality of opportunity. It particularly welcomes applications from ethnic minority candidates.

CASE PhD Studentship (Experimental)
in Synchrotron-based Spectroscopy of Ferromagnetic Semiconductors
University of Nottingham & Daresbury Laboratory, UK

The III-V dilute ferromagnetic semiconductors (FS) represent a new class of magnetic material, in which a long range magnetic ordering between dopant ions is mediated by itinerant charge carriers. Such materials have potential applications in information storage and processing as well as quantum computation, and also are an ideal testing ground for studying magnetic interactions at the nanoscale. A CASE PhD studentship is available, in collaboration between the University of Nottingham and Daresbury Laboratory, for an investigation of the electronic and magnetic properties of FS-based structures, using synchrotron-based x-ray spectroscopy. X-ray magnetic dichroism will be exploited to investigate the detailed interactions between the magnetic impurities and the semiconductor host, and the origins of the complex magnetic anisotropy effects displayed by these materials. Also, central to the programme will be the development of a novel combined photoemission, magnetic dichroism, and x-ray standing wave technique, which will reveal unique site-specific magnetic information.

The experiments will be conducted at leading international laboratories, and there will be several opportunities for travel. For information, contact: Kevin Edmonds (kevin.edmonds@nottingham.ac.uk) or Bryan Gallagher (bryan.gallagher@nottingham.ac.uk) at the School of Physics and Astronomy, University of Nottingham; or Tarnjit Johal (t.k.johal@dl.ac.uk) or Gerrit van der Laan (`g.van_der_laan@dl.ac.uk`) at Daresbury Laboratory.

Postdoc Position in Theoretical Solid State Physics at IFW Dresden

We would like to announce an open postdoc position at the Institute for Solid State and Materials Research Dresden

(http://www.ifw-dresden.de).

The project includes

(1) density functional studies of magnetism on transition metal, lanthanide, and actinide elements and compounds, using the recently developed FPLO code (http://www.ifw-dresden.de/FPLO/);

(2) code development with respect to non-collinear magnetic structures.

Close contact with related experimental work at IFW Dresden, University of Technology Dresden (http://www.tu-dresden.de), and the Max-Planck Institute for the Chemical Physics of Solids Dresden (http://www.cpfs.mpg.de) is envisaged, as well as collaboration with several Dresden groups active in solid state theory.

The applicant should preferably have a safe background in solid state physics, good knowledge of density functional theory, and experience in the understanding and development of extended code for numerical purposes (FORTRAN 90 and C).

We offer a one-year position, extendable up to 3 years, at the level BAT IIa-O (annual net income about kEUR 20, depending on age and family status).

The Department of Theoretical Solid State Physics at IFW Dresden consists of thirteen PhDs in solid state theory, five PhD students, and several guest scientists, see

http://www.ifw-dresden.de/agtheo/eagtheo1.htm.

The group has up-to-date computer facilities, regular coffee meetings, and a lively exchange with a number of other groups inside and outside of Dresden (theoretical and experimental, physics and chemistry). The city of Dresden is situated mid-way between Berlin and Prague, in the valley of river Elbe. With a population of about 500,000, it is known for a rich cultural live and for its baroque silhouette.

Interested candidates should send their application together with a curriculum vitae, a list of publications, a statement about current research activities, and other relevant material to:

Dr. Manuel Richter
Dept. of Theoretical Solid State Physics
IFW Dresden e.V.
P.O. Box 270016
D-01171 Dresden, Germany

email m.richter@ifw-dresden.de
 http://www.ifw-dresden.de/~manuel/

PhD Studentship in Theoretical Chemistry Cambridge, UK

COMPUTATIONAL MODELLING OF AQUEOUS REDOX REACTIONS

A candidate is sought for an EPSRC Studentship in the research group of Dr Michiel Sprik. The project involves a computational study of model redox reactions in aqueous solutions using density functional based ab initio molecular dynamics simulation ("Car-Parrinello"). This approach is ideally suitable to gain a microscopic understanding of the coupling between electronic states and solvent fluctuations and the aim of the project is to compare such an orbital based picture to the more classical electrostatic models developed for redox reactions, such as Marcus theory of electron transfer. The project combines electronic structure calculation and statistical mechanics addressing fundamental questions regarding reactivity in solution.

Candidates should have, or be about to receive, an honours degree (at least II.1 or equivalent) in Chemistry or Physics. Experience with computer simulations is helpful, but not required. Full funding (fees and maintenance) is available to UK citizens, and partial funding to EU citizens. Appointments must be made by 31 March 2004, so applications should be submitted well ahead of this date.

Applications should include a full CV (two copies) and the names of two referees, and should be sent to: Dr Michiel Sprik, Department of Chemistry, Lensfield Rd, Cambridge CB2 1EW, UK. Informal enquiries may also be made to Dr Sprik (tel: +44-(0)1223-336314, email: ms284@cam.ac.uk). See also the department webpage: http://www.ch.cam.ac.uk.

POST-DOCTORAL POSITION in CONDENSED MATTER THEORY

Department of Physics, University of Missouri

One position of a post-doctoral Fellow is available beginning July 1, 2004 or thereabout in the area of theoretical and computational condensed matter physics to work with Prof. Sashi Satpathy on the topic of Electronic and Magnetic properties of solids, especially, on the oxides. The successful candidate must have a Ph. D. in Condensed Matter Theory and should have experience in the area of density-functional methods and / or physics of any of the wide variety of phenomena exhibited by the oxides, such as Jahn-Teller effects, colossal magneto-resistance, 1D Luttinger liquid behavior, etc. The position is for two years and may be renewed for a third year.

Interested candidates should send a letter of interest, a curriculum vita, and arrange to have three letters of reference sent either electronically to: satpathys@missouri.edu (please put the word "postdoc" and the name of the applicant on the Subject heading in your email - same for letters of reference also) or by regular mail to: Prof. S. Satpathy, Department of Physics, University of Missouri, Columbia, MO 65211, USA. Consideration of applications will begin immediately and will continue until the position is filled. It is anticipated that the position will be filled by end of April or so.

Permanent position, Paris

We are advertising a permanent position for an "ingenieur de recherche" (the highest position available for a technician at CNRS) to work with the theoretical group of the Laboratoire de Mineralogie-Cristallographie de Paris (LMCP). One of our main activities is the developement of numerical methods for the computation of material properties, based on electronic structure via Density Functional Theory. The role of the selected candidate will be to organize the developement of a user-friendly scientific software for ab-initio prediction of properties of materials. Such software will be made available to a large community of users, including non-experts in electronic structure theory, and will be distributed under the "GNU General Public License". The candidate will assure the links between the users and the developers. He will also be encouraged to pursue an original research activity in the domain of electronic structure theory.

The candidate will be selected in the coming spring 2004, to start the activity in autumn 2004.

More details about the required profile can be found at the URL:

`http://www.lmcp.jussieu.fr/~calandra/Poste/ing.html`

Interested candidates should e-mail a curriculum vitae and a brief letter of motivation as soon as possible to

Matteo Calandra

LMCP - Université Pierre et Marie Curie

Case 115, 4 Place Jussieu, F-75252, PARIS cedex 05, FRANCE

Tel: +33-1-44275216, Fax: +33-1-44274541

E-mail: matteo.calandra@lmcp.jussieu.fr

For any additional information please contact directly one of the followings:

matteo.calandra@lmcp.jussieu.fr

michele.lazzeri@lmcp.jussieu.fr

francesco.mauri@lmcp.jussieu.fr

POSTDOCTORAL RESEARCH POSITION

Theoretical Condensed Matter Physics
Theory Group, Physics Department, University of Warwick, UK

A three-year post-doctoral research position is available from 1 May 2004 to work on a project with Prof.Julie Staunton to develop a 'first-principles' theory of electrons in disordered systems with short-range order. This project is being undertaken in collaboration with Prof.Balazs Gyorffy at the University of Bristol.

Order-disorder phenomena in solids are driven by the energetics of their electrons. Whilst simple models frequently suffice to give an account of particular phenomena, in general, a description in terms of the electronic structure in unavoidable. This is particularly so when the symmetry of the lattice is broken by defects. Disorder has profound effect on the electronic structure and typically there is order over small length scales, namely Short Range Order (SRO). This can vary dramatically with the type of defect. A method, recently invented at Warwick and Bristol, provides an effective way of dealing with this problem which successfully combines treatment of disorder and SRO with an ab-initio quantum mechanical description of the electrons. (see D.A.Rowlands et al. Phys. Rev. B67, 115109, (2003)). This project will be directed at developing this approach and showing its potential as a tool for designing materials and understanding their properties. Three problems from alloy physics and magnetism of broad scientific and technological interest have been identified to demonstrate this.

The project is funded by the Engineering and Physical Sciences Research Council of the UK and the salary for the postdoctoral position is on the RA1A scale (currently 20,311 - 27,339 UK pounds, pay award pending).

Candidates for this post must have (or expect to obtain soon) a Ph.D in theoretical or computational condensed matter physics or related discipline. Experience with electronic density functional theory and electronic structure calculations (e.g. KKR techniques) is desirable.

Further information including recent publications can be found at `http://www.warwick.ac.uk/~phrjz`

Specific enquiries should be directed to Prof.Julie Staunton
E-mail address: j.b.staunton@warwick.ac.uk.
Tel: (44) 024 76523381

Application forms can be obtained from the Personnel Office,
University of Warwick, Coventry CV4 7AL.
Telephone: (44) 024 76 523627
Email:recruit@warwick.ac.uk
Please quote reference 52773

Closing date for applications is 16 April 2004.

Two Postdoctoral Positions in Molecular Electronics
Department of Chemistry & Biochemistry, University of Maryland

Two postdoctoral positions are available starting September 2004 to work with D. Kosov at the University of Maryland. The research projects focus on the development and applications of theoretical and computational methods for the investigation of electron transport in molecular wire junctions.

Topical Areas:

(1) Development of ab initio transport code to compute molecular I-V characteristics, geometry and its evolution during transport;

(2) vibrational and electronic spectroscopy to monitor and to control transport properties of molecular wires;

(3) Non-equilibrium, current-dependent Born-Oppenheimer potential energy surfaces of molecular devices (current induced forces, electromigration, and current-induced device breakdown; heating in molecular junction via current-induced vibrations).

Familiarity with modern electron transport theory (e.g. non-equilibrium Green's functions), profound knowledge of electronic structure methods or scattering theory and programming experience are desired. Both positions are available for a year with a possibility of extension for another year.

Interested applicants should contact D. Kosov (kosov@theochem.uni-frankfurt.de)

Ph. D. Position, Mainz-Montpellier
Development of empirical potentials

Applications are invited for a Ph.D. position in a joint project of the University of Mainz with the University of Montpellier II. The position is for three years, it is now already available, and the payment is according to the standard German public employee salary scheme (BAT IIa/2). The applicant is expected to work based at Montpellier for about two years and based at Mainz for about one year (there will be the opportunity and funding to visit frequently the other group to maintain an intense collaboration). The candidate shall defend the doctoral thesis at Mainz. The project is on the development of empirical potentials for amorphous silicates based on ab initio methods. This is of interest for the research laboratory of SCHOTT GLAS which company provides the funding for this project. The applicant is expected to have special interest in statistical and quantum mechanics and their application to computer simulations of realistic models of viscous liquids and glasses.

Requirement: fluent in English

Interested candidates should e-mail a curriculum vitae and a brief letter of motivation as soon as possible to

Dr. Simona ISPAS (simona.ispas@ldv.univ-montp2.fr)
Laboratoire des Verres, cc 069
Universite Montpellier 2
34095 Montpellier Cedex 05
Tel: +33 (0)4 67 14 49 79
Fax: +33 (0)4 67 14 34 98,
FRANCE

Postdoctoral Position for Ab Initio Interface Calculations

National Institute of Advanced Industrial Science and Technology
AIST-Kansai, Osaka, Japan

The reseach invloves first-principles supercell calculations of stable configurations and mechanical behavior of oxide/ metal interfaces and the development of interatomic potentials for classical molecular-dynamics simulations. This is performed as "Nano-Coating Project" sponsored by NEDO. The candidate should have good knowledge on ab initio calculations, materials science or solid state physics, and basic computer languages (FORTRAN).

The salary is in the range of 4000k Yen (USD 35k) to 4500k Yen (USD 40k), depending on experience. Applications, CV and recommendation letters should be sent by 15 April 2004 to m-kohyama@aist.go.jp.

Dr. M. Kohyama

Interface Res. Group

National Institute of Advanced Industrial Science and Technology,

AIST-Kansai, 1-8-31, Midorigaoka, Ikeda, Osaka 563-8577, Japan

POSTDOC POSITION IN THEORETICAL PHYSICAL CHEMISTRY

Theoretical Chemistry, Rijksuniversiteit Groningen, The Netherlands

Project Title: Development and Application of Time-Dependent Density Functional Theory: Nonlinear Optical Properties of Organo-Metallic Compounds

Duration: Three Years

Fields: Theoretical/Computational Physics/Chemistry

SUBJECT: A three year Post-Doc position in theoretical physical chemistry is immediately available at the Theoretical Chemistry group of the Rijksuniversiteit Groningen, Groningen, The Netherlands. The position is financially supported by the Royal Dutch Academy of Sciences within the program for Strategic Scientific Alliances between China and the Netherlands. This project is part of a research program that focuses on the new approach of time-dependent (current)-density-functional theory for calculating excitation and response properties in solid state physics and quantum chemistry. Currently four PhD students and two senior researchers are developing this theoretical and computational method for solids, surfaces, polymers, and large molecules. Jointly with them the successful applicant will develop the method for nonlinear response properties, and will extend it to facilitate the analysis of the effectiveness of complex chemical compounds as nonlinear media in terms of the functional groups and their interactions. This fragment analyses, which is available for energetic properties but not yet for response properties, will help in understanding and designing molecules for nonlinear applications. On the Chinese side the Fuzhou institute of the Chinese Academy of Sciences synthesizes and characterizes various organo-metallic compounds, and will analyze them using the methods developed in Groningen. The project involves frequent exchanges between China and the Netherlands: each year a one-month visit to China by Dutch post-doc and senior researcher, and a two-month visit from Chinese post-doc and senior researcher. At the end of the project phase a one-week symposium will be organized by both sides.

INTERNET: Theoretical Chemistry Group http://theochem.chem.rug.nl, Materials Science Centre: http://www.msc.rug.nl, Rijksuniversiteit Groningen: http://www.rug.nl

APPOINTMENT AND SALARY: The Post-Doc will be appointed for a period of three years, and will be offered a monthly salary (before subtraction of taxes and health and social insurance fees, typically 35ranging between 2600 and 2800 euro depending on previous experience. Additionally, they receive a holiday allowance ($\sim$8%) and an end-of-year supplement.

QUALIFICATION: The position is open to EU and non-EU citizens. Successful candidates should hold a PhD, in theoretical chemistry or theoretical solid-state physics. They should have good communicative skills and should master the English language. Experience with density

functional and numerical methods is highly recommended.

APPLICATION: requests for further information and applications (application letter explaining your motivation and suitability for this job, plus a full CV including a list of publications as well as the summary of the doctor thesis, and the names and addresses of two academic referees should be sent to dr. ir. Paul L. de Boeij (mailto:p.l.de.boeij@chem.rug.nl) Theoretical Chemistry, Rijksuniversiteit Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands. Phone:+31.50.363.4287, Fax:+31.50.363.4441.

Deadline for submission is April 15 2004, although the search will continue until the position is filled.

POSTDOCTORAL POSITION: University of Edinburgh, U.K.

Modelling interatomic interactions in steels from first principles

Applications are invited for a research associate position starting immediately, to calculate alloying and impurity effects in iron and to parameterise interatomic potentials.

The ideal candidate would have strong programming skills and experience in areas such as theoretical metallurgy, interatomic potentials, function optimisation and DFT/MD calculations. Typically you will hold a PhD in a relevant subject. She or he would use electronic structure methods based on preexisting code in order to model configurations relevant to the complex processes involved radiation damage in steels. These configurations will then be used to parameterise interatomic potentials for use in large-scale molecular dynamics.

The School of Physics at Edinburgh University provides an intellectually inspiring environment and excellent facilities. The work will be part of close ongoing collaboration with departments in Princeton, Barcelona and Liverpool, and is funded by the EU 6th framework through the 28-site "Prediction of Irradiation Damage Effects in Reactor Components" collaboration.

Candidates should send a detailed resume including an outline of their research achievements and interests as well as contact information for academic references.

Consideration of candidates will begin immediately and continue until the position is filled. The position will be for one year initially, with the possibility of extension to up to five years. Salary will be on the AR1A scale.

Apply to

Graeme Ackland
Professor of Computer Simulation
School of Physics
The University of Edinburgh
Edinburgh EH9 3JZ
(tel) +44 131 650 5299
gjackland@ed.ac.uk

Further Particulars

Applications are invited for a postdoctoral research position in the condensed matter group at the School of Physics at the University of Edinburgh. The position is part of the EU's nuclear safety "Prediction of Irradiation Damage Effects in Reactor Components" (PERFECT) programme, and results will be fed directly to other members of the programme.

The multi-million atom molecular dynamics modelling required to understand radiation damage depends entirely on the existence reliable interatomic potentials. Much recent work in the area

of ferritic steels has been done using an iron potential derived in collaboration between the Edinburgh and Liverpool groups. Unlike other available potentials, this describes the geometry of the iron self-interstitial and can thus be sensibly used for radiation damage cascades and subsequent evolution. Although this model correctly describes the known experimental facts, and has been used to make plausible simulations, our recent work using quantum mechanical calculation has provided a different window to the atomistic world, and revealed deficiencies in the model. In particular the short range repulsion which keeps atoms apart is weaker than previously thought, and the energy require to form interstitials (and dislocations) is less than was believed. Incorporating these results is essential to improve models, and there is ongoing work in this area in conjunction with Profs D.Srolovitz, and M.Mendelev (Princeton).

At the same time, there is a need for potentials to describe iron interactions with solutes (Cu, P, Mn, Cr, C) and this is where the project will concentrate. Quantum simulation gives us, for the first time, the capacity to generate reliable data for various configurations of these solute relevant in parameterising the potential. It also enables us to determine whether the functional form of the potential is adequate. Changes in chemical composition affect the electron density, and some strange features such as the nonlinear solubility of Cr may be describable by including a density dependent pair potential. Recently, we have introduces a two-band variant of the embedded atom method which, for similar computational cost, successfully described the s-d band interaction in caesium. In iron, a similar relationship exists between the two spin bands and there is the possibility of including the physics of magnetism in a simple MD potential.

It is envisaged that potentials for iron with and without solutes can be derived and interatively tested upscale through molecular dynamics and downscale through quantum mechanical simulations. The parameters for an interatomic potential for iron in the embedded atom form, consistent with both experimental data and quantum mechanical calculations will be determined. New forms of interatomic potential, including the two-band model and potentials with explicit dependence on Fermi energy, will be derived.

There are ample computing resources. The condensed matter group has a cluster of 40 LINUX workstations and its own 12 processor IBM SP2. We also have access to the EPCC's 52 processor Sun Fire E15k and the HPCx national supercomputer.

You will be responsible for:

Developing code to use empirical and ab initio data in parameterising interatomic potentials

Running and analysing density functional theory calculations for impurities in iron using pre-existing code.

Devising computer-efficient representations of interatomic interactions for use in molecular dynamics calculation.

6 Abstracts

Stability of reduced $V_2O_5(001)$ surfaces

M. V. Ganduglia-Pirovano and J. Sauer

Humboldt Universität zu Berlin, Institut für Chemie,

Unter den Linden 6, D-10099 Berlin, Germany

Abstract

The defect-free $V_2O_5(001)$ surface and ordered structures involving oxygen vacancies have been studied for a wide range of defect concentrations, Θ ($1/6 \leq \Theta \leq 1$ monolayer, ML), combining density functional theory and statistical thermodynamics. At $\Theta=1/4$ ML the oxygen vacancy formation energy for the singly coordinated surface oxygen atoms (vanadyl oxygen, O^1) is by ~ 1.7 eV/atom and ~ 2.0 eV/atom lower than the corresponding values for two- and three-fold coordinated surface oxygen atoms, respectively. Between 1/3 and 1/2 ML the alignment of vanadyl oxygen vacancies (O^1_{vac}) along the [010] direction is by 70 meV/atom ($\Theta=1/3$ ML) and 120 meV/atom ($\Theta=1/2$ ML) more favorable than along the [100] direction, with the concentration induced change of the vacancy formation energy for structures with vacancies aligned along the [100] direction being smaller than 20 meV/atom. The lowest vacancy formation energy of 1.87 eV/atom corresponds to the (1×1)-O^1_{vac} ($\Theta=1/2$ ML) phase with defects forming a trenchlike structure with rows along the [010] direction. Above 1/2 ML the vacancy formation energy increases up to 2.07 eV/atom ($\Theta=1$ ML). The ease of formation of non-random vacancy structures with a favored alignment along the [010] direction is discussed in terms of special vacancy induced lattice distortions. It is also argued that the trenches along the [010] direction provide preferred paths for continuous reduction of the surface starting from isolated defect sites. However, this missing-row structure would be stable only at very low oxygen partial pressures close to conditions for which V_2O_5 decomposes into VO_2 and O_2.

From stripe to speckle–the magnetic attraction of nanostructures

G. van der Laan

Magnetic Spectroscopy, Daresbury Laboratory, Warrington WA4 4AD, UK

Abstract

We discuss the principles and advantages of soft X-ray resonant magnetic scattering using polarized synchrotron radiation for the study of magnetic domain structures on a length scale from 1 to 1000 nm. This new technique is ideally suited to study magnetic superlattices and magnetic stripe domains. Speckle patterns, obtained using coherent radiation, give information on the local magnetic configuration.

Soft X-ray resonant magnetic scattering from FePd thin films: a study of the micromagnetic components

G. Beutier, A. Marty, K. Chesnel, M. Belakhovsky

CEA Grenoble-SP2M, Grenoble, France

J-C. Toussaint

Laboratory Louis Nel, CNRS, Grenoble, France

G. van der Laan, S.P. Collins, E. Dudzik

Magnetic Spectroscopy, Daresbury Laboratory, Warrington WA4 4AD, UK

Abstract

Soft X-ray resonant magnetic scattering (SXRMS) was performed on a FePd alloy thin film at the L_3 edge of Fe. This film exhibits perpendicular magnetic anisotropy giving rise to periodic alternation of up and down magnetisation domains with closure domains. Rocking curves performed in transverse geometry allowed us to measure the magnetic periodicity and correlation length of domains. Micromagnetic simulations of the FePd layers and SXRMS calculations were made to analyse the asymmetry ratio of magnetic satellite intensities, hence allowing us to quantify the magnetic anisotropy.

Polarization effects in X-ray resonant magnetic scattering patterns from striped FePd films

K. Chesnel, M. Belakhovsky, A. Marty, G. Beutier

DRFMC, CEA-Grenoble, France

G. van der Laan and S. P. Collins

Magnetic Spectroscopy, Daresbury Laboratory, Warrington WA4 4AD, UK

Abstract

We recorded X-ray resonant magnetic scattering (XRMS) patterns from a 40 nm thin FePd film that exhibits magnetic stripes with ∼100 nm period. Measurements were performed using a CCD camera in reflection geometry for different light polarizations at the Fe L_3 resonance. We observed dichroic effects using circular polarization. By combining the scattering patterns obtained with both helicities we obtain the symmetric and antisymmetric part of the pattern. The experimental results are in agreement with a simple theoretical model.

Analytical Hartree-Fock gradients with respect to the cell parameter for systems periodic in three dimensions

K. Doll

Institut für Mathematische Physik, TU Braunschweig,

Mendelssohnstrasse 3, D-38106 Braunschweig

R. Dovesi, R. Orlando

Dipartimento di Chimica IFM, Università di Torino,

Via Giuria 5, I-10125 Torino, Italy

Abstract

Analytical Hartree-Fock gradients with respect to the cell parameter have been implemented in the electronic structure code CRYSTAL, for the case of three-dimensional periodicity. The code is based on Gaussian type orbitals, and the summation of the Coulomb energy is performed with the Ewald method. It is shown that a high accuracy of the cell gradient can be achieved.

Fe $M_{2,3}$ X-ray resonant magnetic reflectivity on epitaxial Fe$_{3-\delta}$O$_4$ thin films

N. D. Telling

Magnetic Spectroscopy, Daresbury Laboratory, Warrington WA4 4AD, UK

A. Haznar

Magnetic Spectroscopy, Daresbury Laboratory, Warrington WA4 4AD, UK
Inst. Low Temp. and Struct. Res., Polish Acad. Sci., Wroclaw, Poland

G. van der Laan, M. D. Roper

Magnetic Spectroscopy, Daresbury Laboratory, Warrington WA4 4AD, UK

F. Schedin, G. Thornton

Chemistry Department, University of Manchester, UK

Abstract

We report the use of soft X-ray resonant reflectivity at the Fe $M_{2,3}$ edges to probe the magnetic circular dichroism of non-stoichiometric Fe$_{3-\delta}$O$_4$ thin films grown epitaxially on Al$_2$O$_3$. Photon energy scans of the magnetic dichroism display features that arise from the different Fe cation sites, with relative intensities that depend on the incident angle of the X-rays. Comparisons are made between the dichroism measured with this technique and X-ray magnetic circular dichroism calculated for the three Fe sites in magnetite.

Electron-energy-loss spectroscopy and X-ray absorption spectroscopy as complementary probes for complex f-electron metals: cerium and plutonium

K. T. Moorey, M. A. Wall, A. J. Schwartz,

B.W. Chung, S. A. Morton, J. G. Tobin

Chemistry and Materials Science Directorate,

Lawrence Livermore National Laboratory, Livermore, California 94550, USA

S. Lazar, F. D. Tichelaar, H. W. Zandbergen

National Center for High Resolution Electron Microscopy,

Delft University of Technology, The Netherlands

P. Söderlind

Department of Physics, Lawrence Livermore National Laboratory,

Livermore, California 94550, USA

G. van der Laan

Magnetic Spectroscopy Group, Daresbury Laboratory,

Warrington WA4 4AD, UK

Abstract

In this paper, we demonstrate the power of electron-energy-loss spectroscopy (EELS) in a transmission electron microscope by investigating the electron structure of two f-electron metals: Ce and Pu. It is shown that EELS in a transmission electron microscope may be used to circumvent the difficulty of producing singlephase or single-crystal samples owing to its high spatial resolution, and that diffraction patterns and images can be acquired, providing unambiguous phase determination when acquiring spectra. EELS results are supported by synchrotron-radiation-based X-ray absorption, multielectron atomic spectral simulations, and local density approximation calculations based on density-functional theory with the generalized gradient approximation. For Ce, it is shown that changes in 111 stacking sequences can drive substantial modifications in the electronic structure of close-packed phases of Ce that have similar atomic volumes, contrary to previous assumptions in literature. For Pu, it is shown that Russell-Saunders (L-S) coupling fails for the $5f$ states and that either a j-j or an intermediate scheme must be used for the actinides because of the considerable spin-orbit interaction in the $5f$ states. We present a model showing how the $5f$ states behave along the light actinide series.

Probing InAs/GaAs(001) heteroepitaxy from first principles

Evgeni Penev, Peter Kratzer, and Matthias Scheffler

Fritz-Haber-Institut der Max-Planck-Gesellschaft,

D–14195 Berlin-Dahlem, Germany

Abstract

Density-functional theory calculations are employed to obtain important information about the morphology of III-V semiconductor surfaces and kinetics of epitaxial growth. In this way, insight into the microscopic processes governing quantum dot formation in InAs/GaAs(001) heteroepitaxy is gained. First, we investigate theoretically the atomic structure and thermodynamics of the wetting layer formed by InAs deposition on GaAs(001), including the effect of strain in our discussion. Secondly, we present results about In adatom diffusion both on the wetting layer and on the $c(4 \times 4)$-reconstructed GaAs(001) surface. In the latter case, we demonstrate the importance of mechanical stress for the height of surface diffusion barriers. Implications for the growth of InAs quantum dots on GaAs(001) are discussed.

Above we have tried to develop a microscopic picture of the early stages of quantum dot formation. At the fundament of our knowledge lies an understanding of the atomistic processes in epitaxial growth which are best explored through suitably conducted first-principles DFT calculations. In this contribution, we have attempted to demonstrate the application of the latter to the specific problems of surface atomic structure and adatom diffusivity in InAs/GaAs(001) heteroepitaxy. From the typically used growth temperatures and the calculated energy barriers for diffusion, we conclude that the time and length scales involved in quantum dot formation in InAs heteroepitaxy on GaAs(001) span a few decades in magnitude. The importance of a wide range of length and time scales is a very general phenomenon in epitaxial growth. It is therefore clear that the theoretical description of this phenomenon requires more than a single theoretical tool. DFT calculations must be complemented by calculations on larger scales using elasticity theory or analytical interatomic potentials. Kinetic Monte Carlo simulations are able to integrate input form various sources, and enable us to bridge the gap between the atomic scale and experimentally relevant scales. The results from our first-principles calculations constitute important input to such kinetic Monte Carlo simulations. The feasibility of this method has already been demonstrated for homoepitaxy of GaAs. A typical problem where its usage is indispensable is the treatment of structural disorder in the WL, observed in some samples. Future research will therefore be focused on kinetic Monte Carlo simulations of In diffusion on a disordered WL and possible consequences for QD growth.

First-principles study of ferromagnetism in epitaxial Si-Mn thin films on Si(001)

Hua Wu, Mahbube Hortamani, Peter Kratzer, and Matthias Scheffler

Fritz-Haber-Institut der Max-Planck-Gesellschaft,

D–14195 Berlin-Dahlem, Germany

Abstract

Density-functional theory calculations are employed to investigate both the epitaxial growth and the magnetic properties of thin Mn and MnSi films on Si(001). For single Mn adatoms, we find a preference for the 2nd-layer interstitial site. While a monolayer Mn film is energetically unfavorable, a capping Si layer significantly enhances the thermodynamic stability and induces a change from antiferromagnetic to ferromagnetic order. For higher Mn coverage, a sandwiched Si-Mn thin film (with CsCl crystal structure) is found to be the most stable epitaxial structure. We attribute the strong ferromagnetic intralayer coupling in these films to Mn $3d$-Si $3s3p$ exchange.

Oxygen adlayers on Pd(111) studied by density-functional theory

Mira Todorova, Karsten Reuter, and Matthias Scheffler

Fritz-Haber-Institut der Max-Planck-Gesellschaft,
D–14195 Berlin-Dahlem, Germany

Abstract

Using density-functional theory we analyze the on-surface adsorption of oxygen on Pd(111) for coverages up to one monolayer and compare the results with corresponding data for the other late $4d$ transition metals, namely Ru, Rh, and Ag. Besides the known effect of the continued d-band filling on the oxygen-metal bond strength, we also discern trends in the adsorption geometries, work functions, and electron density of states. The repulsive lateral interactions in the overlayer give rise to a pronounced reduction of the adsorption energy at higher on-surface coverages. In fact, for oxygen coverages $\theta > 0.5$ monolayers the thermodynamic equilibrium phase of O/Pd(111) is known to be a surface oxide. The calculations reported in this paper show that on-surface adlayers at such higher coverages, that may exist as metastable phases, still possess qualitatively the same surface chemical bond as that which is found at low coverages. The dependence of the surface relaxation on oxygen coverage exhibits some unexpected behavior.

Adsorption and vibrational spectroscopy of ammonia at mordenite: Ab-initio study

T. Bucko, J. Hafner, and L. Benco

Materials Physics Institute and Center of Computational
Materials Science, University of Vienna,
Sensengasse 8/12, A-1090 Vienna, Austria

Abstract

The adsorption of ammonia at various active centers at the outer and inner surfaces of mordenite, involving Brønsted acid (BA) sites, terminal silanol groups and Lewis sites has been investigated using periodic ab-initio density-functional theory. It is shown that ammonia forms an ammonium ion when adsorbed at strong BA sites. The calculated adsorption energies for different BA sites vary in the interval from 111.5 kJ/mol to 174.7 kJ/mol depending on the local environment of the adduct. The lowest adsorption energy is found for a monodentate complex in the main channel, the highest for a tetradentate configuration in the side pocket. At weak BA sites such as terminal silanol groups or defect with a BA site in a two-membered ring ammonia is H-bonded via the N atom. Additional weak H-bonds are formed between H atoms of ammonia and O atoms of neighboring terminal silanol groups. The calculated adsorption energies for such adducts range between 61.7 kJ/mol to 70.9 kJ/mol. The interaction of ammonia with different Lewis sites is shown to range between weak (ΔE_{ads} 17.8 kJ/mol) to very strong ($\Delta E_{ads} = 161.7$ kJ/mol), the strongest Lewis site being a tri-coordinated Al atom at the outer surface. Our results are in very good agreement with the distribution of desorption energies estimated from temperature-programmed desorption (TPD) and micro-calorimetry experiments, the multi-peaked structure of the TPD spectra is shown to arise from strong and weak Brønsted and Lewis sites.

The vibrational properties of the adsorption complexes are investigated using a force-constant approach. The stretching and bending modes of NH_4^+ adsorbed to the zeolite are strongly influenced by the local environment. The strongest redshift is calculated for the asymmetric stretching mode involving the NH-group hydrogen-bonded to the bridging O-atom of the BA-site, the shift is largest for a monodentate and smallest for a tetradentate adsorption complex. The reduced symmetry of the adsorbate also leads to a substantial splitting of the stretching and bending mode In agreement with experiment we show that the main vibrational feature which differentiates coordinatively bonded ammonia from a hydrogen-bonded ammonium ion is the absence of bending modes above 1630 cm^{-1} and in the region between 1260 cm^{-1} and 1600 cm^{-1}, and a low-frequency bending band in the range from 1130 to 1260 cm^{-1}. The calculated distribution of vibrational frequencies agrees very well with the measured infrared adsorption spectra. From the comparison of the adsorption data and the vibrational spectra we conclude that due to the complex adsorption geometry the redshift of the asymmetric stretching is a better measure of the acidity of the active sites than the adsorption energy.

Sampling the diffusion paths of a neutral vacancy in Silicon with SIEST-A-RT

Fedwa El-Mellouhi, Normand Mousseau

Département de physique and Regroupement québécois sur les matériaux de pointe, Université de Montréal,

C.P. 6128, succ. Centre-ville, Montréal (Québec) H3C 3J7, Canada

Pablo Ordejón

Institut de Ciència de Materiales de Barcelona (CSIC),

Campus de la Universitat Autónoma de Barcelona, Bellaterra,

E-08193, Barcelona, Spain

Abstract

We report a first-principles study of vacancy-induced self-diffusion in crystalline silicon. Starting form a fully relaxed configuration with a neutral vacancy, we proceed to search for local diffusion paths. The diffusion of the vacancy proceeds by hops to first nearest neighbor with an energy barrier of 0.40 eV in agreement with experimental results. Competing mechanisms are identified, like the reorientation, and the recombination of dangling bonds by Wooten-Winer-Weaire process.

A faster way to relax interfaces in supercells

M W Finnis

Atomistic Simulation Group, School of Mathematics and Physics,
Queen's University Belfast, BT7 1NN, Northern Ireland, UK

Abstract

The usual way of minimizing the total energy of a planar boundary between two crystals by relaxing the atomic positions is inefficient, because it does not exploit the physical insight that forces are localised near the interfaces or surfaces. I introduce a simple change of variables, which leads to much faster and more accurate relaxation in such systems. In general the method is formulated for three-dimensional monoclinic supercells with sides $(\mathbf{a}, \mathbf{b}, \mathbf{c})$, subject to periodic boundary conditions. If the crystals fill space the method exploits the stress tensor in the supercell to adjust its side $\mathbf{c}$, where the boundary lies in the $(\mathbf{a}, \mathbf{b})$-plane, but the stress tensor is not required for a slab of finite thickness, which would be simulated by including a vacuum layer in the supercell. In either case the number of conjugate gradient steps required to relax the atomic positions does not increase with the thickness of the system. The power of this method is demonstrated by calculations on one-dimensional chains, both finite and infinite, using a pair potential to calculate the energy, forces and stresses.

Quenching of atomiclike properties upon solid-state formation: Quantitative comparison between Co and Ni in ferrites studied by x-ray resonant Raman scattering at the L_3 edge

G. van der Laan

Magnetic Spectroscopy, Daresbury Laboratory, Warrington, WA4 4AD, UK

G. Ghiringhelli, A. Tagliaferri, L. Braicovich

INFM, Dipartimento di Fisica del Politecnico, Milano, Italy

N. B. Brookes

European Synchrotron Radiation Facility, Grenoble, France

Abstract

We have measured the spin and orbital coupled multipole moments for the ground state of the divalent Co and Ni ions in the ferrites using the technique of integrated x-ray resonant Raman scattering (IRRS). This method exploits the sum rules characteristic of a second-order process which gives access to moments higher than those obtained from magnetic circular and linear dichroism in x-ray absorption. Moreover, IRRS is complementary to the latter techniques concerning the lower-order moments. The experimentally deduced values for the quadrupole and octupole moments are small in Ni ferrite but large in Co ferrite. Except for the spin moment, this difference between both ions is in contrast with the ground-state values given by the Hund's rule that gives the same absolute value for both isolated ions. The difference is due to the quenching of the spin-orbit interaction (its first-order contribution vanishes) in the octahedral crystal field for the Ni d^8 ion, which does not occur for the Co d^7 ion. We compare the experimental results with a cluster calculation that includes crystal field and hybridization effects, which gives the values of the orbital moment, the quadrupole and octupole moments for both ions. The present results show the extent to which the atomiclike properties are retained in the higher-order multipole moments. This can be used to assess the modification of the atomic behavior due to solid-state effects.

Ab-initio study of the electric transport in gold nanocontacts

K. Palotás[1], B. Lazarovits[1], L. Szunyogh[1,2], P. Weinberger[1]

[1] *Center for Computational Materials Science,*
Vienna University of Technology,
Gumpendorferstr. 1.a., A-1060 Vienna, Austria [2] *Department of Theoretical Physics,*
Center for Applied Mathematics and Computational Physics,
Budapest University of Technology and Economics,
Budafoki út 8., H-1521 Budapest, Hungary

Abstract

By employing a real-space formulation of the Kubo-Greenwood equation based on a Green's function embedding technique combined with the fully relativistic spin-polarized Korringa-Kohn-Rostoker method a detailed investigation of the electrical transport through atomic-scaled contacts between two Au(001) semi-infinite systems is presented. Following a careful numerical test of the method the conductance of Au nanocontacts with different geometries is calculated. In particular, for a contact formed by a linear chain of Au atoms a conductance near 1 G_0 is obtained. The influence of transition metal impurities (Pd, Fe and Co) placed on various positions near the center of a particular contact is also studied. We found that the conductance is very sensitive to the position of the magnetic impurities and that the mechanism for the occurring relative changes can mainly be attributed to the impurities' minority d-band inducing resonant line-shapes in the s-like DOS at the center of the contact.

Ab-initio spin dynamics applied to nanoparticles: canted magnetism of a finite Co chain along a Pt(111) surface step edge

B. Újfalussy[1], B. Lazarovits[2], L. Szunyogh[2,3], G. M. Stocks[1] and P. Weinberger[2]

[1] *Metals and Ceramics Division, Oak Ridge National Laboratory,*
Oak Ridge, Tennessee 37831, USA
[2] *Center for Computational Materials Science,*
Technical University Vienna,
A-1060, Gumpendorferstr. 1.a., Vienna, Austria
[3] *Department of Theoretical Physics and Center for Applied Mathematics*
and Computational Physics, Budapest University of Technology and Economics,
Budafoki út 8, H-1521, Budapest, Hungary

Abstract

In order to search for the magnetic ground state of surface nanostructures we extended *first principles* adiabatic spin dynamics to the case of fully relativistic electron scattering. Our method relies on a constrained density functional theory whereby the evolution of the orientations of the spin–moments results from a semi–classical Landau–Lifshitz equation. This approach is applied to a study of the ground state of a finite Co chain placed along a step edge of a Pt(111) surface. As far as the ground state spin orientation is concerned we obtain excellent agreement with the experiment. Furthermore we observe noncollinearity of the atom–resolved spin and orbital moments. In terms of magnetic force theorem calculations we also demonstrate how a reduction of symmetry leads to the existence of canted magnetic states.

Sum rules for resonant inelastic x-ray scattering: explicit form and angular dependence in perpendicular geometry

F. Borgatti

INFM - TASC, Basovizza, S.S. 14, km 163,5, 34012 Trieste, Italy

G. Ghiringhelli

INFM - Dip. di Fisica, Politecnico di Milano, Italy

P. Ferriani and G. Ferrari

INFM - Dip. di Fisica, Università di Modena e Reggio Emilia, Italy

G. van der Laan

Magnetic Spectroscopy, Daresbury Laboratory, Warrington WA4 4AD, UK

C. M. Bertoni

INFM - Dip. di Fisica, Università di Modena e Reggio Emilia, Italy

Abstract

Resonant inelastic x-ray scattering (RIXS) and resonant photoemission spectroscopy (RPES) can be used to selectively measure the ground-state properties of atoms in solid materials. We compare the theoretical RIXS cross section integrated over the energy of the emitted photons with that of RPES and show that they become very similar when the measurements are not dependent on the polarization or spin state of the emitted particles. This similarity extends to the sum rules, which provide quantitative information on the charge and magnetic multipole moments of the atoms. They differ only by a few numerical coefficients in some multipole combinations. Finally, we give the sum rules for RIXS in the so called *perpendicular geometry* for all cases of interest. These rules can serve, in combination with the well known x-ray magnetic circular dichroism sum rules in absorption, to evaluate the quadrupole and octupole moments of the scattering atoms.

7   SCIENTIFIC HIGHLIGHT OF THE MONTH

Non-reactive metal-oxide interfaces: from model calculations towards realistic simulations

Jacek Goniakowski[a,b], Christine Mottet[a], and Claudine Noguera[b]

[a] *Centre de Recherche en Matiére Condensée et Nanosciences, CNRS, Campus de Luminy Case 913, 13288 Marseille Cedex 9, France*

[b] *Groupe de Physique des Solides, Universités Paris 6 - 7 and UMR CNRS 7588, 140, rue de Lourmel, 75015 Paris, France*

Abstract

In the last decade two principal factors have stimulated the progressive regain of interest for non-reactive metal/oxide interfaces. On one hand, the efforts invested by the community of model catalysis in analysing the reactivity properties of supported metal nano-clusters have resulted in an abundance of high quality experimental data. They have also risen several precise questions on the direct and indirect role played by the substrate, and have thus reiterated the interrogations concerning the nature of interactions at the metal/oxide interfaces. On the other hand, conceptual improvements of first-principles calculations, such as implementations of various GGA functionals, have added enormously to the reliability of these methods, and have enlarged considerably their field of application. However, most ab initio simulations are sooner or later confronted by the constrains on the computational cost, inherent of this kind of approaches. It concern principally the limited size of systems which can be treated in practice, a factor which turns out to be particularly limiting in realistic studies of interfaces, where the mismatch of lattice parameters is at the origin of incommensurate interface structures, long-range reconstructions, or/and complex structural deformations and dislocations.

In this paper we give an overview of an effective approach to simulate non-reactive deposition of nano-scale metal objects on a surface of highly ionic oxide. The core of this approach is a many-body potential energy surface (PES) constructed on the basis of results of ab initio calculations for model metal/oxide interface structures. We present its application to a study on substrate-induced change of equilibrium atomic structure and morphology of metal nano-clusters, to an analysis of stress release at the interface, and to an investigation of the role of oxide substrate on the melting properties of supported clusters. We end the paper by a brief discussion of defects. Since in the case of highly ionic substrates, surface defects modify strongly the electronic and adhesion properties of the interface, they become often a key ingredient of realistic simulations. At present, more dedicated experimental investigations, supported by model ab initio studies, are still necessary in order to fully access their impact on the observed properties of metal deposits.

1 Introduction

Recent progress of ab initio methods and a continuous improvement of computer performances, enable first-principles simulations on systems of growing complexity and reduce systematically the gap between what can be modelled and what is of direct interest in the real world. On one hand, this concerns a better account of approximations underlying the existing ab initio approaches and aims at a more reliable description of the electronic interactions in, and beyond, the electronic ground state. On the other hand, the concern is focused on the structural and chemical complexity of simulated systems and aims directly at a more realistic representation of the experimental conditions.

1.1 Realistic simulations on large systems

Very often, a relatively large number of independent degrees of freedom needs to be taken into account in order to obtain a satisfactory structural model of a large-cell reconstruction, a dislocation, or a complex grain boundary. The very same issue of calculation size reappears somewhat differently in simulations which tackle the effects of finite temperature, where the computational effort is related to the length of calculated temporal evolution of the system. For the latter, statistical averages need to be performed over series of configurations (electronic, atomic, compositional, etc.) and the convergence with respect to their number may, quite obviously, represent a challenge even for a system of a moderate number of particles. It is worth keeping in mind that in the case of a large system, a seemingly simple task of searching for a structural ground state gives often rise to similar computational problems. In most cases, an efficient treatment of both classes of problems requires adequate tools, such as molecular dynamics or Monte Carlo simulations. Depending upon the problem, the generated series of configurations are used to minimize the potential energy, to evaluate thermodynamic averages, or to follow the trajectory of the system.

There exist several cases where ab initio techniques were successfully applied to large/dynamic simulations. In fact, the Car-Parrinello[1] pseudopotential plane wave technique was designed to carry out first-principle molecular dynamics simulations on the fly, and is particularly useful for an efficient exploration of atomic trajectories in an insulating or semi-conducting system. However, it is much less well suited for Monte Carlo simulations, and its direct use for dynamic simulations remains of limited use, either because the pseudopotential method is computationally too demanding (for atoms like transition metal atoms or oxygen, which require a high energy cut-off), or because the number of atoms/configurations that can be explicitly treated remains not large enough. As an example, most of prototype systems considered in the field of model catalysis require a full structural optimization of a supported, late transition metal cluster of a few tens/hundreds of atoms. Such a task remains at present by far out of the reach of ab initio calculations.

An alternative approach consists in using the first-principle calculations to parametrize an energetic model, which is then coupled to an adequate statistical method. Depending on the problem, its complexity may range from a mere estimation of energies of selected configurations or activation barriers, to a full parametrization of a set of effective inter-atomic potentials.

Whereas similar in spirit to various existing semi-empirical methods, this approach is limited neither by the existing experimental data, nor by the transferability of the information which can be deduced from the experiments. This is particularly important for systems where the latter is insufficient or difficult to extract from the complex experimental results. In this domain, the first principles calculations offer the unique possibility of tailoring the model systems, at and beyond the structural ground sate, in view of extracting the necessary information. The present study on metal/MgO(100) interfaces is an example of application of this latter strategy.

1.2 Case of non-reactive metal-oxide interfaces

Although systems involving non-reactive metal-oxide interfaces may appear simple compared to those where inter-diffusion or oxidation takes place, their difficulty resides in the not yet fully understood microscopic nature of interactions responsible for the adhesion at the interface cohesion, and in particular, of mechanisms which drive the structural, electronic and growth characteristics of metal deposits. For metals at the end of the transition series, which are the most interesting for their applications in catalysis, this difficulty is enhanced by the overall weakness of interactions at the interface. In these cases, the chemical bonding is often assumed to be negligible, and the adhesion is assigned principally to the van der Waals and image charge contributions. However, no rigorous estimation of the relative strength of these contributions has yet been proposed [2, 3, 4, 5, 6, 7, 8].

Due to the weakness and complex character of interactions at the interface, the applicability of the state-of-the-art first-principles techniques has also been questioned. Whereas the concern is often focused principally on the van der Waals contribution, the method-dependent degree of localization of valence electronic density may contribute to imprecisions in estimation of the image charge effects as well. Presently, after a decade of systematic comparisons with high quality experimental results, we are confident that *ab initio* calculations predict the correct preferential adsorption geometries and give a correct estimation of principal features of adsorption energetic. However, since the comparison of electronic or precise energetic characteristics of the interface is much more challenging the complete microscopic description is still far from being settled.

As a model highly ionic substrate, the MgO(100) surface is probably the most studied oxide surface and constitutes one of the most widely used oxide substrates. From the experimental point of view, its low reactivity, weak tendency to deviate form stoichiometry or to oxidise the deposited metal, are accompanied by a relative easiness of preparation of mono-crystalline samples with large terraces and limited number of defects. Its wide gap and its strong ionicity minimize the effects due to interface electron transfers, but are at the origin of strong electrostatic field which polarizes the metal at the interface. The weakness of interactions at the interface limits the extent of the reciprocal influence of one material upon the other. Although the distortion of the metal electronic structure by the substrate electrostatic field can be quite significant, from the point of view of interface cohesion or interactions within the metal itself, this effect seem to have only a secondary importance. This, together with the rigidity of the crystalline structure and the resulting relatively simple atomic structure of the metal/MgO interface, privileged approaches based on a potential energy surface as probably the most efficient tool for large scale simulation.

2 Model ab initio calculations

In order to get an insight into the basic microscopic mechanisms that drive the adhesion properties of a metal/MgO(100) interface, we have performed DFT calculations (within full-potential LMTO [9] and LAPW [10] methods and both LDA and GGA [11] functionals for the exchange-correlation energy) for a series of model systems, chosen as to shed light on the relevant factors. In the following, with a set of chosen examples, we focus on the characteristics specific to the highly ionic substrate (MgO), and emphasize their relationship to the interface atomic structure and adhesion energetics. Further on, in a more general context, we discuss trends in the series of transition metals.

2.1 Choice of model systems

One of the advantages of first principle calculations resides in the fact that the quality of results does not depend directly on the proximity to the structural ground state. In fact, contrary to methods with adjustable parameters, which work the best in the direct proximity of the adjustment conditions, first principle approaches describe equally well any reasonably chosen system. This concerns in particular the atomic structures and chemical compositions which, due to their elevated total energy, could never be observed experimentally. This aspect, which at first glance may seem somewhat academic, enables, by an adequate choice of model systems, a quasi-direct access to selected aspects of the problem. It is also essential for construction of effective interactions, such as potential energy surface (PES) methods, for which the energetics of configuration far from structural equilibrium needs also to be assessed.

In the present case of metal deposited on an oxide substrate, due to the mismatch between oxide and metal lattice parameters, the energetic and electronic characteristics of a realistic interface are a complex mixture of these corresponding to various local interface structures. The big advantage of the model calculations is to enable a quasi-independent treatment of the different components and contributions, by fixing selected structural degrees of freedom. The essential drawback of this procedure is the additional constrain on the lattice parameter of the deposited metal, necessary to assure the matching of the two lattices at the interface. Its effect is partially compensated by a tetragonal distortion of the metal lattice, which acts towards a conservation of the atomic volume. Although necessary in order to reduce the size of the system and to make it treatable on ab initio level, it is clear that this procedure may lead to non-negligible errors in the case of interfaces with large lattice mismatch.

Due to the simplicity of the MgO(100) surface, once a pseudomorphic structure of the interface is assumed, three factors only are necessary to characterize the essential features of the local atomic structure at the interface.

1. The relative position of the deposited metal atoms with respect to ions of the substrate. The continuum of possibilities can be spanned by three high-symmetry adsorption geometries: metal atoms on-top surface oxygen, on-top surface magnesium, or in intermediate (hollow) adsorption sites.

2. The coverage of the surface. Since it is relatively well established that the cohesion in

metallic system does not have a pair-wise character, it is necessary to investigate to what extent local atomic environment in the metal influences the metal-oxide interaction. Three model cases span the principal coverage-dependent effects: adsorption of an isolated metal atom (in the periodic calculations represented by 0.25 ML or less), deposition of a full metal mono-layer (one metal atom per substrate adsorption site), and an interface between MgO and a thicker metal deposit (2ML or more).

3. The interface separation d_{sep} between the metal deposit and the substrate. Whereas the parameter of first interest is often the optimal interface separation for which the total energy is minimal, one needs to remember that at a realistic interface an important number of atoms is located off their preferential adsorption site and/or at distances different from those estimated in model calculations. This is why the PES needs to also account for the whole spectrum of d_{sep}.

In the presentation that follows we freely benefited of the above advantages of ab initio calculations, and we chose the model examples which more clearly reveal the effects under consideration.

2.2   Electronic structure of the interface

The physics of metal-insulator interfaces largely relies on the nature of interface electronic states close to the Fermi level, which drives the value of the interface dipole moment, and the band alignment at the interface. The best known and the most often referred states in phenomenological models of interface, the Metal Induced Gap States (MIGS) result from the matching of delocalized metal wave functions with exponentially decaying insulator states in the gap energy range. On the other hand, "polarization" states result from strong distortions of the metal valence band by the electrostatic field of the substrate. They are specific to strongly ionic substrates and are responsible for image charge effects. Finally, bonding and anti-bonding interface states refer to chemical bonds across the interface, which appear at well-defined energies, and not only in the insulator band gap energy range. They have often been neglected, especially at weakly adhesive interfaces.

2.2.1   Metal-oxygen bonds across the interface

Formation of an interface chemical bond between oxygen and metal orbitals is at the origin of appearance of bonding (B) and anti-bonding (AB) states located respectively at and below the oxide valence band and above the metal band. They are associated to an enhancement or depletion of the electronic density at the interface, respectively. Although this precise criterion cannot be unambiguously estimated due to the complex deformation of dispersive bands, any occupied state whose energy is lowered during the interface formation enhances the adhesion, the opposite being true for the states pushed upwards on the energy scale. The position of the Fermi level within the AB band is decisive: a fully occupied AB band always overcompensates the cohesive contribution of its B counterpart.

Presence of interface metal-oxygen bonding can be detected even when late transition metals are involved. For example, at the Pd/MgO(100) interface, Fig. 1, the hybridization between
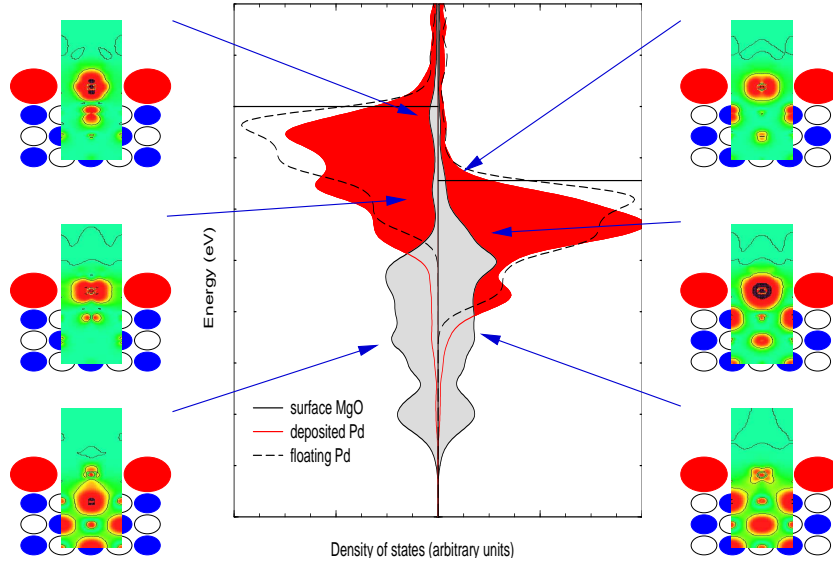
Figure 1: Pd/MgO(100) interface. Metal-oxygen bonds are traced in the local density of states calculated for a Pd monolayer at oxygen (left panel) and magnesium (right panel) adsorption sites, for fixed interface separation of 2.37 Å. Projections on the surface oxide valence band (grey) and on the palladium band (red) are explicitly plotted. The energy scales are aligned by the core levels of oxygen ions in the slab center. LDOS of an unsupported Pd layer (dashed line) with the same lattice parameters and the same Fermi level is plotted as a reference. Side panels present the corresponding maps of the electron density in the plane perpendicular to the interface, calculated in energy windows of 1 eV centered at LDOS features indicated by the arrows. The presented maps are centered on the oxygen (magnesium) ion. Colours red and yellow depict the regions of elevated electron density, whereas green corresponds to zero. From [12].

oxygen and palladium orbitals is clearly visible: interface Pd-O states can be detected below the Pd band, and within the MgO band gap. Among the latter, some contribute to a featureless LDOS in the whole MgO gap (they correspond to MIGS and will be discussed in Sec. 2.2.3), while others are at well-defined energies and represent the AB states of the Pd-O bond. Due to the different spatial orientation of the atomic orbitals involved in the bond formation, their energy and their character are strongly geometry dependent.

In the case of Pd atoms on-top of surface oxygen, the interaction mainly involves the O p_z and the Pd $d_{3z^2-r^2}+sp$ orbitals, whose shape is clearly visible in the electron density maps. The relatively well pronounced splitting of the B and AB contributions is due to strong spatial overlap of the two orbitals. It results in a partial depopulation of the AB component and contributes directly to the cohesion of the interface.

When adsorption takes place on-top magnesium, due to the core-core repulsion between palladium and surface magnesium, the overlap between Pd and O orbitals is smaller. It is not fully compensated by a smaller separation between the Pd and O bands on the energy scale and, although present in this adsorption geometry, the Pd-O bonding gives only a negligible contribution to adhesion.
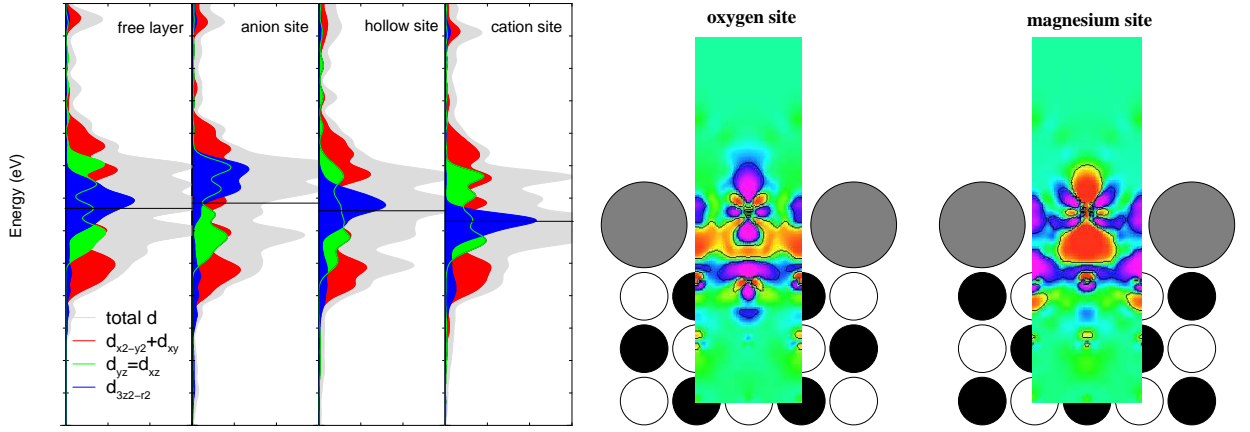
Figure 2: Mo/MgO(100) interface: polarization of the Mo layer by the MgO electrostatic field. Left panel presents the Mo LDOS decomposition (total (grey), $d_{x^2-y^2} + d_{xy}$ (red), $d_{yz} = d_{xz}$ (green), and $d_{3z^2-r^2}$ (blue)), obtained for an unsupported, strained Mo layer, and for the same layer deposited in three alternative adsorption geometries. The energy scales are aligned by the oxygen core levels in the center of the slab, except for DOS of the free layer, whose Fermi level is aligned to that of Mo at the hollow site. Right panel presents maps of differential electron density (difference between the density of constituted interface and the sum of separate systems), plotted in the plane perpendicular to the interface and centered on surface oxygen (oxygen adsorption site) or surface magnesium (magnesium adsorption site). Red and yellow colours correspond to an enhancement of electron density, whereas blue and violet represent a reduction. From [13].

2.2.2 Polarization by the substrate electrostatic field

Additionally to metal-oxygen hybridization, the metal valence band is polarized by the electrostatic field of the substrate. Indeed, an upward (downward) shift of metal orbital energies is systematically registered when adsorption takes place on top oxygen (magnesium) sites. However, due to the different spatial orientation of the different components of the d band with respect to the substrate electrostatic field, this shift is strongly non-uniform and produces a crystal-field-like distortion of the metal band. As a consequence, it modifies the positions of orbitals with respect to the Fermi level and is accompanied by an electron redistribution between the different components. This process does not involve any charge transfer across the interface, and corresponds thus to a substrate-induced polarization of the metal interface layers.

We illustrate this effect on the Mo/MgO(100) interface, Fig. 2. Due to its angular orientation, the largest shift concerns the $d_{3z^2-r^2}$ orbital, whose lobe points towards the substrate. With respect to its relative energy in the unsupported monolayer, it is shifted upwards (and above the Fermi level) when above the surface anion and downwards (and partially below the Fermi level) above the surface cation, whereas its position is only little modified in the surface hollow site. For orbitals with lobes in the plane of the metal layer ($d_{x^2-y^2} + d_{xy}$) the displacement with respect to the Fermi level is much smaller. As shown in the maps of differential electron density, Fig. 2, this non-uniform shift is accompanied by an electron redistribution among the components of the metal d band. Namely, above oxygen the $d_{3z^2-r^2}$ component transfers its electrons to the other d orbitals, the opposite being true for adsorption above cations. By emptying the space
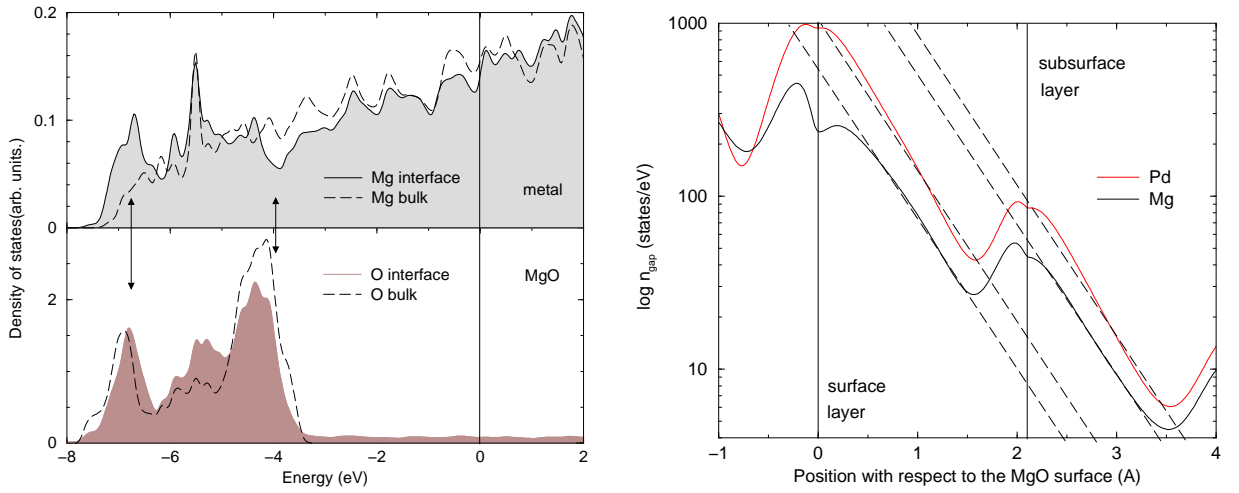
Figure 3: Conventional MIGS: Left panel presents the LDOS of Mg multilayers deposited on the MgO surface. Although, with respect to the bulk DOS (dashed lines), the deformation of interfacial oxygen and magnesium bands is clearly visible (cf. zones marked with arrows), it does not give rise to localised states in the gap region. The structureless continuum of gaps states visible in the LDOS of interface oxygen corresponds to the conventional MIGS. Their penetration into the oxide is exemplified by the electron density n_{gap} (obtained by integrating states between the bulk MgO VBM and the Fermi level), plotted as a function of the coordinate perpendicular to the interface (full black line in the right panel). An equivalent plot for the Pd/MgO(100) interface is also given (full red line). Note the logarithmic scale for n_{gap}. From [14].

above surface oxygen and by populating that above surface magnesium, this process mimics the macroscopic "image charge" effect.

2.2.3 Conventional MIGS

Conventional MIGS, which are produced by the exponential decay of delocalized metal states within the insulator, are also present at metal/oxide interface. This is also true for interfaces with small or absent chemical bonding, in which cases MIGS produce a structureless continuum of states above the substrate VBM. Their decay within the oxide, which can be characterized by their penetration length, is determined principally by the nature of the oxide and nearly independent of the metal [14], in agreement with the MIGS theory developed in Ref. [15]. On the other hand, the MIGS density of states at the interface is strongly metal-dependent.

Presence of MIGS can be detected at the Pd/MgO(100) interface, Fig. 1, where however they coexist with more localized bands due to Pd-O bonds. At the Mg/MgO(100) interface, Fig. 3, the Mg-O chemical bonding is weak, the deformation of interfacial bands is less pronounced, and the Mg-induced MIGS in the MgO band gap are practically structureless. Aside from oscillations on the MgO cores, they display a clear exponential decay, characterized by a penetration length $l_p \sim 0.5$ Å.
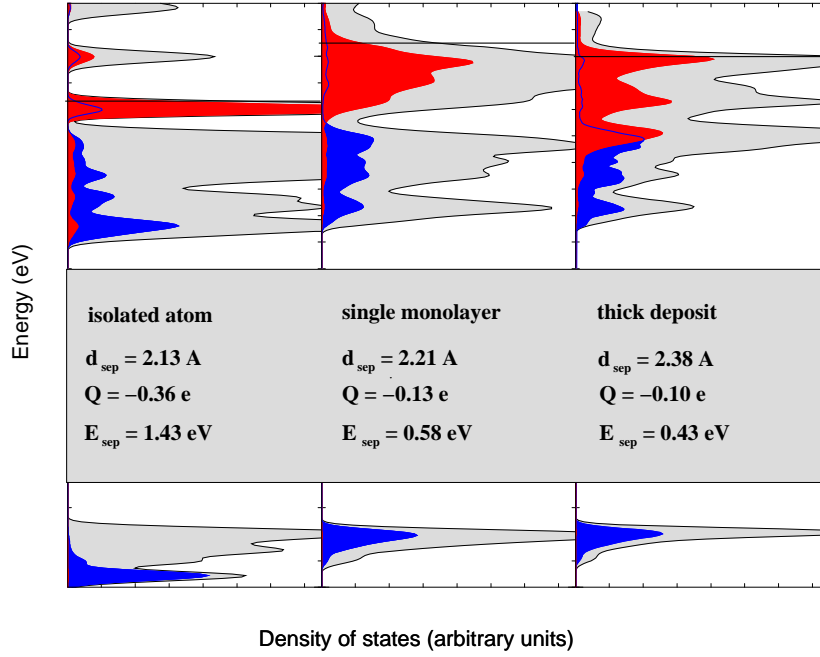
Figure 4: LDOS at a Pd/MgO(100) interface as a function of Pd coverage: an isolated Pd atom (0.25 ML), a single Pd monolayer, and a thicker (5ML) Pd deposit. Are given: total and projected DOS (total (gray), surface oxygen (blue), and palladium (red); energy scales are aligned by the core levels of bulk oxygen ions), equilibrium interface separation d_{sep} (Å), interface charge transfer (electron/oxygen adsorption site, negative sign corresponds to electrons transferred from the substrate towards deposited metal), and separation energy E_{sep} (eV/oxygen adsorption site) defined as a difference of total energy between constituted metal/oxide system and its two separated components: clean MgO(100) slab and floating (strained) metal layer. From [16].

2.3   Dependence on the metal coverage

Whereas it is relatively well established that cohesive interactions in transition metal and transition metal compounds do not have a pair-wise character (see Sec. 3.1), the interactions at metal/oxide interfaces, and their relation to the local environment of the deposited metal atoms is not entirely elucidated. One of the difficulties resides in the fact that, as a function of metal coverage, the various contributions (van der Waals, image charge, and chemical bonding) do not behave in the same way.

Considering again the Pd/MgO(100) interface in its ground state atomic configuration (palladium atoms on-top surface oxygen), we illustrate the strong dependence on the metal coverage by considering three adsorption models, Fig. 4. The metal-oxide interaction is clearly the strongest in the limit of isolated adatoms and weakens progressively with increasing Pd coverage, as shown by the variation of E_{sep}. The decrease of E_{sep} is accompanied by an expected increase of the equilibrium interface separations d_{sep} and by a weakening of the interface electron transfer.

The origin of this evolution can be traced back to the changes of hybridization between oxygen and Pd orbitals at the interface [17]. At low coverages, the Pd LDOS is narrow and located close to the MgO VBM. The coupling is strong, the splitting of bonding and antibonding states is well

pronounced: the B component is below the bulk O $2p$ band, and the AB component is partially depopulated. This corresponds to an important electron transfer across the interface. At higher Pd coverages the width of the Pd band increases progressively and so does the separation between Fermi level (fixed mainly by the Pd band) and the MgO VBM. Hybridization between palladium and oxygen orbitals is thus weaker and, taking into account the increasing width of the Pd band, more and more inefficient to push the AB band above the Fermi level. This progressively reduces the related gain of energy and the interface electron transfer.

The correlation between the changes of Pd-O hybridization and E_{sep} points out to the chemical bonding as the dominant contribution to the separation energy in the Pd/MgO(100) system. Whereas such a behaviour may indeed be expected at interfaces where adhesion is dominated by chemical bonding, it is worth mentioning that this is not the general trend. In fact, at weakly adhesive interfaces, the behaviour is rather determined by van der Waals and image charge contributions. Additionally, also the relative weight of the various contributions may also vary as a function of coverage. This is the case at Ag/MgO(100) interfaces, where the evolution of E_{sep} is opposite to that of Pd/MgO(100), and dependent on the precise choice of the exchange-correlation functional [18, 19].

2.4 General trends along the transition series

In order to generalize the preceding approach and to put it in a wider context, in Fig. 5 we present the evolution of interface characteristics for metals along two transition series.

The general trends are the following:

- The interface ground state always corresponds to adsorption above oxygen. This trend is relatively strong at the beginning and in the middle of the series, where in addition, due to the core-core repulsion, no (meta)stable adsorption takes place above magnesium sites.

- The separation energy E_{sep} displays a well pronounced decrease in the second half of the series (oxygen site). This trend is mainly ascribed to changes in the interface metal-oxygen bonding. Indeed, following the arguments of Sec. 2.2.1, we observe in Fig. 5 a progressive filling of the Me $d_{3z^2-r^2}$ -O p_z AB component and a strong polarization of the metal layer by the electrostatic field of the substrate. The electron redistribution between the different d orbitals contributes also to a weakening of metal cohesion of the deposited layer, and thus to an additional weakening of the separation energy.

- For the metals of the very end of the transition series (Ag, Cu), the sp character of the electronic states close to Fermi energy is associated to a considerably smaller separation energy. The contribution due to the formation of interface bonds is smaller and the part of image charge and van der Waals interactions is likely more important.

3 Calculations on large systems

If the DFT-based methods have proved their usefulness for treating model metal/oxide interfaces, the computational effort needed for a realistic treatment of large-size systems limits considerably
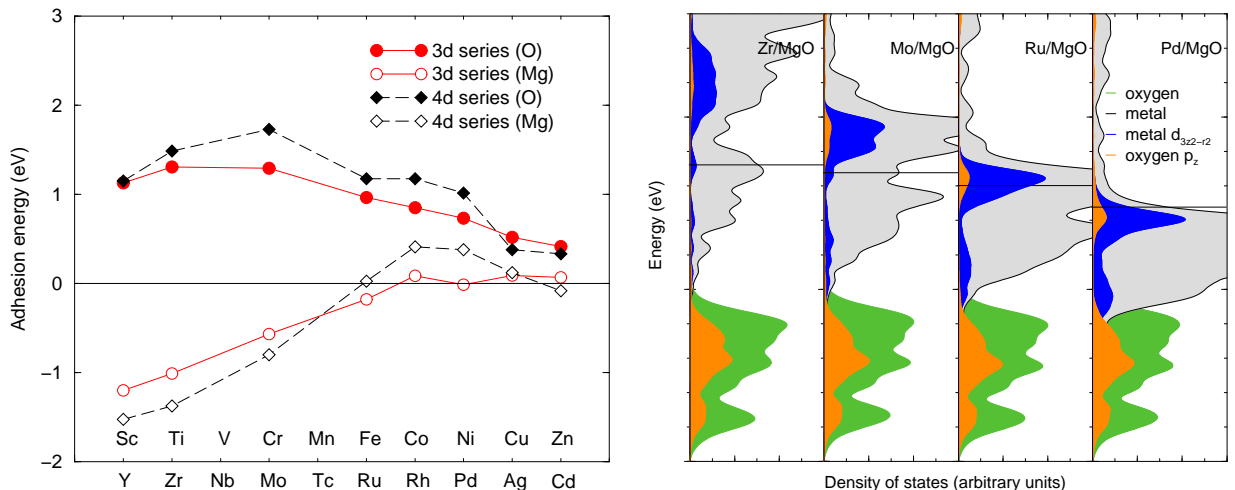
Figure 5: Interface characteristics as a function of the deposited metal. Left panel presents the separation energies for deposition of $3d$ (red circles) and $4d$ (black squares) transition metal monolayers on the oxygen (full symbols) and magnesium (empty symbols) sites of the MgO(100) surface. For sake of a direct comparison, all energies correspond to fixed interface separations: $d_{sep} = 2.4$ Å (oxygen adsorption site) and $d_{sep} = 2.6$ Å (magnesium adsorption site). Relaxation of this constrain does not modify the depicted tendency. Right panel gives the interface LDOS: transition metal band (grey) and its $d_{3z^2-r^2}$ component (blue), oxygen band (green), and its p_z component (yellow), for Zr, Mo, Ru, and Pd monolayers deposited on the oxygen sites of the MgO(100) surface. Energy scales are aligned by the core levels of bulk oxygen atoms. Effects due to spin-polarization are not taken into account. From [13, 20].

their field of application. In particular, it is not yet possible to use them directly for modelling the complex interfaces involving inhomogeneous relaxations, large cell reconstructions, dislocation networks, etc. which have been experimentally observed. This drawback is particularly constraining in modelling of nano-cluster structures, which usually require an extensive search in configurational space. On the other hand, because many fundamental questions on the character of interfacial interactions remain unanswered, there exists no straightforward and reliable semi-empirical methods for modelling these systems. For these reasons, several effective approaches, derived from first principles methods, have been proposed these last years in order to treat metal/MgO interactions [21, 22, 23, 24, 25].

As a model catalyst, Pd clusters supported on MgO(100) have been the subject of many detailed experimental and theoretical studies. Understanding the cluster morphology, the relation between their size and detailed atomic structure, and their interaction with the oxide substrate is a necessary step towards the control of their reactivity. In the following, we describe the Potential Energy Surface approach we have applied to study Pd clusters on MgO(100) [25].

3.1   Second Moment Approximation for the Pd-Pd interactions

Since the cohesion of transition and noble metals is governed by the characteristics of the metal d band [26], several successful semi-empirical approaches have been conceived in order to rationalize the dependence of the cohesive energy on the local environment (coordination) of metal
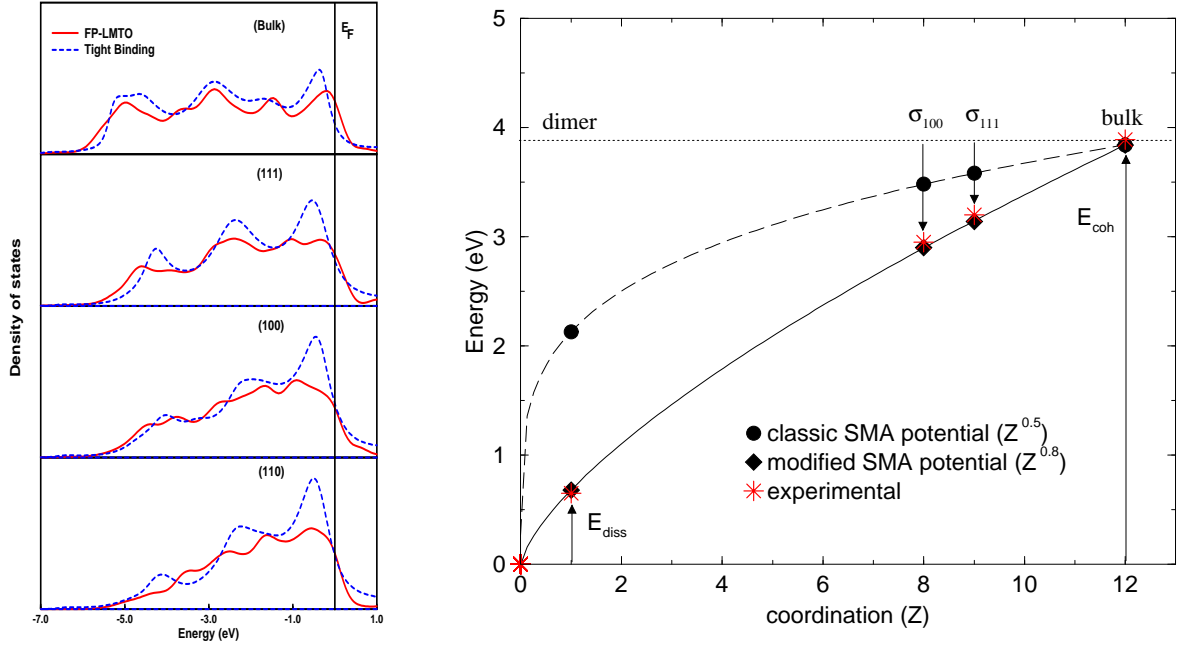
Figure 6: Adjustment of the Pd-Pd potential. Left panel gives LDOS for bulk Pd and for surface Pd atoms at three low index surfaces: (111), (100), and (110). Results obtained within tight-binding calculations with $sp-d$ hybridization based on the charge neutrality per orbital (dashed blue lines) are compared to results of ab initio FP-LMTO calculations (solid red line) [27]. Right panel displays a schematic representation of site energies (E) of Pd atoms as a function of their coordination (Z) obtained within the classic ($E_b \sim Z^{0.5}$: dashed line) and modified ($E_b \sim Z^{0.8}$: solid line) SMA approach. Experimental values of bulk cohesive energy (E_{coh}), surface energies (σ_{111} and σ_{100}), and Pd dimer dissociation energy (E_{diss}) are plotted with red stares.

atoms.

In the so-called second moment approximation (SMA) [28], the attractive part (E_b) of the potential is fitted to the band energy, assuming a rectangular density of states of the same second moment μ_2 as the actual one: $E_b \sim \mu_2^{1/2}$. Moreover, since in the tight-binding approximation, μ_2 is known to be linear in the effective first neighbour coordination number Z, one obtains the usual square-root many-body character of this potential $E_b^{TB} \sim Z^{1/2}$. However, in spite of its overall success, this potential fails to reproduce accurately the experimental variation of the energy as a function of the coordination number in the whole Z-range. The surface energy is generally slightly underestimated [29] and the deviation increases with decreasing Z. This is for example the case for Pd [30].

The alternative is thus either to go beyond the second moment approximation and account for details of the LDOS, or to stay within such an approximation but calculate the second moment as accurately as possible. In both cases this requires to go beyond the tight-binding d-band approximation and an adequate introduction of the $sp-d$ hybridization in tight binding approach. Results of a successful implementation, based on the charge neutrality condition derived from ab initio calculations [27], are illustrated by matching of tight-binding and FP-LMTO densities of states projected at atomic sites of different coordination, Fig. 6. The first
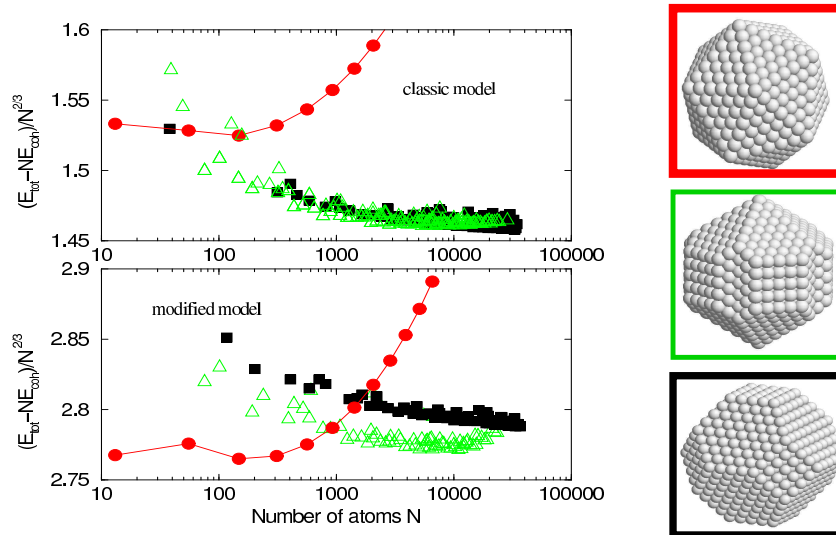
Figure 7: Stability of free Pd clusters: excess energy $((E_{tot}(N) - N.E_{coh})/N^{2/3})$ with respect to bulk Pd cohesion energy $((E_{coh})$ is plotted as a function of cluster size (N) for icosahedron (red circles), decahedron (green triangles), and truncated fcc polyhedron (black squares) cluster structures. Results of both classic (top panel) [34] and modified (bottom panel) SMA approaches are given.

solution, without $sp - d$ hybridization, yields $E_b^{TB} \sim Z^{2/3}$ [31], or to $E^{TB} \sim Z^{4/3}$ when taking this hybridization into account [32]. In second solution, with μ_2 derived either from FP-LMTO results or from tight binding calculations with $sp - d$ hybridization (see Fig. 6) $(\mu_2^{LMTO} \sim Z^{3/2})$, one obtains $E_b^{LMTO} \sim Z^{3/4}$. The proper treatment of $sp - d$ hybridization thus leads to a dependence of the band term which is intermediate between square-root and pairwise. This result seems to be confirmed in the particular case of Pd, for which the experimental variation of the energy with coordination number is found to be almost pairwise. The best account for the experimental data is obtained $Z^{0.8}$ dependence on the coordination number, Fig. 6.

SMA potentials have been used to determine the size range of stability of icosahedral and decahedral structures of free transition and noble metal clusters [33]. The case of Pd, within both classic $(E_b \sim Z^{0.5})$ and modified $(E_b \sim Z^{0.8})$, is illustrated in Fig. 7. For the fcc structures, the excess energy (with respect to bulk cohesion energy) converges monotonically towards a constant value proportional to an average surface energy. For icosahedral and decahedral structures it initially decreases, reaches a minimum, and finally, due to the elastic strain induced in the cluster core by the fivefold symmetry, it diverges at large cluster sizes. Indeed, whereas at small sizes these quasi-periodic structures minimize the surface energy, as the size increases the energy gain due to minimization of surface energy compensates less efficiently the energy of core distortion. Within the modified SMA potential, the critical size increases significantly for both icosahedron to decahedron (from 100 to 1000 atoms) and decahedron to truncated fcc octahedron (from 10000 to 20000 atoms) transitions. This difference is principally due to the increase of the energy of defects (see Fig. 6), which favours cluster structures of minimal surface energy. As a consequence, the stability of quasi-periodic structures is extended towards larger sizes.
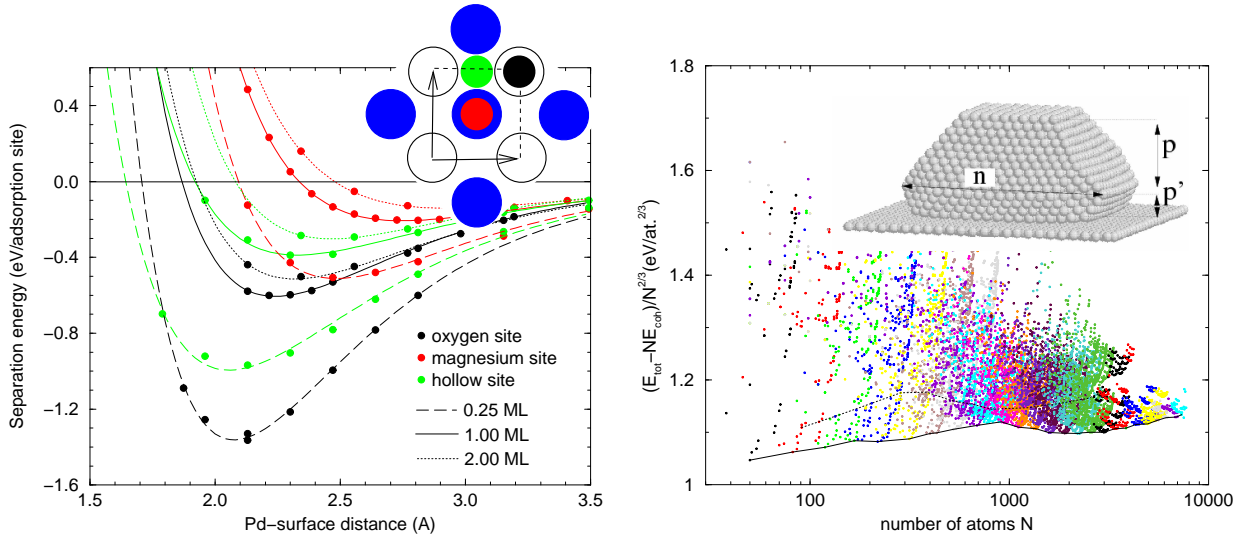
Figure 8: Left panel: adjustment of the Pd-MgO(100) Potential Energy Surface. Circles represent the separation energies (E_{sep}) issued from ab initio calculations, lines correspond to the fitted potential. Oxygen (black), magnesium (red), and hollow (green) sites are considered (see the inset for a schematic representation of the MgO(100) surface) at Pd coverage of 0.25 ML (dashed lines), 1 ML (solid lines), and 2 ML (dotted lines). Right panel: excess energy (see Fig. 7) plotted as a function of cluster size (number of atoms) for Pd clusters supported on MgO(100). Various cluster morphologies have been considered, as defined by parameters depicted in the inset. The doted line corresponds to perfect pyramidal shape and the full line corresponds to minimum potential energy, i.e. the equilibrium cluster morphology. From [35].

3.2   Many-body Potential Energy Surface for Pd-MgO(100) interactions

We derived the many-body potential energy surface representing Pd-MgO(100) interaction, which supplements the SMA Pd-Pd interaction from model DFT calculations, as to take into account the main energetic characteristics described in Section 2. Sites on-top oxygen are energetically the most favourable for Pd adsorption (minima), while magnesium and hollow sites represent respectively maxima and saddle points of the potential energy surface. In addition, the Pd-MgO interaction depends upon the Pd coverage: it is the strongest for isolated ad-atoms and decreases progressively as the number Z of Pd-Pd bonds grows. This ingredient is particularly important in the case of small clusters, characterized by a large proportion of under-coordinated atoms.

The Pd/MgO interaction is assumed to be additive with respect to the number N of Pd atoms: $E^{Pd-MgO} = \sum_{i=1}^{N} E(x_i, y_i, z_i, Z_i)$. It depends on their lateral position (x_i, y_i) with respect to the MgO lattice, on their elevation z_i above the MgO surface, and on the number Z_i of their nearest Pd neighbours. $E(x_i, y_i, z_i, Z_i)$ assures an analytical interpolation between the ab initio results obtained for model interface structures described in Section 2.1. The non-linear dependence of E^{Pd-MgO} on the coordination number Z confers to the fitted PES an effective many-body character. Results of ab initio calculations and the fitted dependence are depicted in Fig. 8.
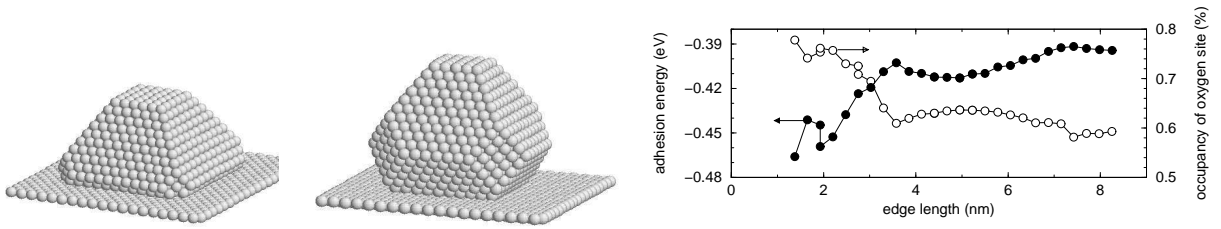
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Figure 9: Pd clusters supported on the MgO(100) surface: typical cluster morphologies obtained within the classic (left) and modified (right) SMA potentials. Right panel displays the evolution of the adhesion energy (black dots) and of the average occupancy of oxygen adsorption sites (open circles) as a function of cluster size. From [25].

3.3 Morphology of supported Pd clusters

Structure and morphology of free metallic clusters described in Section 3.1 are modified by the interaction with the substrate. Indeed, experiments on MgO(100) supported Pd clusters have revealed the truncated fcc octahedron structure already at very small cluster size (less than 2 nm) [36]. Following this experimental indication we have focused on clusters of different sizes (edge length) and morphologies (aspect ratio, corner truncations) under the constraint of [100]Pd//[100]MgO epitaxy relation. For each of them, a series of quenched molecular dynamics runs, of different lengths, at various temperatures and initial conditions has been performed (a few nanoseconds of MD runs per cluster), in order to find the potential energy minimum. Typical results are given in Fig. 8.

The most stable clusters have the shape of "flattened" pyramids with truncated edges. Their aspect ratio varies from 0.5 (classic SMA potential)[25] to about 0.75 (modified SMA potential), Fig. 9, in a nice agreement with the Wulff-Kaishew or Winterbottom argument relying on the ratio between metal surface energy and interface adhesion (in analogy to the Young-Dupré equation in case of a liquid droplet wetting a surface). Indeed, the increase of aspect ratio can be directly related to the higher energy of the Pd(100) surface in the modified SMA approach, in good agreement with experimental observations on larger clusters [36].

Whereas for larger clusters, their morphology does practically not depend on cluster size, the smaller ones (less than 4 nm) are subject to detectable structure changes, induced by the variations of interface adhesion energy, Fig. 9. The latter is driven by the Pd-MgO interaction, and thus follows closely the changes of average occupancy of the preferential (oxygen) adsorption site. If small clusters adhere stronger to the MgO(100) surface, it is due to the strain of their structures, which accommodates the lattice mismatch at the interface.

3.4 Substrate induced stress and dislocations

Due to the lattice mismatch between Pd and MgO ($a_{Pd} \sim 0.92 a_{MgO}$) the substrate induces a tetragonal distortion of small clusters, with a dilation in the interface plane and a contraction in the direction perpendicular to the interface, Fig. 10 (A). As the cluster size increases, the energy gain due to the interface adhesion is no longer sufficient to compensate the elastic energy due to strain induced by the lattice mismatch. At about 5 nm, rows of Pd atoms leave their preferential
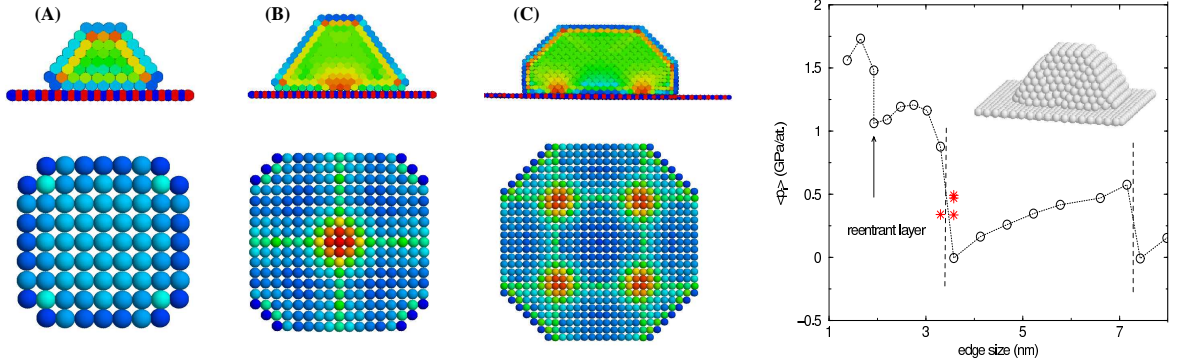
Figure 10: Stress release in supported Pd clusters. Left panel: maps of atomic pressure along a cut perpendicular to the interface (top row), and within the interface Pd layer (bottom row) for clusters of 2.5 (A), 4.7 (B), and 7.4 (C) nm. Red zones correspond to a positive pressure (compression, i.e. negative stress) whereas blue zones correspond to a negative pressure (tension, i.e. positive stress). Intermediate green zones are neutral. Right panel: average stress per cluster and per atom as a function of cluster size. Red stars correspond to clusters whose stress is released via sliding along (111) planes, as depicted in the inset. From [35].

adsorption sites (see the compression zones in Fig. 10 (B)): an interface misfit dislocation is created, which totally releases the strain. As the cluster size further increases, the dislocations organize themselves in a periodic network, leading to a (10x10) superstructure (Fig. 10 (C)), approaching closely the (11x11) incommensurate structure observed at extended Pd/MgO(100) interfaces ($11a_{MgO} \sim 12a_{Pd}$). Stress release by a progressive introduction of the interface misfit dislocations is quantified in the right panel of Fig. 10. An alternative way of partial stress release in small clusters is illustrated in the inset: introduction of (111) sliding planes across the cluster reduces the compression zone around the off-site Pd atomic row and improves the adhesion of smaller prismatic parts at the cluster base. However, since the energy of the sliding plane is proportional to its area, this defect is less energetically favourable in large clusters.

Since at higher metal coverage, the deposited clusters coalesce and a bidimensional layer begins to form, it is interesting to investigate the atomic structure of thin deposited metal films. In particular, Pd and Ag thin films deposited on MgO(100) display interface dislocations similar to those described for the clusters. The dislocation network depends on the lattice misfit: the smaller the misfit, the larger the super-lattice (from 3.3 nm for Pd to 10 nm for Ag). The residual stress, induced by the interface dislocations propagates across the metal film and is at the origin of a nano-structuration of the film's surface, see Fig. 11. As the stress propagates across the metal film, the topology of the local nano-structuration may vary from one atomic layer to another. In the present case of Ag films, in films thicker then ten layers the network of misfit dislocations is recovered on the surface, but the compression and tension zones are inverted. For thinner films (see the intermediate layer in Fig. 11), new tension zones (light blue) appear in the middle of the initial periodic structure and modify its periodicity. Since the elastic strain network acts as a patterning for an adsorbate, a nano-structured metal film may be seen as a promising substrate for the self-organized growth [37].
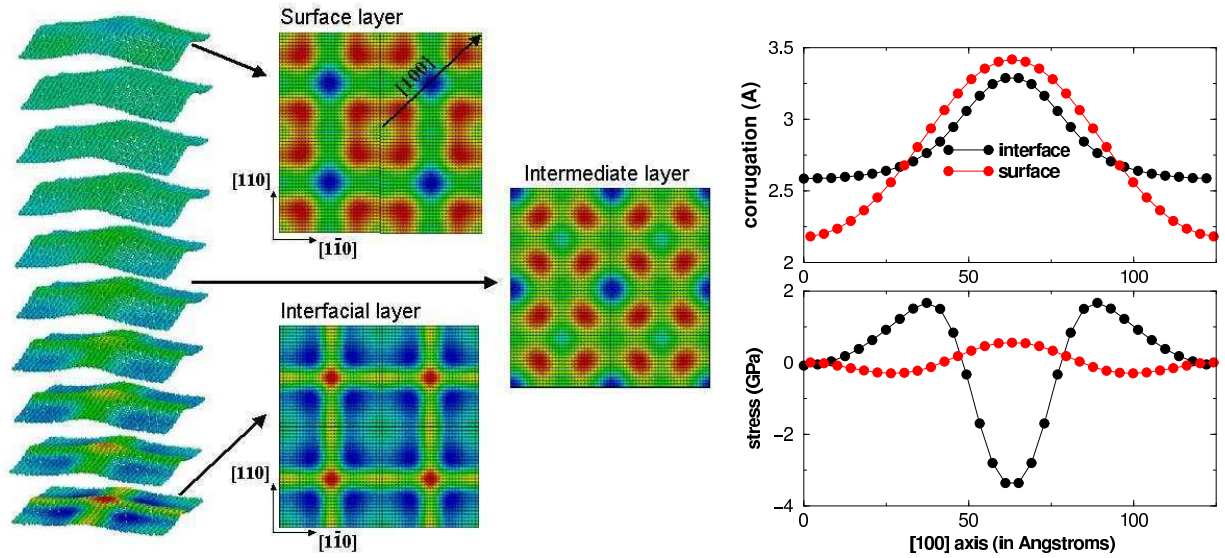
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Figure 11: On the left: side view of maps of atomic pressure within the atomic layers of Ag thin film supported on MgO(100) (the same colour code as in Fig. 10): the coordinate perpendicular to the substrate has been dilated artificially as to get a better insight into the corrugation. In the middle: top view of the maps corresponding to surface, interface, and intermediate layer, each on a separate colour scale. Right panel gives the corrugation and the local stress plotted along the [100] direction for the surface and interface Ag layers. From [19].
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To summarize, the use of model inter-atomic potential derived from first principles calculations permits to take into account all interface degrees of freedom, and to perform an extensive search of minimum-energy structures, without the constraints of pseudomorphic metal/oxide structures. These simulations give access to different mechanisms of strain release in the supported metal clusters of thin films, and enable studies on coupling between the interactions at the interface and the stability and atomic structure of metal deposits.

4   Towards realistic simulations

In the preceding section we have used the results of ab initio calculations on model metal/oxide interfaces as a base of a study on complex metal deposits on the MgO(100) surface. The size of the systems considered in this study and the absence of constrain on the local interface structure bridge two essential aspects separating the experimental reality from results of model calculations. However, several additional ingredients need to be taken into account in order to bring the simulations closer to the reality. In the following we focus on just two of them, chosen because of their qualitatively different character. On one hand, by extending our PES approach described in Sec. 3, we will show a possibility of accounting for the effect of finite temperatures on the properties of deposited clusters. Indeed, since temperature is one of the key factors influencing, eg. different stages of cluster growth and equilibration, it may be seen as an essential ingredient of any realistic simulation. On the other hand, by extending our model ab initio calculations beyond the perfect interfaces described in Sec. 2, we will give examples of

situations in which, due to substrate defects, an otherwise weakly-interacting interface suffers a strong modifications of both electronic and adhesion properties. At present, it is relatively well established that defects determine the characteristics of cluster growth and, potentially, also some of their catalytic properties. Results going beyond the perfect interfaces are thus needed for interpretation of experimentally observed phenomena.

4.1 Finite temperature effects

The main advantage of the PES approach used in the study described in Sec. 3, was to enable an efficient treatment of a large number of structural degrees of freedom (number of independent particles), as to access clusters of "experimental" sizes. Quenched molecular dynamics was employed in those calculations as a tool for an efficient search of equilibrium atomic structures. In the following we present a study which aims an efficient description of oxide-supported metal clusters at finite temperatures. This time, due to atomic vibrations and diffusion, statistical averages need to be calculated in order to quantify cluster properties, and these are the atomic trajectories obtained in molecular dynamics which are used for estimation of various, temperature dependent characteristics and observables. We focus on the melting and re-crystallization of Pd clusters deposited on the MgO(100) surface and analyse the essential substrate-induced characteristics [39].

Since the late transition metals interact weakly with the perfect MgO(100) surface and their cohesive properties are little influenced by the underlying substrate, a prescription for an efficient molecular dynamics simulations is to neglect the complete description of the substrate vibrational degrees of freedom and account for the heat exchange between the substrate and the adsorbate in an effective way. Two different levels of approximation can be conceived. On one hand, the energy exchange between the cluster and the substrate can be ensured by an Andersen thermostat, involving stochastic collisions of interface metal atoms with virtual particles representing the MgO heat bath at fixed temperature. On the other hand, one can use the surface oscillator approach [38], where the motion of the oxide substrate is described through a set of harmonic oscillators of amplitude and frequency derived from ab initio calculations. In the case of our PES model these two methods give equivalent results.

4.1.1 Effect of the oxide substrate on cluster melting

The effect of substrate on the cluster melting and crystallization properties can be deduced from a comparison of caloric curves obtained during heating and cooling of free and supported metal clusters, Fig. 12. The most important effect is the substrate-induced modification of the solid-liquid transition. Both melting (obtained when heating the cluster) and crystallization (obtained when cooling a melted cluster) temperatures increase considerably. The hysteresis (which corresponds to the coexistence loop of the two phases in first order transitions) narrows in the case of deposited clusters and disappears completely at smaller cluster size. The jump of energy representing the latent heat of transition is little affected. The other substrate-induced effect, visible already at relatively low temperatures, is the modification of cluster's morphology. In fact, as soon as diffusion processes are activated, metal clusters deposited in their free equi-
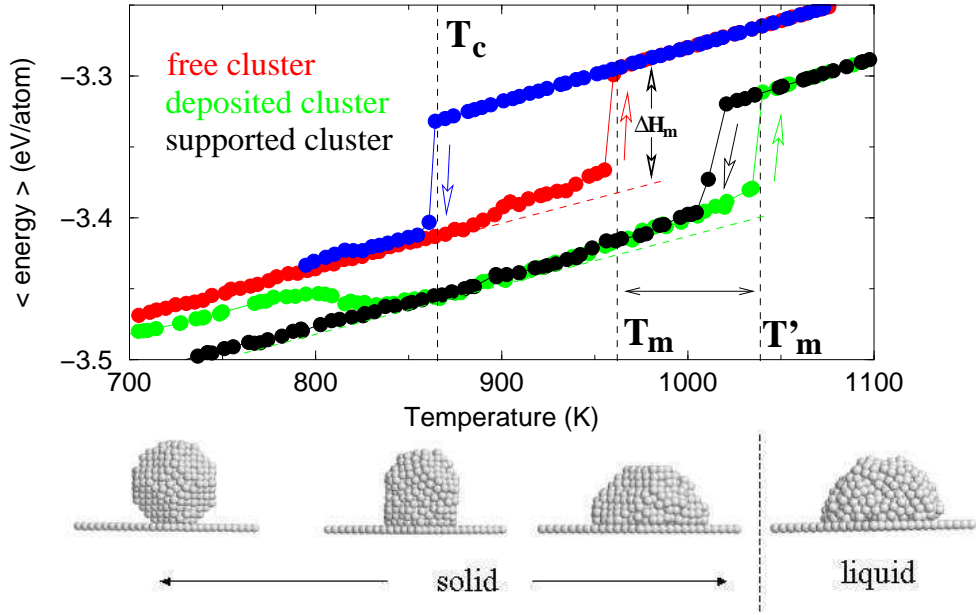
Figure 12: Melting and re-crystallization of a small Pd cluster (about 200 atoms). Top panel gives the caloric curves obtained for free (red), deposited (green), and supported (black) clusters of the same size. Temperature variations (heating and cooling) are indicated with arrows. Latent heat of melting ΔH_m crystallization temperature (T_c), as well as melting temperatures for free (T_m) and deposited (T'_m) clusters are shown. Bottom panel gives the series of snapshots of the deposited cluster atomic structure taken at temperatures below and above T'_m. From [39].

librium shape (first snapshot in the bottom panel of Fig. 12) distort progressively as to adopt their supported equilibrium shape on the MgO(100) surface (third snapshot in the bottom panel of Fig. 12).

4.1.2 Surface premelting and dependence on the cluster size.

The maps of averaged structural characteristics (position, mobility) taken at different temperatures along the caloric curve, Fig. 13, help visualizing the process of cluster melting. The atoms which diffuse at the lowest temperatures are the lowest coordinated ones (at the edge of re-entering layer at the interface). As temperature is progressively increased, more and more atoms, first at cluster edges, than at its (100) top facet, and finally at its (111) side facets become mobile. This formation of a thin liquid layer in equilibrium with the underlying solid core (surface premelting), starts at temperatures well below the actual solid-liquid transition and disappears for very small cluster sizes (where there are practically no core atoms). In the present case of supported Pd clusters, the surface premelting clearly does not involve the metal atoms at the interface, whose mobility is systematically close to that of cluster core sites. However, since the mobility properties of metal atoms directly at the interface depend on the strength of the metal-oxide interaction they are expected to approach those of the metal itself at weakly interacting interfaces.
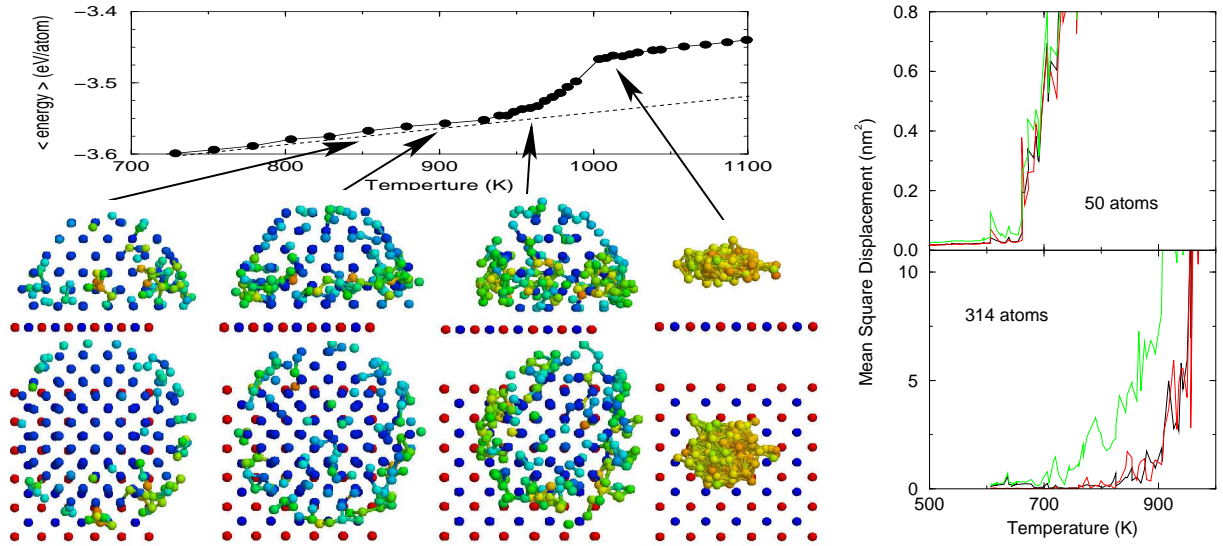
Figure 13: Melting of supported Pd clusters. Left panel presents a series of images of a progressively heated cluster: metal atoms are plotted at their average atomic positions, their colours represent their mean square displacement. Colour scale ranges from dark blue (immobile), through green, to yellow and red (highly mobile). Right panel displays the evolution of the mean square displacement as a function of temperature for three types of Pd atoms in the supported cluster: core (black), interface (red), and surface (green). Small (50 atoms) and medium size (314 atoms) clusters are considered. From [39].
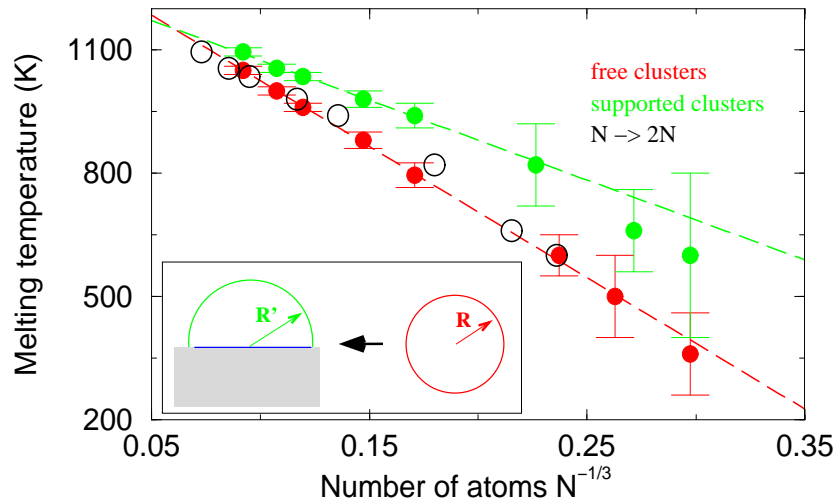

Figure 14: Substrate-induced modifications of the melting temperature of supported Pd clusters. Melting temperature as a function of cluster size (inverse cluster radius $N^{-1/3} \sim R^{-1}$) for free (red) and supported (green) clusters. Black circles represent the melting temperature of supported clusters corrected for the modification of the surface/volume ratio (see text). The inset displays a schematic representation of substrate-induced modification of equilibrium form of Pd clusters: perfectly spherical free shape (red) and half-spherical supported shape (green). From [39].

4.1.3 Interface-induced delay of melting

In order to relate the observed absence of premelting at the Pd/MgO(100) interface to the substrate-induced modification of the melting temperature of the deposited clusters we use the phenomenological law of Gibbs-Thompson. It gives the general relation between the melting temperature T_m of a given cluster and its size (radius R): $T_m(R) \sim -R^{-1}$, and accounts for the well known effect of reduction of the melting temperature in spherical particles of finite size. Indeed, for both free and supported clusters we find a linear variation of melting temperature as a function of inverse cluster radius ($R^{-1} \sim N^{-1/3}$), Fig. 14. Higher melting temperatures in the case of supported clusters gives somewhat smaller proportionality constant. In order to access the mechanism underlying this difference we remind that this is the surface ($\sim R^2$) to volume ($\sim R^3$) ratio which is at the origin of the R^{-1} argument in the Gibbs-Thompson law.

Upon the cluster deposition two effects are to be taken into account. On one hand, the cluster morphology changes and the overall cluster surface increases. On the other hand, depending on the strength of interactions on the metal/substrate interface, the extent of premelting in the interfacial metal layer varies. In the present case of Pd clusters on the MgO(100) surface, the deposition-induced change of cluster shape (full sphere into half sphere, inset of Fig. 14) reinforces the surface/volume ratio. However, since the interface atoms do not show any premelting, only the external cluster facets act as melting precursors. As a consequence the effective surface diminishes by $2^{-1/3}$, and so does the surface/ratio entering the Gibbs-Thompson equation. The corresponding transformation does align the melting temperatures of supported and free clusters, Fig. 14. It emphasis that it is the interface-induced reduction of premelting rather than to the change of cluster morphology which is responsible for the calculated delay of melting.

Although the present results on Pd clusters deposited on the MgO(100) surface present a very particular scenario of cluster melting, they reveal the principal underlying mechanisms which give basis for a more general conclusion. Whereas at weaker interacting interfaces, the properties of deposited clusters shall approach these of the free ones, in the case of strong interaction at the interface one may expect a delay of melting of the interface layer with respect to the cluster core, giving potentially rise to an interesting case of interface "post-melting".

4.2 Substrate polarity and the role of point defects

Any attempt to simulate realistic metal/oxide interfaces has to take into account the possibility of structural, chemical, or electronic defects, stabilized either by the specific metal/oxide environment, or by the conditions of sample preparation. Especially as regards the characteristics of metal growth, the substrate defects are widely recognized to play an essential role. Their characterization and the analysis of their influence on the initial stages of nucleation has recently become a subject of extensive theoretical and experimental studies. Much less is know on the role of defects in the catalytic properties of supported metal nano-clusters. In the following, we focus our attention on the influence of substrate defects on the properties of constituted interfaces. We have chosen two qualitatively different cases: an interface with a polar, or with an oxygen deficient oxide surface, representative respectively, for model extended and point defects. Although their physical origin is very different, both these kinds of defects are responsible for
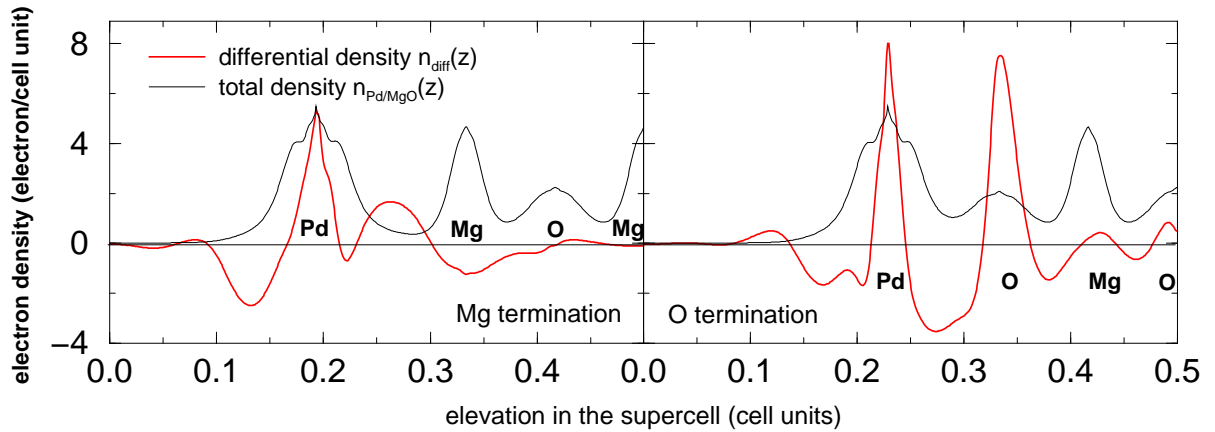
Figure 15: Electron redistribution upon deposition of a Pd layer on the two terminations of MgO(111) surface. Red lines represent profiles of differential electron density across the interface $n_{\text{diff}}(z) = n_{\text{Pd/MgO}}(z) - n_{\text{Pd}}(z) - n_{\text{MgO}}(z)$. Black lines give the (scaled) total electronic density $n_{\text{Pd/MgO}}(z)$, whose maxima indicate the positions of the atomic layers in the supercell. From [20].

important modifications of the interface electronic structure. Even in the case of metals from the end of the transition series, they are at the origin of a strong interaction at the interface.

4.2.1 Polar metal-oxide interfaces

The problematics of metal/oxide interface gains an additional dimension in the case of polar orientations of the substrate surface. Although polar oxide surfaces are well recognized to be unstable and thus difficult to prepare unreconstructed and defect-free [40, 41, 42, 43, 44, 45], there exists both experimental and theoretical evidence that formation of a metal/oxide interface can stabilize polar oxide terminations [46, 47, 48].

Indeed, a simple electrostatic argument explains the instability of polar oxide surfaces, such as the MgO(111) one, and suggests how they can be stabilized. The presence of equidistant layers, with charge densities equal alternatively to $+\sigma$ and $-\sigma$ yields a macroscopic dipole moment which increases with the number of layers. This divergent component can be cancelled out by the introduction of additional (compensating) charge densities $\mp\sigma/2$ on the outer layers of the slab. Various mechanisms leading to this compensation at the MgO (111) surface were described in the literature, among which non-stoichiometric reconstructions [49] and hydroxylation [49, 50]. Adsorption of metals is an equally efficient way of stabilizing of the MgO(111) surface [20].

The metal adsorption characteristics on MgO(111) are controlled by its strong polar character and thus differ substantially from those reported for the MgO (100) face. In particular, strong electron transfers between the metal atoms and the substrate take place, resulting in a strong interface adhesion.

We recall that on the clean MgO (111) substrate, the condition of polarity healing is fulfilled thanks to a modification of the surface valence and conduction band filling: on the oxygen (magnesium) termination, the valence (conduction) band is partly depleted (filled). This leads to a
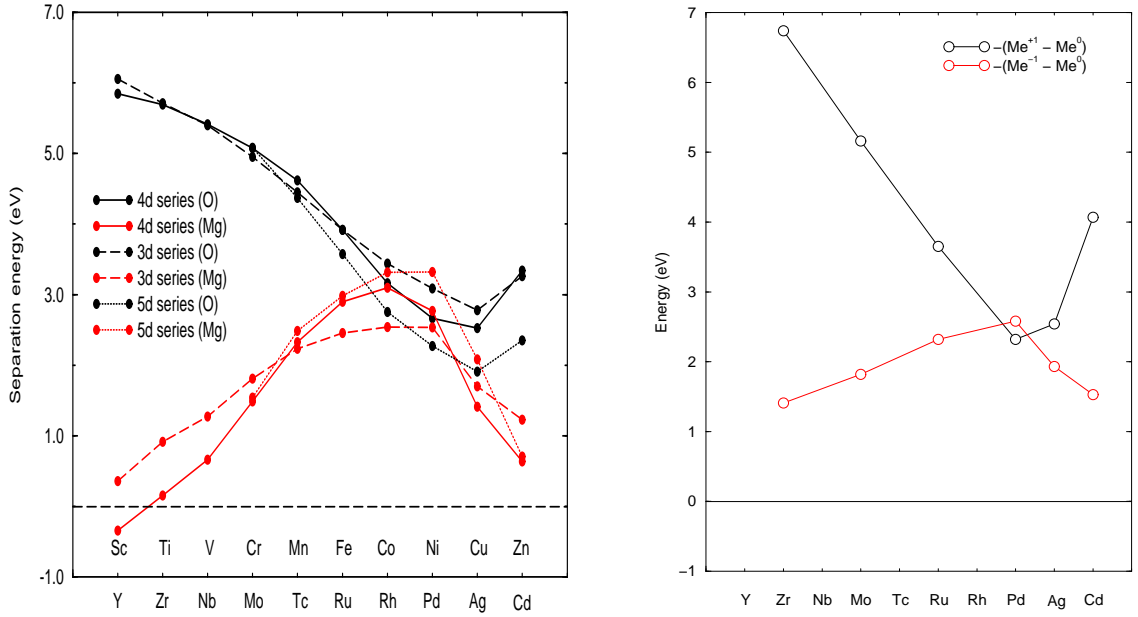
Figure 16: Adhesion at polar metal/oxide interface. Left panel: separation energy (eV/interface metal atom) for a single transition metal layer deposited on oxygen (black) or magnesium (red) termination of the MgO(111) surface (FP-LMTO calculations). Right panel: Energy (eV/atom) required to positively or negatively ionize an unsupported strained metal layer ($4d$ transition series, FP-LAPW calculations). Only the evolution is meaningful. Since this energy represents the metallic band filling contribution to E_{sep}, global shifts have been made to align the curves with the separation energy curves (left panel). From [20].

reduction (in absolute value) of the surface charges and to a metallization of the two terminations. We have shown in Ref. [48] that this mechanism yields charge compensation but results in a high surface energy. When a metal layer is deposited on the MgO(111) surface we find a completely different situation. The substrate bands recover a normal filling and the metal band filling changes. The metal overlayer gives electrons to the MgO surface oxygen (oxygen termination) and receives electrons from the MgO surface magnesium (magnesium termination), in such a way that electrostatic criterion is fulfilled, Fig. 15. Thus, on metal/MgO(111) interfaces, the compensating state is mainly localized at the adsorbed metal interface layer. The fact that the electronic density of the second and following metal layers remain practically unchanged is a manifestation of strong screening effects present in metallic systems.

The evolution of separation energies at metal/MgO(111) interfaces along the transition series, Fig. 16, is driven by the contribution associated to the transfer of the compensating state from the substrate towards the metal. It induces an energy gain (positive contribution to E_{sep}), function of the relative positions of the magnesium, oxygen, and metal bands on the energy scale. It can be qualitatively estimated by the energy required to charge positively or negatively all atoms in an unsupported strained metal layer. As shown in Fig. 16, this contribution accounts for the principal characteristics of the E_{sep} behaviour along the transition series. Although the behaviours of metal/MgO(111) and metal/MgO(100) (Fig. 5) separation energies along the transition series present an overall similarity, the separation energies at metal/MgO(100) interfaces are systematically smaller. The difference is due to different surface energies of the

clean MgO(111) and MgO(100) surfaces and amounts to about 2.1 eV/surface MgO unit. Since the separation energy of metal on the MgO (111) surface is high (the adsorption process stabilizes significantly the polar surface), an estimation of the contact angle θ through the Young-Dupré equation ($E_{sep} = \gamma(1 + \cos\theta)$, where γ is the energy of metal surface), for metals at the end of transition series we find the possibility of total wetting ($\theta = 0$) of the unreconstructed (111) surface by the deposit, whereas bad wetting ($\pi/2 < \theta < \pi$) is found for the (100) orientation.

In summary, the interaction of transition metal with a polar surface of a highly ionic oxide is dominated by the band filling modification which is necessary for suppressing the macroscopic dipole moment in the polar substrate. Transfer of the compensating state from the substrate to the adsorbed metal results in a strong energy gain which enhances thus the adhesion at the interface. As a consequence, the very same transition metal may interact weakly with non-polar faces of a given oxide and wet perfectly the polar ones.

4.2.2 Palladium on oxygen deficient MgO(100) surface

The improvement of experimental techniques enables a better characterization of surface point defects, of their effect on the interaction between oxide substrate and the adsorbate, and finally, of their influence on chemical activity of metal deposits [51]. On one hand, Atomic Force Microscopy experiments have shown that the nucleation kinetics is governed by point defects with a high trapping energy [52]. Also the peculiar catalytic properties of supported clusters have been tentatively attributed to defect-induced modification of the electronic properties of the deposited metal [53]. On the other hand, it has recently been show that in oxygen-poor (UHV) conditions, the surface oxygen vacancies - probably the most widely studied point defects on MgO(100) - are thermodynamically more stable than magnesium or di-vacancies (missing surface MgO units) [54]. The theoretical studies reveal also an important increase of the adsorption energy of metal ad-atoms and a considerable electron transfer induced by oxygen vacancies [55, 56, 57, 58, 59, 16, 60]. Whereas most of results concerns the isolated metal ad-atoms, dimers, or nano-clusters composed of a few atoms only, and are thus representative of the very early stages of cluster growth, in the following we focus on the effect of oxygen vacancies on electronic and adhesion properties of extended metal deposit (Pd/MgO(100) interface).

We recall that the most stable, neutral oxygen vacancies, are characterized by trapping of two electrons by the surface electrostatic field on the site of the missing oxygen atom and by the existence of an occupied state in the MgO band gap. Compared to metal deposition on the defect-free MgO(100) surface, they are responsible for an enhanced electron transfer from the substrate towards the deposit. The transferred electrons remain well localized on the metal atom directly above the vacancy site, which also receives some electrons from its metal neighbours. This electron redistribution can be correlated to the relative position of the vacancy state and the metal band on the energy scale, but the band shift and deformation due to the electron transfer needs to be taken into account self-consistently. In the case of Pd/MgO(100) interface, the LDOS of Pd atom directly above the vacancy is shifted downwards on the energy scale, and its width is considerably reduced, Fig. 17. The electronic population at this atom is enhanced, but the reduced LDOS width reflects a high degree of localization of the transferred electrons. In view of this result on may expect that the enhanced catalytic activity suggested for isolated
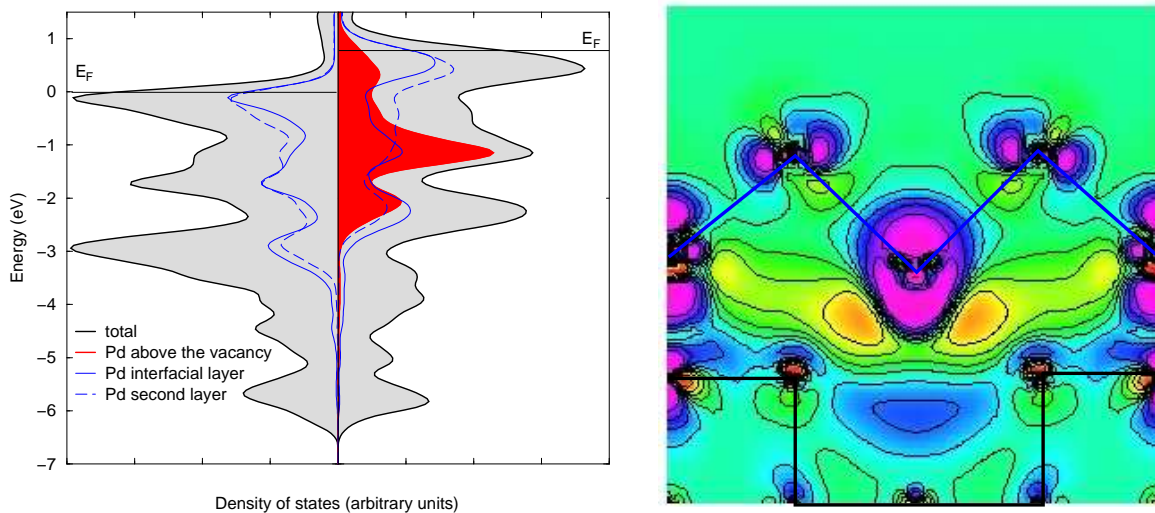
Figure 17: Palladium bi-layer deposited on the oxygen-deficient MgO(100) surface (0.25 ML of neutral oxygen vacancies). Left panel: local density of states calculated for Pd deposited on perfect (left column) and oxygen deficient (right column) surface. Projections on the Pd atoms above the vacancy (red), in the interface layer (solid blue), and in the second layer (dashed blue) are plotted. The energy scales are aligned by the core levels of oxygen ions in the slab center. Right panel presents the map of differential electron density in the plane perpendicular to the interface, and centered on the Pd atom above the vacancy. Black (blue) line interconnects substrate (adsorbate) atoms. Colours yellow and red correspond to an enhancement of electron density, whereas blue and violet represent a reduction. From [16].

metal ad-atoms trapped at oxygen vacancies [58], may also exist for extremely flat clusters or at the edges and corners of three dimensional clusters deposited of defected surface. However, similarly to the case of polar interfaces, the electronic redistribution remains fairly localized to the interface region and is likely to be completely screened in larger three-dimensional deposits.

Due to the stabilizing effect of the electron transfer just described, oxygen vacancies enhance considerably the adhesion energy. Although, compared to adsorption of isolated metal atoms, their effect attenuates rapidly for more extended deposits, and remains much smaller than this of a polar substrate, oxygen vacancies may yield a modification of the aspect ratio of deposited particles. A simple argument based on the Wulff theorem and applied to the known, pyramidal form of Pd clusters on MgO(100) suggests a reduction of the cluster height and thus an increase of the proportion of (100) facets with respect to (111) ones. This effect, together with the related change of edge lengths will necessarily modify the cluster catalytic properties. Although the controlled generation of surface defects may seem to be a tool for a fine tuning of catalyst reactivity, one should not forget that the presence of vacancies may also induce structural defects within the deposit, modify the kinetics of cluster growth, and the cluster size distribution.

5   Conclusion

We have proposed a novel approach to simulation weakly interacting metal/oxide interfaces which couples the advantage to relay on results of model ab initio calculations (and to account

thus for the many-body character of the interactions), with the efficiency of PES-type methods. We have given an example of its application to a study on oxide-supported metal clusters and thin metal films, and have shown the possibility to perform finite temperature simulations at a relatively small computational expense. Both, the large number of treated atoms, and the account of temperature, do unquestionably approach the realistic experimental conditions. In the particular case of the described systems, this two ingredients have helped to reveal physical effects which at present are clearly beyond the reach of ab initio calculations.

We have also introduced the substrate defects - an another factor which often determines the observed characteristics and is responsible for the most interesting properties. The two qualitatively different examples (a polar and an oxygen-deficient substrate surface) reveal an enhanced electron transfer and adhesion energy, which are inherent of most substrate defects. Corresponding modifications of the properties of deposited metal may complicate any possible extension of the PES method towards this kind of interfaces but, at present, more model ab initio results are still necessary in order to rationalize the apparently complex behaviour of metals on defected oxide surfaces.

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