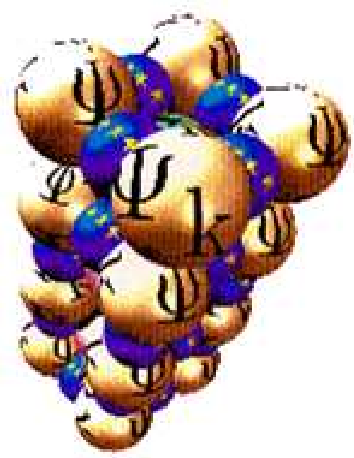
Ψ_k Newsletter

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

Number 78 December 2006



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Contents

1 Editorial

This December issue of the Psi-k Newsletter contains two reports on workshops/meetings in the ESF Psi-k Programme section, and another one in the U. K.'s CCP9 Programme section. Some contain also abstracts of presented papers. In this issue, we also have the final report on the activity and scientific accomplishments of the RTN on ”f-electrons”. With this report we say good-bye to this last, successful, RTN of the recent years.

In addition to the reports, in this issue there is a number of position and workshops/meetings announcements. In particular, we would like to turn readers attention to the announcement of the Psi-k Training Graduate School to take place next March in Bristol, UK. The earlier graduate school is happening in Uppsala, early in December 2006.

The abstracts of the newly submitted and/or recently published papers are in their usual section, followed by the announcement of a new journal of the IOP Publishing, and this can be found just before an impressive scientific highlight by M. Heide, G. Bihlmayer, Ph. Mavropoulos, A. Bringer and S. Blügel (Jülich) on **”Spin Orbit Driven Physics at Surfaces”**. Please check the table of content for further details.

As the year 2006 is also approaching its end, we would like to take the opportunity and thank all of you for your contributions, time and cooperation. May the New Year be full of new challenges and great scientific accomplishments.

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 forthcoming Psi-k 2007 workshops and hands-on courses (subject to funding).

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@dl.ac.uk	**messages to the coordinators, editor & newsletter**
psik-network@dl.ac.uk	**messages to the whole Ψ_k community**

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2 General News

2.1 Special Issue of physica status solidi (b) and Call for Scientific Highlights for 2007

We hope that most of our readers are aware that each Psi-k Newsletter contains a scientific highlight, usually contributed by different Working Groups of the ESF Psi-k Programme "Towards Atomistic Materials Design", but sometimes also by other researchers from all over the world. The purpose of the highlights is to review and dissiminate our research accomplishments to a broader scientific audience. The rather unique and special feature of those highlights was the fact that they were written specifically for the Psi-k Newsletters and their readers. They have been distributed to the Psi-k mailing list which at the present time contains about 1850 e-mail addresses from all the parts of the world. In addition they are easily accessible on-line at the Psi-k web pages

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

All the highlights have been of a very high standard and thus some of the journals offered to publish them as their special issues. The first of such special issues, containing the most recent highlights, spanning the past three years or so, has just been published by physica status solidi (b) and can be viewed at

http://www3.interscience.wiley.com/cgi-bin/jissue/112681548.

If you have not seen this issue yet, please do take time to at least browse through it.

This special issue has been a great success and the editors of the physica status solidi (b), in cooperation of the Psi-k Newsletter, would be interested in publishing also the future highlights, if their authors wished to have them published, in addition to the on-line publication in the Psi-k Newsletters.

Unfortunately, it has become more and more difficult to motivate our readers to contribute a scientific highlight to the future Psi-k Newsletters, as they usually do not count as a regular scientific publication. However, now that we have the option to have them published in the physica status solidi (b), but only if the author of the highlight chooses to do so, we hope that more of our readers and members of the Psi-k family would like to write a highlight of their choice for the 2007 Psi-k Newsletters. So, if you would like to write a highlight and contribute to the development of the Psi-k please do contact us at

psik-coord@dl.ac.uk.

We have been promised highlights for the February and April issues of 2007, but need four more for the June, August, October and December 2007. Note that the template for the scientific highlight is available on-line in the Psi-k Newsletter No 67. The deadline for submissions into a specific issue is about a week before the end of the month preceding the month of the issue, namely e.g. a week before the end of May 2007 for the June 2007 issue, and so on.

3 News from the RTN on "f-electrons"

"Ab-initio Computation of Electronic Properties of f-electron Materials"

3.1 Fourth Annual and Final Report

Final Report: RTN2 'psi-k f-electrons'

Network co-ordinator	:	Associate Prof. Axel Svane
Full report	:	http://www.fysik.uu.se/rtnfelektron/rtn-main.htm

Scientific Highlights

Fourth network year:

Actinide progress

The electronic structure and magnetic properties of δ-Pu [68] and $PuCoGa_5$ [67] were calculated based on the LDA+DMFT approach with the spin-polarized T-matrix +FLEX (SPTF) solver, which has been developed by the Nijmegen group. The calculations give a very satisfactory description of the photoemission spectra for the superconducting $PuCoGa_5$ compound: the correlation effects on the Pu atoms change drastically the electronic structure near the Fermi level, whereas taking into account Hubbard correlations on the Co atoms have relatively weak effect. A giant Van Hove singularity near the Fermi level is predicted for $PuCoGa_5$, which might be important to clarify the mechanism of its superconductivity. For δ-Pu a description of the strongly correlated nonmagnetic ground state is obtained with good agreement with the photoemission spectra including the many-body resonances near the Fermi level. At the same time, the absence of magnetic moments in δ-Pu, being a long-standing problem, has been explained on the base of the self-consistent LDA+DMFT calculations.

The $NpCoGa_5$ system, a sister compound to $PuCoGa_5$, for which superconductivity is not observed, was investigated by the Dresden and Uppsala groups [4], specifically the Fermi surface was calculated and extremal areas compared to experimental de Haas van Alphen frequencies.

Furthermore, the SPFT solver has been implemented into the full potential LMTO code in collaboration between the Nijmegen and Uppsala groups. First application has just been submitted

[17]. It opens a way for systematic investigation of the correlation effects on total energies and related properties (elastic moduli, equation of states, etc.) for both f- and d-electron systems.

The cohesive and magnetic structures of the actinide elements from Pu to Cf were revisited with the self-interaction corrected total energy scheme by the Aarhus-Daresbury teams [9].

Rare earth systems:

The pressure dependence of the mixed-valent state of Yb has been investigated [1] by the Nijmegen and Uppsala groups. The dynamical screening of core-holes is taken into account in a multiband Mahan-Nozieres-deDominici model [2,3], with the effective Yb valency derived from the Falicov-Kimble model.

Trends of the electronic structure of rare earth impurities in GaAs and GaN semiconductors have been studied with the self-interaction corrected local spin density approach by the Aarhus and Daresbury groups [14]. The impurities are found to have large atomic-like spin and orbital moments with only a weak influence on the host carriers, hence the gigantic enhancements of dilute moment magnetism observed in experiments cannot be explained by the isolated substitutional rare-earth impurities.

Cerium sulphides have been investigated by the LeMans postdoc with emphasis on optical properties of γ-cerium sesquisulfide doped with alkali and alkaline-earth elements [69].

The multiplet effects in photoemission of rare earth systems have been further investigated by the multiplet Hubbard-I approach in a collaboration between Uppsala, Nijmegen and Aarhus [10,11], spearheaded by the former Uppsala network post-doc, now permanently employed in Nancy, France. This method is well suited for systems in the atomic limit, i.e. where the influence of the solid may be assumed minimal. The multiplet spectra of rare earth elements are well reproduced in a wide ~ 10 eV range below and above the Fermi level.

For all network period:

Methodological Developments

The Dynamical Mean Field Theory methodology has been extensively developed during the four network years, much of which has been reviewed in [5]. Most significantly, the extension of DMFT to clusters of correlated atoms has been implemented and applied [28,32], and the ambitious GW+DMFT scheme has been formally developed, while implementation is still in progress. (Paris, Nijmegen, Rutgers and Uppsala teams) Work on ab-initio derivation of many-body Hamiltonians, in particular the computation of the Hubbard U parameter, based on the DMFT(GW) method is on-going, first results being published [34]. (Nijmegen, Paris, Rutgers collaboration).

Several new and improved impurity solvers for DMFT have emerged: Within the Exact Muffin Tin Orbital method a charge and self-energy self-consistent spin-polarized T-matrix plus FLEX (SPTF) scheme has been implemented and applied [53,31,67,68] A continuous time, full-interaction vertex, multiorbital Quantum Monte Carlo scheme for fermions has been developed and used to investigate the interplay of the on-site Kondo effect and inter-site exchange interactions, which is of crucial importance for physics of anomalous f-electron systems like Kondo lattices (Nijmegen group). The QMC scheme has been generalized to allow for a non-diagonal and low-symmetry matrix form of the local temperature-dependent Green-function within the Nth order MTO method [54]. A fully relativistic exact MTO (FREMTO) method has been developed including CPA to treat disorder, and a paper has been published [35].(Nijmegen).

A new LDA+U scheme for intermediate localization has been checked with the LDA+DMFT for the transition from magnetic to non-magnetic ground state for correlated metallic systems (Nijmegen team).

A local version of the self-interaction corrected (L-SIC) local spin density approach has been developed and applied to Ce [29]. The L-SIC is implemented in the multiple scattering band theory and therefore the Green's function is easily evaluated. This allows to implement the CPA to treat not only substitutional disorder but also charge and spin disorder. (Daresbury and Aarhus teams). Several applications to dilute Ce alloys and other alloy systems are in the pipeline.

The Uppsala group has developed a many-body projector orbitals method for electronic structure theory of strongly correlated electrons, with the purpose of computing crystal-field excitations in f-materials in a DFT framework [77].

The FPLO method has been implemented for surfaces, including the implementation of the appropriate multipole compensation method for the solution of the Poisson equation [70]. (Dresden)

A new method to describe intermediate valence based on LDA calculations of the competing integral valencies has been developed and tested on the continuous pressure induced valence transition observed in Yb [36,1] including pressure dependant photoemission. (Uppsala and Nijmegen)

Pu and other actinides

The cohesive properties of Pu were calculated in the LDA+DMFT as a function of volume by the Rutgers group [5], elucidating the double-well structure corresponding to the α- and δ-phases. The phonon spectrum of δ-Pu was calculated, and the thermal expansion of δ-Pu discussed. Also the volume dependance of Pu photoemission spectrum was derived. The Rutgers group also calculated the equation of state of Am up to 35 GPa by LDA+DMFT.

The electronic structure and magnetic properties of δ-Pu [68] were calculated based on the LDA+DMFT approach with the SPTF solver, (Nijmegen group). In particular, the absence of magnetic moments in δ-Pu, being a long-standing problem, has been explained on the base of these self-consistent DMFT calculations.

The electronic structure of the exotic superconducting compound $PuCoGa_5$ has been calculated [67]. Other aspects of this relatively high-T_c superconductor, and its non-superconducting sister compound, $NpCoGa_5$, most notably the Fermi surface properties have been investigated by conventional LSD calculations [37,4] (Dresden and Uppsala teams). The pairing of itinerant Pu $5f$ electrons has been identified as the cause of superconductivity.

The electronic structure of $PuO_{2\pm x}$ was studied using first-principles quantum mechanics, realized with the self-interaction corrected local spin density method. In the stoichiometric PuO_2 compound, Pu occurs in the Pu(IV) oxidation state, corresponding to a localized f^4 shell. If oxygen is introduced onto the octahedral interstitial site, the nearby Pu atoms turn into Pu(V) (f^3) by transferring electrons to the oxygen. Oxygen vacancies cause Pu(III) (f^5) to form by taking up electrons released by oxygen. At $T = 0$ the PuO_2 compound is stable with respect to free oxygen, but the delicate energy balance suggests the possible deterioration of the material during long-term storage [55,38] (Aarhus and Daresbury teams). The study of the oxydation processes in PuO_2 and its similarities to ceria has also been studied in Uppsala by complementary methods. Likewise, the crystal fields in PuO_2 have been calculated (Uppsala team).

The intricate U f-electron manifold in UPd_2Al_2 has been investigated within the SIC-LSD approach [56], as has magnetism of UO_2 (Århus and Daresbury teams).

The trends in localization of the f-shell in the series of actinide pnictides and chalcogenides [39] showed the relative destabilization of the f-electrons in the earlier U and Np compounds towards primarily trivalent actinides in the Pu, Am and Cm compounds. At the same time the lighter ligands were found to destabilize the f-electrons more than the heavier ones.

The cohesive and magnetic structures of the actinide elements from Pu to Cf were revisited with the self-interaction corrected total energy scheme by the Aarhus-Daresbury teams [9].

The $\alpha - \gamma$ transition in cerium

The $\alpha - \gamma$ isostructural transition in cerium has been studied by the Daresbury and Aarhus collaboration [29] and by the Paris group [30], by two different models. The first approach involves self-interaction corrected density-functional calculations in a disordered alloy of α-like and γ-like cerium atoms, the disorder being described by the coherent potential approximation. The second approach involves the dynamical mean-field treatment of the cerium solid with extensive quantum Monte Carlo calculations of the ensuing Kondo impurity problem. Common to both approaches is the conclusion that it is the entropy of the γ-phase that drives the transition.

The Mott transition in f-systems, with emphasis on the CeTh alloy, has been studied in a DMFT treatment of the Hubbard model including hybridization and finite temperature, and a first order transition between Kondo screened phase and local moment behavior is found [20] (Paris-Rutgers collaboration). Additionally, it is demonstrated that both an upper and a lower critical temperature exist, a fact corroborated by experimental evidence.

The equation of state of the $Ce_{43}Th_{57}$ alloy has also been studied using DFT and CPA for disorder by the Nijmegen post-doc [74].

Other rare-earth systems

Full geometry optimization of both lattice parameters and the internal atom positions in the crystal unit cell has been completed for a series of cerium compounds including CeS, Ce_2S_3 and Ce_3S_4. Comparisons with available experimental structural data show a level of agreement which is typical for DFT-GGA calculations, i.e. deviations between computed and experimental structural parameters in the range of a few percent [69]. Optical excitations have been calculated with the LDA+U method, including the effect of alkali dopants (LeMans team).

Electronic structure calculations were performed for the rare-earth high T_c superconductors $CeBa_2Cu_3O_7$, $PrBa_2Cu_3O_7$, $NdBa_2Cu_3O_7$, $GdBa_2Cu_3O_7$, and $TbBa_2Cu_3O_7$. Special emphasis was put to the valency of the rare-earth ion, which is computed with the self-interaction corrected local-spin-density energy functional. These studies indicated that the non-superconductivity in $PrBa_2Cu_3O_7$ is due to the tetravalency of Pr which leads to a magnetic and divalent Cu for which superconductivity cannot occur. The situation for the rare-earths in the superconductors is quite parallel to that of the rare-earth oxides, for which the tetravalent dioxides are only found for Ce, Pr and Tb [21,16].

The electronic structure of Sm monopnictides and monochalcogenides has been investigated with the self-interaction corrected LSD method. The localized f^5 and f^6 shells of the ground-state of the pnictides and chalcogenides, respectively, are well described, as evidenced by the excellent quantitative agreement with the lattice constants and bulk modulii. The high pressure intermediate valence state of the chalcogenides is described by a mixture of f^5 localized shells and a partially occupied f-band [40]. The fundamental gap of the chalcogenides in their semi-conducting phase is defined by excitations of a localized f-electron into the conduction band. This we calculate by total energy differences. The absolute values of the gaps are only in fair agreement with experiment, while the pressure coefficient are excellent, i.e. similar trends to what is observed in conventional semiconductors [41]. (Aarhus-Daresbury collaboration).

Eu chalcogenides, candidates for spin-filtering devices, as well as trends of magnetism through the series of rare-earth nitrides have been studied with the same methodology [42,43].

The Fermi surfaces and charge density waves were studied in rare-earth tritellurides [26].

Photoemission spectra of f-electron solids.

The spectral functions of several actinide systems have been calculated within the dynamical mean-field theory. The spectra of Ce and δ-Pu and Am were studied by Rutgers [5]. The spectral function of δ-Pu at high-temperature has been computed and compared with photoemission experiments (Nijmegen, Uppsala and Rutgers teams). The electronic structure and magnetic properties of $PuCoGa_5$ [67] were calculated based on the LDA+DMFT approach with SPTF solver (Nijmegen group). The calculations give a very satisfactory description of the photoemission spectra for the superconducting $PuCoGa_5$ compound: the correlation effects on the Pu atoms change drastically the electronic structure near the Fermi level, whereas taking into account Hubbard correlations on the Co atoms have relatively weak effect. A giant Van Hove singularity near the Fermi level is predicted for $PuCoGa_5$, which might be important to clarify the mechanism of its superconductivity.

For δ-Pu a description of the strongly correlated nonmagnetic ground state is obtained with good agreement with the photoemission spectra including the many-body resonances near the

Fermi level [68].

The spectra of PuSe and Am have been obtained using a simplified model of the conduction electron combined with an exact diagonalization of the ensuing impurity problem (Aarhus). The comparison to experimental photoemission spectra is quantitatively accurate, and allows for a detailed identification of the origin of the most distinct features of the spectra in terms of the quantum state of the f-shell. In another study by the Nijmegen post-doc [73] the spectra of USe, UTe, PuSe and PuTe have been calculated solving the impurity problem in the SPFT approach, emphasizing improvement over the static LDA+U results.

In a series of joint papers, the Aarhus, Nijmegen and Uppsala groups have calculated the photoemission of rare-earth systems TmCh (Ch=S, Se and Te) [22] and of the elemental metals [10,11]. In these cases the photoemission is dominated by the atomic-like multiplets of the photoexcited f-shell, and these featues are quantitatively accurately reproduced with the Hubbard-I type approximation for the f spectral function.

The pressure dependence of the mixed-valent state of Yb has been investigated [1] by the Nijmegen and Uppsala groups. The dynamical screening of core-holes is taken into account in a multiband Mahan-Nozieres-deDominici model [2,3], with the effective Yb valency derived from the Falicov-Kimble model.

Surfaces, magnetism and Fermi surface properties

The interpretation of scanning tunneling spectroscopy (STS) data taken on U/W(110) surfaces was facilitated by ab-initio calculation. It is demonstrated by fully relativistic total energy calculations including full optimization of all lattice parameters that the prepared structure can be a hexagonal Uranium phase, stabilized by the substrate, as seen in LEED and STM. Further, local densities of states are found to compare well with scanning tunneling spectra. This gives evidence for the possibility to observe f-states with STS. (Dresden team).

The lattice parameter and valence transition ($3+ \rightarrow 2+$) of the surface of Sm was calculated and good agreement with experimental photoemission work was obtained. (Uppsala team).

The origin of the magneto crystalline anisotropy of hcp Gd has been subject to intense study. Several mechanism have been proposed, e.g. the mixing of higher multiplets into the otherwise spherically symmetric S-state, or the effect of relativity of the $5d$ valence band. The latter contribution has been shown to reproduce the experimental data with good accuracy. Based on Hartree-Fock theory the mixing in of high multiplet configurations to the $4f^7$ configuration is found to be very small [57] (Uppsala team).

The spontaneous anisotropic magnetostriction of hcp Gd has been investigated within the LSDA and the LSDA+U approximations. As a rough model for the paramagnetic state with persisting $4f$ moments several static antiferromagnetic arrangements were considered. The calculated values of the spontaneous volume magnetostriction are in reasonable agreement with the experiment, but the sign of the anisotropic magnetostriction is wrong in the LSDA+U approach (Dresden team).

Metallic Magnetism in $LaCrSb_3$ has been investigated. This system is a non-collinear ferromagnet with a spin reorientation at about 95 K. Coexistence of itinerant and localized spins at one and the same Cr site has been suggested to explain the experimental results. Strong arguments against this model have been presented on the basis of electronic structure calculations and re-evaluation of experimental information. (Dresden team)

The electronic structure and magnetic properties of compounds formed between f-electron materials and transition metals have revealed many intriguing properties, ranging from quenched orbital moments and electron states that are on the border between localized and delocalized. In addition these materials sometimes exhibit complex non-collinear magnetic interactions which have been studied theoretically for several of these systems. The agreement with experiment is good, and mechanisms that determine if a non-collinear or collinear magnetic coupling occurs have been identified (Uppsala team). The Fermi surface of U dipnictides were studied by the Uppsala post-doc [71].

Magnetic x-ray scattering of praseodymium has been calculated (Daresbury with external team members) [23]. The cerium 115 compounds $CeMIn_5$ (M=Co, Rh, and Ir) have been studied using the LDA implemented in the FPLO method with both itinerant and localized description of the f-electrons. Fermi surface details (de Haas-van Alphen frequencies) show best agreement with experiments for itinerant f-treatment in the M=Co and M=Ir compounds, but localized f-treatment in the M=Rh case [24,25] (Dresden and Uppsala).

Joint Publications

Network post-docs are underlined.

fourth year:

1. C. Dallera, O. Wessely, M. Colarieti-Tosti, O. Eriksson, R. Ahuja, B. Johansson, M. I. Katsnelson, E. Annese, J.-P. Rueff, G. Vanko, L. Braicovich, and M. Grioni, *Understanding mixed-valent materials: Effects of dynamical core-hole screening in high-pressure x-ray spectroscopy*, Phys. Rev. B **74**, 081101(R) (2006). KUN and UU partners.
2. O. Wessely, M. I. Katsnelson, and O. Eriksson, *Ab-initio thory of Dynamical Core-Hole Screening in Graphite from X-Ray Absorption Spectra*, Phys. Rev. Lett. **94**, 167401 (2005). KUN and UU partners.
3. O. Wessely, O. Eriksson, and M. I. Katsnelson, *Dynamical Core-Hole Screening in the x-ray absorption spectra of graphite, C_{60}, and carbon nanotubes: A first principles electronic structure study*, Phys. Rev. B **73**, 075402 (2006). KUN and UU partners.
4. I. Opahle, S. Elgazzar, V.D.P. Servedio, M. Richter, and P.M. Oppeneer, *Calculated de Haas-van Alphen frequencies of $NpCoGa_5$*, Europhys. Lett. 74, 124 (2006). IFW-DRESDEN and UU partners.
5. G. Kotliar, S. Y. Savrasov, K. Haule, V. S. Oudovenko, O. Parcollet, C. A. Marianetti, *Electronic Structure Calculations with dynamical Mean-Field Theory*, Rev. Mod. Phys. **78**, 865 (2006). RUTGERS and ENS-ULM partners.
6. M. Le Tacon, A. Sacuto, A. Georges, G. Kotliar, Y. Gallais, D. Colson, and A. Forget, *Two energy scales and two distinct quaiparticle dynamics in the superconducting state of underdoped cuprates*, Nature Phys. **2**, 537 (2006). RUTGERS and ENS-ULM partners.
7. T. C. Schulthess, W. M. Temmerman, Z. Szotek, A. Svane, and L. Petit, *First Principles Electronic Structure of Mn doped GaAs, GaP and GaN semiconductors*, submitted, JPCM (2006) cond-mat/0610378. UAA and CCLRC partners.

8. W. M. Temmerman, A. Svane, Z. Szotek, P. Strange, L. Petit, and M. Lüders, *Pressure induced valence transitions in f-electron systems*, (submitted, Phase Transitions, 2006) cond-mat/0610263. UAA and CCLRC partners.
9. A. Svane, L. Petit, Z. Szotek, and W. M. Temmerman, *Self-interaction Corrected Local Spin Density Theory of 5f electron delocalization in Actinides*, (submitted, PRB, 2006) cond-mat/0610146. UAA and CCLRC partners.
10. S. Lebègue, A. Svane, M. I. Katsnelson, A. I. Lichtenstein, and O. Eriksson, *Multiplet effects in the electronic structure of heavy rare-earth metals*, J. Phys.: Condens. Matter **18**, 6329 (2006). UAA, UU and KUN partners.
11. S. Lebègue, A. Svane, M. I. Katsnelson, A. I. Lichtenstein, and O. Eriksson, *Multiplet effects in the electronic structure of light rare-earth metals*, Phys. Rev. B**74**, 045114 (2006). UAA, UU and KUN partners.
12. V. Kanchana, G. Vaitheeswaran, A. Svane, and A. Delin, *First-principles study of elastic properties of CeO$_2$, ThO$_2$ and PoO$_2$*, J. Phys.: Condens. Matter **18**, 9615 (2006). UAA and UU partners.
13. L. Petit, T. C. Schulthess, A. Svane, W. M. Temmerman, Z. Szotek, and A. Janotti, *Valency Configuration of Transition Metal Impurities in ZnO*, J. Elec. Mat. **35**, 556 (2006). UAA and CCLRC partners.
14. A. Svane, N. E. Christensen, L. Petit, Z. Szotek, and W. M. Temmerman, *Electronic structure of rare-earth impurities in GaAs and GaN*, Phys. Rev. B **74**, 165204 (2006). UAA and CCLRC partners.
15. Z. Szotek, W. M. Temmerman, D. Ködderitzsch, A. Svane, L. Petit, and H. Winter, *Electronic Structure of Spinel Ferrites*, Phys. Rev. B, accepted (2006). UAA and CCLRC partners.
16. L. Petit, A. Svane, Z. Szotek and W.M. Temmerman, *Electronic Structure of rare earth oxides*, (Topics in Applied Physics, Springer Verlag, to appear 2006) UAA and CCLRC partners.
17. A. Grechnev, I. Di Marco, M. I. Katsnelson, A. I. Lichtenstein, J. Wills, and O. Eriksson, *Theory of quasiparticle spectra for Fe, Co, and Ni: bulk and surface*, cond-mat/0610621 (2006). UU and KUN partners.

first three network years:

18. A. Grechnev, V. Yu. Irkhin, M. I. Katsnelson, and O. Eriksson, *Theromodynamics of a two-dimensional Heisenberg ferromagnet with dipolar interaction*, Phys. Rev. B **71**, 024427 (2005). KUN and UU partners.
19. H. Rathgen, M. I. Katsnelson, O. Eriksson, and G. Zwicknagl, *Polar magneto-optical Kerr effect for low-symmetric ferromagnets*, Phys. Rev. B **72**, 014451 (2005). KUN and UU partners.
20. L. de'Medici, A. Georges, G. Kotliar and S. Biermann, *Mott transition and Kondo Screening in f-electron Metals*, Phys. Rev. Lett. **95**, 66402 (2005). ENS-ULM and RUTGERS partners.
21. L. Petit, A. Svane, Z. Szotek and W.M. Temmerman, *First principles Study of rare earth oxides*, Phys. Rev. B **72**, 205118 (2005). UAA and CCLRC partners.
22. S. Lebègue, G. Santi, A. Svane, O. Bengone, M. I. Katsnelson, A. I. Lichtenstein, and O. Eriksson, *Electronic structure and spectroscopic properties of thulium monochalcogenides*, Phys. Rev. B **72**, 245102 (2005). UAA, KUN and UPPSALA partners.
23. E. Arola, M. Horne, P. Strange, H. Winter, Z. Szotek and W.M. Temmerman, *Self-interaction corrected relativistic theory of magnetic scattering of x-rays: Application to praseodymium*, Phys. Rev. B **70**, 235127 (2004). CCLRC with external team members in Keele and Karlsruhe.
24. S. Elgazzar, I. Opahle, R. Hayn, and P.M. Oppeneer, *Electronic Structure and de Haas-van Alphen quantities of CeMIn$_5$ (M=Co, Rh, and Ir) compounds*, J. of Magn. and Magn. Mater. **290-291**, 388 (2005). DRESDEN and UPPSALA partners.
25. S. Elgazzar, I. Opahle, R. Hayn, P.M. Oppeneer, *Calculated de Haas-van Alphen quantities of CeMIn$_5$ (M=Co, Rh, and Ir) compounds*, Phys. Rev. B **69**, 214510 (2004). DRESDEN and UPPSALA partners.
26. J. Laverock, S. B. Dugdale, Zs. Major, M. A. Alam, N. Ru, I. R. Fischer, G. Santi and E. Bruno, *Fermi surface nesting and charge-density wave formation in rare-earth tritellurides*, Phys. Rev. B **71**, 85114 (2005). UAA with CCLRC external team member Bristol.

27. S. Y. Savrasov, A. Toropova, M. I. Katsnelson, A. I. Lichtenstein, V. Antropov, and G. Kotliar, *Electronic structure and magnetic properties of solids*, Z. Kristallogr. **220**, 473 (2005). RUTGERS and KUN collaboration.

28. S. Biermann, A. Poteryaev, A. I. Lichtenstein, and A. Georges, *Dynamical Singlets and Correlation-Assisted Peierls Transition in* VO_2, Phys. Rev. Lett. **94**, 026404 (2005). ENS-ULM and KUN partners.

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4 News from the ESF Programme

”Towards Atomistic Materials Design”

4.1 ESF Psi-k Programme Workshop Announcements

4.1.1 13th International Workshop on ”Computational Physics and Materials Science: Total Energy and Force Methods”

11-13 January 2007, Trieste, Italy

The 13th International Workshop on ”Computational Physics and Materials Science: Total Energy and Force Methods” will take place in Trieste (Italy), 11-13 January 2007.

More information and application forms can be found at

`http://cdsagenda5.ictp.trieste.it/full_display.php?ida=a06178`
`http://www.democritos.it/events/totalenergy-XIII.php`

The registration deadline was 15 November 2006. There is no registration charge to attend the workshop, but accommodation is provided on a first-registered basis.

The conference will last for three full days - invited speakers are listed below. In addition, there will be three plenary lectures from Federico Capasso (Harvard University), Marvin Cohen (University of California, Berkeley), and Joshua Zak (Technion, Haifa), to celebrate the 60th birthdays of Alfonso Baldereschi, Roberto Car, and Raffaele Resta (Happy birthdays !).

The conference is supported by ICTP, Sissa, Democritos, and Psi-k. US-based participants can apply for travel funding through the Materials Computation Center (http://www.mcc.uiuc.edu/travel/).

Invited Speakers - Trieste Total Energy 2007

Igor A. Abrikosov (Linkopings University)
Hadi Akbarzadeh (Isfahan University of Technology)
Stefano Baroni (SISSA/Democritos)
Aitor Bergara (Universidad del Pais Vasco)
Stefan Bluegel (IFF Julich)
Fabien Bruneval (Ecole Polytechnique, Paris)
Kieron Burke (UC Irvine)
Gerbrand Ceder (MIT)
David Ceperley (University of Illinois, Urbana-Champaign)
David Drabold (Ohio University)

Stefano de Gironcoli (SISSA/Democritos)
Alessandro De Vita (King's College, London)
Dario Estrin (*) (University of Buenos Aires)
Pablo Garcia Gonzales (UNED, Madrid)
Antoine Georges (*) (Ecole Polytechnique, Paris)
Feliciano Giustino (University of California, Berkeley)
Xingao Gong (Fudan University)
Thomas Kuehne (ETH Zurich/USI Lugano)
Nicolas Lorente (Universite Paul Sabatier)
Bengt Lundqvist (Chalmers University)
Igor Mazin (Naval Research Laboratory)
Francesco Mauri (Universite Pierre et Marie Curie)
Richard Needs (University of Cambridge)
Eva Pavarini (IFF Julich)
Patrick Rinke (Fritz-Haber Institute, Berlin)
Annabella Selloni (Princeton University)
Massimiliano Stengel (University of California, Santa Barbara)
Axel Svane (University of Aarhus)
Timo Thonhauser (Rutgers University/MIT)
Ilya Tokatly (*) (Erlangen/Nurnburg)
Paolo Umari (Democritos)
Umesh Waghmare (JNCASR Bangalore)

(*) to be confirmed

We look forward to seeing you in Trieste !

Nicola Marzari, Pablo Ordejon, and Sandro Scandolo

4.1.2 CECAM Tutorial ”Programming Parallel Computers”

January 22-26, 2007

Research Centre Juelich, Germany

This tutorial aims to provide a thorough introduction to parallel programming. After an overview of the basic parallel computing concepts the main part of the course will cover the use of the message-passing interface, MPI. The third part will give an introduction to shared-memory programming with OpenMP.

The tutorial is organised by the John von Neumann Institute for Computing (NIC) on behalf of the Centre Europeen de Calcul Atomique et Moleculaire (CECAM). It will be held at the Central Institute for Applied Mathematics (ZAM) of Research Centre Juelich, Germany.

For further information, and to register, please visit

http://www.cecam.fr

and click on Tutorials-¿Programming Parallel Computers (at the bottom of the Tutorials 2006 page).

The deadline for registrations was November 20, 2006.

Please note that only registrations including a fully completed online application form will be considered.

Contact:

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4.2 Reports on ESF Psi-k Programme Workshops/Meetings

4.2.1 Report on the International Workshop on "Multiscale Modeling of Extended Defects and Phase Transformations at Materials Interfaces"

Place : University of Wrocław, Wrocław, Poland

Date : September 24-26, 2006

Sponsors : Psi-k Programme "Towards Atomistic Materials Design";
COST Action P19: "Multiscale modeling of materials";
University of Wrocław

Organizers : Adam Kiejna, University of Wrocław, Poland;
Mojmir Šob, Masaryk University Brno, Czech Republic

Web Page : `http://www.ifd.uni.wroc.pl/mmds-wroclaw/`

Summary

In order to understand in detail industrially relevant processes such as mechanical properties and fracture, chemical reactions at surfaces, micromagnetism, and polymer processing one has to combine different time and length scales. The aim of the workshop was to bring together distinguished representatives of physics, chemistry, materials science, and metallurgy communities to present and discuss state-of-the-art developments and the perspectives of theory, techniques, and applications, in multiscale modeling of such processes.

The programme of the workshop has included both the activities of the WG6 and WG15 of the Psi-k Network and of the COST Action P19 "Multiscale modeling of materials". During three full days of the workshop (Sunday through Tuesday) there were 19 keynote invited talks (40 min.), presented by internationally well-recognized speakers. These invited lectures were accompanied by 5 contributed talks (20 min.) and by 20 posters, which were presented by young participants of the Workshop. The total attendance of the Workshop was 60 registered participants from 16 countries, including 30 junior scientists (PhD students or post-docs). An important part of the workshop were two panel discussions entitled "Multiscale modelling, where do we stand". The first part was moderated by Prof. Sidney Yip (MIT Cambridge, USA), the second part, concluding the Workshop, by Prof. Matti Alatalo (Lappeenranta University of Technology, Finland), the Chairman of the COST Action P19: Multiscale Modelling of Materials.

Scientific content

A brief summary of the invited talks is as follows:

Sidney Yip described a class of atomic and charge transport problems at the interface of chemical physics and materials science where electronic-level calculations and atomistic calculations required to resolve the basic mechanisms.

Jörg Neugebauer discussed the key role of extended defects and grain boundaries in grain growth and recrystallization and recalled the importance of grain-boundary engioneering.

Igor Abrikosov presented an overview of recent theoretical results in the field of first-principles simulations of phase stabilities of alloys. The first-principles approach is combined with the statistical mechanics within the Ising Hamiltonian with parameters determined ab initio, and the Monte-Carlo method is applied.

François Willaime presented a systematic study of the structure and migration of small defect complexes in Fe from first principles. The results enabled an improvement of empirical interatomic potentials for iron and its alloys by including the first-principles results on defect properties into the database used for the fitting the potentials.

Gabor Csanyi presented recent developments in atomistic hybrid QM/MM simulation methodology, focussing on the problematic areas of matching at the boundary between the classical and quantum-mechanical regions.

Takayuki Kitamura was discussing the strength of interface edge in small (nanoscale) components. He discussed the delamination of cracks at the "interface edges", the junctions, where an interface meets a surface or another interface.

Mikko Alava dealt with statistical physics of material with defects; the main subject of his talk was the strength of brittle materials and the role of disorder.

Adrian Sutton reviewed recent results regarding the structure of twist grain boundaries in silicon. He discussed new, lower energy and ordered configurations of these grain boundaries.

Risto Nieminen reported first-principles calculations of the structure and electronic properties of several different silicon-hafnia interfaces. The simulations show that oxygen always diffuses towards the interface to form a silicon dioxide layer.

Dieter Suess discussed a micromagnetic model allowing for the calculation of process of information writing in the magnetic recording devices. This multiscale method may be applied to design advanced magnetic recording media.

Oksana Chubykalo Fesenko outlined the development of an atomistic model of magnetisation process and applied it to calculations of static and dynamical magnetic properties of nanogranular FePt. She demonstrated finite-size effects in elements used for magnetic recording.

Yuan Ping Feng proposed a new method for chemical tuning of metal effective work function at the interfaces between a high-K oxide and a metal gate. His approach was illustrated at the Ni/HfO2/Si stacks.

Guy Courbebaisse reviewed applications of the lattice Boltzmann method in the field of fluid mechanics. It also enables to use microsopic models to simulate macroscopic behaviour of fluid flows. As an illustration, he presented polymer injection moulding, where some industrial applications may be expected.

Dieter Wolf demonstrated how the materials-physics based insights into the underlying deformatioon and grain-growth mechanisms extracted from molecular dynamics simulations can be incorporated into a mesoscopic simulation model, overcoming the length and time-scale limitations inherent to the molecular dynamics approach. As an example, he discussed diffusion creep in a material containing a large number of grains with arbitrary sizes.

Göran Wahnström presented ab initio results for interfaces in two different systems: sintered WC-Co cemented carbides and ferritic steels. He showed the findings of a quantitative analysis of WC grain shape using the density functional theory and transmission electron microscopy. In steels, he considered VN presipitates which form platelets in ferrite due to a small (2 misfit parallel to the platelet and appreciable misfit (44 the platelet.

Karsten Reuter sketched multiscale modeling attempts for the field of heterogenous catalysis, concentrating particularly on the relevance of treating the surrounding gas phase, as well as the statistical interplay of the manifold of elementary processes at a catalyst surface. He also discussed atomistic thermodynamics.

Vasyl Tokar presented a lattice gas model of coherent strained epitaxy and discussed the size calibration od self-assembled nanoparticles. He was able to explain the discrepancy between the low atomic mobility predicted by a naive application of the ab initio approach and the high mobility presented experimentally.

Matous Mrovec reviewed the theoretical background of bond-order potentials and discussed the latest developments. The applicability of the bond-order potentials was demonstrated by several examples of studies of extended defects, in particular dislocations and grain boundaries which control the mechanic properties in metallic systems.

Vaclav Paidar compared various approaches to the grain boundary classifications and the interpretation of recent experimental results in the context of the complex relationship between microstructure, local chemistry and material properties. Such findings are essential for grain boundary engineering proposed to improve the performance of polycrystalline materials.

Panel discussion: Summary

The first part of the panel discussion was moderated by Sidney Yip. The panelist were François Willaime, Dieter Wolf and Adrian Sutton. **François Willaime** dealt with materials under irradiation. These materials exhibit non-equilibrium steady states and there are complex phenomena to be studied. Ab initio calculations often reconcile simulations with experiments. Computer simulations are increasingly important in the field of materials under irradiation and there are numerous international initiatives: CEA/Saclay & UK (Culham), European Fusion and Fission Project (since 2004), collaboration between the USA and CEA, between the EU and Japan etc. **Dieter Wolf** indicated that computer simulations are rather complementary to experiment. In the multiscale modelling, a great challenge is the time-scale problem. We have defined greater and greater details which we know with the double precision. Everyone giving a simulation talk should state how the results can be used e.g. for higher-level simulations - definitely not the pictures! It should be clearly indicated what can be passed to a higher level. **Adrian Sutton** summarized the main problems in the multiscale modelling:

1. Grand-canonical simulations for interfaces
2. Fracture toughness of polymer-inorganic interfaces and of nanocomposites
3. Beyond Ehrenfest non-adiabatic simulations with excited electrons

4. A continuing need for simple models to gain insights into complex materials and processes, e.g. (a) TB vs. DFT, (b) a possibility for massive simulations of radiation damage and defect processes in ferromagnetic iron

5. Education and training in Materials Modelling. Materials Science and Modelling has been diversified and post-graduate education would be desirable. Recent example: About 5 institutions in London try to share lessons and seminars and provide eduvation and training for students of MSE in UK.

6. Disconnect between fashion and industrial requirements: we need to look outwards and not inside. Materials Modeling seems to be divorced from the needs, seems to be "self-oriented". Challenges in real life are often different from those pursued in materials modelling community.

Part two of the panel discussion was moderated by Matti Alatalo. First, he has given information about the COST Action P19: Multiscale Modelling of Materials (MMM). It is possible to include projects in MMM into this Action. He also announced a Summer School on MMM. It will take place in Lappeenranta, May 23-26, 2007. It should be reasonably cheap and nice to visit, also e.g. in the range of short-term scientific mission within the above-mentioned COST Action P19. **Josef Fidler** informed about the activity of the WG3 (Micromagnetism) of the COST Action P19. At present, about 10 groups are participating. **Guy Courbebaise** outlined the activities of the WG4 on Hybrid Simulation Methods (COST Action P19). In particular, he showed the possibilities of the lattice Botzmann method in the field of fracture in solids. **Matti Alatalo** presented some thoughts of **Mike Finnis**, who could not attend the Workshop. His views concerned hybrid vs. hierarchical modelling and some examples of problems belonging to one or other mode of modelling. **Marc Hou** informed the other participants about an European initiative on radiation damage.

In conclusion, we may state that the primary goal of the Workshop, namely to provide a forum for the exchange of ideas on state-of-the-art developments, perspectives, and challenges of multiscale modeling at materials interfaces was fulfilled. Let us note that especially young participants of the Workshop benefited a lot from the Workshop. They had a possibility of a direct contact with the leading experts in the field and most of them could present their results. Discussions at posters brought them new ideas for their future work.

Final programme

Sunday, September 24

9:00 – 10:00	Registration
10:00 – 10:05	Opening

10:05 – 10:45	X. Lin, J. Li, X. Qian, C. Först, Sidney Yip (Cambridge, USA) *Multiscale Materials Modeling of Reactive Transport*
10:45 – 11:25	Jörg Neugebauer (Düsseldorf, Germany), L. Lymperakis *Extended defects and grain boundaries in Al-based materials*
11:25 – 11:40	Coffee/tea break
11:40 – 12:20	Igor Abrikosov (Linköping, Sweden) *Phase stabilities and phase transformations in alloys from first-principles*
12:20 – 13:00	François Willaime (Saclay, France) *Structure and mobility of defect clusters and defect complexes in iron from first principles*
13:00 – 15:00	Lunch
15:00 – 15:40	Gabor Csanyi (Cambridge, UK) *Hybrid classical and quantum-mechanical molecular dynamics simulations*
15:40 – 16:10	Coffee/tea break
16:10 – 16:50	Takayuki Kitamura (Kyoto, Japan) *Strength of Interface Edge in Small Components*
16:50 – 17:30	Mikko Alava (Helsinki, Finland), P. Nukala, S. Zapperi *Statistical physics of materials with defects*
17:30 – 19:00	Poster session/ snacks

Monday, September 25

9:15 – 9:55	Adrian P. Sutton (London, UK), S. von Alfthan, K. Kaski *Twist boundaries in silicon: a new look at an old problem*
9:55 – 10:35	Risto M. Nieminen (Helsinki, Finland), M. H. Hakala, A. S. Foster *Modeling the silicon-hafnia interface*
10:35 – 11:00	Coffee/tea break
11:00 – 11:40	Dieter Suess (Vienna, Austria) *Multiscale modeling of advanced magnetic recording devices*
11:40 – 12:20	R. Chantrell, U. Nowak, Oksana Chubykalo-Fesenko (Madrid, Spain) *Modelling of the dynamic properties of structured magnetic materials*
12:20 – 13:00	Panel discussion I: *Multiscale modelling, where do we stand?* Moderator: Sidney Yip (Cambridge, USA)
13:00 – 15:00	Lunch

15:00 – 15:40 Yuan P. Feng (NUS, Singapore), Y.F. Dong, Q. Li, Y.Y. Mi, S.J. Wang, C.K. Ong, A. Huan
First-Principles Study on Interfaces of High-K Oxides with Silicon and Metal Gate

15:40 – 16:20 Guy Courbebaisse (Lyon, France)
The Lattice Boltzmann Method

16:20 – 16:40 Coffee/tea break

16:40 – 17:00 Andreas Pedersen (Reykjavik, Iceland), G. Henkelman, J. Schiøtz, H. Jónsson
Long Time Scale Simulations of Atomic Structure and Dynamics at Defects in Metals

17:00 – 17:20 P. Piekarz, Krzysztof Parliński (Cracow, Poland), A.M. Oleś
The mechanism of Vervey transition in magnetite Fe_3O_4

17:20 – 17:40 Victoria Yardley (Sendai, Japan), H. Fujii, S. Tsurekawa
Modelling magnetic field effects on the crystallisation of amorphous Fe-Si-B alloys

19:00 – Conference dinner

Tuesday, September 26

9:15 – 9:55 Dieter Wolf (Idaho Falls, USA)
Atomistically-informed Mesoscale Simulation of Grain Growth and Grain-boundary Diffusion Creep in Nanocrystalline Materials

9:55 – 10:35 Göran Wahnström (Gothenburg, Sweden)
Ab-initio studies of interface energies

10:35 – 11:00 Coffee/tea break

11:00 – 11:40 Karsten Reuter (Berlin, Germany)
First-Principles Statistical Mechanics Approaches to Heterogeneous Catalysis

11:40 – 12:20 Vasyl I. Tokar (Strasbourg, France), H. Dreyssé
Fracture of coherent nanoislands during submonolayer strained epitaxy

12:20 – 13:00 Matous Mrovec (Freiburg and Karlsruhe, Germany), C. Elsaesser
Bond-order potentials for simulations of phases, interfaces and dislocations in metallic and covalent materials

13:00 – 15:00 Lunch

15:00 – 15:40 Vaclav Paidar (Prague, Czech Republic), P. Lejček
Segregation to grain boundaries of different types

15:40 – 16:00 Antti Puisto (Lappeenranta, Finland)
Cu oxidation: effect of surface modifications

16:00 – 16:20 E.E. Zhurkin, T. Van Hoof, Marc Hou (Brussells, Belgium)
Modelling plasticity and superplasticity of cluster assembled nanoalloys

16:20 – 16:40 Coffee/tea break

16:40 – 18:00 Panel discussion II: *Multiscale modelling, where do we stand?*
Moderator: Matti Alatalo (Lappeenranta, Finland)

18:00 Closing

Posters

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1. Juan Beltran (Madrid, Spain), M.C. Muñoz
   Adhesion at transition metal-ZrO_2 *interfaces*
2. Miroslav Čák (Brno, Czech Republic), M. Šob, J. Hafner
   First-principles study of the $\Sigma5(310)$ *grain boundary in iron*
3. Christopher W.M. Castleton (Uppsala, Sweden), A. Höglund, S. Mirbt, K. Hermansson
   Scaling the supercell errors in charged defect calculations: Correlations, band gaps and the LDA dielectric constant
4. Miroslav Cerny (Brno, Czech Republic), J. Pokluda
   First Principles Study of Vanadium Based Composites Reinforced by Tungsten Nano-fibres
5. Maria G. Ganchenkova (Helsinki, Finland), V.A. Borodin, S. Nicolaysen, and R. M. Nieminen
   Planar vacancy cluster formation in a non-hydrostatically loaded Si and SiGe crystals
6. Jerzy Gawd (Cracow, Poland), M. Pietrzyk
   Multiscale CAFE model of hot working process accounting for dynamic recrystallization
7. Jana Houserová (Brno, Czech Republic), M. Šob
   Ab initio study of thermodynamics and structure of Ta-X (X=Cr, Fe, W) C14 Laves phases
8. Karen Johnston (Espoo, Finland), R. M. Nieminen
   Understanding Polymer Adhesion: First-principles Calculations of the Adsorption of Organic Molecules onto Si Surfaces

9. Jan Kuriplach (Prague, Czech Republic), O. Melikhova, M. Šob
   Magnetic moment and segregation at selected grain boundaries in nickel

10. Dominik Legut (Brno, Czech Republic), M. Šob
    Magnetism along ideal tensile tests of Ni_3Al *and* Fe_3Al

11. Tomasz Ossowski (Wrocław, Poland), A. Kiejna
    Surface and $\Sigma5(210)$ *grain boundary properties of chromium*

12. Tomasz Pabisiak (Wrocław, Poland), A. Kiejna
    One-dimensional Au on rutile TiO_2*(110)*

13. Grzegorz Pawlik (Wrocław, Poland), A. C. Mitus
    Monte Carlo study of diffraction gratings in azopolymers

14. P. Scharoch, Jerzy Peisert (Wrocław, Poland)
    Thermal properties of Al(110) surface – ab initio study

15. R. Sot, Jacek Piechota (Warsaw, Poland)
    First principles study of selected Al twisted interfaces

16. Marian Radny (Callaghan, Australia), P.V.Smith, T.C.G. Reusch, O. Warschkow, N.A. Marks, N.J. Curson, S.R. Schofield, D.R. McKenzie, M.Y. Simmons
    Charging in Atomic Resolution Scanning Tunneling Microscopy – Modelling from First Principles

17. Paweł Scharoch (Wrocław, Poland), J. Peisert
    First principles thermodynamics of fcc Al crystal

18. Elwira Wachowicz (Wrocław, Poland), P. Błoński, A. Kiejna
    First principles study of grain boundary impurities in iron

19. Urszula D. Wdowik (Cracow, Poland), K. Parliński
    Lattice dynamics and electronic structure of Mott-Hubbard insulator from ab initio calculations

20. Martin Zelený (Brno, Czech Republic), D. Legut, M. Šob
    First-principles study of magnetic phase transition in cobalt along the bcc-fcc transformation paths

List of participants

Abrikosov Igor, Linköping University, Sweden
Alatalo Matti, Lappeenranta University of Technology, Finland
Alava Mikko, Helsinki University of Technology, Espoo, Finland
Ballo Peter, Slovak University of Technology, Bratislava, Slovak Republic

Beltran Juan, Instituto de Ciencia de Materiales de Madrid, Spain
Błoński Piotr, University of Wrocław, Poland
Cak Miroslav, Academy of Sciences, Brno, Czech Republic
Castleton Christopher, Uppsala University, Sweden
Cerny Miroslav, Brno University of Technology, Czech Republic
Chubykalo-Fesenko Oksana, ICMM Madrid, Spain
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Kiejna Adam, University of Wrocław, Poland
Kitamura Takayuki, Kyoto University, Japan,
Kuriplach Jan, Charles University, Prague, Czech Republic
Legut Dominik, Academy of Sciences, Brno, Czech Republic
Mrovec Matous, Fraunhofer-Institut für Werkstoffmechanik, Freiburg, Germany
Muzyk Marek, Warsaw University of Technology, Poland
Neugebauer Jörg, Max-Planck-Institute for Iron Research, Düsseldorf, Germany
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Paidar Vaclav, Academy of Sciences, Praha, Czech Republic
Parliński Krzysztof, Institute of Nuclear Physics PAS, Cracow, Poland
Pawlik Grzegorz, Wrocław University of Technology, Poland
Pedersen Andreas, University of Iceland, Reykjavik, Iceland
Peisert Jerzy, Wrocław University of Technology, Poland
Piechota Jacek, University of Warsaw, Poland
Pietrzyk Maciej, AGH University of Science and Technology, Cracow, Poland
Puisto Antti, Lappeenranta University of Technology, Finland
Radny Marian, University of Newcastle, Callaghan, Australia
Reuter Karsten, Fritz-Haber-Institut Berlin, Germany
Rogowska Jolanta, University of Wrocław, Poland
Scharoch Paweł, Wrocław University of Technology, Poland
Sestak Peter, Brno University of Technology, Czech Republic
Šob Mojmir, Masaryk University Brno, Czech Republic
Spychalski Maciej, Warsaw University of Technology, Poland
Suess Dieter, Vienna University of Technology, Austria

Sutton Adrian P., Imperial College, London, UK
Szlagowska Justyna, Warsaw University of Technology, Poland
Tokar Vasyl, IPCMS-GEMM, UMR 7504 CNRS Strasbourg, France
Wachowicz Elwira, University of Wrocław, Poland
Wahnström Göran, Chalmers University of Technology, Gothenburg, Sweden
Wdowik Urszula D., Pedagogical University Cracow, Poland
Wejrzanowski Tomasz, Warsaw University of Technology, Poland
Willaime François, CEA/Saclay, France
Wolf Dieter, Idaho National Laboratory, USA
Xu Dongsheng, Chinese Academy of Sciences, Shenyang, China
Yardley Victoria, Tohoku University, Sendai, Japan
Yip Sidney, Massachusetts Institute of Technology, Cambridge, USA
Zelený Martin, Masaryk University Brno, Czech Republic

4.2.2 Report on the Workshop “Progress in ab initio modelling of biomolecules: methods and applications

Progress in *ab initio* modelling of biomolecules: methods and applications

Lorentz Center, Leiden University, Leiden, NL

July 3-7, 2006

Sponsored by the Lorentz Center and Psi-k ESF Programme

Organizers

Francesco Buda, Leiden Institute of Chemistry, Leiden University, NL

Paolo Carloni, International School for Advanced Studies, Trieste, Italy

Ursula Roethlisberger, EPFL, Lausanne, Switzerland

Web page : www.lorentzcenter.nl/lc/web/2006/197/info.php3?wsid=197

Summary

The workshop focused on the recent developments in the computational study of structure, dynamics and function of biomolecules. Particular attention was devoted to Density Functional Theory based methods providing an effective and accurate inclusion of the electronic structure in the simulation. The main goal of the workshop was to bring together researchers active in this field for exchanging expertise and ideas on how to deal with the multi-scale problems encountered in the simulation of macromolecules and bio-systems. The workshop has been a stimulating event for all the participants and an opportunity for young researchers to show their results in an international setting. One of the strategies for the next future which were underlined during this workshop was the need to further develop hybrid methods combining approaches with different degree of accuracy from quantum mechanics to coarse grain simulations. The workshop was held at the Lorentz Center of the Leiden University and it has been funded by the Lorentz Center and by the Psi-k ESF Programme.

Scientific content and discussion

Computer simulation methods based on first principles calculations are increasingly being used to study the structure, dynamics and function of biomolecules. Specifically, the explicit inclusion of the evolving electronic structure (for example by means of Density Functional Theory) in the simulation allows for a proper description of e.g. enzymatic reactions and drugs activity. The primary aim of the workshop was to bring together several researchers active in this field with the double purpose of (i) exchanging the expertise and the progress done in the last few years, and (ii) to envisage strategies for the next future which can increase the effectiveness and scientific impact of this field of research.

While a considerable effort in computational life science is focused on gene sequence and on a mesoscopic description of protein-protein interaction, a detailed microscopic understanding of the activity of biomolecules plays an important role and represents a major scientific and computational challenge. The *ab initio* simulations constitute a crucial tool, complementary to experiments, to elucidate at the atomic level the interplay between microscopic structure and function of a biological system. Such detailed understanding can be a useful ingredient in e.g. drug design, and can have also an impact on optoelectronic, enabling for instance the design of biomolecules with properly tuned optical properties by selective mutations.

In this workshop we discussed methodological developments within *ab initio* simulations and recent efforts to broaden the range of applications to more complex systems. There are a number of technical problems in *ab initio* simulations which are not unique to biological applications but are particularly severe and unavoidable there. (i) A serious limitation is the number of atoms in a simulation, which can only cover the central active region of a protein though longer ranged electrostatic and elastic forces are also important. Therefore a large effort has been devoted recently in the development of hybrid methods which include the protein environment around the active site by using a classical force field approach (QM/MM). Linear scaling methods are also being developed to increase the size of the system treated with *ab initio* methods (ii) The correct calculation of hydrogen bonds and Van der Waals interactions, as well as the correct description of spin states in transition metal complexes present throughout biological systems, are particularly sensitive to the precise choice of correlation and exchange functional in the Density Functional Theory method. We have thus also discussed progress done in improved functionals and the comparison with other *ab initio* many body calculations. (iii) Another issue is the time scale of biological processes that are often very slow compared to the atomic motion so that one has to invoke and compute activated processes through complex pathways. Moreover, biological processes take place at room temperature and therefore it is crucial to calculate efficiently free energy barrier and the lowest free energy reaction path. (iv) A final issue discussed during the workshop is the current state-of-the-art in the calculation of excitation energies and in excited-state molecular dynamics simulations. Here is a list of the main topics that were discussed during the workshop:

Drug-DNA interaction
Photo-activated biological processes
Structure/functionality changes induced by mutation
Hybrid methods

Linear scaling methods
Excitation energies and excited-state dynamics
Improved exchange-correlation functionals
Metadynamics and Free energy calculation
Transition path sampling
Simulation and interpretation of spectroscopic probes (e.g. NMR chemical shift)

Assessment of the workshop

The workshop has been successful in creating an opportunity to discuss several outstanding issues in *ab initio* simulations for biomolecules. The program has been organized in such a way to give ample time to discussions which played a key role. There were a total of 33 participants from Finland, Germany, Italy, The Netherlands, Spain, Switzerland, UK, and USA, all of them playing an active role during the workshop. The workshop has been a stimulating event for all the participants and many young scientists had been given the opportunity to present their research in this international setting either as an oral presentation or in the form of a poster. Poster sessions constituted a useful occasion for informal and fruitful discussions. One of the strategies for the next future which were underlined during this workshop was the need to further develop hybrid methods combining approaches with different degree of accuracy from quantum mechanics to coarse grain simulations. The participants clearly enjoyed the workshop both for the scientific aspects as well as for the excellent facilities provided by the Lorentz Center. This workshop would not have been possible without the financial support of the Lorentz Center and the ESF Psi-k program. The organizers are particularly grateful to Martje Kruk and Wies Groeneboer at the Lorentz Center for their help and assistance.

Program

Monday, July 3

9.30-10.00	Registration
10.00-10.10	Opening
10.10-11.00	M. Swart, *Computational Study on the Structure of DNA*
11.00-11.30	Coffee / Tea
11.30-12.20	U. Landman, *Microscopic simulations of macroscopic consequences: fixing the continuum and hybrid methods*
12.30-13.30	Lunch
14.00-15.00	Poster session
15.00-15.50	A. Magistrato, *Understanding Anticancer Drug-DNA Interactions via Molecular Dynamics Simulations*
15.50-16.10	Coffee / Tea
16.10-16.40	C. Gossens, *DNA-Binding of Ruthenium-arene anticancer drugs*
16.40-17.10	A. Karawajczyk, *The Mechanism of the Bleomycin Activity*
17.10-18.30	Wine & cheese party

Tuesday, July 4

9.00-9.50	B. Ensing, *Metadynamics as a Tool for Exploring Free Energy Landscapes of Chemical Reactions*
9.50-10.40	G. Bussi, *Free energy landscapes from combined metadynamics and parallel tempering*
10.40-11.10	Coffee / Tea
11.10-12.00	U. Roehrig, *Amyloid Fibril Formation Studied by Molecular Dynamics and Metadynamics Simulations*
12.30-13.30	Lunch
14.00-14.50	S. Raugei, *A Quantum chemistry study of the redox potential and electronic properties of Rubredoxin*
14.50-15.40	E.J. Meijer, *Structure, dynamics and proton transfer in aqueous ion solutions*
15:40-16:10	Coffee / Tea
16:10-17:00	C. Rovira, *Substrate distortion in the Michaelis complexes of glycoside hydrolases*

Wednesday, July 5

9.00-9.50	C. Filippi, *Excitations in (bio)molecules from quantum Monte Carlo*
9.50-10.40	V. Tozzini, *Variation of color and photodynamics within the family of intrinsically fluorescent proteins*
10.40-11.10	Coffee / Tea
11.10-11.40	M. Guglielmi, *Microsolvation effects on protonated tryptophan*
11.40-12.20	E. Lenders, *Protonation of the chromophore in the photoactive yellow protein*
12.30-13.30	Lunch
15.00-15.30	L. Guidoni, *Absorption Spectra in Solution by Quantum Monte Carlo/ Molecular Mechanics (QMC/MM)*
15.30-16.00	M. Zaccheddu, *Green Flourescent Protein: Shedding Light with Quantum Monte Carlo*
16.00-16.20	Coffee / Tea
16.30	Departure to Conference Dinner (BBQ at the beach starting at 18.00)

Thursday, July 6

9.00-9.50	J. Ireta, *Why helices are right-handed and beta-sheets left-handed? : Insight from first-principles calculations.*
9.50-10.40	L. Colombi Ciacchi, *Selective inhibition of CDK proteins by small ligands: the roles of hydrogen bonding, solvation, and dispersion forces*
10.40-11.00	Coffee / Tea
11.00-11.50	C. Molteni, *Mutagenesis computer experiments on ligand gated ion channels*
11.50-12.30	P. Bolhuis, *Transition path sampling of biomolecular processes using ab initio and classical molecular dynamics*
12.30-13.30	Lunch
14.30-15.20	D. Sebastiani, *Ab-initio modeling of environmental packing effects of biomolecules in their environment: solvation and crystal NMR chemical shift*
15.20-16.00	J. Neugebauer, *Environmental Effects on Molecular Properties Modeled by Frozen-Density Embedding*
16.00-16.30	Coffee / Tea
16.30-17.00	I-Chun Lin,
17.00-17.30	P. Wawrzyniak, *A DFT study of the special pair in Bacterial Reaction Center: Effect of histidine protonation state on the chemical shift*

Friday, July 7

9.00-9.50	F. Krajewski, *A new stochastic linear scaling electronic structure method and accurate sampling with noisy forces*
9.50-10.30	G. Canters, *Theoretical analysis of structure and function of Cu containing redox proteins: azurin and quercetinase*
10.30-11.00	Coffee / Tea
11.00-11.50	J. VandeVondele, *A combination of linear scaling and QM/MM techniques for the study of electron transfer reactions in biological systems and solar cells*
11.50-12.30	Concluding remarks

List of participants

Peter Bolhuis (Amsterdam, Netherlands)
Francesco Buda (Leiden, Netherlands)
Giovanni Bussi (Lugano, Switzerland)
Gerard Canters (Leiden, Netherlands)
Paolo Carloni (Trieste, Italy)
Lucio Colombi Ciacchi (Freiburg, Germany)
Ivan Degtyarenko (Espoo, Finland)
Bernd Ensing (Lugano, Switzerland)
Claudia Filippi (Leiden, Netherlands)
Christian Gossens (Lausanne, Switzerland)
Matteo Guglielmi (Lausanne, Switzerland)
Leonardo Guidoni (Roma, Italy)
Joel Ireta (Berlin, Germany)
Anna Karawajczyk (Leiden, Netherlands)
Florian Krajewski (Lugano, Switzerland)
Uzi Landman (Atlanta, Georgia, United States)
Elske Leenders (Amsterdam, Netherlands)
I-Chun Lin (Lausanne, Switzerland)
Alessandra Magistrato (Trieste, Italy)
Evert Jan Meijer (Amsterdam, Netherlands)
Carla Molteni (London, United Kingdom)
Johannes Neugebauer (Zurich, Switzerland)
Simone Raugei (Trieste, Italy)
Arturo Robertazzi (Trieste, Italy)
Ute Roehrig (Rome, Italy)
Ursula Roethlisberger (Lausanne, Switzerland)
Carme Rovira (Barcelona, Spain)
Daniel Sebastiani (Mainz, Germany)
Marcel Swart (Girona, Spain)
Valentina Tozzini (Pisa, Italy)
Joost Vandevondele (Zurich, Switzerland)
Piotr Wawrzyniak (Leiden, Netherlands)
Maurizio Zaccheddu (Leiden, Netherlands)

5 Psi-k Training

5.1 Psi-k Training Graduate School

Bristol University, U. K.

25-31 March 2007

Scientific Summary

This Graduate School is an activity of the Psi-k Training Programme in the EU-funded 'Series of Events' Marie Curie Conferences and Training Courses. - The other two activities are Hands-on Tutorials and Summer Schools. - The Bristol University Graduate School is aimed towards giving masters and beginning PhD students (1) an understanding of the theories underlying electronic structure calculations; (2) hands-on experience in electronic structure calculation codes; (3) a perspective how these methods are used in state of the art research.

The Graduate School is motivated by

- The importance of electronic structure calculations of materials at the nano scale (such as catalysis, fuel cell research, magnetic recording and spin electronics, semiconductor technology, pharmacy etc.), has resulted in a sharp increase in the number of European groups (including industrial groups) starting with electronic structure calculations; these groups, however, do not have the optimal knowledge expertise for adequate training of their PhD students.
- The field of electronic structure calculations has become so broad that single institutions do not have the expertise to provide training of the entire field; only at the European level this expertise exists.
- The gap between education provided by university lectures and the much higher level of science in real research and at international workshops and conferences is steadily increasing.
- The combined training and research program, will give young researcher the opportunity to develop in the European Psi-k network at a very early stage of their career.

Abstract

The Psi-k Graduate School aims to provide an understanding of electronic structure calculations, hands-on experience in running a variety of codes and their usefulness in state of the art research.

Meeting Programme

The combined theory-hands-on Graduate School on electronic structure methods will take place at Burwalls and the Physics Department in Bristol from Sunday March 25 until Saturday March 31, 2007. There will be 20 lectures over 6 days, 10 lectures on theory and 10 lectures on electronic structure methods. The rest is all hands-on experience with relevant codes. Of the 10 lectures on theory there would be 5 on Density Functional Theory (DFT), 3 on many body theory (MBT) and 2 on dynamical mean field theory (DMFT). Of the 10 lectures on methods we will give a bird's eye view of 5 methods: plane-wave methods (PW), the full potential local orbital method (FPLO), linear augmented plane waves (LAPW), the linearized muffin tin orbital method (LMTO) and the Korringa-Kohn-Rostocker (KKR) method, each introduced by two lectures followed by hands on experience with a modern state of the art code.

Speakers/Participants

Lecturers:

Density Functional Theory (including fundamentals of Time Dependent Density Functional Theory); 3 hours (**Hardy Gross**)
Many Body Perturbation Theory; 3 hours (**Rex Godby**)
Bethe-Salpheter Equation and Time Dependent Density Functional Theory; 1 hour (**Francesco Sottile**)
Dynamical Mean Field Theory; 3 hours (**Misha Katsnelson**)

PW 2 hours (**Xavier Gonze**)
FPLO 2 hours (**Manuel Richter**)
LAPW 2 hours (**Peter Blaha**)
LMTO 2 hours (**Ole Andersen**)
KKR 2 hours (**Hubert Ebert**)

Tutors: **James Annett, Dzidka Szotek, Martin Lüders, Peter Hogg and Walter Temmerman**.

Participants:

The school will accommodate about 25-30 enthusiastic students at the start of their Ph.D., or at Master's level. For participants from EU countries most living costs will be paid, although a small workshop fee will be charged. Some participants may be eligible for the fee to be reimbursed after completion of the workshop.

Applications for participation and further details can be obtained by email to *tracie.anderson@bristol.ac.uk*.

5.2 The Uppsala Graduate School on Modern Electronic Structure Theory

Venue : Angstrom Laboratory, Uppsala University, Sweden

December 11 - 18, 2006

The Uppsala graduate school on Modern electronic structure theory, for chemists and physicists will be held to give a basic theoretical background in electronic structure theory, and to provide a hands-on experience for the calculations of materials properties with general applications in solid state physics and chemistry. These properties involve phase stability, structural properties, optical properties, magnetism, and correlated electron behaviour. The teaching will be done as a mixture of regular lectures combined with tutorials, and will be given by world leading experts in the field. The tutorials involve learning the fundamental and practical aspects of electronic structure methods such as the exact muffin-tin orbital method (EMTO), the linear combination of atomic orbital method (LCAO) and the LDA+U method as implemented in the linear combination of plane wave method (LAPW). The Nobel prize lectures will be given in Uppsala during this week and a break in the programme will be made to enable the school attendants to listen to these lectures.

Lecturers:

Dr. R. Ahuja, Uppsala University, Sweden
Dr. A. Delin, Royal Institute of Technology, Stockholm, Sweden
Prof. M. Katsnelson, Institute for Molecules and Materials, Radboud
University Nijmegen, Nijmegen, The Netherlands
Prof. P. Mohn, Center for Computational Materials Science, Vienna, Austria
Prof. M. Richter, IFW Dresden, Germany
Dr. A. Shick, Institute of Physics, ASCR, Prague , Czech Republic
Dr. L. Vitos, Royal Institute of Technology, Stockholm, Sweden
Dr. P.M. Oppeneer, Dept. of Physics, Uppsala University, Sweden

Expected background for the course: quantum physics, atomic and molecular physics and solid state physics.

Registration, Conference fee and scholarships:

The conference fee is 250 Euro. A limited number of scholarships will be available for young researchers to cover travel, hotel and living expenses. Registration is done via email to Dr. Biplab Sanyal (Biplab.Sanyal@fysik.uu.se).

Deadline for the registration is November 30, 2006.

More details are available in the following website:

http://www.fysik.uu.se/cmt/

6 News from UK's CCP9 Programme

UK's Collaborative Computational Project 9 (CCP9) on "Computational Studies of the Electronic Structure of Solids"

6.1 Report on the KKR Workshop

KKR Workshop: new developments, applications and collaborations

October 20-22, 2006

Burwalls (University of Bristol, Bristol UK)

Summary

The KKR method is a well established versatile tool for calculating the electronic structure of a wide variety of systems, including periodic solids, disordered alloys, surfaces and nanostructures. In addition it supplies a very efficient and powerful basis for the calculation of spectroscopic properties and the inclusion of many-body effects. The Bristol workshop brought together the leading experts in KKR calculations throughout Europe, together with their students and postdocs and selected invited participants from USA and Japan. Recent advances in the theory of disordered alloys, such as the non-local coherent potential approximation (NLCPA), local self-interaction correction (L-SIC), and first principles many-body dynamical mean field theory (DMFT), were among the topics discussed. Physical problems ranging from magnetism in bulk materials to, electronic structure of surfaces, electronic transport, and ab initio modelling of spectroscopy in pump-probe experiments and scanning tunnelling microscopy.

Scientific content of the workshop

The workshop was opened by H. Ebert, who described the recent development of KKR LDA+U and KKR DMFT methods for first principles many-body theory. He showed that the LDA+U formalism was possible with a relatively straightforward extension of the KKR t-matrices, to include Hubbard U and exchange integrals J on a single site. The KKR DMFT formalism is more complex to implement, involving construction of a suitable single-site self-energy, evaluated within the FLEX approximation. Different schemes of analytic continuation of complex frequencies were discussed. Results were presented for spin and orbital magnetic moments in pure fe Ni Co and for Fe-Ni alloys. Spin dependent photoemission spectra for Ni(001) were also presented.

J. Staunton showed how the disordered local moment model (DLM) can be used to describe the onset of magnetic order and the paramagnetic susceptibility of metals. Using the local Self Interaction Correction (L-SIC) to remove the spurious self energy associated with electrons interacting with themselves that the LSDA includes, she demonstrated how the magnetism of metals with strongly correlated electrons can also be treated using the DLM picture. Prof. Staunton illustrated the approach by describing a study of heavy rare earth systems which was interpreted in terms of an ab-initio RKKY interaction.

A. Ernst presented a the use of multiple scattering theory for spintronics applications. He showed that convergence problems with the KKR method at high angular momenta values, can be corrected by use of the Lloyd formula for the density of states. Corrections to the atomic sphere approximation were compared, including the atomic sphere approximation (ASA), muffin tin approximation (MTA) and full-charge approximation (FCDA). Calculation of exchange integrals and spin-waves were discussed, and results were shown for the magnetization and critical temperature in RPA or mean field theory for Co and Fe. The extension of self-interaction-correction (SIC) to multiple scattering theory was also described. Calculated critical temperatures for transition metal oxides were presented, as obtained with the SIC-KKR method.

I. Abrikosov presented the talk of L. Vitos who was unable to attend the workshop. He described the construction of exact muffin-tin orbitals, and their implementation in a CPA formalism for alloys, EMTO-CPA. Results were presented for the elastic constants of the Hume-Rothery alloys Ag-Zn and for the Fe-Si alloys, occurring in the Earth's core. Finally the problems presented by two center expansions of the slope matrix, in cases with semi-core states, and it was shown that a two centre expansion with extra screening spheres was able to give accurate results for a wide range of energies around the muffin tin zero.

The next session focused on the non-local coherent potential approximation, NLCPA, for alloys. This is a cluster generalisation of the CPA which includes nonlocal correlations and hence a description of short-range order. Dr. Rowlands presented an overview of the idea and formalism of the NLCPA both within a tight-binding framework and the KKR framework. The new fully charge self-consistent (SCF)-KKR-NLCPA was also presented. This enables the total energy to be investigated as a function of short-range order, whilst systematically taking into account the charge-correlation (Madelung) contribution missing in the CPA. Dr. Tulip described the formalism for calculating the spectral function within the KKR-NLCPA. The coarse-grained spectral function was calculated by averaging the spectral functions for each NLCPA tile in the Brillouin zone. A new formalism was presented in which the Green function is split into cluster diagonal and cluster off diagonal components which allows the calculation of the spectral function at specific k-space points. G. Batt described a new method for obtaining a fully continuous spectral function within the NLCPA formalism. The key idea is to use different sets of boundary conditions and to combine these together to yield a continuous spectral function and Fermi surface, unlike in standard NLCPA where both have unphysical discontinuities for small cluser sizes. Dr. D. Ködderitzsch described the KKR-NLCPA formalism in a fully relativistic implementation. This requires an efficient implementation which uses symmetry in the **k**-space coarse-graining procedure and several means to stabilise the NLCPA-algorithm. Results were presented for an application to the alloy system $\mathrm{Fe}_x\mathrm{Pt}_{1-x}$.

The following session concerned magnetism. J. Minar described how the fully relativistic spin-polarized KKR method has been used to study the magnetic and spectroscopic properties for supported alloy clusters. For a variety of clusters supported on various transition metal substrates it was shown that the magnetic properties depend on several different parameters such as substrate type, cluster size as well as shape etc. The magnetic coupling constants of these clusters were calculated and used within a Monte Carlo simulations in order to obtain temperature-dependent magnetic properties. S. Mankovsy presented the results of a theoretical study of the high-field magnetic susceptibility of ferromagnetic metals and alloys. The approach presented has been applied for calculations of the high-field susceptibility of some 3d transition metals (Fe, Ni, Co) and alloys ($\mathrm{Fe}_x\mathrm{Co}_{1-x}$, $\mathrm{Ni}_x\mathrm{Cu}_{1-x}$) and all results of the calculations are found to be in good agreement with experiment. In the case of $\mathrm{Fe}_x\mathrm{Co}_{1-x}$ alloy the high-field susceptibility was found to be strongly dependent on the ordering of the system. S. Lounis described non-collinear magnetism in 3d nanostructures on surfaces, focusing on small magnetic $3d$ clusters on Ni(001), on *fcc* Fe/Cu(001) and on Ni(111). The size and orientation of the local moments and the stabilization of noncollinear magnetic solutions were investigated. While clusters of Fe, Co, Ni atoms are magnetically collinear, noncollinear magnetic coupling is expected for Cr and Mn clusters on surfaces of elemental ferromagnets. P. Mavropoulos described two methods to obtain temperature dependence of magnetization in half metals. The first approach, uses the full-potential linearized augmented plane-wave (FLAPW) method to deduce magnon dispersion relations. Fourier transformation yields the real-space exchange constants J_{ij} of the Heisenberg model from which we find the thermodynamic quantities, such as the magnetization curve $M(T)$, susceptibility and the Curie temperature T_C. The second approach is based on the disordered local moment (DLM) state $\mathrm{NiMn}^{\uparrow}_{1-x}\mathrm{Mn}^{\downarrow}_{x}\mathrm{Sb}$, with $0 \leq x \leq 0.5$ representing the temperature range $0 \leq T \leq T_C$. This approach describes the system at $T > 0$ in a mean-field manner. The DLM calculations are done within the coherent-potential approximation (CPA) and the Korringa-Kohn-Rostoker full-potential Green function method. In the last talk of this section, R. Zeller described the use of the Lloyd formula, which is an important concept in the KKR Green function method since it directly gives the integrated density of states with a considerably better angular-momentum convergence than the the truncated multiple-scattering representation of the Green function. It was shown how the disadvantages of the Lloyd formula can be avoided in numerical applications and that rather accurate results can be obtained. It is also shown how the charge density obtained from the Green function can be made consistent with the Fermi level obtained from the Lloyd formula. These points were illustrated by calculations for the temperature dependence of the Fermi level in GaN. and the magnetic moments of zincblende CrAs, dilute $\mathrm{Mn}_x\mathrm{Ga}_{1-x}\mathrm{N}$ and a FeSi multilayer.

I. Abrikosov presented theoretical models used for the calculation of core-level shifts, including the initial state, transition state, and final state. He discussed core level shifts and Auger energy shifts in the bulk of random alloys, and disorder broadening of core spectral lines. He concluded with comments on implications for the structure of thin film alloys, such as $\mathrm{Ag}_{50}\mathrm{Pd}_{50}$ alloy deposited at Ru (0001).

E. Bruno described the ab initio theory and simulation of metallic alloys within the Charge Excesses Functional Theory - Monte Carlo Method (CEF-MC). He showed that CEF theory constitutes a simple, very realistic model for the energetics of metallic alloys. It is a coarse grained density functional in which the full density is replaced by effective charges q_i. The resulting CEF defines an configurational Hamiltonian that includes an infinite series of many-body interactions, for which no truncation for the range of interactions is necessary. A Monte Carlo-CEF algorithm allows for the study of order-disorder phase transitions. Order-disorder phase transitions have been reviewed as charge-monodisperse to charge-polydisperse transitions

The session on self-interaction corrected DFT (SIC) featured talks by W. Temmerman, Z.Szotek, M. Lüders and M. Toyoda. W. Temmerman showed that SIC-LSD leads to an useful definition of valency in strongly interacting systems, important examples of which include systems such as Ce, LiNiO_2, Fe in MgO, the rare earths, the actinides and Mn in GaAs and ZnO. Z. Szotek discussed energy gaps calculated using self-interaction corrected local spin density (LSD) approximation. Results were presented for rare gas solids, transition metal oxides, parent compounds of high temperature superconductors, and Europium chalcogenides. The SIC-LSD energy gaps were compared to such approaches as LSD, GGA, LDA+U and hybrid functionals. M. Lüders described the two ways in which SIC can be implemented in the KKR method, namely local SIC and Pseudo-SIC. In particular the differences and similarities in the technical implementation, as well as in the philosophy of the applications were described. M. Toyoda investigated the electronic structure and magnetic properties of dilute magnetic semiconductors from first principles calculations in the self-interaction-corrected local density approximation (LDA+SIC). The implementation is based on the pseudopotential-like self-interaction correction scheme (pseudo-SIC) implemented with the Korringa-Kohn-Rostocker coherent potential approximation (KKR-CPA) method. It was found that the electronic structures calculated by LDA+SIC are in better agreement with the photoemission spectrum than those calculated by LDA. Magnetic properties and Curie temperature calculated by LDA+SIC also differ from those calculated by LDA. For example, showing enhancement of ferromagnetic interactions between the Mn ions in GaMnAs.

The Sunday morning session focussed on surfaces and nanostructures. I. Mertig started the session with the theory of tunnel magnetoresistance in Fe/MgO/Fe multiyayers with amorphous Fe electrodes. She described the structure models and electronic structure of amorphous Fe, and then TMR tunnelling with such amorphous electrodes, compared to free electron leads. It was found that a crystalline Fe layer is important to act as a spin filter and so giant TMR arises from by the matching of crystalline Fe to the MgO barrier. W. Hofer described calculations of high resolution tunnelling microscopy within a multiple scattering formalism. Multiple electron scattering in a vacuum barrier are obtained using real-space single-electron wavefunctions for the separate surfaces. The Green functions in the vacuum barriers are calculated to first order, showing that the zero-order current is equal to the usual Bardeen approach only in the limit of zero bias and derive the modifications in the finite bias regime. A first-principles formulation for the energy of interaction between the two surfaces, is shown to be proportional to the tunnelling current and hence the tunnelling current can in principle be computed to any order in the Dyson expansion. L. Szunyogh discussed the size dependent Kondo effect under the assumption that a magnetic impurity near a surface experiences spin-orbit induced anisotropy. The splitting of the states of a Kondo impurity interacting with the neighboring host atoms is calculated via perturbation technique up to second order in the exchange coupling strength. Two models were investigated, namely, an impurity subject to a host-induced magnetic anisotropy and an impurity with a strong local spin-orbit coupling. It is found that in both cases the anisotropy energy is an oscillating function of the distance d from the surface. The numerical estimates suggests that second mechanism gives rise to an anisotropy energy of the desired order of magnitude whereas the first mechanism seems to be of negligible importance. S. Shallcross described the calculation of exchange integrals using an expansion based upon the Lloyd formula. In particular the RKKY interaction between moments was derived in an asymptotic expansion from this formula.

In the final session of the workshop, A. Vernes described calculation of pump-probe spectroscopy within KKR. The Kubo response theory was extended by linearizing the density of both pump- and probe-excited states and neglecting the overlap between the femtosecond pulses. The time-dependent zeroth order dynamic conductivity as obtained by means of the spin-polarized relativistic screened Korringa-Kohn-Rostoker method for fcc Ni(100) predicts a relatively fast demagnetization process over 100 fs after the impact of the probe pulse, which is in a reasonably good agreement with available experimental data. Calculations for Co/Pt(111) and Pt/Co/Pt(111) systems show that the layer-resolved demagnetization time is not necessarily dominated by the demagnetization time of the ferromagnetic Co layer. B. Lazarovitis described calculations of artificial atomic structures, notably quantum corrals. In particular the density of states was obtained for magnetic adatoms, leading to spin-dependent properties, and surface states which can be compared with the STM dI/dV experiments. M. Stocks described the LSMS multiple scattering code, and its applications to various nanostructures as carried out at Oak Rigde National Laboratory USA. Finally, L. Udvardi described the calculation of relativistic exchange interactions. A relativistic extension of the magnetic torque theorem was combined with the Lloyd formula for the band energy to obtain closed formulas for various derivatives of the free energy. The resulting magnetic anisotropy energies were presented for thin Fe layers on a range of non-magnetic transition metal surfaces. The Dzyaloshinsky-Moria interaction was shown to dominate and to play the key role in domain formation.

Assessment of results and impact

The KKR method is a versatile computational tool for a wide range of electronic structure problems. The workshop has highlighted this versatility in terms of the range of applications, such as nanostructures, spectroscopy, surface physics, and spintronics. The KKR method is also evolving and expanding its applicability with a number of exciting new developments, such as the improved cluster methods for alloys (NLCPA and CEF-QMC), and with novel many-body methods for strongly interacting systems (eg L-SIC and DMFT). The workshop provided a timely opportunity for all the main practitioners of the KKR method in Europe to meet and exchange ideas on these new devlopments. The workshop was attended by a number of PhD students, postdocs and young researchers, who will continue these developments in the future.

Final Program of Meeting

October 20

Arrival, Registration and Welcoming reception

October 21

8:30-9:00	H.Ebert	*Combination of the LDA+U and DMFT methods with KKR*
9:00-9:30	J.B.Staunton	*DLM and the LSIC: a description of magnetism in the heavy rare earths*
9:30-10:00	A.Ernst	*GW with KKR*
10:00-10:30	I. Abrikosov	*The Exact Muffin-Tin Orbitals-CPA method and applications*
10:30-11:00	Coffee	
11:00-11:30	D.A. Rowlands	*KKR nonlocal coherent-potential approximation*
11:30-11:50	P.R. Tulip	*First-principles spectral function in the KKR-NLCPA*
11:50-12:10	G.Batt	*Fermi Surfaces of Random Alloys*
12:10-12:30	D.Ködderitzsch	*An efficient and fully relativistic implementation of the KKR-NLCPA making use of symmetry*
12:30-1:30	Lunch	
1:30-1:50	J. Minar	*Magnetic properties of deposited transition metal clusters*
1:50-2:10	S.Mankovskyy	*Spin and orbital high-field susceptibility of ferromagnetic alloys calculated using the SPR-KKR*
2:10-2:30	S.Lounis	*Non-Collinear KKR Green function method: application to 3D nanostructures on surfaces*
2:30-2:50	P.Mavropolous	*Temperature dependence of spin polarization of half-metallic ferromagnets: an approach from first principles*
2:50-3:10	break	

3:00-3:20	R.Zeller	*The Lloyd Formula*
3:20-3:40	I.Abrikosov	*Core Level Spectroscopy in Alloys*
3:40-4:00	E.Bruno	*First-principles calculations of phase diagrams in metallic alloys through the CEF-QMC method*
4:00-4:30	Tea	
4:30-5:00	W.E.Temmerman	*Valency and SIC*
5:00-5:30	Z.Szotek	*Gaps and SIC*
5:30-6:00	M.Lüders	*Local SIC*
6:00-6:30	M. Toyoda	*Electronic Structure of Dilute Magnetic Semiconductors from LDA+SIC calculations*

October 22

9:00-9:30	I. Mertig	*Tunnelling magnetoresistance with amorphous electrodes for Fe/MgO/Fe*
9:30-10:00	W. Hofer	*Simulation of high-resolution tunnelling microscopy and spectroscopy*
10:00-10:30	L. Szunyogh	*Kondo Impurity near a Surface*
10:30-10:50	S. Shallcross	*Asypmtotics of exchange integrals*
10:50-11:20	Coffee	
11:20-11:40	A.Vernes	*Ab initio description of pump-probe spectroscopy using KKR*
11:40-12:00	B. Lazarovits	*Quantum Corrals*
12:00-12:30	G.M.Stocks	*LSMS*
12:30-1:00	L.Udvardi	*Relativistic Exchange Interactions*

Posters

H. Akai and M. Ogura	*Magnetic properties of* $La_{1-x}Ca_xMnO_3$
M. Ogura	*Magnetic properties of 3d pyrite-type mixed crystals calculated by the full potential KKR-CPA method*
S. Gallego	*Magnetic anisotropy of free and capped Co/Ru(0001): strain and stacking*
P. Mavropoulos	*Complex magnetic order and transition to half metallicity in Mn-doped* Fe_3Si

Abstracts

The DLM and the LSIC: a description of magnetism in strongly correlated electron systems.

I.Hughes[1], M.Däne[2], A.Ernst[3], W. Hergert[2], M.Lüders[4], J.Poulter[5], J.B.Staunton[1], Z. Szotek[4], W.M.Temmerman[4]

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[2] Martin-Luther-Universität, Halle, Germany.
[3] Max Planck Institut für Mikrostrukturphysik, Halle, Germany.
[4]Daresbury Laboratory, U.K.
[5]Mahidol University, Thailand

We investigate the onset of magnetic order in materials using a 'first-principles' theory of finite temperature metallic magnetism, in which the effects of strong electron correlations are included. Thermally induced spin fluctuations are treated within a mean-field 'disordered local moment' (DLM) picture [1] and the Self-Interaction Correction (SIC) is used to remove the spurious energy associated with electrons interacting with themselves that is inherent in the LSDA [2]. The scheme is implemented using the Korringa-Kohn-Rostoker (KKR) multiple scattering method. We describe our first applications to rare earth systems and interpret our results in the language of a first-principles RKKY interaction.

1. B.L. Gyorffy et al., J. Phys. F 15, 1337 (1985); J.B. Staunton et al., J. Phys. F 15, 1387 (1985).
2. M. Lüders et al., Phys. Rev. B 71, 205109 (2005).

Multiple-scattering theory for spintronics

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Multiple-scattering theory (MTS) is a very efficient technique for calculating the electronic properties of an assembly of atoms. Combined with the coherent potential approximation this method can be used as well for studying the electronic structure of alloys and pseudo-alloys. The MTS provides the explicit Green function, which can be used in many applications such as spectroscopy, transport and many-body physics. The main application field of the multiple-scattering theory are mostly metallic systems because semiconductors and insulators can not be correctly described in frame of the local density approximation (LDA). However, even within the LDA the most of existing implementations of the MST can not reproduce results obtained by conventional basis methods. The main reason are the construction and some convergence

properties of the Green function. Here I shall present an approach based on the LDA, which provides an absolutely converged Green function and can be used for half-metals, semiconductors and insulators.

The Exact Muffin-Tin Orbitals-CPA Method and Applications

Levente Vitos[1], Igor Abrikosov[2]
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The implementation of the Exact Muffin-Tin Orbitals (EMTO) theory [1] within the Spherical Cell Approximation [2] is reviewed. We present an investigation of the energy dependence of the EMTO slope matrix in the complex energy plane [3]. We show that a two-center Taylor type expansion of the slope matrix accurately reproduces the exact values within a complex energy range covering the usual energy window used in electronic structure calculations.

Combined with the Coherent Potential Approximation (CPA), the EMTO method [4,5] is found to be suitable for an accurate determination of the electronic structure and total energy of completely random alloys with a substitutional disorder on any kinds of underlying crystal structure. The accuracy of the EMTO-CPA method is demonstrated in the case of cubic and hexagonal Hume-Rothery alloys (CuZn and AgZn) [4,6]. As applications, our recent results obtained for Fe-Si [7] and Fe-Mg [8] are discussed.

[1] O. K. Andersen, O. Jepsen and G. Krier, Lectures on Methods of Electronic Structure Calculation pp. 63-124 (1994). [2] L. Vitos, Phys. Rev. B, 64, 014107, (2001).
[3] A. E. Kissavos, L. Vitos, and I. A. Abrikosov, to be published.
[4] L. Vitos, I. A. Abrikosov, and B. Johansson, Phys. Rev. Lett. 87, 156401 (2001).
[5] L. Vitos, I. A. Abrikosov, and B. Johansson, in Complex Inorganic Solids, Structural, Stability, And Magnetic Properties Of Alloys, eds. A. Meike, P. E. A. Turchi, A. Gonis, K. Rajan, pg. 339 (14), Springer Verlag (2005).
[6] B. Magyari-Kope, L. Vitos, and G. Grimvall, Phys. Rev. B, 70, 052102(4) (2004).
[7] L. Dubrovinsky, et al., Nature, 422, 58-61 (2003).
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Korringa-Kohn-Rostoker nonlocal coherent potential approximation

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The nonlocal coherent-potential approximation (NLCPA) [1] has emerged as a viable method for generalising the CPA by systematically including nonlocal fluctuations about the single-site mean field. In this talk the idea and formalism of the NLCPA is first introduced within the tight-binding framework, and then the KKR-NLCPA [2] formalism described by analogy. Results are presented for the CuNi system, illustrating the effects of nonlocal scattering correlations and short-range order. The combination of the KKR-NLCPA with density functional theory is then described, which results in a fully charge self-consistent (SCF)-KKR-NLCPA method [3] which systematically takes into account the charge-correlation (Madelung) contribution to the total energy missing in the conventional KKR-CPA. An application to the CuZn system is presented, demonstrating how the total energy varies as a function of short-range order.

[1] M. Jarrell and H. R. Krishnamurthy, PRB 63, 125102 (2001)

[2] D. A. Rowlands, J. B. Staunton, B. L. Gyorffy, PRB 67, 115109 (2003)

[3] D. A. Rowlands, A. Ernst, B. L. Gyorffy, J. B. Staunton, PRB 73, 165122 (2006)

Fermi Surfaces of Random alloys

G. M. Batt

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The effects of short range ordering (SRO) on the Fermi Surface for random metallic alloys was discussed. Specifically how well the nonlocal coherent-potential approximation (NLCPA) [1], predicts deviations from the Fermi Surfaces predicted by the single-site mean field theory of the CPA. It was shown that when the difference is large between the two, one sees in the NLCPA the introduction of discontinuities in **k**-space across coarse grained tile boundaries. The consequence is that the resulting Fermi Surface becomes unphysical leading to large fluctuations in the density of states (DOS). A solution [2] to overcome this problem was introduced that uses all possible boundary conditions when transforming between lattice and cluster quantities in the NLCPA. Where all discontinuities are removed, resulting in an improved DOS over the standard implementation of the NLCPA. The procedure was demonstrated for the 2D tight-binding analogue of CuPd. Giving dramatic **k**-dependent corrections to both the topology and lifetime of the Fermi Surface over the CPA. Also preliminary results for the KKR-NLCPA [3] prediction for the Fermi Surface of CuPd were given. Where a small change was observed over the KKR-CPA. It is expected that a combination of the new method [2] with [3] will improve further on this prediction.

[1] M. Jarrell and H. R. Krishnamurthy, PRB 63, 125102 (2001)

[2] G. M. Batt and D. A. Rowlands J. Phys.: Condens. Matter 18 (2006) 11031-11046

[3] P. R. Tulip, J. B. Staunton,D. A. Rowlands, B. L. Gyrffy, E. Bruno, and B. Ginatempo,Phys. Rev. B 73, 205109 (2006)

An efficent and fully relativistic implementation of the KKR-NLCPA

D. Ködderitzsch

Ludwig-Maximilians-Universität München, Department Chemie und Biochemie, Physikalische Chemie

The KKR-method allows to elegantly make use of the coherent-potential approximation (CPA). As a single-site mean field theory the CPA is not able to describe short-range order (e.g. clustering) effects. Recently the so called non-local CPA (NLCPA) has been devised which remedies these shortcomings. We present our fully relativistic extensions of this formalism. Also we devise an efficient implementation which uses symmetry in the **k**-space coarse graining procedure and several means to stabilise the NLCPA-algorithm. Finally we present an application to the alloy system $\mathrm{Fe}_x\mathrm{Pt}_{1-x}$.

Spin and orbital high field susceptibility of ferromagnetic alloys calculated using the SPRKKR

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The results of a theoretical study of the high-field magnetic susceptibility of 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. This approach accounts not only for the Pauli spin and Van Vleck orbital susceptibilities, but also for the spin-orbit induced susceptibility as well as the Landau susceptibility. Calculation of the Landau susceptibility shows that it can give an substantial contribution to the total susceptibility. It can be positive in the case of transition metals and alloys and should be taken into account to get a proper value of magnetic susceptibility.

In contrast to the paramagnetic state, the spin-charge response function as well as contributions to the susceptibility related to a Fermi level shift become important in ferromagnetic materials. Therefore, these effects have been also taken into account in the present calculations of the magnetic susceptibility.

The approach presented has been applied for calculations of the high-field susceptibility of some 3d transition metals (Fe, Ni, Co) and alloys ($\mathrm{Fe}_x\mathrm{Co}_{1-x}$, $\mathrm{Ni}_x\mathrm{Cu}_{1-x}$). All results of the calculations are found in good agreement with experiment. It is shown that the orbital Van Vleck and Landau contributions are dominating terms in the magnetic susceptibility of the pure Fe, Ni and Co ferromagnetic metals.

In the case of $\mathrm{Fe}_x\mathrm{Co}_{1-x}$ alloy the high-field susceptibility was found to be strongly dependent on the ordering of the system. In the Fe reach limit the results of our calculations obtained for disordered alloy are in a very good agreement with experiment, while in the middle region of concentrations the experimental results are in a better agreement with those calculated for partially ordered alloys.

Non-collinear KKR Green function method: Application to 3d nanostructures on surfaces

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Rather few *ab-initio* calculations for small magnetic nanostructures exists, especially when noncollinear magnetic configurations have to be considered. Motivated by this, we developed and extended the Jülich version of the full-potential scalar–relativistic Korringa-Kohn-Rostoker (KKR) Green–function code to treat noncollinear magnetic nanostructures on surfaces. We focus on small magnetic $3d$ clusters on Ni(001), on *fcc* Fe/Cu(001) and on Ni(111). The size and orientation of the local moments and moreover the stabilization of noncollinear magnetic solutions are investigated. While clusters of Fe, Co, Ni atoms are magnetically collinear, noncollinear magnetic coupling is expected for Cr and Mn clusters on surfaces of elemental ferromagnets.

The origin of the noncollinear states is frustration, *i.e.* the competition of the antiferromagnetic exchange coupling among the Cr or Mn atoms with the antiferromagnetic (for Cr) or ferromagnetic (for Mn) exchange coupling between the impurities and the substrate.

For the Ni(001) surface, we find that Cr and Mn first-neighbouring dimers show noncollinear behavior nearly degenerate with the most stable collinear configuration. Increasing the distance between the dimer atoms leads to a similar behavior as the single impurities. In the case of fcc Fe surface, the exchange interaction with the impurities is stronger leading then to the formation of new complex magnetic configurations. The Cr-trimer, tetramer and pentamer all prefer noncollinear magnetic coupling. For the Ni(111) surface, we examine the Cr- and Mn-trimer, which shows the well-known triangular frustration.

Finally, we compare some of the ab-initio results to the results for a classical Heisenberg model, where the exchange constants were fitted to total energy results of the collinear state; the agreement is sometimes surprisingly good, in other cases it fails, however.

Temperature dependence of spin polarization in half-metallic ferromagnets: an approach from first principles

Ph. Mavropoulos, M. Ležaić, and S. Blügel
Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany

Half-metallic ferromagnets (HMF) are ferromagnetic metallic compounds showing, under ideal circumstances, e.g. at zero temperature and no structural disorder, a spin-polarization P of 100% at the Fermi level. This makes them, at least hypothetically, ideal candidates for spintronics applications. However, it is also clear that the ideal half-metallic property ($P = 100\%$) may not be realized at elevated temperatures. Combining first-principles calculations with a Monte Carlo method, we investigate the effect of temperature on the band gap of HMF. In particular, we examine HMF which contain more than one magnetic atom in the unit cell, and describe the mechanisms which lead to the drop of polarization at elevated temperatures.

We follow two approaches to the excited magnetic states. The first approach is based on the full-potential linearized augmented plane-wave (FLAPW) method[1]. Using the force theorem we deduce magnon dispersion relations. A subsequent Fourier transformation yields the real-space exchange constants J_{ij} of the Heisenberg model. We use a Monte Carlo method to find the thermodynamic quantities, such as the magnetization curve $M(T)$, susceptibility and the Curie temperature T_C. The second approach is based on the disordered local moment (DLM) state $\mathrm{NiMn}^{\uparrow}_{1-x}\mathrm{Mn}^{\downarrow}_{x}\mathrm{Sb}$, with $0 \leq x \leq 0.5$ representing the temperature range $0 \leq T \leq T_C$. This approach describes the system at $T > 0$ in a mean-field manner. The DLM calculations are done within the coherent-potential approximation (CPA) and the Korringa-Kohn-Rostoker full-potential Green function method[2].

For multicomponent HMF we cannot confirm the proposed model which assumes that $P(T) \sim M(T)$ [3]. The presence of different magnetic components can, in principle, lead to a drop of the spin-polarization at $T > 0$ which is much faster than the drop of magnetization in these systems. This effect can be quite drastic and depends largely on the strength of the hybridization among the components [4]. We describe the effects of temperature in more detail for the compounds NiMnSb and $\mathrm{Co_2MnSi}$.

[1] The `FLEUR` code, http://www.flapw.de

[2] The SPR-TB-KKR package, H. Ebert and R. Zeller,
http://olymp.cup.uni-muenchen.de/ak/ebert/SPR-TB-KKR

[3] R. Skomski and P. A. Dowben, Europhys. Lett. **58**, 544 (2002)

[4] M. Ležaić, Ph. Mavropoulos, J. Enkovaara, G. Bihlmayer, and S. Blügel, Phys. Rev. Lett. **97**, 026404 (2006)

The Lloyd formula

Rudolf Zeller
Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich

The Lloyd formula is an important concept in the KKR Green function method since it directly gives the integrated density of states with a considerably better angular-momentum convergence than the one obtained by the use of the truncated multiple-scattering representation of the Green function. A disadvantage of the Lloyd formula is its dependence on multivalued imaginary parts of logarithms of complex arguments. It is shown how this difficulty can be avoided in numerical applications and that rather accurate results can be obtained as illustrated by calculations for the temperature dependence of the Fermi level in GaN. It is also shown how the charge density obtained from the Green function can be made consistent with the Fermi level obtained from the Lloyd formula. The consistency, which is achieved by renormalizing the Green function at each point of the complex energy charge-density integration contour, is important, e. g. in spintronic materials, where it leads to integer moments in ferromagnetic half metals and to properly aligned energetic states in metal-semiconductor systems as illustrated by density-functional calculations for zincblende CrAs, dilute $\mathrm{Mn}_x\mathrm{Ga}_{1-x}\mathrm{N}$ and a FeSi multilayer.

Core-Level Spectroscopy in Alloys

I.A. Abrikosov

Department of Physics, Chemistry and Biology, Linkping University, SE-581 83 Linkping, Sweden

We show that core-level binding energy shifts (CLS) can be reliably calculated within Density-functional theory [1]. The scheme includes both the initial (electron energy eigenvalue) as well as final state (relaxation due to core-hole screening) effects in the same framework. The results include CLS as a function of composition in substitutional random bulk [2,3] and surface alloys [4]. Sensitivity of the CLS to the local chemical environment in the bulk and at the surface is demonstrated [5]. A possibility to use the CLS for structural determination is discussed. Finally, an extension of the model is made for Auger kinetic energy shift calculations [6].

[1] W. Olovsson, C. Gransson, T. Marten, and I.A. Abrikosov, Phys. Stat. Sol. (b) 243, 2447 (2006).
[2] I. A. Abrikosov, W. Olovsson, and B. Johansson, Phys. Rev. Lett. 87, 176403 (2001).
[3] W. Olovsson, C. Gransson, L. V. Pourovskii, B. Johansson, and I. A. Abrikosov, Phys. Rev. B 72, 064203 (2005).
[4] W. Olovsson, L. Bech, T. H. Andersen, Z. Li, S. V. Hoffmann, B. Johansson, I. A. Abrikosov, J. Onsgaard, Phys. Rev. B 72, 075444 (2005).
[5] T. Martin, S. I. Simak, W. Olovsson, and I. A. Abrikosov, Phys. Rev. B 72, 054210 (2005).
[6] W. Olovsson, I. A. Abrikosov, B. Johansson, A. Newton, R. J. Cole, and P. Weightman, Phys. Rev. Lett. 92, 226406 (2004)

Valency and SIC

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

In this talk I will show how the application of the self-interaction correction to the local spin density (SIC-LSD) leads to an useful definition of valency. This is then explicity demonstrated on the basis of several examples which include systems such as Ce-the prototypical system showing the localization/delocalization transition-, $LiNiO_2$-transition from trivalent Jahn-Teller (JT) active Ni to divalent JT inactive Ni-, Fe in MgO-transition from high spin to low spin-, the rare earths-the discovery of two types of f-electrons-, the actinides-ls versus jj coupling- and Mn in GaAs and ZnO- applications in the field of spintronics.

Gaps and SIC

Z. Szotek
Daresbury Laboratory, Daresbury, Warrington, WA4 4AD, Cheshire, U. K.

We provide critical assessment and deeper understanding of energy gaps calculated using self-interaction corrected local spin density (LSD) approximation. We discuss the underlying formulations of the SIC-LSD method and how they impact the formal definition and interpretation of the energy gap. We present results for rare gas solids, transition metal oxides, parent compounds of high temperature superconductors, and Europium chalcogenides. Wherever possible we compare the SIC-LSD energy gaps to such approaches as LSD, GGA, LDA+U and hybrid functionals.

Single-Site Self-Interaction Correction in KKR-CPA

Martin Lueders, Daresbury Laboratory, Daresbury, Warrington, WA4 4AD, Cheshire, U. K.

Strongly correlated materials including d- and f- electrons are of common interest in many areas. For this class of systems, the standard local spin density approximation (LSD) to density functional theory often fails, which is due to a spurious self-interaction of the localized electrons. It has long been shown that this can be corrected by the so-called self-interaction corrected (SIC) LSD. The SIC-LSD is so far implemented in two ways in the KKR method.

In my talk I will overview the background of SIC in general, and then discuss in detail the approximations underlying the two current implementations, namely local SIC and Pseudo-SIC. In particular the differences and similarities in the technical implementation, as well as in the philosophy of the applications will be investigated.

Electronic Structures of Dilute Magnetic Semiconductors from LDA+SIC calculations

M. Toyoda[1], H. Akai[2], K. Sato[1] and H. Katayama-Yoshida[1]
[1] *Department of Computational Nanomaterials Designm The Institute of Scientific and Industrial Research, Osaka University, Ikaraki 567-0047, Japan.*
[2] *Department of Physics, Osaka University, Toyonaka 560-0043, Japan.*

We investigate the electronic structure and magnetic properties of dilute magnetic semiconductors from first principles calculations. Since the 3d electrons of transition-metal impurities are strongly localized[1], the local density approximation (LDA) gives a poor description of them. Thus we use the self-interaction-corrected local density approximation (LDA+SIC). Our implementation is based on the pseudopotential-like self-interaction correction scheme (pseudo-SIC) proposed by Filipetti and Spaldin[2]. We implement the pseudo-SIC with the Korringa-Kohn-Rostocker coherent potential approximation (KKR-CPA) method[3]. In order to investigate the magnetic properties, we use a classical Heisenberg-type Hamiltonian for the DMS system. The parameters of the Hamiltonian, the magnetic exchange interaction J_{ij}, are calculated from the first-principles results using Lichtenstein's formula[4]. We found that the electronic structures calculated by LDA+SIC are in better agreement with the photoemission spectrum than those calculated by LDA. We will also discuss about the difference of magnetic properties and Curie temperature calculated by LDA+SIC from those calculated by LDA. For example, we found the enhancement of ferromagnetic interactions between the Mn ions in GaMnAs. This is because the antiferromagnetic super-exchange interaction is suppressed due to the increase of the exchange splitting. A contrary example is ZnCoO in which we found antiferromagnetic interaction between Co ions due to a large gap opening between the occupied and unoccupied d states.

[1] J. Okabayashi *et al.*, J. Appl. Phys. **95**, 3537 (2004).
[2] A. Filippetti and N.A. Spaldin, Phys. Rev. B **67**, 125109 (2003).
[3] H. Akai, Phys. Rev. Lett. **81** 3002 (1998); H. Akai, http://sham.phys.sci.osaka-u.ac.jp/ kkr/.
[4] A. Lichtenstein *et al.*, J. Magn. Matter. **67**, 65 (1987).

Magnetic anisotropy of an impurity in the vicinity of a surface

L. Szunyogh
Department of Theoretical Physics, Budapest University of Technology and Economics, Budapest, Hungary
and
Center for Computational Materials Science, Vienna, Austria

The most successful explanation of the size dependent Kondo effect relies on the assumption that a magnetic impurity near a surface experiences spin-orbit induced anisotropy. I present numerical investigations in terms of a simple tight–binding model that accounts correctly for the semi–infinite geometry of the host metal, while the splitting of the states of a Kondo impurity interacting with the neighboring host atoms is calculated via perturbation technique up to second order in the exchange coupling strength. Two models are investigated, namely, *(i)* an impurity with a half-filled p-shell subject to a host-induced magnetic anisotropy and *(ii)* an impurity of D^1 configuration with a strong local spin-orbit coupling. It is found that in both cases the anisotropy energy is an oscillating function of the distance d from the surface with an amplitude that, however, decays as $1/d^2$ in case *(i)*, while as $1/d^3$ in case *(ii)*. This observation is clearly supported by an asymptotic analysis of the spectral function of the host. Furthermore, numerical estimates suggests that mechanism *(ii)* gives rise to an anisotropy energy of the desired order of magnitude whereas mechanism *(i)* seems to be of negligible importance [1]. Corresponding attempts towards an ab-initio description of the phenomenon based on the Screened KKR method are also discussed.

[1] L. Szunyogh, G. Zaránd, S. Gallego, M. C. Muñoz, and B. L. Györffy, Phys. Rev. Lett. **96**, 067204 (2006)

Ab initio description of pump-probe experiments using KKR

A. Vernes and P. Weinberger
Center for Computational Materials Science, Technical University Vienna, Gumpendorferstr. 1a, A–1060 Vienna, Austria

The Kubo response theory is extended to describe pump-probe experiments by linearizing the density of both pump- and probe-excited states and neglecting the overlap between the femtosecond pulses. Although the derived formalism includes also second order responses, as illustrated - for example - in the case of double exponential envelopes, the scheme is formally linear and all deduced formulas, e.g. in particular those of the optical conductivities, are straightforwardly implementable within any standard bandstructure method. In particular, even the time-dependent zeroth order dynamic conductivity as obtained by means of the spin-polarized relativistic screened Korringa-Kohn-Rostoker method for fcc Ni(100) predicts a relatively fast demagnetization process over 100 fs after the impact of the probe pulse, which is in a reasonably good agreement with available experimental data. Furthermore, calculations for Co/Pt(111) and Pt/Co/Pt(111) layered systems show that due to the high polarizability of Pt layers, the layer-resolved demagnetization time is not necessarily dominated by the demagnetization time of the ferromagnetic Co layer.

Magnetic properties of 3d pyrite-type mixed crystals calculated by the full potential KKR-CPA method

Masako Ogura,
Department of Physics, Graduate School of Science, Osaka University 1-1 Machikaneyama, Toyonaka, Osaka 560-0043, Japan

3d pyrite-type crystals AB2 (A=Fe, Co, Ni; B=S, Se) show various magnetism depending on the combination and concentration of elements. Due to their anisotropic structure, this system can not be treated in the conventional KKR method in which the muffin-tin potential approximation is used. In the present study, we investigate the electronic structure of the 3d pyrite compounds using the full potential KKR method combined with the CPA. The full potential treatment improves the description of this system and the results reproduce the experiments well.

6.2 CCP9 Meeting Announcements

6.2.1 Computational Magnetism Meeting

13 December 2006, Institute of Physics, London

Organised by the Computational Physics Group of the Institute of Physics
Co-sponsored by the Magnetism Group of the Institute of Physics
`http://www.iop.org/Conferences/Forthcoming_Institute_Conferences/event_5517.html`

Introduction

A one-day meeting on computational magnetism ranging from the atomic scale up to length-scales of micrometres. The relevant computational techniques focus around micromagnetism, Heisenberg models with dipolar interaction and ab-initio methods.

For each of these computational methods there will be an introductory talk providing an overview of the computational methods before leading researchers present their most recent methods and results.

See this link for the full event:

`http://www.iop.org/Conferences/Forthcoming_Institute_Conferences/event_5517.html`

Programme

12:00 - 13:00	Registration and Lunch
13:00 - 15:00	Session 1 - Ab-initio calculations
13:00 - 13:30	Professor Balasz Gyorffy (Bristol, UK) "Introduction to Ab-initio methods"
13:30 - 14:00	Dr Dzidka Szotek (Daresbury, UK) "Ab-initio materials modelling for spintronics"
14:00 - 14:20	Mr Ian Hughes (Warwick, UK) "Magnetic Ordering in Heavy Rare Earth Systems from ab initio"
14:20 - 14:40	Professor Ray Bishop (Manchester, UK) "Quantum phase transitions in spin-lattice systems: an ab initio treatment via the coupled cluster method"
14:40 - 15:00	Dr Balazs Ujfalussy (Budapest, Hungary)

	"Magnetic anisotropy in small metallic nanostructures"
15:00 - 16:00	Coffee and Poster Session
16:00 - 18:00	Session 2 - Heisenberg models and Micromagnetism
16:00 - 16:30	Uli Nowak (York, UK) "Heisenberg models"
16:30 - 17:00	Bob McMichael (NIST, USA) "Micromagnetics (OOMMF is developed and maintained at NIST)"
17:00 - 17:20	Dr Thomas Fischbacher (Southampton, UK) "Multiphysics extension to micromagnetic calculations"
17:20 - 17:40	Dr Wyn Williams (Edinburgh, UK) "Configurational anisotropy in equidimensional grains of magnetite"
17:40 - 18:00	Professor Thomas Schrefl (Sheffield, UK) Title to be confirmed
18:00 - 20:00	Buffet Dinner and Drinks Reception

The meeting Computational Magnetism takes place on Wednesday 13 December 2006 at Institute of Physics, London.

Please note that there are a few spaces available for this meeting.

To obtain registrations details please go to

`http://www.iop.org/Conferences/Forthcoming_Institute_Conferences/event_5517.html`

Looking forward to seeing you there,

Hans Fangohr and Walter Temmerman

7 General Workshop/Conference Announcements

7.1 Workshop on Interaction Energies and the Structure of Surfaces and Nano-structures

RMIT University, Melbourne, Victoria 3001, Australia

Monday 19th, Tuesday 20th and Wednesday 21st of February 2007

Sponsored by:
RMIT International
Australian Research Council of the Australian Government
Nanotechnology Network

Professor Ian Snook and Associate Professor Salvy Russo
Applied Physics, School of Applied Sciences
RMIT University, Melbourne, Victoria 3001, Australia

www.rmit.edu.au/applied-sciences/workshop

The theme is the calculation of interaction energies of atoms in condensed matter systems by quantum mechanical and empirical methods with special emphasis on predicting the properties of surfaces, and nano-structures. There will be keynote talks given by invited speakers Abstracts of proposed shorter talks should be submitted to Ian Snook Papers arising from this meeting may be submitted to a special edition of "Molecular Simulation"

Keynote Speakers

Professor Richard Needs, TCM Group, Cavendish Lab., Cambridge University, UK

Quantum Monte Carlo Calculations Professor John Dobson, Griffith University, Queensland

The Theory of van der Waals Interactions Professor Mukunda Das, RS Phys. Sci., ANU, Canberra, ACT

The Fundamentals of Density Functional Theory Professor Julian Gale, Curtin University of Technology, Perth, WA

Applications of DFT using the SIESTA Code and The Use of Empirical Force Laws Associate Professor Mike Ford, Physics, UTS, Sydney, NSW

The Applications of DFT and Empirical Force Laws to Au Nanostructures Dr Manolo Per, Applied Physics, RMIT, Melbourne

Quantum Monte Carlo and Weak Interactions

8 General Job Announcements

POSTDOCTORAL OPENING

Condensed Matter Theory

Institute for Theoretical Physics, University of Regensburg, Germany

A postdoctoral position is open in the theory of low-dimensional semiconductor ferromagnetism at the Institute for Theoretical Physics in the University of Regensburg, starting in January 2007. The successful canditate will perform numerical ab initio computations of the electronic structure, as well as Monte Carlo simulations of transport properties of low dimensional ferromagnetic semiconductors. The project is a collaboration with Prof. Dr. Claudia Ambrosch-Draxl of the University Leoben. The candidate is also expected to interact with experimental groups in Regensburg.

The Institute for Theoretical Physics in Regensburg provides an excellent environment for research and teaching. The atmosphere of the Institute and the Department as a whole is friendly and informal, providing a nice international mixture of young graduate and postdoc researchers who whish to launch a successful career in physics. Living in Regensburg is also very nice and pleasant, the city is one of the most charming in the middle of Europe:

http://www.regensburg.de/tourismus/international/english/index.shtml

The applicant should have a PhD in condensed matter theory from a respected higher education institution. Experience with ab initio electronic structure calculations is very helpful. The position is funded by the Sonderforschungsbereich 689, ”Spin phenomena in reduced dimensions.” The salary is on the German BATIIa scale, being commensurate with age, family status, and experience.

Please send a cover letter and professional CV to Prof. Dr. Jaroslav Fabian at jaroslav.fabian@physik.uni-r.de. Recommendation letters will be solicited after an initial selection.

Prof. Dr. Jaroslav Fabian

University Regensburg
Institute for Theoretical Physics
jaroslav.fabian@physik.uni-regensburg.de
http://www.physik.uni-regensburg.de/forschung/fabian/
phone: (49-941) 943 2031
fax: (49-941) 943 4382

Research Associate/Postdoc Position

Quantum Simulations of Complex Molecular Systems

Center for Theoretical Chemistry, University of Bochum, Germany

Applications are invited for a research associate that is expected to become available as early as January 2007 but a later starting date is possible.

The ideal candidate would have significant experience in path integral MC/MD methods, electronic structure calculations, and computer simulation; a PhD in theoretical chemistry, physics or related field is required.

The position is focused on applying and improving our novel ab initio Quantum Monte Carlo technique based on path integrals and will strongly benefit from collaborations with experimental groups. In addition, you are most welcome to get involved in other challenging research projects including both method development and large-scale applications. Information on the techniques used and developed at CTC are accessible via

http://www.theochem.rub.de/go/cprev.html.

The Center for Theoretical Chemistry at RUB offers an exciting interdisciplinary environment with excellent working conditions including several high-performance parallel platforms in house, see

http://www.theochem.rub.de/go/jobs.html.

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

Professor Dominik Marx
Lehrstuhl für Theoretische Chemie
Ruhr-Universität Bochum
44780 Bochum, Germany
Email: office@theochem.rub.de

Consideration of candidates will begin immediately and continue until the position is filled. The university particularly welcomes applications from women.

Postdoctoral & Ph. D Position
IZBS, University of Karlsruhe (TH), Germany

The Institute for Reliability of Systems and Devices (izbs) of the University of Karlsruhe (TH) has two openings in the field of atomistic modeling for Research - Scientists (physics, chemistry or material science).

Our research interests are mainly focused on atomistic mechanisms of plastic deformation, fracture and interfacial phenomena. The topics are closely related to a multiscale materials modeling framework, which is in development at the institute. The atomistic modeling activities covers quantum mechanical approaches, development of interatomic potentials and non-equilibrium molecular dynamics simulation on high performance computing facilities.

The first position is open for an outstanding experienced scientist, with the prospective the lead the atomistic modeling group. The second position is open for a PhD student or post-doc. Both positions are closely related to research projects financed the BMBF or DFG.

We expect an outstanding record in the field of atomistic modeling or an excellent degree and a background in at least one of the following fields: physics, chemistry, material science and engineering. Excellent knowledge of the English language is required.

The University of Karlsruhe (TH) is an equal opportunity employer. The salary scheme follows the BAT /TV-L. The position is for an initial period of 2 years.

Please send your application to:

Universität Karlsruhe(TH)
Institut für Zuverlässigkeit von Bauteilen und Systemen (IZBS)
Prof. Dr. Peter Gumbsch
Kaiserstrae 12
D-76131 Karlsruhe.
E-mail: sekretariat@izbs.uni-karlsruhe.de
www.izbs.uni-karlsruhe.de

POSTDOCTORAL POSITION

Electronic Structure of Strongly Correlated Systems.

Forschungzentrum Juelich, Germany

A postdoctoral position is available immediately at the Institute of Solid State Research (IFF), Forschungzentrum Juelich, Department Theory I.

We are building a vigorous group in many-body physics and seek a motivated researcher to strengthen our team. The focus of our activity is understanding the effects of strong correlations in real materials and developing methods for the realistic description of strongly correlated systems. We use Wannier functions as basis for material-specific model building (first- principles NMTO downfolding method), and solve these models with a modern many-body method, the dynamical mean-field theory (DMFT) and/or its cluster extension (CDMFT).

The goal of this project is the calculation of the magnetic response in strongly correlated systems. It involves extending our code to calculate four-point correlation functions with DMFT and CDMFT (quantum Monte Carlo solver), both for simple models and for realistic models obtained through the downfolding procedure. Once the methodology is developed, it will be applied to understand NMR relaxation rates and Knight shifts, and to calculate exchange coupling constants and spin-wave spectra. Applications to strongly correlated transition metal oxides with orbital order, orbital liquids, frustrated systems and high-temperature superconductors are envisioned. As a further goal, we aim to extend the method to the full Hamiltonian by means of an upfolding procedure.

The DMFT and CDMFT calculations will be performed at the NIC supercomputer center on a BlueGene/L with 16384 processors, one of the top-ten computers worldwide.

Candidates should have a Ph.D. degree in physics or a related subject, a strong background either in many-body physics and/or density functional theory, and good computational skills. The position (salary at the level 13 of TV=D6D) is available for two years (with a possible extension of one more year) starting immediately.

The Research Center Juelich is an equal opportunity employer. Applications and further information inquiries should be addressed to

E. Pavarini
Institut fuer Festkoerperforschung
Forschungzentrum Juelich
52425 Juelich
e.pavarini@fz-juelich.de

Applications should include a letter of motivation, a curriculum vitae, a list of publications, a summary of past accomplishments, and the full contact details of 2 referees. Information about the department is provided at

`http://www.fz-juelich.de/iff/e_th1`

Postdoctoral Position in Computational Electronic Structure Theory

Rutgers University

A postdoctoral position is available to begin as early as January 2007 in the group of David Vanderbilt in the Department of Physics and Astronomy at Rutgers University. The research will be in the general area of DFT-based computational studies of ferroelectric and piezoelectric materials, and may cover the construction of DFT-based models for describing high-strain perovskite piezoelectrics, the piezoelectric properties of alloys and solid solutions, the nonlinear dielectric properties of bulk and superlattice perovskites in finite electric field, and the properties of novel ferroelectric and multiferroic materials. Experience with density-functional electronic-structure methods is essential.

Interested applicants should email to dhv@physics.rutgers.edu with CV attached (PDF preferred), and should supply names and contact information for two or three references. Consideration of candidates will begin immediately and will continue until the position is filled.

Prof. David Vanderbilt
Department of Physics and Astronomy
Rutgers University
136 Frelinghuysen Road
Piscataway, NJ 08854-8019, USA

Phone: (732) 445-2514
Fax: (732) 445-4400
Email: dhv@physics.rutgers.edu
`http://www.physics.rutgers.edu/~dhv`

Postdoctoral Position

Condensed Matter Physics Department
Universidad del Pais Vasco, Bilbao, Spain

A postdoctoral position to perform ab-initio calculations in mineral physics is available at the Condensed Matter Physics Department of the Universidad del Pais Vasco, in Bilbao (Spain).

The position is funded by the Spanish Ministry of Education in the framework of the European Science Foundation EUROCORES Eurominsci program. The project, "Ordering of Ions in Minerals", involves the following institutions and senior scientists:

- Bilbao (JM Perez Mato, K. Friese, A. Grzechnik): ab-initio calculations, superspace analysis methods, high-pressure research, state-of-the art crystallographic structure determination.
- Innsbruck (V. Kahlenberg): high-pressure synthesis, structural analysis.
- Bochum (M. Fechtelkord): NMR spectroscopy.
- Prague (V. Petricek, M. Dusek): refinement of non-standard structures.
- Copenhaguen (T. Balic-Zunic, E. Makovicky): mineralogical analysis.

The project is led by Alberto Garcia, at the Materials Science Institute in Barcelona but with close ties with the Bilbao group.

The successful candidate will join the group in Bilbao, performing ab- initio or in general first-principles-based calculations to analyse the relative stability of different ionic orderings in representative minerals, to predict and suggest new structural configurations, and to study related properties. It is expected that there will be strong interaction with the other nodes in the project, including short stays.

Prospective applicants must hold a PhD degree in physics, chemistry, materials science, or related field. Experience with density- functional calculations, numerical methods, and programming is essential. Familiarity with other relevant methods (such as the Monte Carlo simulation of effective hamiltonians) is a plus.

Salary is at the level of a starting associate professor (around 30,000 EUR gross p.a.), through a contract which also includes the standard Spanish health benefits and social-security contributions. The appointment is in principle for two years, with an initial period of one year extended by mutual agreement. The starting date is January/February 2007.

Interested candidates should write a cover letter to Alberto Garcia (albertog@icmab.es) or J.M Perez Mato (wmppemam@lg.ehu.es), attaching a CV and the names and contact information of two references.

(An earlier announcement for this position was posted in June, but a funding delay has changed the starting date. We are now seeking candidates who might have missed the previous announcement, and will review applications until the position is filled.)

Research Associate - Computational Surface Science

School of Physics, Faculty of Science, The University of Sydney, Australia

The School of Physics is a core discipline within the Faculty of Science. Located on the Universitys Camperdown campus, the School hosts world-class facilities and is renowned for excellence in the a reas of teaching and research. The School currently has an outstanding opportunity available for a results-driven Research Associate to conduct specialised research into Computational Surface Science.

The appointee will be in involved in the study of surfaces of, and reactions at, metal-oxide-based materials in relation to heterogeneous catalysis relevant to renewable energy production. This will include the development and application of ab initio based thermodynamic and statistical mechanical schemes for determining surface structures and reaction rates. The School attracts high-profile scientists and research groups, so an ability to communicate and work with others will be crucial. In addition, the appointee will need an ability to write quality manuscripts that are suitable for publication in peer-reviewed journals.

To succeed, a recent PhD in physics, chemistry, or materials science, and a sound knowledge of the ab initio density-functional theory or quantum-mechanical electronic structure theory will be essential. The appointee will also be required to have experience with first-principles calculations such as Density Functional Theory. This is the perfect opportunity for a recent graduate to conduct innovative research in a specialised field that attracts significant research coverage and funding.

The position is full-time fixed term for 2 years, subject to the completion of a satisfactory probation period for new appointees. There is the possibility of further offers of employment for 12 months, subject to funding and need. Membership of a University approved superannuation scheme is a condition of employment for new appointees. Remuneration package: $72,327 - $77,638 p.a. (which includes a base salary Level A $61,117 - $65,605 p.a., leave loading and up to 17% employer's contribution to superannuation)

Closing: 17th December 2006.

For further information, contact Professor Catherine Stampfl e-mail:
stampfl@physics.usyd.edu.au (http://www.physics.usyd.edu.au/cmt) or
Dr. Oliver Warschkow e-mail: oliver@physics.usyd.edu.au.

To apply, please do this online at: http://www.usyd.edu.au/positions/ where the job reference code is: 90076.

The University is a non-smoking workplace and is committed to the policies and principles of equal employment opportunity and cultural diversity. The University reserves the right not to proceed with any appointment for financial or other reasons.

PostDoc and PhD Positions (Theoretical Solid State Physics)

Institute for Theoretical Solid State Physics, ITF,

at Leibniz-Institute for Solid State and Materials Research Dresden, IFW,

Dresden, Germany)

We would like to announce several open PhD and PostDoc positions at the Institute for Theoretical Solid State Physics, ITF (http://www.ifw-dresden.de/agtheo/agtheo1.htm), at Leibniz-Institute for Solid State and Materials Research Dresden, IFW (http://www.ifw-dresden.de).

The projects include

(1) density functional theory of orbital magnetism in transition metal, lanthanide, and actinide elements and compounds (further development of the theory and related implementation/calculations);

(2) electronic structure calculations for heterosystems of dielectric substrates and metallic films (magnetic properties of stressed films in external fields);

(3) phenomenological theory and simulations of magnetic shape memory alloys using micromagnetism;

(4) electronic and magnetic structure of lanthanide molecules in fullerens (chemical bonding, crystal field, and magnetic ground state).

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 groups active in solid state theory and in applied mathematics, in particular at the Max-Planck Institute for Mathematics in Sciences, Leipzig.

The applicant should preferably have a strong background in solid state physics, good knowledge of theoretical physics, and experience in the understanding and skillful use of code for numerical simulations. Command of one or several programming languages and Linux is favorable.

For PostDocs, we offer a one-year position, extendable to 2 years, at the level BAT IIa-O (annual net income about kEUR 22, depending on age and family status); for PhD students, we offer a two-year position, extendable to 3 years, at the level 50% BAT IIa-O (annual net income about kEUR 14).

The Institute for Theoretical Solid State Physics at IFW Dresden employs fourteen scientists, five PhD and Diploma students, and several guest scientists. The Institute has up-to-date and well-managed computer facilities 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 picturesque valley of river Elbe. With a population of about 500,000, it is known for an exceptionally rich cultural live, for its beautiful surroundings, 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, references and other relevant material to:

m.richter@ifw-dresden.de

Prof. Dr. Helmut Eschrig
Dr. Manuel Richter
Dr. Ulrich Röler
IFW Dresden e.V.,
P.O. Box 270016,
D-01171 Dresden,
Germany

Ph.D. Studentship

Theory Department of the Fritz Haber Institute of the Max-Planck-Society

Berlin, Germany

The Theory Department of the Fritz Haber Institute of the Max-Planck-Society invites applications for a Ph. D. studentship funded through the Marie Curie early stage training network, MONET: Molecular Networks at Phase Boundaries.

Research in our department is aimed at understanding important phenomena in surface-, materials-, and nano-science. With about 50 scientists from many countries the Theory Department provides a lively and stimulating international atmosphere for students in one of Europe's most vibrant capital cities.

For more information of the Theory department see:

http://www.fhi-berlin.mpg.de/th/th.html

We are looking for highly qualified students from physics, chemistry, and materials science that hold a Masters Degree (or equivalent) and fulfill the requirements of nationality and residence as outlined on the MONET website:

http://www.sljus.lu.se/monet/index.html

Further details of the proposed Ph. D. project can also be found at the MONET site.

Please send your application including a detailed CV by email to Dr Angelos Michaelides (michaeli@fhi-berlin.mpg.de) or to Dr Karsten Reuter (reuter@fhi-berlin.mpg.de).

Postdoctoral and/or Research Staff Position

Institute of Physics, CAS, Beijing & Göteborg University, Sweden

”Theory and simulation of excited states and nanoplasmons”

A postdoctoral and/or research staff position is available at the Institute of Physics, Chinese Academy of Sciences (IOP-CAS), Beijing & Department of Physics, Göteborg University, Gothenburg, Sweden. The research project focuses on the theory and simulation of optical properties of surfaces and nanomaterials, excited states in particular collective excitations. It involves both theoretical developments and numerical simulation with available codes based on linear response theory and time-dependent density functional theory (TDDFT). Candidates with experiences in electronic structure, time-dependent density functional theory, many-body theory, optical properties of nanomaterials are encouraged to apply. The postdoc position will be jointly appointed at both the IOP-CAS, Beijing, and the Gothenburg University, Sweden. The initial appointment is for one year for postdoc, with possibility to extend for another year or a tenured staff positions at IOP-CAS after two years.

For further information and applications, please send your CV, list of publications, and arrange two letters of recommendations to Professor Shiwu Gao, Email: tfysg@fy.chalmers.se, Institute of Physics, Chinese Academy of Sciences, 100080 Beijing, China, or Department of Physics, Göteborg University, Sweden.

Experienced Researcher

National Hellenic Research Foundation (NHRF)

Athens, Greece

We wish to recruit an experienced researcher (see below) for two years. The salary of the recruited scientist will be funded by the Transfer of Knowledge programme of the European Union. This person will work at the National Hellenic Research Foundation (NHRF), Athens, Greece. The successful applicant must have an expertise in the SIESTA methodology. This technique will be used to compute the linear and non-linear optical properties of a series of fullerenes. In addition the employed researcher will transfer his expertise, in the SIESTA technique, to the other members of the NHRF team. Researchers, from the Universities of Cambridge, Girona and Nagoya will participate in the project. The job is available from the 1/10/06.

Applications consisting of CV and the names two referees should be sent by e-mail to Dr M. G. Papadopoulos, mpapad@eie.gr.

Experienced researchers are defined as

i)researchers having at least 4 years of research experince (full-time equivalent) since gaining a university diploma giving them access to doctoral studies (the degree must entitle the holder to embark on doctoral studies, without having to acquire any further qualifications), in the country in which the degree/diploma was obtained or

ii) researchers already in possession of a doctoral degree, independently of the time taken to acquire it.

Postdoctoral Position

Department of Chemical & Biological Engineering

University of Wisconsin, Madison, USA

I have an immediate postdoctoral position opening in my research group. The ideal candidate would have PhD-level experience with molecular modeling techniques, particularly with DFT planewave codes, and would be interested in working with reactions on transition metal surfaces. The position is sponsored by DOE-Basic Energy Sciences Office and the work will be conducted in Madison, WI, located 2 hours drive away from Chicago.

Interested applicants should contact me via email: manos@engr.wisc.edu and send me their CV and a list of 2-3 references.

Manos Mavrikakis
Associate Professor
Department of Chemical & Biological Engineering
University of Wisconsin, Madison
1415 Engineering Dr.
Madison, WI 53706-1691

Phone: (608) 262-9053
Fax: (608) 262-5434
Email: manos@engr.wisc.edu
Web: `http://www.engr.wisc.edu/che/faculty/mavrikakis_manos.html#address`

Postdoctoral Research Position

School of Chemistry, University of Southampton, U. K.

A postdoctoral research position in the computational modelling of semiconductor nanocrystal quantum dots using linear-scaling first-principles quantum mechanical calculations is available in Southampton.

Details about the position and the application procedure can be found by going to

http://www.jobs.soton.ac.uk/

and entering the job reference number: 0407-06-E or by going directly to:

`http://www.jobs.soton.ac.uk/soton/jobboard/JobDetails.aspx?__ID=*C3FF88F9919962E1`

The deadline is 1 December 2006.

Dr Chris-Kriton Skylaris
Lecturer & Royal Society University Research Fellow
School of Chemistry, University of Southampton,
Highfield, Southampton SO17 1BJ, UK
Tel. +44 (0)2380 599381 (work)
+44 (0)7952 650563 (mobile) http://www.chem.soton.ac.uk/skylaris.htm

Postdoctoral Position in Computational Condensed Matter Physics and Materials Science

DEMOKRITOS, Trieste, Italy

Applications are invited for one postdoctoral position within DEMOCRITOS "Modeling Center for Research in Atomistic Simulations" in Trieste, Italy extending on 1+1 years.

The selected candidate will participate in a project aimed at developing and implementing new algorithms for the first-principles calculation of optical properties of nanostructured materials. This project is part of an ongoing collaboration between DEMOCRITOS and the Elettra Synchrotron Radiation Laboratory in Trieste.

The candidate should hold a Ph.D. in the field either of theoretical physics/chemistry or materials science and have previous experience with first-principles methods as well as scientific programming.

Perspective applicants are requested to get in touch with Dr. Paolo Umari (umari@democritos.it, Democritos c/o Sincrotrone Trieste, Strada Statale 14 - km 163,5 34012 Basovizza, Trieste ITALY) to whom they should submit a CV, including a list of publications, together with two letters of recommendation (all this by e-mail).

Ph. D. Studentship

School of Mathematics and Physics

Queen's University Belfast, Northern Ireland, U. K.

A PhD studentship is available in the School of Mathematics and Physics, Queen's University Belfast. The position is fully funded, covering both fees and maintenance, and is open to students of all nationalities, over a four year period beginning 1 Feb 2007.

For details, see

http://www.jobs.ac.uk/jobfiles/QF321.html

and for informal enquiries, contact

Professor A T Paxton (Tony.Paxton@QUB.ac.uk).

Applications may be made on-line at

http://pg.apply.qub.ac.uk/home

Postdoctoral Position in Computational Materials Science

University of Minnesota

Department of Chemical Engineering and Materials Science
Minnesota Supercomputing Institute, Minnesota, U.S.A.

A postdoctoral position is available to begin as early as March 2007 in the group of Renata Wentzcovitch in the Department of Chemical Engineering and Materials Science at the University of Minnesota. The research will be in the general area of DFT-based computational studies of spintronic materials under the support of the Materials Research Science and Engineering Center (IRG3) at the University of Minnesota

(http://www.mrsec.umn.edu/irg3.shtml).

The research will be closely related to experimental studies conducted in the interdisciplinary research group on Magnetic Heterostructures. We are also interested in perovskite materials with strongly correlated ions and uncommon properties at low and high temperatures.

Interested applicants should email to wentzcov@cems.umn.edu with CV attached (PDF preferred), and should supply names and contact information for two or three references. Consideration of candidates will begin immediately and will continue until the position is filled.

Ph. D. Position

Bremen Center for Computational Materials Science, Bremen, Germany

The Bremen Center for Computational Materials Science (BCCMS) is a newly founded interdisciplinary research institute aiming at an understanding of technologically relevant materials using atomistic simulations. We are currently looking for a highly motivated PhD student which will work on the following project:

Theoretical simulation of biomolecule-semiconductor nanowire structures

A PhD scholarship is immediately available to investigate the formation of semiconductor nanowire-biomolecule structures for molecular electronic device applications. The project is part of a cooperative research program between Germany and Israel. In this work molecular dynamics simulations, tight-binding and first-principles density-functional theory methods will be used to calculate electronic, electrical and optical properties of biomolecules adsorbed on semiconductor nanowires. The project is of highly multidisciplinary nature and will be performed in close collaboration with experimental groups in order to support and guide the search for novel materials.

A solid background in theoretical solid state physics or theoretical chemistry is required. Existing expertise in electronic structure methods and atomistic modelling of materials will be considered as an advantage. Previous experience in scientific programming (e.g. in Fortran or C) is highly appreciated. The BCCMS is part of an international network of research institutes and has worldwide collaborations, so that good English communication skills are essential. At the same time readiness to learn German in order to contribute to the teaching at the BCCMS is highly welcome.

In order to increase the percentage of female faculty members, female candidates with equal qualification will be given preference. Interested candidates should send their application including a cover letter indicating their motivation to apply for this position, a curriculum vitae, a list of publications, a statement about current research activities and other relevant material to: *farchmin@bccms.uni-bremen.de*

`Contact and further information:`

Prof. Thomas Frauenheim
thomas.frauenheim@bccms.uni-bremen.de
www.bccms.uni-bremen.de

Ph. D. Position

Bremen Center for Computational Materials Science, Bremen, Germany

The Bremen Center for Computational Materials Science (BCCMS) is a newly founded interdisciplinary research institute aiming at an understanding of technologically relevant materials using atomistic simulations. We are currently looking for a highly motivated PhD student which will work on the following project:

Electrical charge transport through single molecules adsorbed on metal and semiconductor surfaces

In the context of molecular electronics, atomistic simulations based on quantum mechanics will be used to study the adsorption of organic molecules on gold, silver and silicon surfaces. In comparison with experiments currently performed at the International University Bremen, the energetically most stable binding configurations are determined and characterized according to their structural, vibrational and electronical properties using density functional theory. With the help of nonequilibrium Greens Function approaches we plan to study the electronic transport through the adsorbed molecules in order to test their potential in the development of new molecular electronic devices. This is a three-year position with a salary at the level of 1/2 BAT IIa.

A solid background in theoretical solid state physics or theoretical chemistry is required. Existing expertise in electronic structure methods and atomistic modelling of materials will be considered as an advantage. Previous experience in scientific programming (e.g. in Fortran or C) is highly appreciated. The BCCMS is part of an international network of research institutes and has worldwide collaborations, so that good English communication skills are essential. At the same time readiness to learn German in order to contribute to the teaching at the BCCMS is highly welcome.

In order to increase the percentage of female faculty members, female candidates with equal qualification will be given preference. Interested candidates should send their application including a cover letter indicating their motivation to apply for this position, a curriculum vitae, a list of publications, a statement about current research activities and other relevant material to: *farchmin@bccms.uni-bremen.de*

`Contact and further information:`

Prof. Thomas Frauenheim
thomas.frauenheim@bccms.uni-bremen.de
www.bccms.uni-bremen.de

Postdoctoral Position

”Modelling Production of Hydrogen”

Theoretical Chemistry Group, Leiden University, The Netherlands

A post-doc (1.5 years) position is available immediately, in the theoretical chemistry group of Leiden University.

The research will focus on the production of hydrogen through water splitting, in a tandem cell set-up involving photoelectrolysis of water. More specifically, the mechanism of the photo-oxidation of water on oxidic semi-conductor surfaces will be studied, using density functional theory and quantum transition state theory. The project will involve a collaboration with the group of Prof. Jens Nrskov at the Technical University of Denmark.

The project is funded by the EC, being part of a new Research Training Network (Hydrogen) under framework 6. The network has started on 1 September. The project will be supervised by Geert-Jan Kroes and Roar Olsen.

Recquirements: Applicants for the post-doc position should have a Ph.D. in Chemistry, Physics, or Applied Mathematics, and have experience with computational methods relevant to the field of Chemical Physics. According to EC-rules, candidates for the post-doc position should have no more than 10 years of research experience, counting from the day they started their Ph.D. study. In view of the composition of the network, the applicant should be a national from a EC member state, or from an Associated state (Associated states are: Bulgaria, Romania, Turkey, Iceland, Israel, Liechtenstein, Norway and Switzerland).

Appointment: The initial appointment will be for a period of 1 year but funding is available for an additional period of 6 months for the post-doc position.

The salary will be according to the Marie-Curie rules. Employees of Marie-Curie Research training networks enjoy special privileges such as a travel allowance, mobility allowance, and career exploration allowance. More information can be found in the Marie-Curie Research Training Networks handbook, available at:

`http://ec.europa.eu/research/fp6/mariecurie-actions/action/training_en.html`

Applications: To be considered for the project, applicants should send an application letter, CV, and publication list, and should arrange themselves that three letters of are sent to Prof. Dr. Geert-Jan Kroes, by email (g.j.kroes@chem.leidenuniv.nl).

The deadline for receiving the material at Leiden is Wednesday 20 December 2006.

G.J.Kroes (g.j.kroes@chem.leidenuniv.nl)
LIC, Gorlaeus Laboratoria
Universiteit Leiden, Postbus 9502
2300 RA Leiden
The Netherlands

Tel: +31 71 527 4396
Fax (new!): +31 71 527 4397
Web: http://rulgla.leidenuniv.nl

Postdoctoral and Research Associate Positions

in NREL's Solid State Theory Group with Alex Zunger

Research Fields:

(1) Theory of Nanostructures
(2) Alloy Theory
(3) Magnetism and conductivity in Oxides
National Renewable Energy Laboratory (NREL)
http://www.sst.nrel.gov

NREL's Solid State Theory Group is looking to fill Postdoctoral and Research Associate positions (depending on qualifications). The research area covers the theory of nanostructures, alloy theory, and magnetism and conductivity in oxides. The positions are available immediately and renewable upon mutual consent for up to 3 years. The salary range is $48,000 - $62,000 per year, depending on seniority, qualification and experience. Applicants are expected to have a strong background in solid-state theory and preferably in the area of nanostructures. For more details about ongoing work, see

http://www.sst.nrel.gov.

The Solid State Theory Group is headed by Alex Zunger and currently consists of ten Ph.D.'s in condensed matter theory and interacts with a broad range of experimentalists. The group has outstanding computational facilities, an excellent basic-research atmosphere, and is located in the beautiful Rocky Mountains. Consult our web page for additional information on the group, its history, research subjects, publications, current and past personnel and facilities.

Interested candidates should send now their curriculum vitae, list of publications (including preprints of unpublished papers, if possible), and arrange for two to three references addressed to:

Dr. Alex Zunger, M/S 3213
Solid State Theory Group
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado 80401

Clarification or further details can be obtained via email to `alex_zunger@nrel.gov`

NREL is an equal opportunity employer and proud of its commitment to diversity. Women and minorities are encouraged to apply.

Postdoctoral Position
Institut des Nanosciences de Paris, France

We have an immediate opening for postdoctoral position in the area of materials modeling and simulation. The project focuses on (1) simulation and theory of the effect of environment on equilibrium and growth properties of oxide nano-objects and (2) development and application of a new, quantum-based approach for modeling large-scale iono-covalent systems.

The project offers the opportunity to collaborate with experimental and simulation groups at the Institut des Nanosciences de Paris, the Centre de Recherche en Matière Condensée et Nanosciences (Marseille), and the Centre de Géochimie de la Surface (Strasbourg). The candidate will have access to computational facilities, which include a local cluster and the supercomputers of the French national facility (IDRIS/CNRS).

Applicants must hold a recent Ph.D. or equivalent in physics, chemistry or materials science. Expertise in materials modeling and simulation would be desired, strong background in programming (f95) would be highly regarded, and a previous experience with semi-empirical approaches would be advantageous. Aptitude to communicate effectively with coworkers and a demonstrated ability to conduct original research, are expected. The position is full-time for one year, with a possible extension.

To apply, send an application addressing the selection criteria, including a CV with a list of publications, and names, addresses, e-mails, and phone numbers of two or more confidential Referees.

Jacek.Goniakowski@insp.jussieu.fr, tel: +33 (0)1 44 27 46 17
Fabio.Finocchi@insp.jussieu.fr, tel: +33 (0)1 44 27 51 16
Claudine.Noguera@insp.jussieu.fr, tel: +33 (0)1 44 27 46 65

Institut des Nanosciences de Paris
Campus de Boucicaut
140 Rue de Lourmel
75015 PARIS, France
http://www.insp.upmc.fr

Ph. D. Studentships and Postdoctoral Positions

The Fraunhofer Institute for Mechanics of Materials IWM, Freiburg, Germany

The Fraunhofer Institute for Mechanics of Materials IWM in Freiburg, Germany, offers several positions for PhD students or postdoctoral researchers to work in the research group ”Physical Modelling of Materials” on collaborative projects funded by the Fraunhofer Society (FhG), the German Research Foundation (DFG) and the German Federal Ministry of Education and Research (BMBF).

We are looking for scientists from physics, chemistry, or materials science, in the fields of theoretical solid-state physics, electronic-structure calculation by ab-initio density functional theory, atomistic modelling and numerical computer simulation of materials.

The research projects include the following material systems and properties:

1. Electronic structure of oxide materials for photovoltaic devices (reference number 2685).

2. Electronic transport in electroceramic thin-film systems for data-storage devices (reference number 2695).

3. Multiscale modelling of ferroelectric materials for sensor and actuator devices, or Ab-initio thermodynamics and atomistic simulation of metal alloys for microelectronic devices (code number 2699).

The option for preparing a Ph. D. thesis on the research topic is provided.

Applicants should have a Ph. D. degree, or an academic degree equivalent to a German University's diploma or master degree to be eligible for a Ph. D. program. Scientific curiosity, ability for team work, knowledge in theoretical materials physics or chemistry, and in numerical computer simulation are expected.

Initially the positions are temporary for two years.

The employment, salary, and social security will be according to the German federal employment contract system (TVöD).

The Fraunhofer Institute for Mechanics of Materials is one of 58 research institutes of the Fraunhofer Society (FhG) in Germany. As a leading organisation for application-oriented research in Europe, the FhG offers challenging research activities to well trained and engaged scientists.

The city of Freiburg provides a very pleasant and stimulating atmosphere for working and living, with its internationally well-known Albert-Ludwig University and a broad variety of scientific and cultural activities, the beautiful location at the rim of the Black Forest in the south-west of Germany, near to both Switzerland and France.

More information on the institute can be found in the internet:

http://www.iwm.fraunhofer.de

Questions? Please contact: Prof. Dr. Christian Elsaesser (phone: +49-(0)761-5142-286, email: christian.elsaesser@iwm.fraunhofer.de).

Interested? Please send your application including curriculum vitae, short essay about research activities, publication list, reference addresses.

Electronically via:

http://www.iwm.fhg.de/stellenmarkt/stellenmarkt.html

(in German only, follow links ”Wissenschaft”, ”Standort: Freiburg”, ”Suchen”)

or by postal mail to:

Fraunhofer-Institut für Werkstoffmechanik IWM
Kerstin A. Druesedau, Personalreferat
Woehlerstrasse 11
79108 Freiburg
Germany

Postdoctoral
National Renewable Energy Laboratory, Golden, Colorado

A post-doctoral position is available immediately in the Theoretical Condensed Matter Physics group at the National Renewable Energy Laboratory to work on the design of new materials for photoelectrochemical hydrogen production. The position is initially for one year, renewable for up to three years subject to mutual agreement and funding availability.

The candidate will explore new semiconductor alloys based on GaN, for the purpose of photoelectrochemical water splitting. The work will require a variety of theoretical and computational methods, including total-energy calculations, thermodynamic simulations, semi-empirical pseudopotential calculations for band-gap engineering, and, for large-scale systems, computationally fast expansions of the total-energy, such as cluster-expansion or valence force field methods. Close collaboration with the group of Alex Zunger is anticipated. The salary will be $48K+, depending on seniority, qualification and experience.

Candidates should have a strong background in computational materials science, as evidenced by experience with first-principles methods or empirical pseudopotential calculations. To apply, please submit (preferably by e-mail) an application letter and a resume including list of publications, and have two letters of recommendation sent directly to:

Stephan Lany (Stephan_Lany@nrel.gov)
or
Alberto Franceschetti (Alberto_Franceschetti@nrel.gov)

National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado 80401, USA

9 Abstracts

Hybrid functionals applied to rare earth oxides: The example of ceria

J. L. F. Da Silva, M. V. Ganduglia-Pirovano and J. Sauer
Humboldt Universität zu Berlin, Institut für Chemie,
Unter den Linden 6, D-10099 Berlin, Germany
V. Bayer
Universität Wien, Institut für Physikalische Chemie,
Sensengasse 8/12, A-1090 Wien, Austria
G. Kresse
Universität Wien, Institut für Materialphysik,
Sensengasse 8/12, A-1090 Wien, Austria

Abstract

We report *periodic* density functional theory (DFT) calculations for CeO_2 and Ce_2O_3 using the PBE0 and HSE hybrid functionals that include non-local Fock exchange. We study structural, electronic, and magnetic ground state properties. Hybrid functionals correctly predict Ce_2O_3 as insulator as opposed to the ferromagnetic metal predicted by the local spin density (LDA) and generalized gradient (GGA) approximations. The equilibrium volumes of both structures are in very good agreement with experiments, improving upon the description of LDA and GGA. The calculated CeO_2 (O $2p$ − Ce $5d$) and Ce_2O_3 (Ce $4f - 5d4f$) band gaps are larger by up to 45% (PBE0) and 15% (HSE) than experiments. Furthermore, we calculate atomization energies, heats of formation and the reduction energy of $2CeO_2 \rightarrow Ce_2O_3 + \frac{1}{2}O_2$. The latter is underestimated by $\sim 0.4 - 0.9$ eV with respect to available experimental data at room temperature. We compare our results with the more traditional DFT+U (LDA+U and PBE+U) approach and discuss the role played by the Hubbard U parameter.

(submitted Phys. Rev. B)
Contact person: Juarez L. F. Da Silva (dasilvaj@chemie.hu-berlin.de);
Veronica Ganduglia-Pirovano (vgp@chemie.hu-berlin.de)

Vanadium oxides on aluminium oxide supports. 3. Metastable κ-Al_2O_3(001) compared to α-Al_2O_3(0001)

T. K. Todorova, M. V. Ganduglia-Pirovano and J. Sauer
Humboldt Universität zu Berlin, Institut für Chemie,
Unter den Linden 6, D-10099 Berlin, Germany

Abstract

Low coverage vanadia species (monomers, dimers, trimers, and 1D vanadia rows) as well as vanadium oxide films of varying thickness supported on the metastable κ-Al_2O_3(001) surface are investigated by density functional theory in combination with statistical thermodynamics. At low vanadium chemical potentials and typical reducing conditions, species with V–$O^{(3)}$–Al interface bonds are stable. These aggregates are partially reduced with vanadium in the V^{III} oxidation state. This correlates with defect formation energy values for the initial removal of lattice oxygen in the range of 1.3–2.7 eV. As the length of the polymeric species increases, the reduction energy decreases. We demonstrate that the support structure does affect the structure of the model catalyst and the lattice oxygen bond strength. On the α-Al_2O_3(0001) surface species with V–$O^{(2)}$–Al interface bonds are also stable. However, the defect formation energy varies between 2.8 and 4.5 eV, with the largest values for monomeric species. Reduction remains more facile for vanadia films on κ-Al_2O_3 than on α-Al_2O_3. The systematic lower values relate to the presence of tetrahedral sites that allow for significant lattice relaxation upon reduction. Using the oxygen defect formation energy as a reactivity descriptor, we discuss possible effects of the support structure and vanadia loading in Mars-van Krevelen-type oxidation reactions. We also analyze the influence of the support structure on the interface vibrational modes.

(submitted J. Phys. Chem. B)
Contact person: M. Veronica Ganduglia-Pirovano (vgp@chemie.hu-berlin.de)

Mesoscopic Magnetic/Semiconductor Heterostructures

Yong Bing Xu, Ehsan Ahmad, Yong Xiong Lu, Jill S. Claydon, Ya Zhai
Spintronics Laboratory, Department of Electronics, University of York,
York YO10 5DD, UK
Gerrit van der Laan
CCLRC Daresbury Laboratory, Warrington WA4 4AD, UK

Abstract

We report the experimental results of Fe and Fe_3O_4 nanostructures on GaAs(100) surfaces and hybrid Ferromagnetic/Semiconductor/Ferromagnetic (FM/SC/FM) spintronic devices. Element specific x-ray magnetic circular dichroism (XMCD) measurements have shown directly that Fe atoms on the GaAs(100) 4×6 surface are ferromagnetic. Within coverages of 2.5 to 4.8 ML superparamagnetic nanoclusters are formed and exhibiting strong uniaxial anisotropy, of the order of 6.0×10^5 erg/cm^3. The coercivities of epitaxial Fe dot arrays films grown on GaAs(100) were observed to be dependent on the separation and size of the dots indicating that interdot dipolar coupling affects the magnetization processes in these dots. In addition Fe_3O_4 films grown on deformed GaAs(100) substrates have been observed to form nanostripes following the topography of the substrate and magneto-optical Kerr effect (MOKE) measurements showed that these nanostripes have uniaxial magnetic anisotropy with easy axis perpendicular to the length of the nanostripes. Meanwhile the FM/SC/FM vertical device has exhibited a biasing current dependent on MR characteristics, with a maximum change of 12% in the MR observed, indicating for the first time a large room temperature spin injection and detection.

Published in IEEE Transactions on Nanotechnology **5**, 455–458 (2006).
Manuscript available from g.vanderlaan@dl.ac.uk.

Spectroscopy of $La_{0.5}Sr_{1.5}MnO_4$ orbital ordering : a cluster many-body calculation

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European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble Cedex, France
S.S. Dhesi
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Abstract

Orbital ordering (OO) in $La_{0.5}Sr_{1.5}MnO_4$ has been studied using soft x-ray resonant diffraction (SXRD) at the Mn $L_{2,3}$ edges in combination with many-body cluster calculations. The SXRD intensity is modelled in second quantization using a small planar cluster consisting of a central active Mn site with first-neighbour shells comprising O and Mn sites. The effective Hamiltonian includes Slater-Koster parameters and charge transfer and electron correlation energies obtained from previous measurements on manganites. The energy dependence of the SXRD OO peak is calculated using the Jahn-Teller distortions of the oxygen octahedra and in-plane spin correlations as adjustable parameters. These contributions are clearly distinguished above the Néel temperature with a good spectroscopic agreement. The results also suggest a significant charge separation between the Mn sites.

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Reprints available from g.vanderlaan@dl.ac.uk

Exchange interactions and correlations in Ni$_{1+x}$MnSb Heusler alloys

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Abstract

In this work we extend our recently published *ab initio* study (Rusz *et al.*, Phys. Rev. B **73**, 214412 (2006)) of finite temperature magnetic properties of Ni$_{1+x}$MnSb Heusler alloy family ($0 \leq x \leq 1$) with particular attention to the role of electronic correlations beyond the local density approximation. Exchange interactions are calculated using the magnetic force theorem on the base of zero-temperature electronic structure obtained within the density functional theory. The resulting effective classical Heisenberg hamiltonian is treated by methods of statistical physics. Our results are in improved agreement with experiment compared to bare local density approximation results, particularly for alloys with lower nickel content.

To be published in: Journal of Magnetism and Magnetic Materials Contact person: Ján Rusz (rusz@mag.mff.cuni.cz)

Influence of correlation effects on the magneto-optical properties of the half-metallic ferromagnet NiMnSb

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Abstract

The magneto-optical spectra of NiMnSb were calculated in the framework of the local spin density approxi- mation LSDA combined with dynamical mean-field theory DMFT . Comparing with results based on the plain LSDA, the additional account of many-body correlations via DMFT results in a noticeably improved agreement of the theoretical Kerr rotation and ellipticity spectra with corresponding experimental data.

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Spectral function of ferromagnetic 3d-metals: a self-consistent LSDA+DMFT approach combined with the one-step model of photoemission

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Abstract

The electronic structure of ferromagnetic 3d-transition metals in the vicinity of the Fermi level is dominated by the spin-polarized d-bands. Experimentally, this energy region can be probed in detail by means of angle-resolved ultraviolet photoemission and inverse photoemission. In several earlier studies the measured spectra were described either within a single particle approach based on the local spin density approximation including matrix-element effects within the so-called one-step model or by sophisticated many-body approaches neglecting these effects. In our analysis we combine for the first time correlation with matrix-element effects to achieve an improved interpretation of photoemission data from ferromagnetic nickel.

(Accepted in: Phys. Rev. Lett.)
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Phase change materials by design: The role of vacancies and local distortions

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Abstract

Many "GeSbTe" based phase change materials contain vacancy concentrations around 10 per cent in their metastable crystalline structure. By employing density-functional theory the origin of these vacancies has been clarified. Our calculations show that the most stable crystalline phases with rocksalt-like structures are characterized by large vacancy concentrations and local distortions. The ease by which vacancies are formed is explained by the need to annihilate energetically unfavorable antibonding Ge–Te and Sb–Te interactions in the highest occupied bands. Understanding how the interplay between vacancies and local distortions lowers the total energy helps to design novel phase change materials as evidenced by new experimental data.

(In press at Nature Mater.)

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Morphology and magnetism of Fe monolayers and small Fe$_n$ clusters ($n = 2 - 19$) supported on the Ni (111) surface

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Abstract

Using the modified embedded atom model in conjunction with a self-consistent tight-binding method, we investigated the lowest-energy structures of Fe monolayers and isolated Fe$_n$ clusters ($n = 2 - 19$) supported on the Ni (111) surface. In keeping with experimental findings, our calculations predict that the atoms of the monolayer occupy fcc rather than hcp sites. Likewise in agreement with experiment we found that Fe layers stack with a pseudomorphic fcc structure up to two monolayers, beyond which they stack as bcc(110). The structures of supported Fe clusters are predicted to be two-dimensional islands maximizing the number of nearest-neighbor bonds among the adsorbed Fe atoms, and their average magnetic moments per atom decrease towards that of the supported Fe monolayer almost monotonically as n increases. Finally, a pair of Fe$_3$ clusters on Ni(111) were found to exhibit virtually no interaction with each other even when separated by only one atomic row, i.e. so long as they do not coalesce they retain their individual magnetic properties.

(Accepted in Nanotechnology)
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Noncollinear magnetism caused by intermixing in ferromagnetic/antiferromagnetic interfaces

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Abstract

Fe-Cr alloy layers on Fe(001) substrates with different atomic environments are theoreticaly investigated through a self-consistent real space tight binding method parameterized to density functional theory and without collinear restriction for the spin directions.We show that the intermixing at the Cr/Fe interface, experimentally observed at the first stages of the Cr growth on Fe, originates noncollinear magnetic arrangements within the system and even induces magnetic walls in the Fe layer with a magnetic domain close to the interface. A different behavior is shown if steps are present at the interface i.e. noncollinear magnetism becomes more localized and the induced magnetic wall in Fe vanishes.

(Accepted in Phys. Rev. B)
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Calculation of the work function with a local basis set

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Abstract

Electronic structure codes usually allow to calculate the work function as a part of the theoretical description of surfaces and processes such as adsorption thereon. This requires a proper calculation of the electrostatic potential in all regions of space, which is apparently straightforward to achieve with plane wave basis sets, but more difficult with local basis sets. To overcome this, a relatively simple scheme is proposed to accurately compute the work function when a local basis set is used, by having some additional basis functions in the vacuum. Tests on various surfaces demonstrate that a very good agreement with experimental and other theoretical data can be achieved.

Surface Science Letters, in press
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Structure of active sites in Pd–exchanged mordenite: A density–functional investigation.

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Abstract

The removal of NO_x from exhaust gases is of major importance for environmental protection. Ammonia as reducing agent is used in stationary power sources, but is highly impractical for vehicles. Selective catalytic reduction (SCR) by hydrocarbons using acid zeolites as catalysts is an appealing alternative, although reaction conditions (high temperature, high water and oxygen content) are very demanding for the catalyst. Promising results were reported with Pd–exchanged mordenite as the catalytic system.

Understanding the SCR process requires a detailed knowledge of the structure of active sites. Location, state and reactivity of Pd cations are influenced by the distribution of aluminum sites within the zeolite framework. Using periodic density functional theory (DFT) the distribution of Al over the tetrahedral framework sites in mordenite has been investigated. A very narrow (0.6 eV) energetic distribution was found for all Al distributions considered, with a slightly lower energy for substitution in T1 and T2 than in T3 and T4 sites.

Pd^{2+} cations were introduced at various positions and the structure was allowed to fully relax. Energy differences between Pd placed in the main channel and the side channel were found to be small (ca. 0.5 eV). However, in most cases, palladium requires a very specific arrangement of two Al ions to be effectively stabilized. Only in the case of Pd placed in the 6–member ring in the wall of the main channel, the detailed Al arrangement did not play a significant role. In fact, even with only one aluminum in the vicinity, palladium is well stabilized (the energy is only 0.43 eV above the optimum). As a result, the cations are more likely to be found in the main rather than the side channel. However, with increasing Al content the Pd distribution should tend to become more random.

KEYWORDS: zeolite, mordenite, palladium, SCR, catalyst, periodic DFT

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Substrate effects on surface magetetism of Fe/W(110) from first principles

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Abstract

Surface magnetic properties of the pseudomorphic Fe(110) monolayer on a W(110) substrate are investigated from first principles as a function of the substrate thickness (up to eight layers). Analyzing the magnetocrystalline anisotropy energies, we find stable (with respect to the number of substrate layers) in-plane easy and hard axes of magnetization along the [1[overline 1]0] and [001] directions, respectively, reaching a value in good agreement with experiment for thick substrates. Additionally, the changes to the magnetic spin moments and the density of the Fe d states are analyzed with respect to the number of substrate layers as well as with respect to the direction of magnetization. With respect to the number of W(110) substrate layers beneath the Fe(110) surface, we find that the first four substrate layers have a large influence on the electronic and magnetic properties of the surface. Beyond the fourth layer, the substrate has only marginal influence on the surface properties. `doi:10.1103/PhysRevB.74.184415`

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Inter-atomic bonds and the tensile anisotropy of trialuminides in the elastic limit: A density functional study for Al_3(Sc,Ti,V,Cr)

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Abstract

The tensile anisotropy in the elastic limit of Al_3(Sc,Ti,V,Cr) intermetallic compounds in both $L1_2$ and $D0_{22}$ crystal structure have been investigated using first-principles density-functional calculations. In both crystal structures the main bonding character comes from the saturation of dominant d^3 ($L1_2$) and d^4 ($D0_{22}$) hybrid orbitals located on the TM atoms. The series $Al_3Sc \rightarrow Al_3V$ corresponds to the gradually d-band filling and leads to a gradual increase of bond-strength and covalent bond formation. The magnetism of Cr breaks this trend in the Al_3Cr compound (for both ferromagnetic and anti-ferromagnetic configurations). In this series, a trend towards an increased anisotropy of the elastic constants, Young modulus Y and Poisson ratio ν is observed. The easy and hard directions of tension can be simply identified by the variation of Y, which corresponds to the presence or absence of covalently bonded –Al–TM– chains. A high anisotropy of Poisson ratio arises also from an alternation of atoms in the lateral directions and can be understood in the same terms.

(Accepted for publication in Phil. Mag.)

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Formation of Magnetic Minerals by Non-Magnetotactic Prokaryotes

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Abstract

Magnetic minerals produced by non-magnetotactic microbes include magnetite (Fe_3O_4), greigite (Fe_3S_4) and pyrrhotite (Fe_7S_8). These are produced by a diverse range of Fe(III)-reducing, Fe(II)-oxidising and sulfate-reducing prokaryotes. The mechanisms of formation of magnetic minerals by bacteria are still under investigation, and have been studied most intensively in Fe(III)- and sulfate-reducing bacteria. In the subsurface, the formation of magnetic Fe(II)-bearing minerals can affect the mobility of contaminants through sequestration of toxic metals such as zinc or the reduction of metals such as uranium(VI) or organic contaminants. This review covers the mechanisms of magnetic biomineral synthesis by a diversity of non-magnetotactic prokaryotes, and also discusses their potential biotechnological exploitation in a range of applications including bioremediation and the construction of magnetic recording devices and catalytic systems.

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High-order Dy multipole motifs observed in DyB_2C_2 with resonant soft x-ray Bragg diffraction

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Abstract

Resonant soft X-ray Bragg diffraction at the Dy $M_{4,5}$ edges has been exploited to study Dy multipole motifs in DyB_2C_2. Our results are explained by introducing the intra-atomic quadrupolar interaction between the core $3d$ and valence $4f$ shell. This allows us to determine for the first time higher-order multipole moments of dysprosium $4f$ electrons and to draw their precise charge density. The Dy hexadecapole and hexacontatetrapole moment have been estimated at -20% and $+30\%$ of the quadrupolar moment, respectively. No evidence for the lock-in of the orbitals at T_N has been observed, in contrast to earlier suggestions. The multipolar interaction and the structural transition cooperate along c but they compete in the basal plane, explaining the canted structure along [110].

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Curvature and chirality dependence of the properties of point defects in nanotubes

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Abstract

This article presents a systematic study of how point defects, such as SW-defects and vacancies, influence the properties of nanotubes. The DFT calculations show that large atomic relaxations at point defects leads to a contraction of the nanotube. The formation energy E_{form}, has a curvature, chirality and a family dependence, where E_{form} is slightly lower in metallic compared to semiconducting nanotubes. The point defects become electrically active due to defect states close to ϵ_{F} and its population depend on the chirality and the position of ϵ_{F}. A model based on the heat of formation of defective nanotubes furthermore provide an upper estimate for the defect concentration, which is in better agreement with values from AFM experiments than the standard equilibrium approximation.

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Composition and strain dependence of the piezoelectric coefficients in $In_xGa_{1-x}As$ alloys

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Abstract

We address the issue of the composition and strain dependence of the piezoelectric effect in semiconductor materials, which is manifested by the appearance of an electric field in response to shear crystal deformation. We propose a model based on expressing the direct and dipole contributions to the polarization in terms of microscopic quantities that can be calculated by Density Functional Theory (DFT). We show that when applied to the study of $In_xGa_{1-x}As$ alloys, the model is able to explain and accurately predict the often observed discrepancies between the experimentally deduced values of e_{14} and those linearly interpolated between the values of InAs and GaAs. The values of the piezoelectric coefficient predicted by our approach compare very well with values deduced from photocurrent measurements of Quantum Well samples grown on (111) GaAs substrates by Molecular Beam Epitaxy.

(submitted to: Phys. Rev. B, accepted)
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Control of fine-structure splitting and excitonic binding energies in selected individual InAs/GaAs quantum dots

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Abstract

A systematic study of the impact of annealing on the electronic properties of single InAs/GaAs quantum dots (QDs) is presented. Single QD cathodoluminescence spectra are recorded to trace the evolution of one and the same QD over several steps of annealing. A substantial reduction of the excitonic fine-structure splitting upon annealing is observed. In addition the binding energies of different excitonic complexes change dramatically. The results are compared to model calculations within 8-band kp theory and the configuration interaction method suggesting a change of electron and hole wavefunction shape and relative position.

(submitted to: Appl. Phys. Lett., accepted)

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The three-dimensional equilibrium crystal shape of Pb: Recent results of theory and experiment

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Abstract

The three-dimensional equilibrium crystal shape (ECS) is constructed from a set of 35 orientation-dependent surface energies of fcc Pb which are calculated by density functional theory in the local-density approximation and distributed over the and zones of the stereographic triangle. Surface relaxation has a pronounced influence on the equilibrium shape. The (111), (100), (110), (211), (221), (411), (665), (15,1,1), (410) and (320) facets are present after relaxation of all considered surfaces, while only the low-index facets (111), (100) and (110) exist for the unrelaxed ECS. The result for the relaxed Pb crystal state is in support of the experimental ECS of Pb at 320-350 K. On the other hand, approximating the surface energies of vicinal surfaces by assuming a linear relationship between the Pb(111) first-principles surface energy and the number of broken bonds of surface atoms leads to a trivial ECS that shows only (111) and (100) facets, with a 6-fold symmetric (111) facet instead of the correct 3-fold symmetry. It is concluded that the broken bond rule in this simple linear form is not a suitable approximation for obtaining the proper three-dimensional ECS and correct step formation energies.

(accepted at: Appl. Phys. A)
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Density-functional theory study of half-metallic heterostructures: interstitial Mn in Si

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Abstract

Using density-functional theory within the generalized gradient approximation, we show that Si-based heterostructures with 1/4 layer δ-doping of *interstitial* Mn (Mn_{int}) are half-metallic. For Mn_{int} concentrations of 1/2 or 1 layer, the states induced in the band gap of δ-doped heterostructures still display high spin polarization, about 85% and 60%, respectively. The proposed heterostructures are more stable than previously assumed δ-layers of *substitutional* Mn. Contrary to wide-spread belief, the present study demonstrates that *interstitial* Mn can be utilized to tune the magnetic properties of Si, and thus provides a new clue for Si-based spintronics materials.

(submitted to: Phys. Rev. Lett.)
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Observation of subsurface Mn on the Si(001)-(2×1) reconstructed surface

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Abstract

The deposition of Mn atoms onto the Si(001)-(2×1) reconstructed surface has been studied using scanning tunneling microscopy (STM) and first-principles electronic structure calculations. Room temperature deposition of 0.1 monolayers of Mn gives rise to a disordered surface structure. After *in situ* annealing between 300–700 °C, most of the Mn is incorporated into three-dimensional manganese silicide islands, and Si dimer rows re-appear in the STM images on most of the substrate surface. At the same time, row-like structures are visible in the atomic-scale STM images. A comparison with calculated STM images provides evidence that Mn atoms are incorporated into the row structures in subsurface interstitial sites, which is the lowest energy position for Mn on Si(001). The subsurface Mn alters the height and local density of states of the Si dimer atoms causing them to appear 0.6 Å higher than a neighboring Si dimer with no Mn below. This height difference that allows the detection the subsurface Mn results from a subtle interplay of geometrical and electronic effects.

(submitted to: Phys. Rev. B)
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Au wetting and nanoparticle stability on GaAs(111)B

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Abstract

Au nanoparticles and Au films for growth of nanowires on the GaAs(111)B surface have been studied by a combination of experimental and theoretical techniques. If Au is present in either form, annealing to temperatures relevant for nanowire growth results in the formation of a thin Au wetting layer. Based on DFT calculations and experimental data, a structural model is proposed with an Au atom on every third threefold hollow hcp site of the Ga lattice. We observe that the stability of Au nanoparticles is governed by the presence of the wetting layer and out-diffusion of Au from the nanoparticles.

(submitted to: Appl. Phys. Lett.)
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Atomic and electronic structure of BeO and the BeO($10\bar{1}0$) surface: An ab initio investigation

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Abstract

We report the atomic and electronic structure of bulk BeO and the nonpolar BeO($10\bar{1}0$) surface as resulting from density functional theory (DFT). Employing norm-conserving pseudopotentials which incorporate self-interaction corrections (SIC) we arrive at structural and electronic properties of bulk BeO which are not subject to the usual shortcomings of the standard local density approximation (LDA), most noticeably the underestimate of the band gap. The latter is particularly large for BeO amounting to more than 3 eV. It turns out that the LDA problems can largely be overcome by employing SIC pseudopotentials in DFT calculations. They cause no additional computational effort, as compared to standard LDA calculations. Our SIC approach yields a bulk band gap of 10.5 eV in excellent agreement with the measured gap of 10.6 eV and calculated structural bulk properties are found to be in very good accord with experiment, as well. Also the surface electronic structure of BeO($10\bar{1}0$) shows very significant SIC-induced changes, as compared to the respective standard LDA surface band structure. For the relaxed surface, showing a bond-lengths contracting rotation relaxation, we find three salient bands of surface states. Two of these occur within the fundamental gap fairly close to the projected bulk bands from which they are derived. The surface band gap resulting in SIC is 9.1 eV, as opposed to the LDA surface band gap of 6.4 eV.

(Physical Review B **74**, December 15 (2006))
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Why H_2 Molecules Adsorb on SiC(001)-c(4×2) and Not on SiC(001)-(3×2) at Room Temperature

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Abstract

In experiment, the amazing observation has been made that H_2 molecules readily adsorb dissociatively on the c(4×2) but not on the 3×2 surface of SiC(001) at room temperature. To unravel this spectacular reactivity difference, we have investigated a variety of H_2 reaction scenarios within density functional theory using the generalized gradient approximation. It turns out that *intradimer* adsorption is unlikely at both surfaces while *interdimer* adsorption depends crucially on the distinct spatial arrangement and dangling-bond topology of the Si dimers at the surfaces. The results clearly reveal barrierless reaction pathways for dissociative H_2 adsorption on the c(4×2) surface as opposed to pathways with significant energy barriers on the 3×2 surface. The latter finding also allows us to explain the inertness of self-organized Si addimer nanolines on the c(4×2) surface to H_2 uptake.

(submitted to: Phys. Rev. Lett.)
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Thermally activated charge reversibility of gallium vacancies in GaAs

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Abstract

The dominant charge state for the Ga vacancy in GaAs has been the subject of a long debate, with experiments suggesting -1, -2, or -3 as the best answer. We revisit this problem using ab initio calculations to compute the effects of temperature on the Gibbs free energy of formation, and we find that the thermal dependence of the Fermi level and of the ionization levels lead to a reversal of the preferred charge state as the temperature increases. Calculating the concentrations of gallium vacancies based on these results, we reproduce two conflicting experimental measurements, showing that these can be understood from a single set of coherent local density approximation results when thermal effects are included.

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Charge-dependent migration pathways for the Ga vacancy in GaAs

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Abstract

Using a combination of the local-basis ab initio program SIESTA and the activation-relaxation technique we study the diffusion mechanisms of the gallium vacancy in GaAs. Vacancies are found to diffuse to the second neighbor using two different mechanisms, as well as to the first and fourth neighbors following various mechanisms. We find that the height of the energy barrier is sensitive to the Fermi level and generally increases with the charge state. Migration pathways themselves can be strongly charge dependent and may appear or disappear as a function of the charge state. These differences in transition state and migration barrier are explained by the charge transfer that takes place during the vacancy migration.

PHYSICAL REVIEW B 74, 205207 2006

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10 Introducing New Journals

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11 SCIENTIFIC HIGHLIGHT OF THE MONTH: "Spin Orbit Driven Physics at Surfaces"

Spin Orbit Driven Physics at Surfaces

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Abstract

The pioneering spintronic proposal of a spin field-effect transistor by Datta and Das motivated largely the research of the spin related behavior of electrons propagating in the potentials with structure inversion asymmetry (SIA). Owing to the spin-orbit interaction, inversion asymmetric potentials give rise to a Bychkov-Rashba spin-orbit coupling causing a spin-splitting of a spin-degenerate electron gas. In this article we show that the rich spin-orbit driven physics in potentials with SIA is effective also for electrons at metallic surfaces. Carrying out first-principles calculations based on density functional theory (DFT) employed in a film full-potential linearized augmented plane-wave (FLAPW) method in which spin-orbit coupling (SOC) is included, we investigate the Rashba spin-splitting of surface electrons at noble-metal surfaces, e.g. Ag(111) and Au(111), at the semimetal surfaces Bi(111) and Bi(110), and the magnetic surfaces Gd(0001) and O/Gd(0001). E.g. on the Bi(110) surface the Rashba spin-splitting is so large that the Fermi surface is considerably altered, so that the scattering of surface electrons becomes fundamentally different. On a magnetic surface, the Rashba splitting depends on the orientation of the surface magnetic moments with respect to the electron wavevector, thus offering a possibility to spectroscopically separate surface from bulk magnetism. Due to the interplay of SIA and SOC effects, magnetic impurities in an electron gas experience spin-spin interactions which arise not only from the common Ruderman-Kittel-Kasuya-Yoshida-type (RKKY) symmetric Heisenberg exchange but in addition also from an Dzyaloshinskii-Moriya-type (DM) antisymmetric exchange. The origin of the latter can be a combination of Moriya-type spin-orbit scattering at the impurities plus kinetic exchange between the impurities and the Fert-Levy type exchange due to relativistic conduction electrons. Assuming that the DM is smaller than the symmetric exchange interaction, we develop a continuum model to explore the rich phase space of possible magnetic structures. Depending on the strength of the DM interaction, we expect in low-dimensional magnets deposited on substrates, such as ultrathin magnetic films, chirality broken two- or three-dimensional magnetic ground-state structures between nanometer and sub-micrometer lateral scale. We present two approaches on how the strength of the DM interaction, the so-called DM vector **D**, can be calculated from *ab initio* methods, either using the concept of infinitesimal rotations applicable to Green function type electronic structure methods or using the concept of homogeneous spin-spirals more applicable to a supercell type electronic structure method. We determine **D** for a doublelayer of Fe on W(110) and show that the quantity is sufficiently large to compete with other interactions. We demonstrate that SOC

effects are essential for the understanding of magnetic structures in these ultrathin magnetic films.

1 Introduction

Two independent experiments carried out in 1988 by Albert Fert [1] in Paris and Peter Grünberg in Jülich [2] mark the beginning of *magnetoelectronics* or *spintronics*. In these experiments it was found that an electrical current passing through ferromagnetic films separated by non-magnetic metallic spacer layers is subject to a resistivity which changes by an unexpectedly large amount (gigantic amount at those days) with the change of the relative alignment of the magnetization in these films from ferromagnetic to antiferromagnetic. This observation was coined the giant-magneto-resistance effect or GMR. Obviously GMR made it possible to turn the information of a two-state magnetic configuration (parallel or anti-parallel associated with bit 0 or 1) into an electrical one, or in a more abstract sense, turn spin information into charge current information. Already 8 years after the discovery, this effect is used for example in sensors embodied in read heads in hard disk drives common to all contemporary PCs. Today spintronics is a very active and driving multidisciplinary field whose central theme is the active manipulation of spin-degrees of freedom in solid state systems combining issues of central importance for fundamental physics with great perspectives in applications [3, 4].

Very recently, in the field of *semiconductor spintronics* a number of spin-electronic devices have been proposed, which explicitly make use of the Rashba effect. Here, the basic idea is the control of the spin orientation by utilizing the Rashba spin-orbit coupling [5] utilizing a spin splitting due to spin-orbit coupling in the presence of a structure inversion asymmetric (SIA) potential. This mechanism opens up the possibility to design electronic devices, where the switching process is realized by changing the spin orientation in the semiconductor without application of an external magnetic field. In fact, this scheme is the basis for the well-known spin transistor proposed by Datta and Das [6].

The Datta-Das proposal motivated largely the research of the spin-orbit driven spin splitting in SIA potentials, which turns out to be a rather general phenomenon, and arises not only in two-dimensional electron gases of semiconductor heterostructures but in particular also at (metallic) surfaces and interfaces. Today, the investigation of the spin-orbit coupling of systems with a SIA, provides a subject involving different fields of science including mesoscopic physics, low-temperature physics, surface science, electron spectroscopy, scanning tunneling microscopy (STM) and spectroscopy (STS), nanomagnetism and electronic structure theory. In this article we review at first in section 2 our theoretical first-principles investigations of the Rashba spin-splitting of surface electrons at noble-metal surfaces, e.g. Ag(111) and Au(111), at the semimetal surfaces Bi(111) and Bi(110), and then at magnetic surfaces Gd(0001) and O/Gd(0001). Electrons subjected to the spin-orbit interaction in magnets with a SIA, generate besides the common symmetric Heisenberg-type [7] of exchange, an antisymmetric exchange between spins, known as the Dzyaloshinskii-Moriya (DM) interaction [8, 9] (although the original work was in the context of weak ferromagnetism of insulating antiferromagnetic oxides crystallized in non-centrosymmetric lattices, which relates rather to a Dresselhaus spin-splitting of electrons than to the Rashba spin-splitting, and to a superexchange mechanism rather than that of conduction electrons, for details see below). As we discuss in section 3, the DM interaction destabilizes collinear magnetic structures and favors non-collinear ones. Although about the existence of the DM interaction at surfaces or in nanomagnets cannot be argued in principle, as the reasoning is based on symmetry considerations, after 20 years of intense experimental research in the field of ultrathin magnetic films there are no experimental reports discussing or concluding on the DM interaction in this context. This may suggest that the DM interaction is small and unimportant. In this article we show this is not so. In fact, nobody knows how strong it actually is. We think it is correct to assume that the antisymmetric exchange is smaller than the symmetric one. Then, depending on the strength of the DM interaction, we expect in low-dimensional magnets deposited on substrates, such as ultrathin magnetic films, magnetic ground-state structures with a lateral length scale between nanometer and sub-micrometer. This encouraged us to develop a micromagnetic continuum model, presented in section 4, in which we explore the rich phase space of possible magnetic structures. Which of the possible two- or three-dimensional magnetic phases are realized in nature depends strongly on the strength of the DM interaction. This makes first-principles calculations very valuable. At the same time, the fact that one deals here with magnetic structures of large lateral extent, at surfaces, requiring spin-orbit interaction and structural relaxation makes first-principles calculations a true challenge. This might be the reason why in fact no hard numbers are known for **D**. In this article we report on two conceptually different approaches to calculate the Dzyaloshinskii-Moriya vector **D** from first-principles. In section 5.1, **D** is derived in the spirit of the Lichtenstein formula [10] using the concept of infinitesimal rotations. The method is optimally suited for Green-function type electronic structure methods. To calculate **D** by wave function based methods we outline in section 5.2 a perturbative treatment of the spin-orbit interaction on top of self-consistently calculated homogeneous periodic spin-spirals. All results are obtained with the full-potential linearized augmented planewave method [11] as implemented in the `FLEUR` code [12]. Our calculations include spin-orbit coupling (SOC) [13] and spin-spirals are implemented in the general context of non-collinear magnetism according to reference [14]. In section 6 we present an example where we actually calculated **D** for a Fe double layer on W(110), and discuss the consequences for the magnetic structures of domain walls for that system. At first, we continue with some simple considerations about Rashba spin-spitting due the spin-orbit interaction in SIA, and what it means for the Datta-Das spin-field-effect transistor. A motivation to study these effects is to translate these concepts to the physics of nanostructures at surfaces.

1.1 Rashba Effect

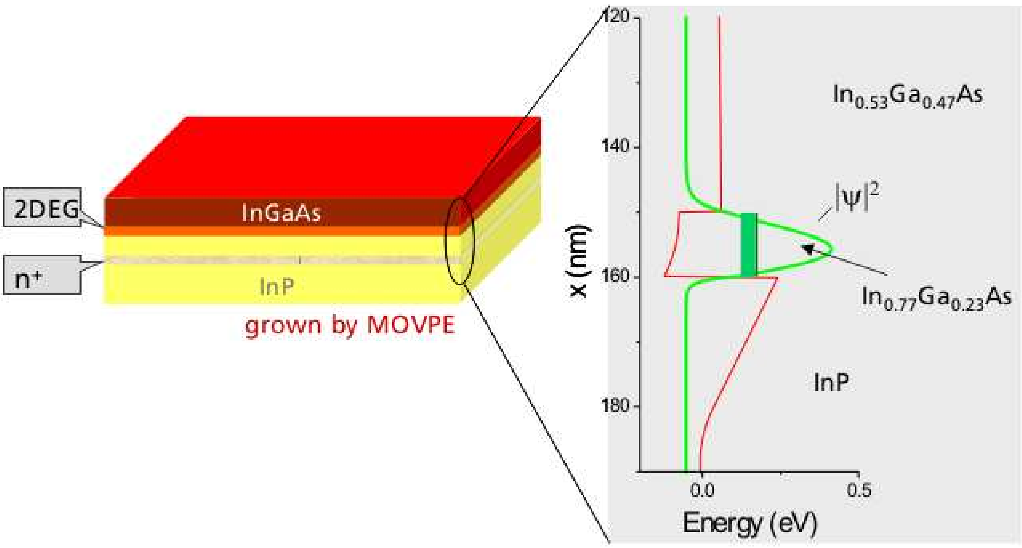


Figure 1: Schematic illustration of a $In_{0.53}Ga_{0.47}As/In_{0.77}Ga_{0.23}As/InP$ heterostructure. The two-dimensional electron gas is located in the strained $In_{0.77}Ga_{0.23}As$ layer. Such a heterostructure is typically grown by metal-organic vapor phase epitaxy on a semi-insulating InP substrate. The two-dimensional electron gas (2DEG) is located in a strained 10 nm thick $In_{0.77}Ga_{0.23}As$ layer. The lower barrier of the quantum well is formed by an InP layer, while for the upper layer a 70 nm thick $In_{0.53}Ga_{0.47}As$ layer is used. The electrons are provided by a 10 nm thick InP dopant layer separated by 20 nm of InP from the quantum well [15].

In order to look in more detail into the principles of the Rashba effect in semiconductors we consider a two-dimensional electron gas (2DEG) as it develops typically in epitaxially grown III-V quantum-well heterojunctions shown for example in figure 1. Considering the 2DEG in a constant potential e.g. $V_0 = 0$, neglecting electron correlation and working in a single-particle picture, in the absence of internal and external magnetic fields, $B = 0$, then the motion of the electrons is described by the simple kinetic energy Hamiltonian $H_{\mathrm{K}} = \frac{\mathbf{p}^2}{2m^*}$. p is the momentum operator and m^* are the masses of the valence or conduction band electrons, respectively. The single particle energy $\varepsilon(\mathbf{k}) = \frac{\hbar^2}{2m^*}\mathbf{k}^2$ depends on the Bloch vector $\mathbf{k}$, indicating the orbital motion of the eigenstate, which is a plane wave $\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}}e^{i\mathbf{kr}}$. Each eigenstate $\varepsilon_{\uparrow\downarrow}(\mathbf{k})$ is two-fold degenerate for spin-up and spin-down electrons which is a combined consequence of inversion symmetry of space and time. Space inversion symmetry changes the wave vector $\mathbf{k}$ into $-\mathbf{k}$ and for each spin-direction σ, $\sigma \in \{\uparrow, \downarrow\}$, the single-particle energy transforms as $\varepsilon_\sigma(\mathbf{k}) = \varepsilon_\sigma(-\mathbf{k})$. Time inversion symmetry flips in addition the spin, i.e. $\varepsilon_\uparrow(\mathbf{k}) = \varepsilon_\downarrow(-\mathbf{k})$, known as the Kramers degeneracy of the single-particle states. Thus, when both symmetry operations are combined we obtain the two-fold degeneracy of the single-particle energies, $\varepsilon_\uparrow(\mathbf{k}) = \varepsilon_\downarrow(\mathbf{k})$. When the potential through which the carriers move is inversion-asymmetric as in the example of the strained heterojunction in figure 1, then the spin-degeneracy is removed even in the absence of an external magnetic field $\mathbf{B}$. Performing a Taylor expansion of the potential $V(\mathbf{r})$, $V(\mathbf{r}) = V_0 + e\mathbf{E}\cdot\mathbf{r} + \cdots$, in lowest order the inversion asymmetry of the potential $V(\mathbf{r})$ is characterized by an electric field $\mathbf{E}$. When electrons propagate with a velocity $\mathbf{v} = d\varepsilon/d\mathbf{p} = \frac{\hbar}{m^*}\mathbf{k}$ in an external electric field $\mathbf{E}$ defined in a global frame of reference, then the relativistic Lorentz transformation gives rise to magnetic field $\mathbf{B} = \frac{1}{c}\mathbf{v}\times\mathbf{E} = \frac{\hbar}{m^*c}\mathbf{k}\times\mathbf{E}$ in local frame of the moving electron. The interaction of the spin with this $\mathbf{B}$ field leads then to the Rashba or Bychkov-Rashba Hamiltonian [16, 17]

$$H_{\mathrm{R}} = \frac{\alpha_{\mathrm{R}}}{\hbar}\,\boldsymbol{\sigma}(\mathbf{p}\times\mathbf{E}) \qquad \text{or} \qquad H_{\mathrm{R}} = \alpha_{\mathrm{R}}\,\boldsymbol{\sigma}(\mathbf{k}\times\mathbf{E}) \qquad \text{or} \qquad H_{\mathrm{R}} = \alpha_{\mathrm{R}}(|\mathbf{E}|)\,\boldsymbol{\sigma}(\mathbf{k}\times\hat{\mathbf{e}}) \tag{1}$$

describing the Rashba spin-orbit coupling as additional contribution to the kinetic energy. $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ are the well-known Pauli matrices. The latter two terms are strictly correct only for plane wave eigenstates as for the 2DEG. α_{R} denotes a materials-specific prefactor, known as Rashba parameter. Different definitions exist, also that for which the strength of the $\mathbf{E}$-field, $|\mathbf{E}|$, is included in $\alpha_{\mathrm{R}}(|\mathbf{E}|)$ and only the direction of $\mathbf{E}$, $\hat{\mathbf{e}}$, enters the Hamiltonian. This Hamiltonian leads then to the structure inversion-asymmetric (SIA) spin splitting, the Rashba effect [5, 16, 17]. Today, it is common practice to use the term *Rashba-effect* both for the Hamiltonian given in equation (1) as well as for the SIA spin splitting in general.

Although we have motivated the Rashba Hamiltonian heuristically by a Lorentz transformed confining external electric field, in general the Rashba parameter α_{R} is not directly proportional to it. Instead a microscopic view is required and the effect is caused by the spin-orbit interaction as described in a Pauli-like (or scalar-relativistic equation plus spin-orbit interaction as for *ab initio* calculations, c.f. subsection 2.1) equation (15), which takes care on the Lorentz transformation locally of the moving electron of quantum number $\mathbf{k}$ in the structure inversion-asymmetric potential. Then, the strength of SIA spin splitting depends on the asymmetry of the electronic structure on the spin-orbit matrix elements, most prominently on the asymmetry of the penetration of the electron wave functions into the barrier, but also on the orbital character, the size of the band gap and the atomic spin-orbit strength which scales typically quadratically with the nuclear number Z. Electronic structure $\mathbf{k}\cdot\mathbf{p}$ calculations of α_{R} can be found in the book of Winkler [18] and references therein.

The general features of the Rashba-model are studied for the 2DEG in a SIA potential and the solution is displayed schematically in figure 2. For electrons propagating in the 2DEG extended in the (x, y) plane subject to an electric field normal to the 2DEG, $\hat{\mathbf{e}}_z = (0, 0, 1)$, the Hamiltonian takes the form

$$H = H_{\mathrm{K}} + H_{\mathrm{R}} = \frac{\mathbf{p}_\parallel^2}{2m^*} + \frac{\alpha_{\mathrm{R}}}{\hbar}\,(\boldsymbol{\sigma}\times\mathbf{p}_\parallel)_{|z} = \frac{\mathbf{p}_\parallel^2}{2m^*} + \frac{\alpha_{\mathrm{R}}}{\hbar}\,(\sigma_x p_y - \sigma_y p_x)\,, \tag{2}$$

which is solved analytically. For a Bloch vector in the plane of the 2DEG, $\mathbf{k}_\parallel = (k_x, k_y, 0) = k_\parallel(\cos\varphi, \sin\varphi, 0)$, the eigenstates written as a product of plane wave in space and two-component spinor are

$$\psi_{\pm\mathbf{k}_\parallel}(\mathbf{r}_\parallel) = \frac{e^{i\mathbf{k}_\parallel \cdot \mathbf{r}_\parallel}}{2\pi} \frac{1}{\sqrt{2}} \begin{pmatrix} ie^{-i\varphi/2} \\ \pm e^{i\varphi/2} \end{pmatrix} \tag{3}$$

with eigenenergies

$$\varepsilon_\pm(\mathbf{k}_\parallel) = \frac{\hbar^2}{2m^*}\mathbf{k}_\parallel^2 + \alpha_\mathrm{R}\left(\boldsymbol{\sigma} \times \mathbf{k}_\parallel\right) = \frac{\hbar^2}{2m^*}\mathbf{k}_\parallel^2 \pm \alpha_R|\mathbf{k}_\parallel| = \frac{\hbar^2}{2m^*}(k_\parallel \pm k_\mathrm{SO})^2 - \Delta_\mathrm{SO}\,, \tag{4}$$

where ± denotes the spin-up and -down states with respect to a spin orientation axis $\hat{\mathbf{n}}(\mathbf{k}_\parallel)$, local in $\mathbf{k}_\parallel$ space. With the exception of the high-symmetry state $k_\parallel = 0$, we find that the original two-fold degenerate energy paraboloid of the 2DEG in a constant potential indeed spin-splits. The spin splitting $\varepsilon_+(\mathbf{k}_\parallel) - \varepsilon_-(\mathbf{k}_\parallel) = 2\alpha_r k_\parallel$ is linear in $k_\parallel$. Due to the presence of the SIA potential and the spin-orbit interaction, the origin of the degenerate parabola is shifted by $k_\mathrm{SO} = m^*\alpha_R/\hbar^2$, but in opposite directions for up- and down-spins with in overall spin-orbit lowering of $\Delta_\mathrm{SO} = m^*\alpha_R/(2\hbar^2)$. The orientation axis is given by the expectation value

$$\hat{\mathbf{n}}_\pm(\mathbf{k}_\parallel) = \langle\psi_{\pm\mathbf{k}_\parallel}|\boldsymbol{\sigma}|\psi_{\pm\mathbf{k}_\parallel}|\rangle = \pm\begin{pmatrix} \sin\varphi \\ -\cos\varphi \\ 0 \end{pmatrix} \quad \perp \quad \mathbf{k}_\parallel = k_\parallel \begin{pmatrix} \cos\varphi \\ \sin\varphi \\ 0 \end{pmatrix}. \tag{5}$$

We find that the orientation axis is independent of the magnitude $k_\parallel$ and depends only on the direction of the $\mathbf{k}_\parallel$ vector. In fact, it is in the plane of the 2DEG and the orientation axis is perpendicular to the propagation direction of the electron. Considering $\mathbf{k}_\parallel \to -\mathbf{k}_\parallel$, φ changes to $\varphi + \pi$, we find that the spin orientation axis reverses. $\hat{\mathbf{n}}_\pm(\mathbf{k}_\parallel) \to \hat{\mathbf{n}}_\mp(-\mathbf{k}_\parallel) \to -\hat{\mathbf{n}}_\pm(-\mathbf{k}_\parallel)$. Thus for $\mathbf{k}_\parallel$ and $-\mathbf{k}_\parallel$ the spin-up and -down states refer to opposite orientations. Defining a global quantization axis along the line $(-\mathbf{k}_\parallel, \mathbf{k}_\parallel)$, e.g. according to $\hat{\mathbf{n}}_\pm(+\mathbf{k}_\parallel)$, then a spin-up state appears as spin-down state if $\mathbf{k}_\parallel$ changes sign. Together with the eigenvalue spectrum given in equation (4) the Kramer degeneracy $\varepsilon_\uparrow(\mathbf{k}_\parallel) = \varepsilon_\downarrow(-\mathbf{k}_\parallel)$ holds. In all, the magnetic moment is zero when averaged over all states $\mathbf{k}_\parallel$. This is consistent with the absence of an **B** field. The Rashba spin-orbit splitting may be observed either by electron photoemission or transport experiments. In both cases experiments have to be carried out at temperatures, k_BT which are lower than the energy difference of the spin-splitting, $\varepsilon_+(\mathbf{k}_\parallel) - \varepsilon_-(\mathbf{k}_\parallel)$. In angle resolved photoemission the eigenvalue spectrum is measured for a selected $\mathbf{k}_\parallel$ value. Two peaks at different energies are expected. Using spin-polarization analysis, for example using a Mott-detector oriented perpendicular to the propagation direction of the electron, different polarizations should be observed for the two peaks.

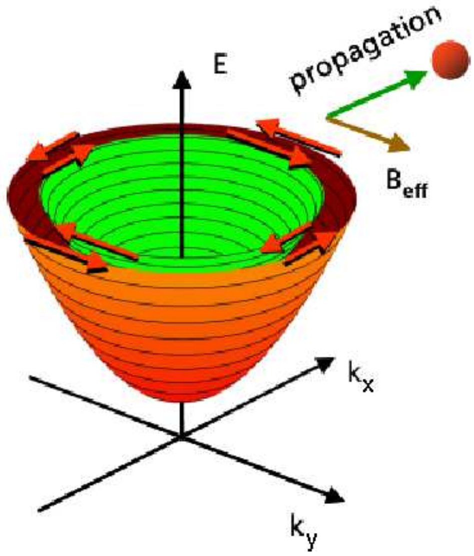


Figure 2: Parabolic energy dispersions of a two-dimensional electron gas in a structure inversion asymmetric (SIA) environment. Indicated are the vector fields of the spin-quantization axes (or the patterns of the spin) at the Fermi surface. As the opposite spins have different energies, the Fermi surface becomes two concentric circles with opposite spins. The effective B-field, $\mathbf{B}_\mathrm{eff}$ is perpendicular to the propagation direction defined by $\mathbf{k}_\parallel$.

Transport experiments work typically on a shell of constant energy ε. Here we expect at a given energy two different wave vectors for up- and down-electrons, which will be exploited in the Datta-Das proposal of a spin-transistor.

That the Pauli-like spin-orbit coupling may have important consequences for the one-electron energy levels in bulk semiconductors was first emphasized by Dresselhaus *et al.* [19] already in 1955. Unlike the diamond structure of Si and Ge, the zinc blende structure, in which for example the III-V semiconductor crystallize, exhibit a bulk inversion asymmetry (BIA), i.e. this crystal structure lacks a center of inversion, so that we can have a spin splitting of the electron and hole states at nonzero wave vectors $\mathbf{k}$ as for the Rashba effect even if $\mathbf{B} = 0$. Today, this is called the Dresselhaus effect. The corresponding Dresselhaus Hamiltonian

$$H_{\mathrm{D}} = \frac{\alpha_{\mathrm{D}}}{\hbar}\left[\sigma_x p_x \left(p_y^2 - p_z^2\right) + \sigma_y p_y \left(p_z^2 - p_x^2\right) + \sigma_z p_z \left(p_x^2 - p_y^2\right)\right] \tag{6}$$

describes the BIA spin splitting due to the Dresselhaus spin-orbit coupling, which produces spin vector fields quite different from those produced by the SIA splitting. One difference is obviously that the Dresselhaus term produced a spin splitting which is proportional to k^3, $\varepsilon_{\mathrm{D}} \propto k^3$, while the spin splitting of the Rashba-term is linear in k, $\varepsilon_{\mathrm{R}} \propto k$. Since we focus in this article on spin-orbit driven physics of SIA potentials this term is not further considered.

1.2 Datta-Das Spin Field Effect Transistor

Figure 3 explains the Datta-Das [6] proposal of a spin field-effect transistor (SFET) exploiting the Rashba effect. What is remarkable about this theoretical transistor model is the fact that the tuning of the precessing spin-orientation is accomplished by applying an electric rather than a magnetic field. Considering the fact that in semiconductor devices it is much easier to generate electric fields as to integrate externally controllable magnetic fields, this paves a way to even more complex devices.

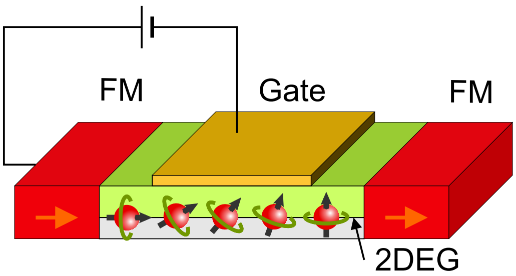


Figure 3: Scheme of the Datta-Das spin field-effect transistor (SFET). The source (spin injector) and the drain (spin detector) are ferromagnetic metals or semiconductors, with parallel alignment of magnetic moments. The injected spinpolarized electrons with wave vector $\mathbf{k}$ move ballistically through the 2DEG (which is actually quantized along a quasi-one-dimensional channel) formed by, for example, a strained InGaAs/InP heterojunction. While propagating from source to drain, electron spins precess about a precession axis, which arises from spin-orbit interaction, which is defined by the structure and the materials properties of the channel. The change of the precession angle with propagation distance is tunable by the gate voltage. The current is large if the electron spin at the drain points in the initial direction, and small if the direction is reversed. Shown is an intermediate situation. For simplicity we call the left ferromagnet the source, which acts as spin injector and the right ferromagnet the drain, which acts as spin analyzer.

To understand the principle of the Datta-Das transistor we consider again a 2DEG in the semiconductor part of the transistor located in the x-y-plane, while the quantum-well potential, as well as the variable gate voltage, are orientated along the z-axis. We develop a simple one-dimensional model. The x-axis is the direction of propagation for the electrons and at the same time the polarization axis of the ferromagnetic source and drain. As we have seen in subsection 1.1, the direction of propagation defined by $\mathbf{k}_{\parallel}$ determines the spin orientation $\hat{\mathbf{n}}$ of the eigenstates in the 2DEG, which is in the plane of the 2DEG pointing perpendicular to the propagation direction, which is the y and $-y$ direction in our frame of reference, i.e. $\mathbf{k}_{\parallel} = (k_x, 0, 0)$, $\varphi = 0$ and $\hat{\mathbf{n}} = \pm(0, 1, 0)$, taken the definitions entering equation (5). Neglecting the spatial plane wave prefactor, according to equation (3) the eigenstates with respect to this quantization axis take the form $| \uparrow\rangle = \frac{1}{\sqrt{2}}(i, 1)$ and $| \downarrow\rangle = \frac{1}{\sqrt{2}}(i, -1)$. An electron at the point of injection into the 2DEG next to the ferromagnetic injector is not in an eigenstate, because both spin and propagation vector point in the same direction. But its spinor quantized along the x direction, $| \rightarrow\rangle = \frac{1}{\sqrt{2}}(1, 1)$ can be expressed in terms of above eigenstate as

$$| \rightarrow\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{2}\left[(1-i)\frac{1}{\sqrt{2}}\begin{pmatrix} i \\ 1 \end{pmatrix} + (-1-i)\frac{1}{\sqrt{2}}\begin{pmatrix} i \\ -1 \end{pmatrix}\right]. \tag{7}$$

Taking into consideration that the eigenstates propagate as plane waves along the x-axis, the x-dependent amplitude $\psi(x)$ of the injected electron of fixed energy ε

$$\psi(x) = \frac{1}{2}\left[(1-i)e^{ik_{\uparrow}x}| \uparrow\rangle + (-1-i)e^{ik_{\downarrow}x}| \downarrow\rangle\right] \tag{8}$$

is a coherent superposition of up- and down-states. The values $k_{\uparrow}$, $k_{\downarrow}$ belong to the opposing spin states at fixed energy ε and can be obtained from equation (4)

$$k_{\uparrow,\downarrow} = \kappa \mp k_{\mathrm{SO}} \qquad \text{with} \qquad \kappa = \sqrt{\frac{2m^*}{\hbar}\varepsilon + k_{\mathrm{SO}}^2}\,. \tag{9}$$

Substituted back into equation (8), this gives the wave function the final form

$$\psi(x) = (\cos(k_{\mathrm{SO}}x)| \rightarrow\rangle \;-\; \sin(k_{\mathrm{SO}}x)| \leftarrow\rangle)\ . \tag{10}$$

The expression includes the spinor eigenstates in x and $-x$ direction. Here we can see for which particular channel length L between the injector and analyzer, the spin is parallel ($k_{\mathrm{SO}} = n\pi/L$) or antiparallel ($k_{\mathrm{SO}} = (n+1/2)\pi/L$) to the magnetization direction of the ferromagnetic analyzer. By calculating the spin orientation axis

$$\hat{\mathbf{n}} = \langle\psi(x)|\boldsymbol{\sigma}|\psi(x)\rangle = \begin{pmatrix} \cos(2k_{\mathrm{SO}}x) \\ 0 \\ -\sin(2k_{\mathrm{SO}}x) \end{pmatrix} \tag{11}$$

we see that the spins precess in the x-z plane. The wavelength of precession $\lambda = \pi/k_{\mathrm{SO}} = \pi\hbar^2/(m^*\alpha_R(E_z))$ depends on the electric field E_z and it should in principle be possible to tune E_z such that either full- or half-integer spin revolutions fit into the gate length L. The spin-precession has also a classical analogon: a electron with a magnetic spin moment m_x pointing into the x-direction is injected into the 2DEG and is subject to an Rashba B_y-field in the y direction. Thus, a torque $\boldsymbol{\tau} = \mathbf{m} \times \mathbf{B}$ is exerted on the magnetic moment which gives rise to a precession of the moment in the x-z plane.

1.3 Spin structure in quantum wires

In the geometry of the SFET (figure 3) the motion of the electrons is restricted to one preferred direction (x). Orthogonal to this direction (y) the wave functions are bound by a wall like potential (cf. figure 4). The lack of circular symmetry causes a non trivial spin distribution across the wire. This may be shown by solving the Schrödinger equation

$$(H_K + H_R + V)\,\Psi = \mathcal{E}\Psi$$

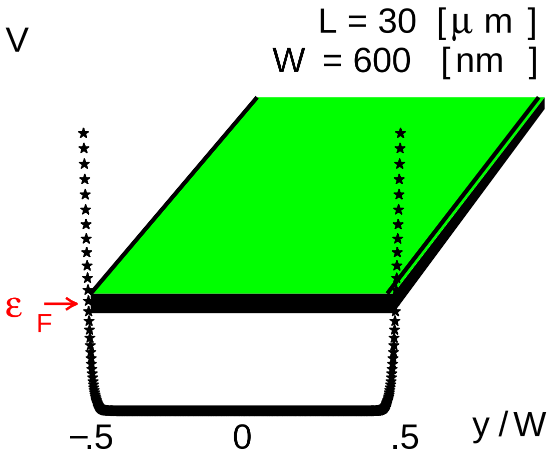


Figure 4: Schematic picture of a quantum wire made out of the heterostructure material of figure 1. The typical width W and length L and position of the Fermi energy ϵ_F are indicated.

with the Hamiltonian of eqn. (2) and a confining Potential V in y-direction. For a long wire the wave functions are separable

$$\Psi = \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix} = e^{ik_x x} \begin{pmatrix} f(y) \\ ig(y) \end{pmatrix}. \tag{12}$$

With the scaled quantities $y = Ws$, $\kappa = Wk_x$, $\eta = \alpha_R m^* W/\hbar^2$, $\epsilon = m^*(W/\hbar)^2\mathcal{E}$, $v = m^*(W/\hbar)^2 V$, this results in two coupled differential equations for the spinor functions f and g:

$$\left[-\frac{1}{2}\left(\frac{d}{ds}\right)^2 + \frac{1}{2}\kappa^2 + v - \epsilon \right] \begin{pmatrix} f \\ g \end{pmatrix} = \begin{bmatrix} 0 & \eta\left(\kappa - \frac{d}{ds}\right) \\ \eta\left(\kappa + \frac{d}{ds}\right) & 0 \end{bmatrix} \begin{pmatrix} f \\ g \end{pmatrix}. \tag{13}$$

They may be solved by standard discretization methods [20]. A typical wave function is shown in the right of figure 5. In a wire a fraction of the kinetic energy rests in the confinement. One observes wave

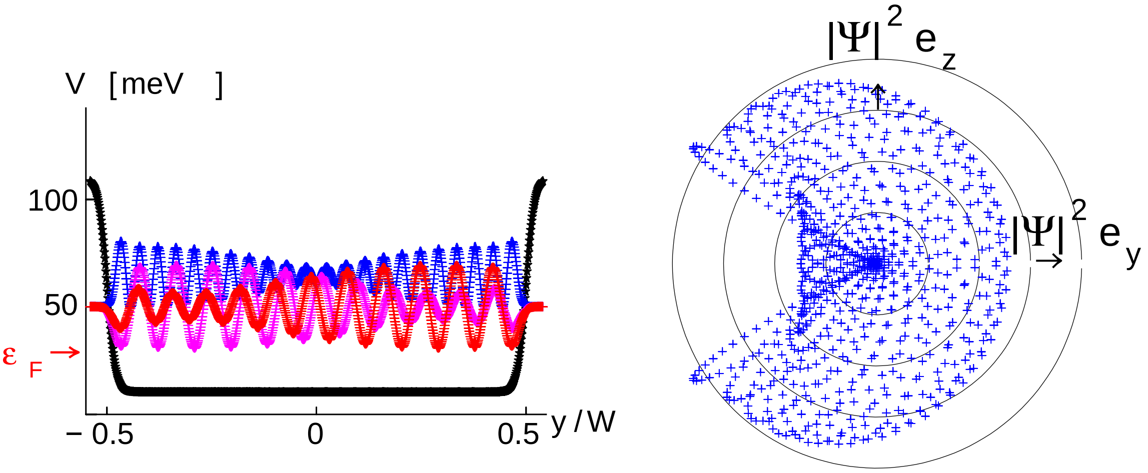


Figure 5: Left: Spinor wave functions (f red, g purple) and density (blue) at ϵ_F across the wire of figure 4. Right: Polar plot of the spin direction across the wire of the wave function shown in the left part.

functions with increasing number of nodes across the wire at higher energies. The local spin direction is defined by

$$(e_x, e_y, e_z) = \left(0 \ , \ \frac{2fg}{f^2+g^2} \ , \ \frac{f^2-g^2}{f^2+g^2} \right) \tag{14}$$

and may be plotted weighted by the density in a polar diagram (right of figure 5). From left to right, the spin direction is turned from the lower to the upper side of the wire plane. This left right asymmetry is present in most of the stationary states and there have been attempts to observe it experimentally [21].

2 The Rashba effect at metallic surfaces

2.1 Nonmagnetic Surfaces

A surface state can be considered as a particular realization of a two dimensional electron gas. Since the surface always breaks spatial inversion symmetry, the effective potential which acts on the surface state will generally have a finite gradient along the surface normal, i.e. there is an electric field in this direction. The physical manifestation of this field is the workfunction.

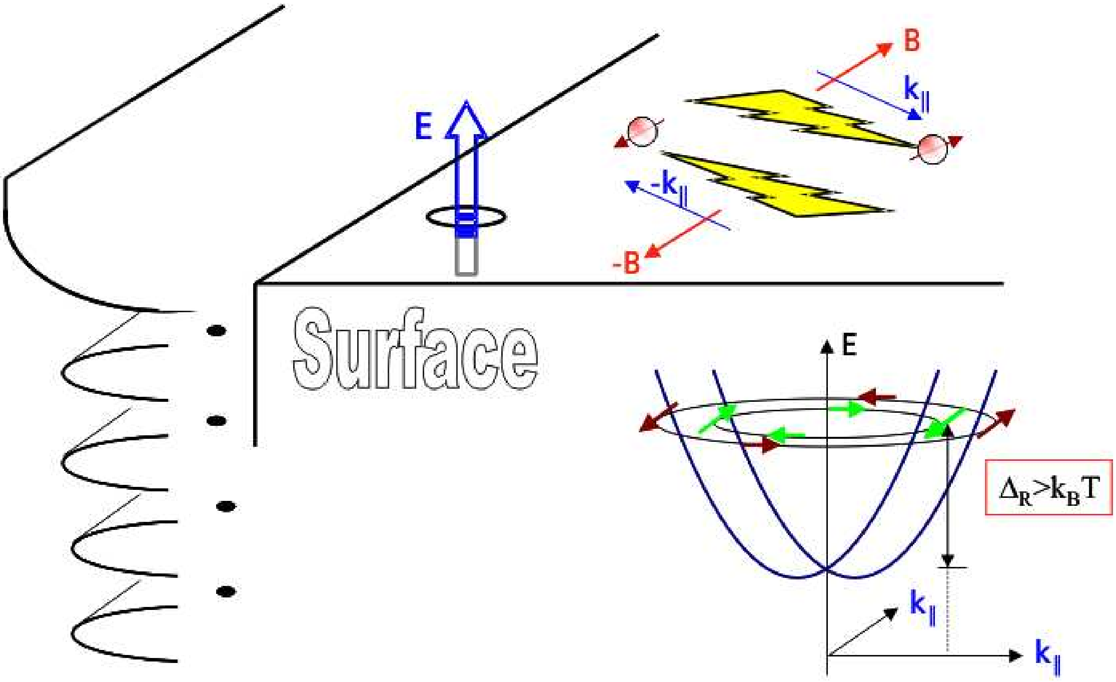


Figure 6: Electrons moving with in-plane wavevectors $\mathbf{k}_\parallel$ and $-\mathbf{k}_\parallel$ in the potential gradient of a surface (indicated on the left). The resulting electric field, $\mathbf{E}$, is seen in the restframe of the moving electrons as a magnetic field $\mathbf{B}$ or $-\mathbf{B}$ which couples to the spin of the electron. This interaction modifies the bandstructure of a spin-degenerate (s, p_z)-like surface state as shown in the lower right picture. The degeneracy is lifted and the electrons at the Fermi level have spin directions perpendicular to their propagation directions as indicated by the small arrows (cf. also preceding section).

Like in the semiconductor heterostructures discussed above, due to the movement of an electron with wavevector $\mathbf{k}_\parallel$ in the surface plane, this electric field appears in the rest frame of the electron as a magnetic field which couples to the spin of the electron. The situation is schematically depicted in figure 6 for two electrons traveling on the surface in opposite directions. For a non-spinpolarized surface state (e.g. on a nonmagnetic surface) this gives rise to a term in the Hamiltonian

$$H_{\mathrm{soc}} = \frac{\hbar}{4m_{\mathrm{e}}^2c^2}\boldsymbol{\sigma}\cdot(\nabla V(r)\times\mathbf{p}) \tag{15}$$

which leads to a k-dependent splitting of the dispersion curves. When we simply use the nearly free electron gas (NFEG) model and substitute $\mathbf{p}$ by the $\mathbf{k}$-vector, for usual workfunctions we would expect this splitting to be very small, in the order of 10^{-6} eV. This would be far too small to observe directly with angle resolved photoemission spectroscopy (ARPES). So it came rather as a surprise, when in 1996 LaShell and coworkers [22] discovered a splitting of the surface state of the Au(111) surface, which was not only k-dependent, but also in the order of 0.1 eV at the Fermi level. They correctly interpreted this splitting as a spin-orbit coupling effect, which obviously was influenced by the strong atomic spin-orbit effects in the heavy Au atom. Spin resolved ARPES experiments finally also analysed the spin distribution of this surface state [23] and found it to be in quite good agreement with the NFEG model (cf. figure 6), as it was also predicted theoretically [24].

While this effect was observed in different studies for the Au(111) surface, on other surfaces which show a similar Shockley state, e.g. Ag(111) or Cu(111), no such splitting was discovered experimentally and in calculations [25] based on density functional theory (DFT). From the calculations it was concluded, that the k-dependent splitting on Ag(111) is by a factor 20 smaller than on Au(111) (cf. also figure 7). This can neither be explained by the difference in atomic spin-orbit coupling of Au ($Z = 79$) and Ag ($Z = 47$) alone, nor by the potential gradients at the surface. Also the amount of p-character in the sp-surface state is larger for Ag than for Au, so that in principle spin-orbit effects should be more prominent in silver. So what is responsible for the size of the effect?

To resolve this issue, we did calculations based on DFT with the full potential linearized augmented planewave method [11] as implemented in the FLEUR code [12]. Our calculations include spin-orbit coupling (SOC) in a self-consistent manner [13] in the muffin-tin (MT) spheres. For the present discussion it might be interesting to note, that actually only the spherically symmetric part of the potential is included in the calculations, which might seem inconsistent with the above discussion which claims that the potential gradients at the surface are responsible for the effect we want to describe. But we will see, that in all considered cases the agreement with experimental data is fine, suggesting that the theoretical approach includes the dominant terms leading to the Rashba-type splitting in question.

In the calculations we can choose the region where to include SOC: in specific spheres around the atoms, i.e. in certain layers of the film, or we can also vary the size of the sphere, where we want to include spin-orbit coupling. In this way, it is possible to show that a bit less 60% of the k-dependent splitting of the Au(111) surface state comes from the surface layer and the contribution in deeper layers decays more or less like the weight of the surface state in these layers [26]. Moreover, this effect is extremely localized in the core region, where the *radial* potential gradient is largest. For Au(111), more that 90% of the effect originate from a sphere with radius 0.25 a.u. around the nucleus. In this region the potential is almost perfectly spherically symmetric, so that our above mentioned approximation, to include only the $l = 0$ part of the potential, is probably well justified. The potential gradient at the surface enters actually only indirectly, via the asymmetry of the wavefunction in the core region. In a tight-binding model, Petersen and Hedegård showed that the size of the Rashba-type splitting is determined by the product of the atomic spin-orbit coupling parameter and a measure for the asymmetry of the wavefunction under consideration [27].

A measure for the asymmetry of the wavefunction of a surface state can be found by analysing the l-like character of the state, i.e. to determine how much s, p or d character a surface state shows at a certain $\mathbf{k}_{\|}$-point, in our case the $\overline{\Gamma}$-point. E.g. a surface state of pure p_z character is inversion symmetric and will – in absence of an electric field – show no Rashba-type splitting. The potential gradient or electric field at the surface will distort the wavefunction, so that some s or d_{z^2} contributions to the surface state will arise. The ratio of l- to $l \pm 1$-type character of a surface state (for a given m, e.g. $m = 0$) will therefore give a measure for the asymmetry of this state. In the case of Ag(111), we find that the surface state is predominantly of p_z-type, with a small d_{z^2} admixture ($p : d$ ratio of 9.5) while in Au the surface state has much stronger d_{z^2} character ($p : d = 3.3$). The fact that the Au d band lies much higher in energy than the Ag d band leads to a stronger d character of the Au surface state and thus to larger asymmetry of the wavefunction [26]. This determines the stronger k-dependent splitting in the Au(111) surface bandstructure.

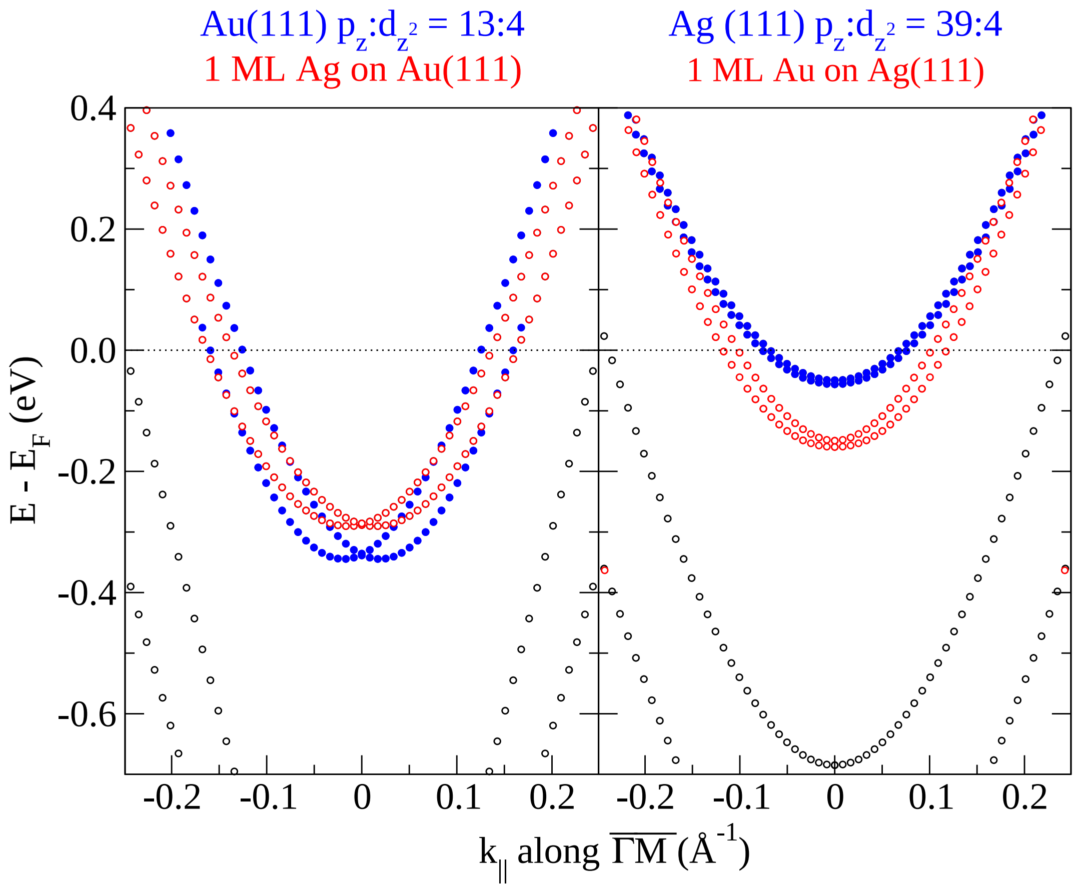


Figure 7: Bandstructure of Au(111) (left, full circles) and one monolayer Ag on Au(111) (left, open circles) as compared to a Ag(111) film (right, full symbols) and a single Au monolayer on Ag(111) (right, open symbols).

This effect can be further demonstrated, when we compare a single monolayer of Ag on Au(111) with a Au monolayer on Ag(111). Just from the point of view of the atomic SOC, we would expect that the Rashba-type splitting of the Au monolayer of Ag(111) is larger than that of the Ag/Au(111) system, since more than 50% of the effect comes from the surface layer. But since the gold d states of the subsurface layers can induce a larger d character of the Ag surface state in Ag/Au(111) while the Au surface state of Au/Ag(111) has less d character than the one of pure Au(111), finally the Rashba-type spin-orbit splitting is larger in Ag/Au(111) (cf. figure 7). Other examples, how the asymmetry of a surface state influences the strength of the Rashba-type splitting can be found on lanthanide surfaces (e.g. Lu(0001) [26]), and a particular case will be presented in subsection 2.3.

2.2 Semimetal Surfaces

Up to now we have discussed examples, where the Rashba-type spin-orbit splitting was in the order of 10 to 100 meV (up to 120 meV for Au(111)), so that experimentally it is not so easy to detect in

ARPES experiments. Now, we turn to another extreme, where the splitting is so big, that it was not a-priori clear, whether the two experimentally observed features were spin-split partners of the same state or two different surface states: the low-index surfaces of Bi. Bismuth is a non-magnetic, rather heavy metal ($Z = 83$) with semimetallic properties, i.e. the Fermi surface consists only of two tiny pockets, so that the density of states (DOS) at the Fermi level (E_F) is almost zero. In the surface projected bulk-bandstructure extended gaps are observed around E_F, in which surface states can be localized.

ARPES measurements on the Bi(110) surface [28] showed the existence of two spectroscopic features in the gap, which could be interpreted as to two surface states. Bismuth has a rhombohedral crystal structure and the (110) surface consists of unreconstructed pseudocubic bilayers [29], where dangling bonds can give rise to surface states. Similarly, on Bi(111) two states were identified spectroscopically [30]. The (111) surface has closed-packed layers and again shows a bilayer structure, but without dangling bonds and with a much larger separation of the bilayers [31]. In both cases of course only the occupied part of the surface bandstructure could be observed spectroscopically. Using DFT calculations, we have the possibility to access also the unoccupied part of the spectrum. It can be seen that the observed spectroscopic features are actually a Rashba-type spin-split pair of a surface state which forms – at least for the (110) and (100) surface – a band through the whole surface Brillouin zone [32, 33]. That these surface state is actually split by spin-orbit coupling can be demonstrated by comparison of a scalar-relativistic calculation without inclusion of SOC and with the inclusion of SOC [34] (cf. also left of figure 8). In this cases, the splittings are very large (in the order of 300 meV) and, since the surface states extend throughout the Brillouin zone, they are also no longer linear in k, except in the vicinity of high symmetry points.

It is not only of academic interest, whether two surface states are a spin-split pair or two spin-degenerate surface states. For example, on the Bi(111) surface the Fermi surface forms a small hexagon around the $\overline{\Gamma}$ point, which led to speculations about the formation of a charge density wave on this surface [35]. If the Fermi surface were indeed formed by spin-degenerate surface states, this would be possible. If, on the other hand, Rashba-type spin-split bands form this part of the Fermi surface, the electrons at $+\mathbf{k}_\parallel$ and $-\mathbf{k}_\parallel$ were of opposite spin and instead of a peak in the (spin) diagonal part of the susceptibility χ, we would expect a large contribution to the spin off-diagonal part, $\chi^\pm$, leading to a modulation of the spin-structure. Since the surface is of course still nonmagnetic, these modulations have to cancel and a direct observation is difficult. When magnetic atoms were present at the surface, their interaction would be modified and this effect could be detected. We will show in a later chapter, that this is actually possible.

Using scanning tunneling microscopy (STM) techniques, consequences of the spin polarization of the surface states have indeed been observed for another Bi surface [32]. If a scanning tunneling spectrum (STS) is recorded for a dense mesh of positions on a surface, this STS map can be Fourier transformed for a given energy within this spectrum. The Fourier transformed (FT) STS map gives then a picture of the energy dispersion in reciprocal space, i.e. a two dimensional cut through the function $\varepsilon(\mathbf{k}_\parallel)$, but with doubled length of the $\mathbf{k}$-vectors, since the STS maps the scattering between two states of different $\mathbf{k}$ but at the same E. In particular, for $E = E_\mathrm{F}$, this yields an image the Fermi surface. It is easily seen, that a surface state with a Fermi surface of a wavevector $\pm\mathbf{k}_\mathrm{F}$ will give rise to standing waves with $2\mathbf{k}_\mathrm{F}$ which can be seen in the STS map. This correspondence between FT-STS and Fermi surface has been used extensively to study the electronic properties of high-temperature superconductors. A Rashba splitting will not change this picture, since for one spin channel the Fermi vectors are changed to $\pm\mathbf{k}_\mathrm{F} + \Delta\mathbf{k}$, while for the other spin we get $\pm\mathbf{k}_\mathrm{F} - \Delta\mathbf{k}$, so that both spin channels will lead to a contribution of $\pm 2\mathbf{k}_\mathrm{F}$ in the STS map, i.e. the picture is indistinguishable from the one without Rashba splitting [27]. But if the Fermi surface is more complex, like in the case of Bi(110), the fact, that the surface states are spin polarized can be seen the FT-STS clearly.

Consider a simple one-dimensional example: along the line $\overline{\Gamma\mathrm{M}}$ in Bi(111) we can see in figure 8 (left, broken line) a surface state obtained without inclusion of SOC. This state originates at -0.3 eV at $\overline{\Gamma}$,

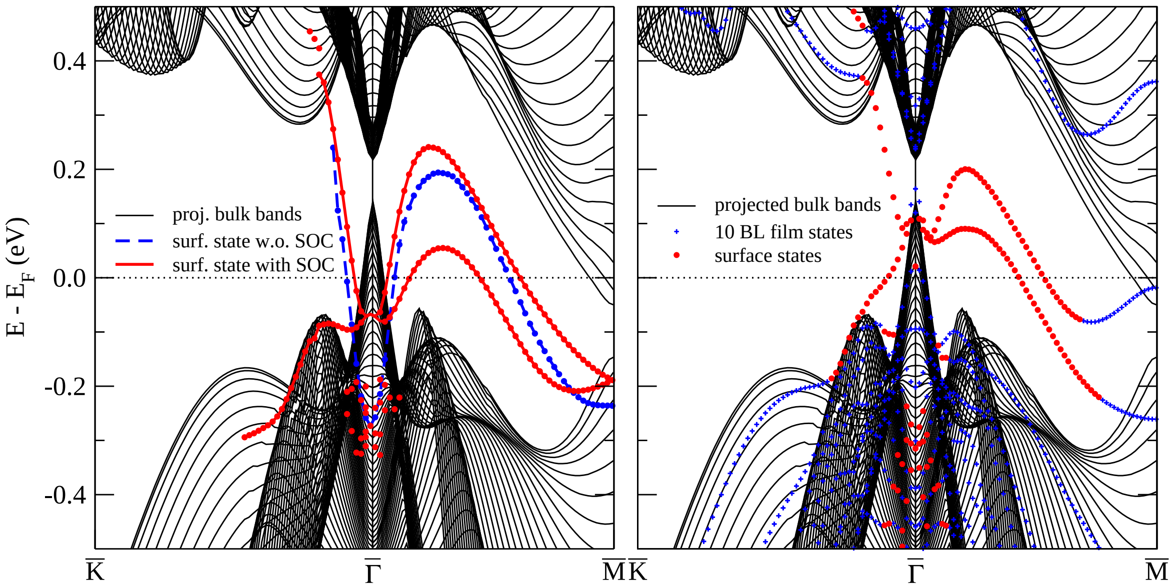


Figure 8: Bulk-projected bandstructure of Bi and surface bandstructure of a 22 layer Bi(111) film with H termination on one side (left) with (full line) and without (broken line) spin-orbit coupling included in the calculation. A similar calculation with SOC included for a symmetric 20 layer film without H termination is shown on the right.

crosses the Fermi level at a wavevector we denote k_a, disperses down again and crosses E_F once more at k_b and reaches $\overline{\mathrm{M}}$ at -0.22 eV. Surface states at E_F can scatter between k_a and k_b and give rise to standing waves with wavelength $2k_a, 2k_b, (k_a + k_b)$ and $(k_a - k_b)$, if the state is spin-degenerate. Now, consider that spin-orbit coupling splits this degeneracy and gives rise to spin-up states at $k_a + \Delta k$ and $k_b - \Delta k$, while spin-down states cross the Fermi level at $k_a - \Delta k$ and $k_b + \Delta k$. In this case, spin conserving scattering events will again give rise to oscillations with wavelength $2k_a, 2k_b$, but also $(k_a + k_b) \pm 2\Delta k$ and $(k_a - k_b) \pm 2\Delta k$. Here, the effect of spin is clearly visible. On the Bi(110) surface, this effect was also verified experimentally in a two dimensional case [32].

The occurrence of spin-polarized surface states of course suggests, that this could be utilized in some way for spintronic applications. In the case of Ag(111), where the surface state contributes very little to the density of states at the Fermi level, this might not seem very promising, but in the case of a semimetal surface, where the DOS at E_F originates almost exclusively from surface states, this might be more realistic. Alternatively, the surface of a thin film on insulating or semiconducting substrates could be interesting, since in this case the relative contribution of the surface state to the conduction electrons is also increased. This works of course only, if the thin film still supports the same surface state as the semiinfinite crystal, i.e. localized Tamm states of d-character as they occur on lanthanide (0001) surfaces will be more suitable for very thin films than the extended s,p-derived Shockley states of the closed packed coinage metal surfaces.

Another effect, that can disturb the surface states in thin films, is the interaction between the two surfaces of the film. If, like in Bi, the screening is very weak, surface states at the upper and lower surface of a symmetric film interact to form even and odd linear combinations. This of course interferes with the concept of broken inversion symmetry at the surface. On the other hand, in our theoretical calculations for Au and Ag surfaces, we always used symmetrical films where a tiny interaction between upper and lower surface cannot be avoided, even in thicker films. For the bandstructures of figure 7 we used 23 layer films and especially in the case of Ag(111), a finite splitting of the surface state parabolas at the $\overline{\Gamma}$ point can be seen. At the first glance it might seem surprising, that the two different splittings, the even-odd and the Rashba-type splitting result in only two dispersion curves. Without the interactions that lead to the splittings, we can think of having two states (spin up, $\uparrow$ and down, $\downarrow$) on each surface. The spin-orbit coupling leads for the spin up states of the upper surface ($\uparrow_u$) to the same shift in energy as for the spin down states of the lower surface ($\downarrow_l$) (since the potential gradient is reversed there) and they will have an energy ε^+. In the same way of course $\varepsilon(\downarrow_u) = \varepsilon(\uparrow_d) = \varepsilon^-$. A hybridization of $\uparrow_u$ and $\downarrow_u$ leads to energies $\varepsilon^+ + \varepsilon^s$ and $\varepsilon^- - \varepsilon^s$, respectively, but in the same way the two downspin states, $\downarrow_u$ and $\downarrow_l$ will be shifted to energy values $\varepsilon^- - \varepsilon^s$ and $\varepsilon^+ + \varepsilon^s$. The stronger the interaction across the film, the more each state will be localized at both sides of the film so that finally the spin-polarization for a given energy and $\mathbf{k}_{\|}$ gets reduced.

A case, where this scenario has been actually observed in experiment are thin Bi films grown on a Si substrate [36]. The interaction with the substrate is very weak, since the Bi film is deposited on a seeding layer of Bi atoms and can adopt (for more than a few bilayers) the structure of Bi(111). Angle resolved photoemission has shown that near the zone center the electronic structure of these Bi films is not so different from what has been observed on single crystal surfaces. But when the $\mathbf{k}_{\|}$ vector approaches the zone boundary at $\overline{\mathrm{M}}$, the crossing of the two spin-split states is no longer observed. Instead, quantum well states (QWS) are formed when the surface state gets near to the bulk continuum at $\overline{\mathrm{M}}$ [36]. The energy levels of these states agree nicely with those obtained by the calculation of symmetric films of the same thickness (cf. right of figure 8). As the surface state character is lost, also the spin-polarization of these states vanishes. The very bad screening of Bi makes this QWS disappear only for very thick films (more than 40 bilayers). Therefore, when we simulate Bi single crystal surfaces, we have to terminate one side of the film with H atoms to saturate the dangling bonds and explicitly remove the inversion symmetry of the film, even if it is 22 layers thick.

2.3 Magnetic Surfaces

Let us finally consider the case of a surface of a magnetic metal, like Gd(0001). On this closed packed surface a bulk projected bandgap around $\overline{\Gamma}$ contains a surface state of d_{z^2} character, like it can be found also on other lanthanide surfaces. Exchange interaction splits this surface state into an occupied majority spin state and an unoccupied minority state. This splitting is mainly controlled by the $4f$ electrons of Gd and amounts to about 0.8 eV, which is large as compared to spin-orbit effects in this system. No matter how SOC affects the electrons of the surface state, their spin will remain more or less parallel to the exchange field, which is oriented in plane in the directions of nearest neighbor atoms by the magnetic anisotropy.

An electron traveling on the surface in a direction *perpendicular* to its spin quantization axis, will experience the potential gradient at the surface as a magnetic field parallel to its spin. Therefore, a magnetic coupling can arise and the dispersion curves will split more or less similar to what is observed on a nonmagnetic surface. If, on the other hand, the propagation direction of the electron is parallel to its spin quantization axis, the field arising from SOC cannot couple to the electron's spin and no Rashba-like splitting can be observed. Schematically, this situation is shown in figure 9. In contrast to the surface state on the nonmagnetic surface, where the spin of the electron is always oriented perpendicular to the propagation direction and the surface normal, $\mathbf{e}_z$, (with some deviation, depending on the shape of the potential [24]), on the spin-polarized surface, the spins are more or less collinear. This changes the shape of the Fermi surface significantly, especially if exchange splitting is considered (figure 9 (c)). If the exchange splitting is large, this leads to a Fermi surface consisting of a single circle shifted away from the zone center. The consequences for the bandstructure are simple: along a certain direction in reciprocal space SOC will have no particular effect. In a direction orthogonal to this one, the dispersion curves for majority and minority spin will be shifted in opposite directions. For the eigenvalues this results in an

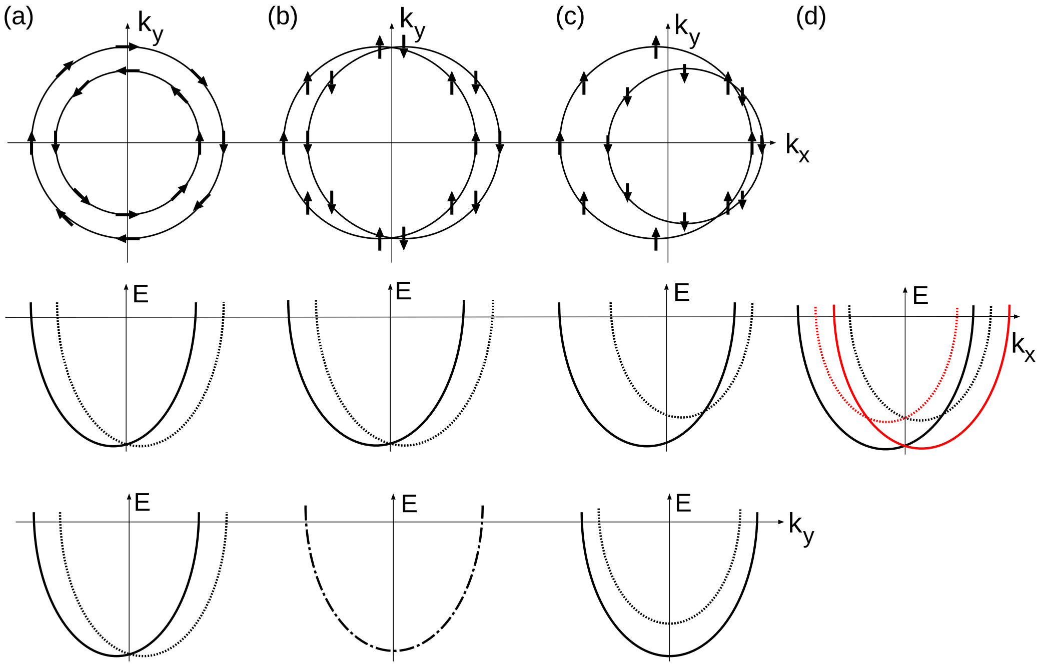


Figure 9: (a): Rashba splitting on a non-magnetic surface: the top panel shows the Fermi surface and the spin-polarization of the states at the Fermi level. In the middle and lower panel the bandstructures along two orthogonal directions in reciprocal space are shown. (b): The same relations as in (a) are shown, but now for the case where the spin-quantization axis of the electrons has been aligned in a particular direction. For electrons propagating in this direction, the Rashba splitting vanishes. (c): Effect of an additional exchange splitting on the situation as described in (b). (d): Surface bandstructure arising from the calculation of a symmetric film, where the surface states from the lower surface are shown in red.

expression

$$\varepsilon_{\downarrow(\uparrow)}(\mathbf{k}) = \varepsilon(\mathbf{k}) \pm IM \pm \alpha_{\mathrm{R}}(\mathbf{k} \times \mathbf{e}_z) \cdot \hat{\mathbf{M}} \tag{16}$$

where $\mathbf{M} = M\hat{\mathbf{M}}$ is the magnetization and IM represents the exchange splitting of the bands. Of course in a calculation of a symmetric film, again on the lower surface ($-\mathbf{e}_z$) the directions of the spin-orbit induced shifts will be exactly opposite to the shifts on the upper surface, so that in total a picture as shown in figure 9 (d) is obtained. From this picture the two splittings for the spin-up and the spin-down surface state can be determined directly as $\Delta\varepsilon(\mathbf{k}) = \varepsilon(\mathbf{k}, \mathbf{M}) - \varepsilon(\mathbf{k}, -\mathbf{M})$.

Experimentally, for a single crystal surface, it is possible to measure with ARPES two spectra of the same surface, but rotated by 180 degrees. In the case of an in-plane anisotropy, as for Gd(0001), this rotation reverses the spin and leads, therefore, also to a picture as figure 9 (d). A comparison of these two spectra allowed to determine the Rashba splitting in Gd(0001), even though its magnitude is rather small [37]. A particular advantage of magnetic surfaces is, that the measurements allow the determination of the sign of the Rashba parameter, α_R, even without the need of spin-analysis via a Mott detector.

Modification of the Gd surface also alters the characteristics of the surface state: if (atomic) oxygen is adsorbed in the surface, the surface state shifts down in energy and both, minority and majority spin states become occupied. Moreover, the dispersion of the surface state changes from almost flat on Gd(0001) to parabolic for O/Gd(0001). Both surface states were observed experimentally, and DFT calculations show, that these states are actually interface states residing between the topmost Gd/O layer and the underlying Gd bulk [37].

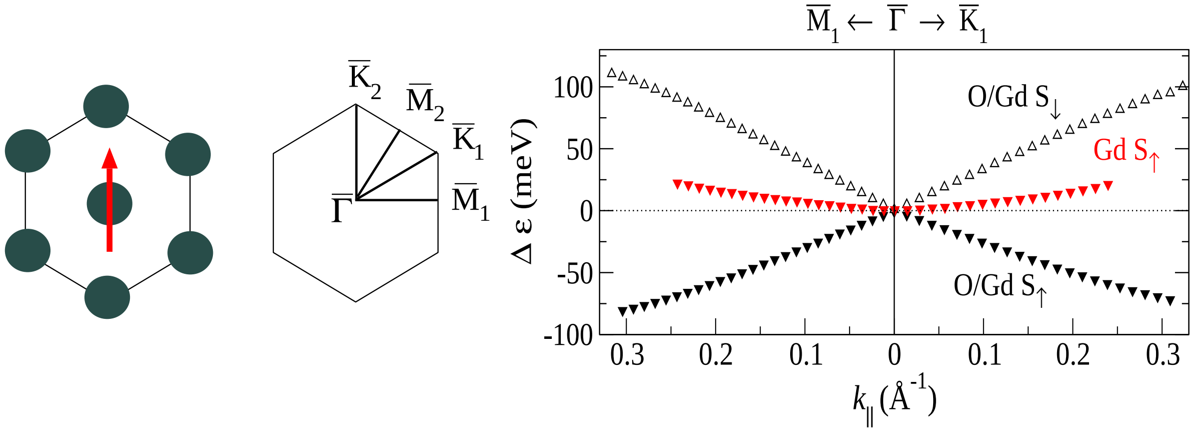


Figure 10: Left: Magnetization direction on the Gd(0001) surface indicated by the red arrow and surface Brillouin zone and labeling of the high symmetry points. Right: Rashba-type splitting of the surface state of Gd(0001) and O/Gd(0001) in the directions $\overline{\Gamma \mathrm{K}_1}$ and $\overline{\Gamma \mathrm{M}_1}$.

Let us now focus on the Rashba-type splitting on O/Gd(0001). In figure 10 we plotted the splitting as a function of $k_{\|}$ for the directions $\overline{\Gamma \mathrm{M}_1}$ and $\overline{\Gamma \mathrm{K}_1}$ as indicated in the figure. Since the magnetization is directed towards nearest neighbours (a-direction), the largest effects on the surface state dispersion should be observed in $\overline{\Gamma \mathrm{M}_1}$ direction while no splitting should be visible in the direction $\overline{\Gamma \mathrm{K}_2}$. A closer look at figure 10 reveals, that the splitting, $\Delta\varepsilon$ is indeed smaller in $\overline{\Gamma \mathrm{K}_1}$ than in $\overline{\Gamma \mathrm{M}_1}$. Furthermore, we observe that $\Delta\varepsilon$ for the majority spin state ($\mathrm{S}_\uparrow$) is not only of opposite sign as compared to $\Delta\varepsilon$ for the minority state ($\mathrm{S}_\downarrow$), but also their absolute values differ. This is also observed experimentally, and can be explained again by the different positions of the states in the bulk-projected bandgap and the different asymmetry of the wavefunctions. One should note here, that also the effective masses of the $\mathrm{S}_\uparrow$ and $\mathrm{S}_\downarrow$ states differ and this shows, that spin is not the only difference of these states.

Even more drastic is the difference of the $\mathrm{S}_\uparrow$ surface state of O/Gd(0001) to the $\mathrm{S}_\uparrow$ state of Gd(0001). We can see from the right of figure 10 that not only the magnitude of the splitting is a factor 3 to 4 smaller, even the sign is different. Since this reversal of sign cannot be attributed to the spin, it must result from a different admixture of p_z-character to the d_{z^2} surface state. A reversal of the gradient of the wavefunction at the position of the Gd nucleus can be interpreted as the result of hybridization with p_z-type wavefunctions of different signs. In some sense we can say, that we see the sign of the wavefunction here in the sign of the Rashba-parameter.

3 Anisotropic exchange of adatoms on surfaces

In the last subsection, we assumed that the magnetic order at the surface is not influenced by spin-orbit coupling effects. If the exchange field is strong, all spins will align accordingly. On the other hand, if the exchange coupling is weak, spin-orbit coupling effects can substantially influence the magnetic interaction. The particular case of two distant impurities, which interact in a RKKY-type manner via a non-magnetic host which shows strong spin-orbit effects has been discussed by Smith [38]. He showed that the interaction between two magnetic atoms A and B (spins $\mathbf{S}_A$ and $\mathbf{S}_B$) via a non-magnetic third atom with a SOC term $\mathbf{l} \cdot \mathbf{s}$ gives rise to an interaction $(\mathbf{S}_A \cdot \mathbf{s})(\mathbf{l} \cdot \mathbf{s})(\mathbf{s} \cdot \mathbf{S}_B)$. Taking the trace over the spin variable $\mathbf{s}$ this term can be written as $(-i/4)\mathbf{l} \cdot (\mathbf{S}_A \times \mathbf{S}_B)$ and thus shows the form of the Dzyaloshinskii-Moriya (DM) interaction $\mathbf{D} \cdot (\mathbf{S}_A \times \mathbf{S}_B)$. Fert and Levy [39] derived an expression for this anisotropic exchange interaction of two magnetic atoms in spin-glasses doped with heavy impurity atoms which is of the form

$$H_{\mathrm{DM}} = -V(\xi)\frac{\sin\left[k_{\mathrm{F}}(R_A + R_B + R_{AB}) + \eta\right]\hat{\mathbf{R}}_A\cdot\hat{\mathbf{R}}_B}{R_A R_B R_{AB}}(\hat{\mathbf{R}}_A\times\hat{\mathbf{R}}_B)(\mathbf{S}_A\times\mathbf{S}_B) \tag{17}$$

where $\mathbf{R}_A = R_A\hat{\mathbf{R}}_A$ and $\mathbf{R}_B = R_B\hat{\mathbf{R}}_B$ are the positions of the magnetic atoms measured from the nonmagnetic impurity and R_{AB} is the distance between the atoms A and B. $V(\xi)$ is a term that depends of the spin-orbit coupling constant of the nonmagnetic atom, ξ, k_{F} is the Fermi vector and η the phase shift induced by the impurity. The sinus term reflects the RKKY-type character of the interaction, while the two cross products determine the symmetry of the interaction.

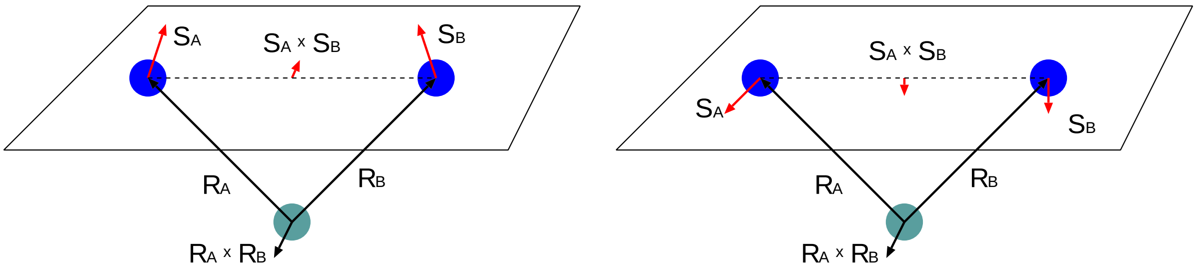


Figure 11: Two magnetic adatoms (A, B) on a surface interacting with a surface atom at the center. The distance between the surface atoms and the adatoms is $\mathbf{R}_A$ and $\mathbf{R}_B$. The spins of the adatoms are almost perpendicular to the surface (left) or in the surface plane (right), but sightly canted to give a finite value for $\mathbf{S}_A \times \mathbf{S}_B$

This model can be translated to the case of two magnetic atoms on a surface, where the magnetic interaction is mediated by surface states which show strong SOC effects. Such a situation might be imagined, if e.g. two Mn atoms are placed on a Bi surface (figure 11). If the easy magnetic axis is out-of-plane, a slight tilting of the magnetic moments results in a finite value for $\mathbf{S}_A \times \mathbf{S}_B$ which is then parallel to $\hat{\mathbf{R}}_A \times \hat{\mathbf{R}}_B$ and leads to a non-vanishing contribution of H_{DM} (equation (17)). If the easy magnetic axis is in-plane (right of figure 11) and the surface normal is the hard axis, a small tilting of the magnetic moments results in a vector $\mathbf{S}_A \times \mathbf{S}_B$ that is normal to $\hat{\mathbf{R}}_A \times \hat{\mathbf{R}}_B$ and equation (17) will give no contribution to the total energy. Of course, on a surface the scattering will involve all surface atoms and in general it will depend not only on the direction of the spins of the adatoms, but also on the symmetry of the surface whether a DM interaction will occur for a specific arrangement of the spins. This will be discussed later in more detail.

If we extend the two impurities in figure 11 to a chain of magnetic atoms, where the spins of two neighbouring atoms, i and j, are canted slightly, an interaction of this kind

$$H_{DM} = \mathbf{D}_{ij}\cdot(\mathbf{S}_i\times\mathbf{S}_j) \tag{18}$$

will favour spin-spiral structure. Since the DM interaction has to compete with the Heisenberg-type (symmetric) exchange interaction, these structures will probably be of long wavelength. Such long-ranged magnetic structures can be found on surfaces in domain walls of thin magnetic films. In the following we will discuss the consequences of the DM interaction on this kind of long ranged, non collinear structures, and show results of *ab initio* calculations for a system that has also been investigated experimentally in some detail.

4 Mesoscale magnetic structures

In this section, we discuss magnetic structures on the mesoscopic length scale that are driven by the DM interaction. Since the DM interaction is a purely relativistic effect, we expect it to be much weaker than the usual exchange interactions. In most cases, it cannot cause more than a small canting angle between the spins on adjacent lattice sites, and the local magnetic structure (typically ferro- or antiferromagnetic) is governed by non-relativistic effects. For spatially slowly varying magnetic structures, however, the DM interaction can become relevant since it is antisymmetric whereas the non-relativistic exchange interactions are all symmetric with respect to the canting angle. The symmetric interactions lack any linear terms in the usual Taylor expansions in the canting angle, whereas an antisymmetric interaction shows such a term. In the following, we employ a simple model in order to describe the mesoscale magnetic structures that can arise from an interplay of spin stiffness, usual anisotropy and the Dzyaloshinskii-Moriya interaction. It is not the aim of this section to give a complete overview of the possible magnetic structures arising from the DM interaction at surfaces, but our simple model already illustrates the variety of possible magnetic structures.

4.1 Micromagnetic model

We restrict our further investigations to a quasi one-dimensional model where the magnetization depends on only one spatial coordinate x, and we denote the corresponding real-space direction as propagation direction (cf. figure 12). The quasi one-dimensional model is justified for anisotropic crystal structures where the magnetization is expected to propagate along a high-symmetry line and for simple domain walls where the magnetization is expected to propagate normal to the real-space orientation of the domain boundary. But our ansatz cannot describe vortices and other mesoscale magnetic structures that are well discussed in literature (cf. e.g. [40]).

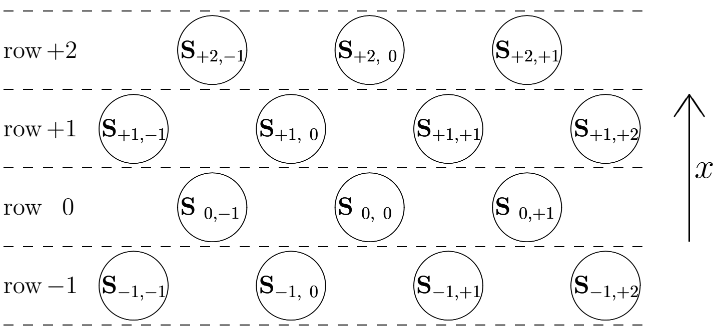


Figure 12: Atomic rows. In the quasi one-dimensional model, we assume that the magnetization direction changes along the x-direction but remains constant within a row normal to the x-direction (i.e. $\mathbf{S}_{j,i} = \mathbf{S}_{j,i'}$). The x-direction is called propagation direction.

As we want to investigate magnetic structures, that change on length scales that are large compared to the lattice spacing, we can employ a micromagnetic model. In such a model, the magnetization direction is not described by a discrete set of unit vectors $\{\mathbf{S}_j\}$ but by a continuous function $\mathbf{m}(x)$ with $|\mathbf{m}| = 1$. This ansatz works for ferromagnetic and antiferromagnetic materials alike: In the case of an antiferromagnetic structure, $\mathbf{m}(x)$ is oriented parallel and antiparallel respectively to every second atomic moment $\mathbf{S}_j$.

If all relevant interactions are reasonably short-ranged, we can estimate the energy of a magnetic configuration (in a homogeneous crystal) by

$$E[\mathbf{m}] = \int \mathrm{d}x\, f(\mathbf{m}, \dot{\mathbf{m}}) \tag{19}$$

with $\dot{\mathbf{m}}(x) = \frac{\mathrm{d}}{\mathrm{d}\,x}\,\mathbf{m}(x)$. The structure of the function f can be deduced from a discrete lattice model, for instance the classical Heisenberg model $\sum_{i,j} J_{i,j}\,\mathbf{S}_i \cdot \mathbf{S}_j$ corresponds to a term of the form $\int \mathrm{d}x\, A\,\dot{\mathbf{m}}(x)^2$ (cf. e.g. [41]). But the integrand $A\,\dot{\mathbf{m}}(x)^2$ can also be regarded as the lowest order Taylor expansion to an arbitrary symmetric $\dot{\mathbf{m}}$-dependent function. Thus, the parameter A includes all non-relativistic exchange effects in the limit of spatially slowly varying magnetic structures, even if the system is badly described by the Heisenberg model.

In the following, we consider a term symmetric in $\dot{\mathbf{m}}$ (that prevents spin rotations on short length scales), a term antisymmetric in $\dot{\mathbf{m}}$ (that favors certain spin rotations), and the lowest order anisotropy term and we work with the energy functional

$$E[\mathbf{m}] = \int \mathrm{d}x \left(A\,\dot{\mathbf{m}}(x)^2 + \mathbf{D}\cdot(\,\mathbf{m}(x) \times \dot{\mathbf{m}}(x)\,) + \mathbf{m}(x)^{\dagger}\cdot\mathsf{K}\cdot\mathbf{m}(x)) \right) \ . \tag{20}$$

The model parameters are the spin stiffness A, the Dzyaloshinskii vector $\mathbf{D}$ and the anisotropy tensor K. As we assume, that the magnetization propagates along a high symmetry line of a rectangular surface, we know the direction of the Dzyaloshinskii vector $\mathbf{D}$ and the structure of the anisotropy tensor K: $\mathbf{D}$ is oriented perpendicular to the x-direction and perpendicular to the surface normal (cf. figure 13), and K is diagonal if we choose our coordinate axis along the high symmetry directions of the crystal. With such a coordinate system, we get:

$$\mathbf{D} = \begin{pmatrix} 0 \\ 0 \\ D \end{pmatrix} \quad , \quad \mathsf{K} = \begin{pmatrix} K_1 & 0 & 0 \\ 0 & K_2 & 0 \\ 0 & 0 & K_D \end{pmatrix} \ . \tag{21}$$

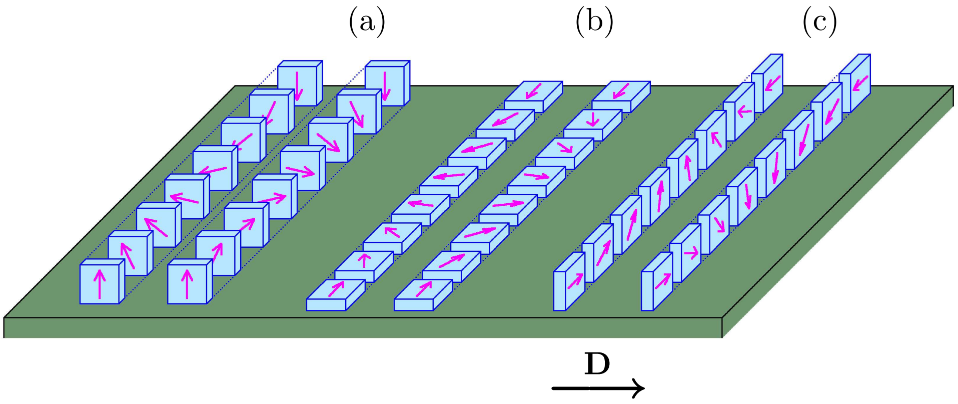


Figure 13: Spin spirals with different rotation axes on a symmetric surface. For each rotation axis, a right- and a left-handed spiral is shown. If we neglect the substrate, the right- and left-handed spirals are mirror images of each other. If we take spin-orbit coupling into account, we need to consider the system consisting of spiral and substrate. For (a) and (b), the mirror plane is oriented normal to the surface, therefore the surface does not break the mirror symmetry (provided that the spirals propagate along a high-symmetry line of the crystal structure). In the case (c), however, the surface breaks the mirror symmetry and there is no other symmetry operation mapping the right- onto the left-handed system. Therefore, the two systems in (c) are not equivalent to each other and may differ in energy. With equation (18), we conclude that $\mathbf{D}$ is orthogonal to the rotation axes of (a) and (b). Of course, the sign of $\mathbf{D}$ cannot be deduced from the symmetry.

4.2 Planar spin structures

From equation (20) it is obvious, that the DM term is minimized if the magnetization rotates in the plane normal to the Dzyaloshinskii vector $\mathbf{D}$. If the hard axis is oriented parallel to $\mathbf{D}$ (i.e. $K_D > K_1$, $K_D > K_2$), then the anisotropy term also favors a magnetization that is confined to the plane normal to $\mathbf{D}$. At first, we restrict our considerations to this case. In such a system with $\mathbf{m} \perp \mathbf{D}$, we can describe the magnetization with only one angle φ ($\mathbf{m} = \hat{\mathbf{e}}_1 \cos\varphi + \hat{\mathbf{e}}_2 \sin\varphi$) and obtain the energy functional

$$E[\varphi] = \int \mathrm{d}x \, \big(A \, \dot{\varphi}(x)^2 + D \, \dot{\varphi}(x) + K \, \sin^2 \varphi(x) + \mathrm{const} \big) \tag{22}$$

with $K = K_2 - K_1$. Without loss of generality, we assume $K > 0$. The functional (22) is well discussed by Dzyaloshinskii. In the following we briefly state some of his results, for further details and analytical derivations cf. [42, 43].

If we neglect the anisotropy term $K \sin^2 \varphi$, we obtain spin rotations for all non-vanishing D. But, for sufficiently large K the DM term cannot compete with the other terms and the energy is minimized by a collinear magnetization that is oriented along the easy axis (i.e. $\varphi(x) = 0 = \mathrm{const}$). The model (22) shows a rotating spin structure as the ground state, if and only if

$$|D| > \frac{4}{\pi} \sqrt{A \, K} \quad \Leftrightarrow \quad |\tilde{D}| = \frac{|D|}{\sqrt{A \, K}} > \frac{4}{\pi} \, . \tag{23}$$

At the transition to the collinear ground state, the spiral's spatial period length λ diverges (cf. figure 14). This transition can be interpreted as a second-order phase transition with order parameter $1/\lambda$ and a kink in $\mathrm{d}E/\mathrm{d}\tilde{D}$.

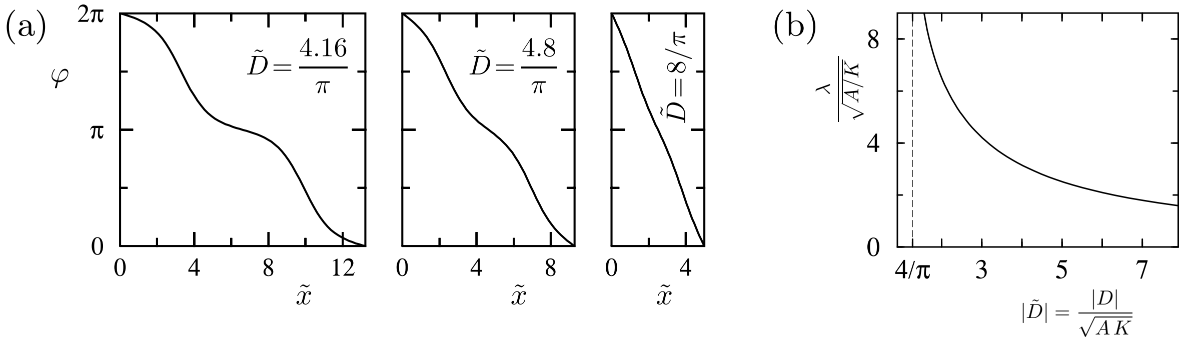


Figure 14: Influence of the model parameters on the ground state of equation (22). The model is characterized by one dimensionless parameter $\tilde{D} = \frac{D}{\sqrt{A \, K}}$. We use the reduced length $\tilde{x} = \sqrt{K/A} \, x$. (a): Magnetization direction of the periodically rotating ground state. For $\tilde{D} \searrow \frac{4}{\pi}$, the period length diverges and two collinear domains with $\sin^2 \varphi = 0$ evolve. For $\tilde{D} < -\frac{4}{\pi}$, the rotational direction is reversed (i.e. $\dot{\varphi}$ changes sign). (b): Spatial period length λ with respect to the model parameters.

If the DM term is not strong enough to cause a rotating spin structure, a ferromagnetic sample of sufficient size usually consists of several domains that posses different spin quantization axes. In this case, we can use equation (22) with the boundary conditions

$$\varphi(x) \xrightarrow{x \searrow -\infty} \pi \qquad , \qquad \varphi(x) \xrightarrow{x \nearrow +\infty} 0 \tag{24}$$

in order to describe a wall between two oppositely magnetized domains. Thereby, the size of the DM term cannot influence the domain-wall shape $\varphi(x)$ but alters the wall energy E:

$$E = \int_{-\infty}^{+\infty} \mathrm{d}x \, \left(A \, \dot{\varphi}^2 + K \, \sin^2 \varphi \right) + \int_{-\infty}^{+\infty} \mathrm{d}x \, D \, \dot{\varphi} \qquad \text{with} \qquad \int_{-\infty}^{+\infty} \mathrm{d}x \, D \, \dot{\varphi} = \int_{\pi}^{\pi \pm \pi} \mathrm{d}\varphi \, D = D \, (\pm \, \pi) \, . \tag{25}$$

Minimizing the (A, K)-dependent term in equation (25) yields two degenerate solutions of opposite rotational directions, i.e. with opposite sign of $\dot{\varphi}(x)$. The D-dependent term is independent of the actual shape of $\varphi(x)$, but its sign depends on the rotational direction. It favors domain walls with $\operatorname{sign} \dot{\varphi} = -\operatorname{sign} D$.

The functional $\int_{-\infty}^{+\infty} \mathrm{d}x \left(A\,\dot{\varphi}^2 + K\,\sin^2\varphi \right)$ with the boundary conditions (24) is minimized by the domain-wall shape $\varphi(x) = \operatorname{arccos}\tanh(\pm\sqrt{K/A}\,x)$ with the energy $4\sqrt{A\,K}$ [44]. Thus, from equation (25) we obtain an optimal domain-wall energy of

$$E = 4\sqrt{A\,K} - \pi\,|D|\ . \tag{26}$$

A negative domain-wall energy indicates, that the the system can gain energy by deviating from the collinear state. Therefore, $E = 0$ in equation (26) corresponds to the condition (23).

4.3 Three-dimensional spin structures

Of course, the assumptions made in equation (22) do not hold for all systems. In the following we still restrict our ansatz to the functional (20) and a crystal structure compatible with the definitions (21), but we do not impose any conditions to the anisotropy constants K_1, K_2, K_D. As a consequence, the magnetization vector $\mathbf{m}$ is not necessarily confined to a single plane but can rotate on a three-dimensional path in spin space. Although we still work with only one spatial coordinate, our model already illustrates the variety of magnetic structures that can arise from an interplay of spin stiffness and spin-orbit-coupling effects in anisotropic crystals.

Our model can be described with two dimensionless parameters $\tilde{D}$ and $\tilde{K}$. For $K_2 \neq K_1$ we can define

$$\tilde{D} = \frac{D}{\sqrt{A\,|K_2-K_1|}} \quad , \quad \tilde{K} = \frac{K_D-K_1}{|K_2-K_1|} \quad , \quad \tilde{x} = \sqrt{\frac{|K_2-K_1|}{A}}\,x \quad , \quad \tilde{E} = \sqrt{\frac{1}{A\,|K_2-K_1|}}\,E \tag{27}$$

and consider the functional

$$\tilde{E} = \int \mathrm{d}\tilde{x}\,\left(\dot{\vartheta}^2 + \sin^2\!\vartheta\,(\,\dot{\varphi}^2 + \tilde{D}\,\dot{\varphi} + \sin^2\!\varphi - \tilde{K}\,)\right) \tag{28}$$

with the $\tilde{x}$-dependent angles defined by $\mathbf{m} = \hat{\mathbf{e}}_1\,\sin\vartheta\,\cos\varphi + \hat{\mathbf{e}}_2\,\sin\vartheta\,\sin\varphi + \hat{\mathbf{e}}_D\,\cos\vartheta$. In the following, we present results that are obtained from a numerical analysis of the functional (28) [45, 46].

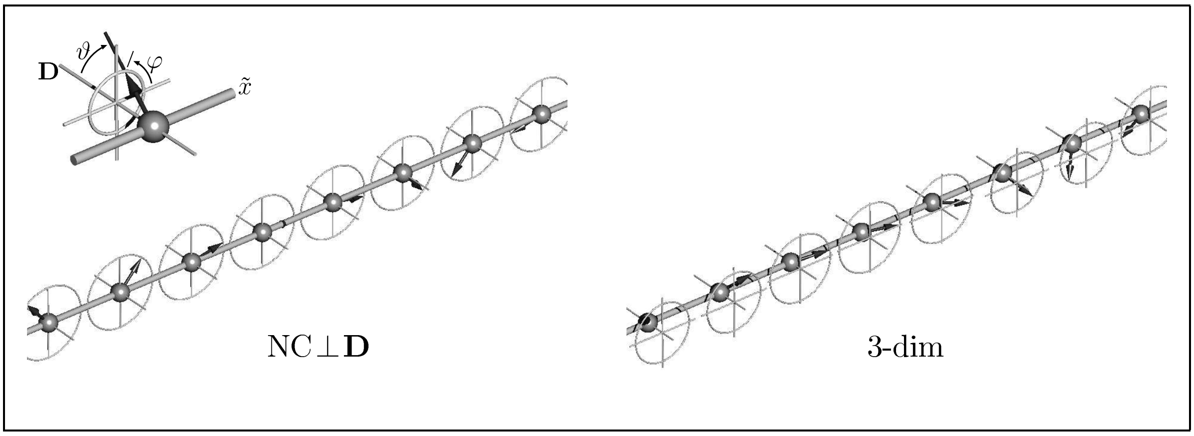


Figure 15: Noncollinear ground state of the functional (28). The left picture shows a planar rotating state ($\vartheta = \pi/2$) that occurs for large $|\tilde{D}|$, the right picture shows the state that occurs for intermediate values of $|\tilde{D}|$. The latter performs a truly three-dimensional path in spin space with $\vartheta \neq \mathrm{const}$. Note, that $\mathbf{m}$ tries to avoid the hard axis that is oriented vertically in this figure.

For small $|\tilde{D}|$, the anisotropy term dominates the DM term and the ground state is collinear ($\vartheta = 0 =$ const), for large $|\tilde{D}|$ the system is dominated by the competition between the DM interaction and the spin stiffness and the rotating magnetization is confined to the plane normal to the Dzyaloshinskii vector

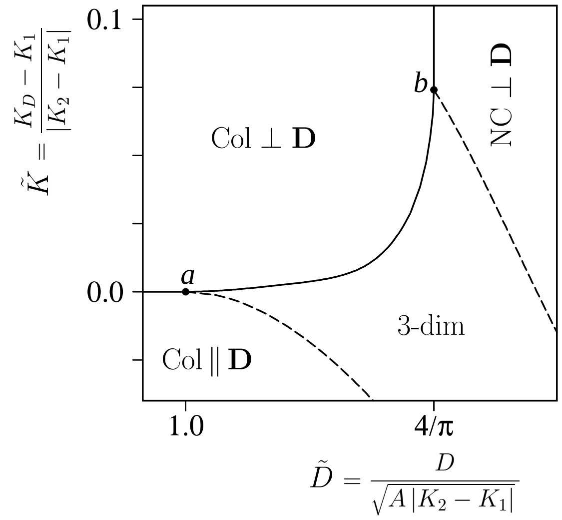


Figure 16: Phase diagram of the ground state of the functional (28). The diagram shows the collinear phase with $\mathbf{m}$ aligned perpendicular (Col $\perp \mathbf{D}$) or parallel (Col $\| \mathbf{D}$) to $\mathbf{D}$, the noncollinear (rotating) phase where $\mathbf{m}$ is confined to a plane (NC $\perp \mathbf{D}$) and the noncollinear phase where $\mathbf{m}$ describes a truly three-dimensional path in spin spin space (3-dim). For $\tilde{D} < 0$ equivalent noncollinear phases occur with reversed rotational direction. The solid line denotes a first-order and the dashed lines denote continuous transitions. The two dashed lines approach each other for increasing $(-\tilde{K})$. For $K_1 = K_2$ the intermediate region (3-dim) vanishes and there is a sharp transition from the collinear state (Col $\| \mathbf{D}$) to the planar rotating state (NC $\perp \mathbf{D}$). Due to our choice of the reduced parameters (equation (27)), this transition point cannot be displayed in this figure.

($\vartheta = \frac{1}{2}\,\pi = \text{const}$, left picture in figure 15). If $\mathbf{D}$ points parallel to the easy axis (i.e. $\tilde{K} < 0$), there is a continuous transition from the collinear to the planar rotating ground state: When $|\tilde{D}|$ exceeds a certain critical value, then the magnetization starts to rotate around the $\mathbf{D}$-vector (i.e. $\operatorname{sign}\dot{\varphi} = -\operatorname{sign}\tilde{D} = \text{const}$), and the average cone angle ϑ increases with increasing $|\tilde{D}|$ (right picture in figure 15). If $\mathbf{D}$ does not point parallel to the easy axis, there is no continuous transition from the collinear to a rotating ground state possible: In this case a rotation around the $\mathbf{D}$-vector cannot be realized by an infinitesimal deviation from the collinear state. In figure 15 we illustrate the rotation path $\mathbf{m}(\tilde{x})$ of the ground state, in figure 16 we show the resulting phase diagram.

Next, we turn our attention to the domain walls that can be described with our ansatz. We minimize the functional (28) under the boundary conditions

$$\tilde{x} \gg 1 \Rightarrow \begin{cases} \hat{\mathbf{e}}_{\text{easy}} \cdot \mathbf{m}(+\tilde{x}) \; > 0 \\ \hat{\mathbf{e}}_{\text{easy}} \cdot \mathbf{m}(-\tilde{x}) \; < 0 \end{cases} \tag{29}$$

where $\hat{\mathbf{e}}_{\text{easy}}$ denotes the unit vector that points parallel to the easy axis. This condition can be applied for the the collinear domains as well as for the three-dimensional ground states that are discussed above (cf. figure 15). A numerical investigation of the expressions (28) and (29) in the $(\tilde{K}, \tilde{D})$ parameter-space shows a variety of domain wall structures that can be classified in several distinct phases. The main results are summarized in the figures 17 and 18.

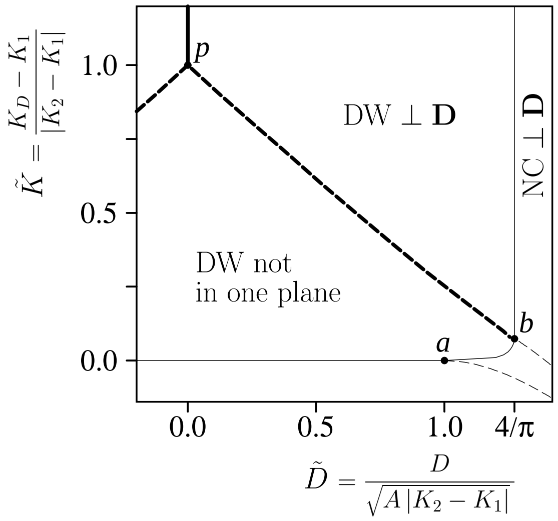


Figure 17: Phase diagram of the domain walls that are described by the functional (28). The thin lines show the transitions of the unconstrained structures (cf. figure 16), the bold lines indicate additional transitions of the domain-wall structures. For $\tilde{K} > 0$ the **D**-vector points parallel to the hard axis. This case is already discussed in section 4.2. The solid line starting at p denotes the first-order transition that occurs when the preferable rotational direction reverses ($\operatorname{sign}\dot{\varphi} = -\operatorname{sign}\tilde{D}$). The dashed line from p to b denotes a second-order transition between wall structures with $\mathbf{m}(\tilde{x})$ confined to one plane (DW $\perp$ **D**) and wall structures with $\mathbf{m}(\tilde{x})$ describing a three-dimensional path in spin space. Note, that the latter can exist also in the case of collinear aligned domain magnetization. The possible domain wall structures are further explained in the caption of figure 18.

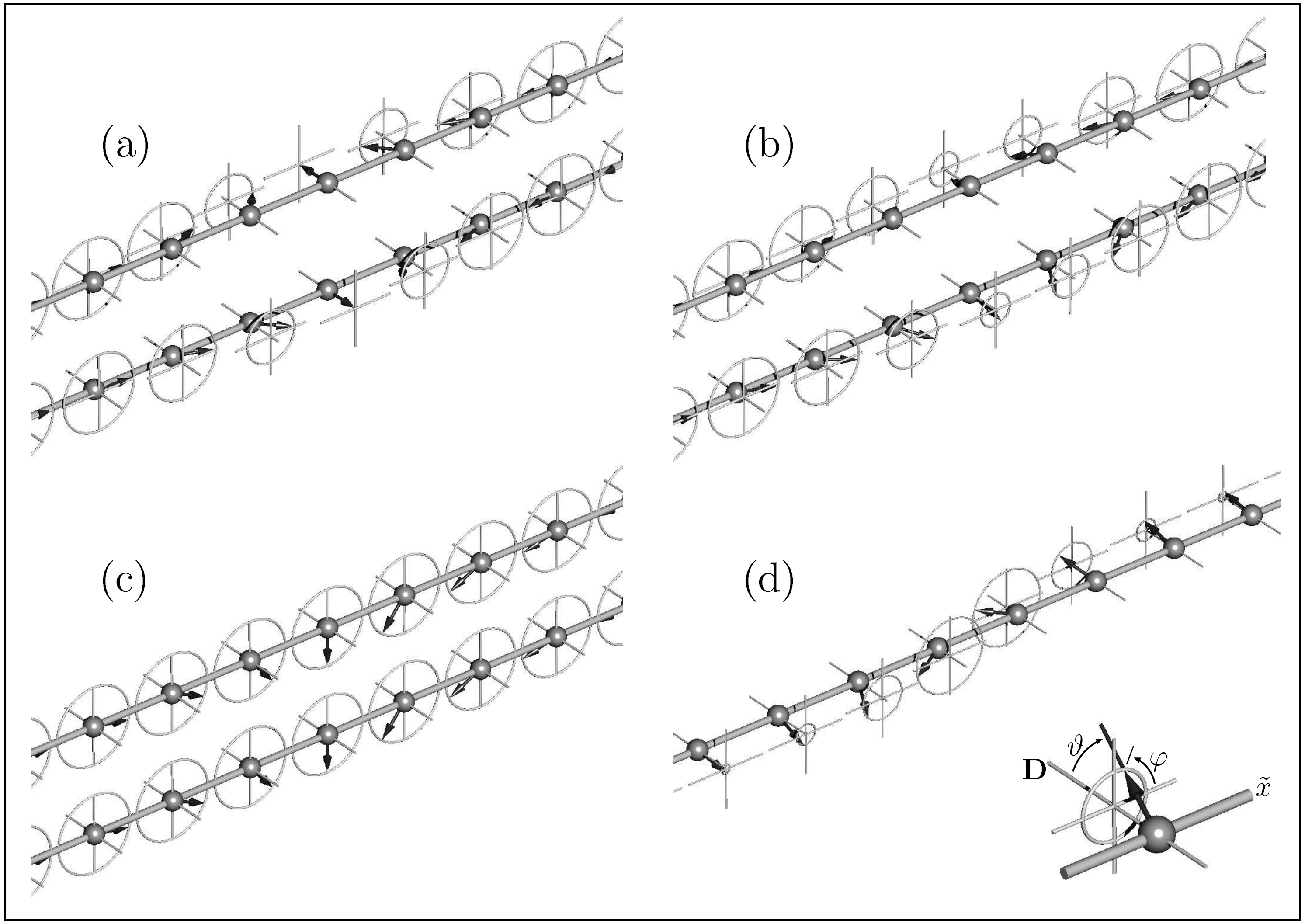
5 Dzyaloshinskii-Moriya interaction from first principles

5.1 DM-interaction within Multiple-Scattering Theory

Within multiple-scattering theory (MST) the DM constants $\mathbf{D}_{ij}$ can be found in an elegant way, as outlined in [47] and more recently in [48]. One employs the so-called "method of infinitesimal rotations", which provides the energy cost of an infinitesimal rotation of two spins, at sites i and j, within second-order perturbation theory. An underlying assumption is that the associated energy is related to the change of the single-particle energy levels only, i.e., one assumes again the validity of the magnetic force theorem. The change in the single-particle levels is then calculated in a straightforward way by utilizing Lloyd's formula, in a way analogous to the derivation of the Lichtenstein formula [10] for the Heisenberg exchange constants. Here, we follow the derivation by Udvardi et al. [48]. It is implied that the spin-orbit coupling is already included in the calculations of the electronic structure, scattering t-matrices, etc., before applying perturbation theory for the infinitesimal rotations.

We distinguish between two models for the description of the solid, which we will then bring in connection: (i) the density-functional model, including the charge and spin density $\rho(\mathbf{r}); \mathbf{m}(\mathbf{r})$ at each point as a degree of freedom, and giving rise to a free energy $F[\mathbf{m}; \rho]$; and (ii) an extended, classical Heisenberg-like model with a Hamiltonian $H(\mathbf{S}_i)$, including spin-spin interactions up to second order, and containing the directions of the magnetic moments at each atom, $\mathbf{S}_i$, as degrees of freedom. It is assumed that, for the system properties in question, a mapping of the free energy F of model (i) to the Hamiltonian H of model (ii) is meaningful. Such a mapping leads obviously to a significant reduction of the degrees of freedom to the essential ones for the problem at hand.

Figure 18: Rotation paths of $\mathbf{m}(\tilde{x})$ in the walls between collinear domains. In figures a-c the **D**-vector is perpendicular to the easy axis (i.e. $\tilde{K} > 0$), in figure d it is parallel to the easy axis (i.e. $\tilde{K} < 0$). (a): For $\tilde{D} = 0$ and $0 < \tilde{K} < 1$ there are two degenerate rotation paths in the plane normal to the hard axis. (b): For small $\tilde{D} > 0$ and $0 < \tilde{K} < 1$ the competition between the anisotropy term and the DM term results in a three-dimensional rotation path in spin space (in this figure, the hard axis is oriented vertically). There are still two degenerate solutions. (c): For larger $\tilde{D}$ or $\tilde{K} > 1$ the magnetization is confined to the plane normal to **D**. In this case, there is only one solution: the continuations of both walls in figure b coincide in the regime of $\mathbf{m} \perp \mathbf{D}$. (d): For **D** parallel to the easy axis, the domain walls reduce their energy by a spatial rotation around **D**.



The spin-spin interaction can be described, up to second order, by the Hamiltonian

$$H = \sum_i K(\mathbf{S}_i) + \sum_{ij(i\neq j)} \mathbf{S}_i \mathsf{J}_{ij} \mathbf{S}_j \tag{30}$$

Here, the first term describes the on-site anisotropy energy and the second term (where $i \neq j$) includes the intersite exchange interactions and the Dzyaloshinskii-Moriya interaction. The quantities J_{ij} are 3×3 matrices (second rank tensors in real space). They can be decomposed in symmetric and antisymmetric parts as:

$$\mathsf{J}_{ij} = J_{ij}1 + \mathsf{J}_{ij}^S + \mathsf{J}_{ij}^A \tag{31}$$

with J_{ij} being the usual exchange interaction

$$J_{ij} = \frac{1}{3}\mathrm{Tr}\mathsf{J}_{ij}, \tag{32}$$

J_{ij}^S the (traceless) symmetric part

$$\mathsf{J}_{ij}^S = \frac{1}{2}\left(\mathsf{J}_{ij} + \mathsf{J}_{ij}^t\right) - J_{ij}1, \tag{33}$$

and J_{ij}^A the antisymmetric part:

$$\mathsf{J}_{ij}^A = \frac{1}{2}\left(\mathsf{J}_{ij} - \mathsf{J}_{ij}^t\right). \tag{34}$$

The latter can be brought in connection with the Dzyaloshinskii-Moriya interaction constants $\mathbf{D}_{ij} = (D_{ij}^x, D_{ij}^y, D_{ij}^z)$ by writing

$$\mathsf{J}_{ij}^A = \begin{pmatrix} 0 & \frac{1}{2}(J_{ij}^{xy} - J_{ij}^{yx}) & \frac{1}{2}(J_{ij}^{xz} - J_{ij}^{zx}) \\ -\frac{1}{2}(J_{ij}^{xy} - J_{ij}^{yx}) & 0 & \frac{1}{2}(J_{ij}^{yz} - J_{ij}^{zy}) \\ -\frac{1}{2}(J_{ij}^{xz} - J_{ij}^{zx}) & -\frac{1}{2}(J_{ij}^{yz} - J_{ij}^{zy}) & 0 \end{pmatrix} = \begin{pmatrix} 0 & D_{ij}^z & -D_{ij}^y \\ -D_{ij}^z & 0 & D_{ij}^x \\ D_{ij}^y & -D_{ij}^x & 0 \end{pmatrix} \tag{35}$$

The spin-spin interaction is then written in terms of the Dzyaloshinskii-Moriya vectors as

$$\mathbf{S}_i \mathsf{J}_{ij} \mathbf{S}_j = J_{ij}\mathbf{S}_i\mathbf{S}_j + \mathbf{S}_i \mathsf{J}_{ij}^S \mathbf{S}_j + \mathbf{D}_{ij}(\mathbf{S}_i \times \mathbf{S}_j) \tag{36}$$

It is now necessary to express the interaction constants J_{ij}^{xy} etc. in terms of H; then the substitution $F \leftrightarrow H$ will make the connection to the density-functional model. We restrict the discussion to the off-diagonal elements, as these enter expression (35) for the Dzyaloshinskii-Moriya interaction. Evidently,

$$J_{ij}^{xy} = \frac{\partial^2 H}{\partial x_i \partial y_j}, \tag{37}$$

and similar expressions hold for the other components. These can be rewritten in terms of spherical coordinates (θ_i, ϕ_i) (defining the direction of magnetization $\mathbf{S}_i$). To obtain, for example, the expression of J_{ij}^{zy} in terms of H, it is convenient to choose a reference system in which the magnetization of the ferromagnetic state is along the x-axis, as sketched in fig. 19. In this reference system we get from eq. (30):

$$J_{ij}^{zy} = -\left(\frac{\partial^2 H}{\partial\theta_i \partial\phi_j}\right)_{\substack{\theta_{i,j}=\frac{\pi}{2} \\ \phi_{i,j}=0}}, \quad J_{ij}^{yz} = -\left(\frac{\partial^2 H}{\partial\phi_i \partial\theta_j}\right)_{\substack{\theta_{i,j}=\frac{\pi}{2} \\ \phi_{i,j}=0}}, \tag{38}$$

By choosing the magnetization along the y-axis, J_{ij}^{xz} and J_{ij}^{zx} can be obtained as:

$$J_{ij}^{zx} = -\left(\frac{\partial^2 H}{\partial\theta_i \partial\phi_j}\right)_{\substack{\theta_{i,j}=\frac{\pi}{2} \\ \phi_{i,j}=\frac{\pi}{2}}}, \quad J_{ij}^{xz} = \left(-\frac{\partial^2 H}{\partial\phi_i \partial\theta_j}\right)_{\substack{\theta_{i,j}=\frac{\pi}{2} \\ \phi_{i,j}=\frac{\pi}{2}}}, \tag{39}$$

while the J_{ij}^{xy} and J_{ij}^{yx} are found by placing the magnetization along the z-axis and taking infinitesimal rotations in the x and y directions (thus we set $\theta = 0$ and $\phi = 0, \frac{\pi}{2}$):

$$J_{ij}^{xy} = \left(\frac{\partial^2 H}{\partial\theta_i \partial\theta_j}\right)_{\substack{\theta_{i,j}=0 \\ \phi_i=0 \\ \phi_j=\frac{\pi}{2}}}, \; J_{ij}^{yx} = \left(\frac{\partial^2 H}{\partial\theta_i \partial\theta_j}\right)_{\substack{\theta_{i,j}=0 \\ \phi_i=\frac{\pi}{2} \\ \phi_j=0}}. \tag{40}$$

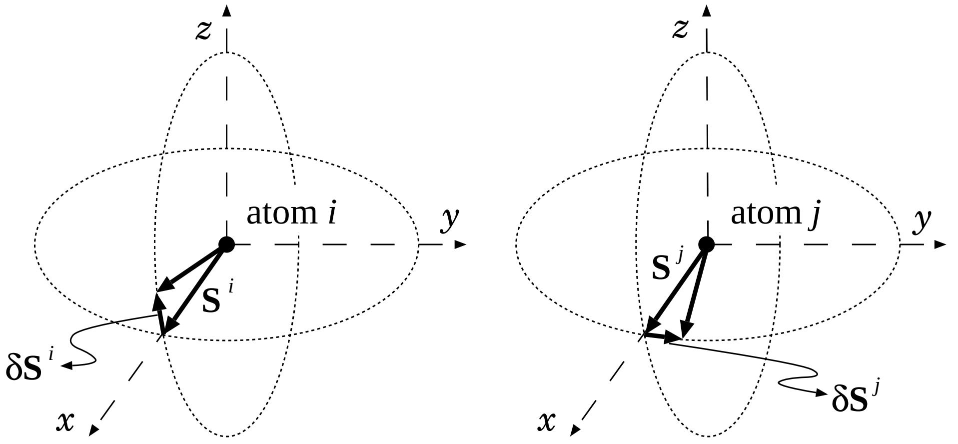


Figure 19: Setup for the calculation of the Dzyaloshinskii-Moriya interaction constants $\mathbf{D}_{ij}$. The magnetic moments of atoms i and j are tilted in different directions. Here, $\mathbf{S}_i$ is tilted in the z direction and $\mathbf{S}_j$ in the y-direction (i.e., $\delta\mathbf{S}_i = -\delta\theta\,\hat{z}$ and $\delta\mathbf{S}_j = \delta\phi\,\hat{y}$) yielding $J_{ij}^{zy} = \partial^2 H/\partial z_i \partial y_j = -\partial^2 H/\partial\theta_i\partial\phi_j$.

We now turn to the expressions of the change of free energy with respect to infinitesimal rotations of the magnetic moments within DFT, as derived by multiple-scattering theory. Again we follow the derivation by Udvardi et al. [48]. The contribution of the single-particle levels to the free energy at zero temperature is given in terms of the density of states $n(E)$, or the integrated density of states $N(E) = \int^E n(E')dE'$, as an integral up to the Fermi level E_F:

$$F = \int^{E_F} (E - E_F) n(E) dE = -\int^{E_F} N(E) dE. \tag{41}$$

By virtue of the magnetic force theorem, changes in the magnetization direction affect, to lowest order, only this single-particle part of the free energy. Therefore, the change in total energy can be directly associated with the changes in the integrated density of states.

Within the Korringa-Kohn-Rostoker Green function method, one considers the atomic potentials as scattering centers at points $\mathbf{R}_i$, each characterized by a scattering t-matrix $t_i(E)$. A central quantity is the scattering path operator $\tau(E)$, which is connected to the site-dependent scattering t-matrix $t_i(E)$ and to the free-space structure constants $g_{ij}(E)$ via the matrix relation

$$\tau(E) = [\mathsf{t}^{-1}(E) - \mathsf{g}(E)]^{-1} = \mathsf{t} + \mathsf{t}\,\mathsf{g}\,\mathsf{t} + \mathsf{t}\,\mathsf{g}\,\mathsf{t}\,\mathsf{g}\,\mathsf{t} + \cdots ; \tag{42}$$

i.e., the matrix $\tau(E)$ describes the coherent scattering from all centers i. Here, $\mathsf{t}(E)$ is to be understood as a site-diagonal matrix with element $(\mathsf{t})_{ij} = t_i(E)\delta_{ij}$ ($t_i(E)$ is also a matrix with angular-momentum and spin indexes). The free-space structure constants (describing the electron propagation in the absence of scattering) relate a free spherical wave (a Hankel function), outgoing from a center j , to incoming free spherical waves (Bessel functions) at a center i [49].

The change of the integrated density of states (with respect to free space) due to the scattering centers can be connected to the scattering path operator $\tau(E)$ via Lloyd's formula:

$$\Delta N(E) = \frac{1}{\pi}\mathrm{Im}\mathrm{Tr}\ln\tau(E) \tag{43}$$

(Expressions (42) and (43) hold also when relating a perturbed system to any reference system (not just free space), with $t_i(E)$ describing the scattering with respect to the reference system and $\mathsf{g}(E)$ being the reference system structural Green function.)

Utilizing expressions (41), (42) and (43) we can express the change of free energy under an infinitesimal change in the direction of the magnetic moments at sites i and j, which in turn is expressed via a corresponding change in the t-matrices $t_i(E)$ and $t_j(E)$. We proceed as follows. Firstly we express the rotated inverse t-matrix of atom i in terms of rotation matrices $\mathsf{R}(\delta\theta_i, \delta\phi_i)$, corresponding to an infinitesimal change in the moment direction described by angles $\delta\theta_i$ and $\delta\phi_i$:

$$t_i'^{-1} = \mathsf{R}(\delta\theta_i, \delta\phi_i)\, t_i^{-1}\, \mathsf{R}^\dagger(\delta\theta_i, \delta\phi_i). \tag{44}$$

In the absence of spin-orbit coupling, the rotation matrices act only in spin space and are of the form $\mathsf{R}(\delta\theta_i, \delta\phi_i) = \exp[-(i/\hbar)\alpha_i \hat{\mathbf{n}}(\delta\theta_i, \delta\phi_i) \cdot \boldsymbol{\sigma}/2]$ where α_i is the angle and $\hat{\mathbf{n}}$ is the unit vector expressing the real-space rotation $(\delta\theta_i, \delta\phi_i)$, and $\boldsymbol{\sigma}$ is the Pauli matrix vector; then the equations are simplified, yielding the result of Lichtenstein for the exchange constants J_{ij} [10]. Here, however, spin-orbit coupling is present, so that the rotation affects also the angular momentum part of the t-matrix; thus, $\mathsf{R}(\delta\theta_i, \delta\phi_i) = \exp[-(i/\hbar)\alpha_i \hat{\mathbf{n}}(\delta\theta_i, \delta\phi_i) \cdot (\mathbf{L} + \boldsymbol{\sigma}/2)]$, where $\mathbf{L}$ is the angular momentum operator.

For the calculation of the exchange and DM-interactions we are interested in the change of the free energy up to second order in $\delta\theta_i$ and $\delta\phi_i$. Thus, the partial derivatives of the inverse t-matrix are needed. These can be expressed via the derivatives of the rotation matrices (see eq.(44)), as [48]:

$$t_{i\,\theta}^{-1} \equiv \frac{\partial t^{-1}}{\partial \theta_i} = \frac{\partial \mathsf{R}}{\partial \theta_i}\, t_i^{-1}\, \mathsf{R}^\dagger + \mathsf{R}\, t_i^{-1}\, \frac{\partial \mathsf{R}^\dagger}{\partial \theta_i} \tag{45}$$

$$t_{i\,\phi}^{-1} \equiv \frac{\partial t^{-1}}{\partial \phi_i} = \frac{\partial \mathsf{R}}{\partial \phi_i}\, t_i^{-1}\, \mathsf{R}^\dagger + \mathsf{R}\, t_i^{-1}\, \frac{\partial \mathsf{R}^\dagger}{\partial \phi_i} \tag{46}$$

Let us denote the change of t^{-1} due to the rotation of t_i^{-1} by $\delta \mathsf{t}_i^{-1}$ (this matrix has non-zero elements only at the (i, i) block). An infinitesimal rotation at sites i and j brings a change in the scattering path operator,

$$\tau' = [\mathsf{t}^{-1} + \delta\mathsf{t}_i^{-1} + \delta\mathsf{t}_j^{-1} - \mathsf{g}]^{-1} = \tau\, [1 + (\delta\mathsf{t}_i^{-1} + \delta\mathsf{t}_j^{-1})\, \tau]^{-1}. \tag{47}$$

We are interested in the change of the integrated density of states caused by these rotations. Having in mind Lloyd's formula (43), we expand the logarithm of τ' up to second order:

$$\delta \ln \tau = \ln \tau' - \ln \tau = 1 + (\delta\mathsf{t}_i^{-1} + \delta\mathsf{t}_j^{-1}) - \frac{1}{2}(\delta\mathsf{t}_i^{-1} + \delta\mathsf{t}_j^{-1})\, \tau\, (\delta\mathsf{t}_i^{-1} + \delta\mathsf{t}_j^{-1})\, \tau + \cdots \tag{48}$$

From equations (37-40) it is evident that we seek the quantity $\partial^2 \ln \tau / \partial\theta_i \partial\phi_j$ etc. Then only the cross terms of the last part of eq. (48) survive, i.e., $\frac{1}{2}(\delta\mathsf{t}_i^{-1}\, \tau\, \delta\mathsf{t}_j^{-1}\, \tau + \delta\mathsf{t}_j^{-1}\, \tau\, \delta\mathsf{t}_i^{-1}\, \tau)$. Using the cyclic property of the trace, we obtain

$$\frac{\partial^2}{\partial\theta_i \partial\phi_j} \mathrm{Tr} \ln \tau = \frac{\partial^2}{\partial\theta_i \partial\phi_j} \mathrm{Tr}\, (\mathsf{t}_i^{-1}\, \tau\, \mathsf{t}_j^{-1}\, \tau) = \mathrm{Tr}_L\, t_{i\,\theta}^{-1}\, \tau_{ij}\, t_{j\,\phi}^{-1}\, \tau_{ji}, \tag{49}$$

where in the last part the trace is only over angular momentum indexes (we have used the fact that $\delta\mathsf{t}_i^{-1}$ has nonzero elements only in the (i, i)-block). Similar are the expressions for the other partial second derivatives with respect to angles at both i and j. Combining this with Lloyd's formula (43) and with the free energy expression (42), we arrive at the following equations:

$$\frac{\partial^2 F}{\partial\phi_i \partial\phi_j} = -\frac{1}{\pi} \mathrm{Im} \int^{E_F} dE\, \mathrm{Tr}_L [t_{i\,\phi}^{-1}(E)\, \tau_{ij}(E)\, t_{j\,\phi}^{-1}(E)\, \tau_{ji}(E)] \tag{50}$$

$$\frac{\partial^2 F}{\partial\theta_i \partial\phi_j} = -\frac{1}{\pi} \mathrm{Im} \int^{E_F} dE\, \mathrm{Tr}_L [t_{i\,\theta}^{-1}(E)\, \tau_{ij}(E)\, t_{j\,\phi}^{-1}(E)\, \tau_{ji}(E)] \tag{51}$$

$$\frac{\partial^2 F}{\partial\theta_i \partial\theta_j} = -\frac{1}{\pi} \mathrm{Im} \int^{E_F} dE\, \mathrm{Tr}_L [t_{i\,\theta}^{-1}(E)\, \tau_{ij}(E)\, t_{j\,\theta}^{-1}(E)\, \tau_{ji}(E)] \tag{52}$$

The final step is the connection of the two models (the Hamiltonian (30) and density-functional theory) by making the substitution $F \to H$ in eqs. (50-52). Thus we arrive at expressions describing the

Dzyaloshinskii-Moriya interaction constants, using also equations (35) and (38-40). We obtain:

$$D^x_{ij} = -\frac{1}{2\pi}\mathrm{Im}\int^{E_F} dE\,\mathrm{Tr}_L \\ \Big[t^{-1}_{i\,\phi}(E)\,\tau_{ij}(E)\,t^{-1}_{j\,\theta}(E)\,\tau_{ji}(E) - t^{-1}_{i\,\theta}(E)\,\tau_{ij}(E)\,t^{-1}_{j\,\phi}(E)\,\tau_{ji}(E)\Big]_{\substack{\theta_{i,j}=\frac{\pi}{2}\\ \phi_{i,j}=0}} \tag{53}$$

$$D^y_{ij} = -\frac{1}{2\pi}\mathrm{Im}\int^{E_F} dE\,\mathrm{Tr}_L \\ \Big[-t^{-1}_{i\,\phi}(E)\,\tau_{ij}(E)\,t^{-1}_{j\,\theta}(E)\,\tau_{ji}(E) + t^{-1}_{i\,\theta}(E)\,\tau_{ij}(E)\,t^{-1}_{j\,\phi}(E)\,\tau_{ji}(E)\Big]_{\substack{\theta_{i,j}=\frac{\pi}{2}\\ \phi_{i,j}=\frac{\pi}{2}}} \tag{54}$$

$$D^z_{ij} = -\frac{1}{2\pi}\mathrm{Im}\int^{E_F} dE\,\mathrm{Tr}_L \\ \left\{\Big[t^{-1}_{i\,\theta}(E)\,\tau_{ij}(E)\,t^{-1}_{j\,\theta}(E)\,\tau_{ji}(E)\Big]_{\substack{\theta_{i,j}=0\\ \phi_i=0\\ \phi_j=\frac{\pi}{2}}} - \Big[t^{-1}_{i\,\theta}(E)\,\tau_{ij}(E)\,t^{-1}_{j\,\theta}(E)\,\tau_{ji}(E)\Big]_{\substack{\theta_{i,j}=0\\ \phi_i=\frac{\pi}{2}\\ \phi_j=0}}\right\} \tag{55}$$

5.2 Calculating the DM interaction with periodic spin spirals

An alternative way to obtain model parameters like the elements of the above discussed matrix J_{ij} from first principles is to fit the energy expression obtained from the model ansatz to the total energies obtained from electronic structure calculations for different magnetic states. We follow this strategy in order to obtain the micromagnetic parameters that are discussed in section 4. If we know the orientation of the Dzyaloshinskii vector from symmetry considerations, we can constrain the magnetization to the plane normal to $\mathbf{D}$ and work with equation (22). For homogeneous spin spirals (i.e. spirals with $\dot{\varphi}(x) = q = \mathrm{const}$ or a constant canting angle $\arccos(\mathbf{S}_i{\cdot}\mathbf{S}_{i+1})$ between the magnetizations of two adjacent lattice sites) the magnetic structure has a period of $\lambda_{\mathrm{hs}} = 2\,\pi/q$ and the energy density E/λ_{hs} of the micromagnetic model gets

$$\frac{q}{2\,\pi}\,E(q) = \frac{q}{2\,\pi}\int\limits_0^{\frac{2\,\pi}{q}} \mathrm{d}x\,\big(\,A\,q^2 + D\,q + K\sin^2(q\,x)\,\big) = A\,q^2 + D\,q + \tfrac{1}{2}\,K\ . \tag{56}$$

Thus, we can obtain our model parameters A and D from a quadratic and a linear fit to the dispersion curve $q\,E(q)$, with latter obtained from first-principles calculations. In order to determine the anisotropy constant K, we can perform independent calculations of collinear configurations with $\varphi = 0$ and $\varphi = \pi$.

Since the micromagnetic model is valid in the limit of slow spatial rotations, relation (56) holds only for homogeneous spin spirals with large period lengths. This presents a formidable problem, since the size of the unit cell that one can treat is limited by the computing facilities. We employ a perturbative scheme in order to deal with these large magnetic superstructures: In contrast to the method described in the previous section, we calculate the rotations selfconsistently but treat the spin-orbit coupling as a perturbation. Thereby, we make use of the local force theorem [10,50]. If we neglect spin-orbit coupling, the orientation of the magnetic moments with respect to the crystal lattice is irrelevant and we can calculate the electronic structure of a homogeneous spin spiral within the chemical unit cell by applying a generalized Bloch theorem [51,52]. The resulting eigenstates of the unperturbed Hamiltonian $\mathcal{H}_0$ have the form

$$\psi_{\mathbf{k},\nu}(\mathbf{r}) = \begin{pmatrix} \psi^{(\uparrow)}_{\mathbf{k},\nu}(\mathbf{r}) \\ \psi^{(\downarrow)}_{\mathbf{k},\nu}(\mathbf{r}) \end{pmatrix} = \exp(i\,\mathbf{k}{\cdot}\mathbf{r}) \begin{pmatrix} \exp(-i\,\frac{1}{2}\,\mathbf{q}{\cdot}\mathbf{r})\ u^{(\uparrow)}_{\mathbf{k},\nu}(\mathbf{r}) \\ \exp(+i\,\frac{1}{2}\,\mathbf{q}{\cdot}\mathbf{r})\ u^{(\downarrow)}_{\mathbf{k},\nu}(\mathbf{r}) \end{pmatrix} \tag{57}$$

with the $\mathbf{q}$-vector of length $|q|$ pointing along the propagation direction of the spiral and the functions $u^{(\uparrow)}_{\mathbf{k},\nu}(\mathbf{r})$, $u^{(\downarrow)}_{\mathbf{k},\nu}(\mathbf{r})$ possessing the period of the chemical lattice. Of course, $\mathbf{k}$ denotes a $\mathbf{k}$-vector of the reciprocal chemical lattice. In a next step, we apply the spin-orbit coupling operator $\mathcal{H}_{\rm so}$ in second variation, i.e. we expand the eigenfunctions of $\mathcal{H}_0 + \mathcal{H}_{\rm so}$ in eigenfunctions of $\mathcal{H}_0$ and construct the Hamiltonian matrix with the matrix elements $\langle \psi_{\mathbf{k}',\nu'} | \mathcal{H}_0 + \mathcal{H}_{\rm so} | \psi_{\mathbf{k},\nu} \rangle$. Since we can neglect all states of high energy, this procedure reduces the size of the Hamiltonian matrix drastically. The spin-orbit coupling is well described by

$$\mathcal{H}_{\rm so} = \sum_\alpha \frac{1}{r_\alpha} \frac{\mathrm{d}V_\alpha(r_\alpha)}{\mathrm{d}r_\alpha} \boldsymbol{\sigma}\cdot\hat{\mathbf{L}}_\alpha = \begin{pmatrix} \mathcal{H}_{\rm so}^{(\uparrow,\uparrow)} & \mathcal{H}_{\rm so}^{(\uparrow,\downarrow)} \\ \mathcal{H}_{\rm so}^{(\downarrow,\uparrow)} & \mathcal{H}_{\rm so}^{(\downarrow,\downarrow)} \end{pmatrix} \tag{58}$$

where the index α denotes the atoms. Since only the spin-independent part of the potential enters $\mathcal{H}_{\rm so}$, its real-space representation possesses the period of the chemical lattice. This allows us to write the matrix elements in the form

$$\begin{aligned}
\langle \psi_{\mathbf{k}',\nu'}^{(\uparrow)} | \mathcal{H}_{\rm so}^{(\uparrow,\uparrow)} | \psi_{\mathbf{k},\nu}^{(\uparrow)} \rangle &= \int\!\mathrm{d}\mathbf{r}\ \mathrm{e}^{i\,(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}\ u^{(\uparrow,\uparrow)}(\mathbf{r})\ , \\
\langle \psi_{\mathbf{k}',\nu'}^{(\uparrow)} | \mathcal{H}_{\rm so}^{(\uparrow,\downarrow)} | \psi_{\mathbf{k},\nu}^{(\downarrow)} \rangle &= \int\!\mathrm{d}\mathbf{r}\ \mathrm{e}^{i\,(\mathbf{k}-\mathbf{k}'+\mathbf{q})\cdot\mathbf{r}}\ u^{(\uparrow,\downarrow)}(\mathbf{r})\ , \\
\langle \psi_{\mathbf{k}',\nu'}^{(\downarrow)} | \mathcal{H}_{\rm so}^{(\downarrow,\uparrow)} | \psi_{\mathbf{k},\nu}^{(\uparrow)} \rangle &= \int\!\mathrm{d}\mathbf{r}\ \mathrm{e}^{i\,(\mathbf{k}-\mathbf{k}'-\mathbf{q})\cdot\mathbf{r}}\ u^{(\downarrow,\uparrow)}(\mathbf{r})\ , \\
\langle \psi_{\mathbf{k}',\nu'}^{(\downarrow)} | \mathcal{H}_{\rm so}^{(\downarrow,\downarrow)} | \psi_{\mathbf{k},\nu}^{(\downarrow)} \rangle &= \int\!\mathrm{d}\mathbf{r}\ \mathrm{e}^{i\,(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}\ u^{(\downarrow,\downarrow)}(\mathbf{r})
\end{aligned} \tag{59}$$

with lattice-periodic functions $u^{(\uparrow,\uparrow)}$, $u^{(\uparrow,\downarrow)}$, $u^{(\downarrow,\uparrow)}$, $u^{(\downarrow,\downarrow)}$. Obviously, these matrix elements are non-zero if and only if the exponents are zero. If we choose a **q**-vector that is commensurate with the reciprocal lattice (i.e. a spiral that is commensurate within a certain supercell) and a **k**-grid that is commensurate to the **q**-vector, then we obtain a block-diagonal and sparse Hamiltonian matrix. Each block contains the matrix elements from all **k**-vectors that are connected by **q** (cf. figure 20). Note, that **q** is a reciprocal lattice vector of the large magnetic unit cell in which the spin spiral is commensurate.

For large systems, the Hamiltonian matrix that is shown in figure 20 is too large for straightforward diagonalization. But since we are applying the local force theorem, we only need to know the sum of occupied eigenvalues. This allows to use a perturbative technique that requires exact diagonalization only in a subspace close to the Fermi energy and exploits the sparseness [45].

$$H_{\{\mathbf{k}\}} = \Big(\delta_{\mathbf{k},\mathbf{k}'} \delta_{\nu,\nu'}\, \epsilon_{\mathbf{k},\nu} + \langle \psi_{\mathbf{k},\nu'} | \mathcal{H}_{\rm so} | \psi_{\mathbf{k},\nu} \rangle \Big)_{\substack{\mathbf{k},\mathbf{k}' \\ \nu,\nu'}} =$$

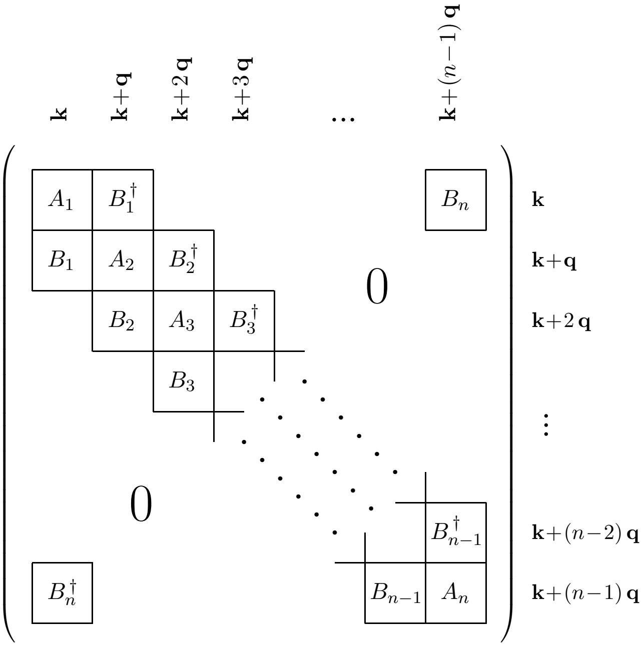


Figure 20: Block of the Hamiltonian matrix for spin-spiral basis functions.

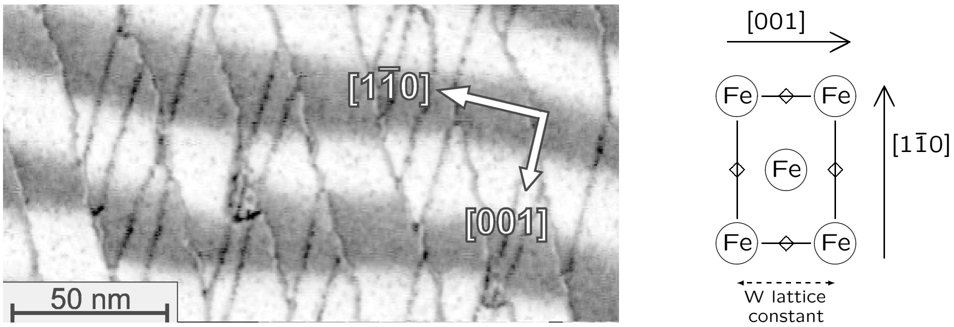


Figure 21: (from [56]) Magnetic domain structure imaged with spin polarized STM. The bright and dark areas correspond to domains with magnetization aligned parallel or antiparallel to the magnetization of the STM tip. The vertical stripes originate from step edges and other geometrical irregularities. The domain walls are oriented normal to the [001]-direction.

6 An example: Domain walls in Fe/W(110)

In this section, we illustrate the relevance of the DM interaction by discussing an exemplary system, namely an ultrathin Fe film consisting of two atomic layers grown on the W(110)-surface. We choose this system, since its magnetic structure is elaborately studied by spin-polarized STM, cf. e.g. [53–55]. A typical STM image is shown in figure 21.

The system shows ferromagnetic domains with the magnetization pointing out-of-plane along the easy axis. The spatial orientation of the corresponding domain walls is determined by the crystal lattice and hardly influenced by the mesoscopic shape of the sample: The walls are preferably oriented normal to the [001]-direction (i.e. the magnetization changes along [001] and remains constant along [1$\bar{1}$0]). In the following, we want to investigate this effect on the basis of the previously introduced micromagnetic models. If the DM term is irrelevant, the magnetization in the domain walls tries to avoid the hard axis and the magnetization rotation axis does not depend on the propagation direction. In this case, the energies $\sqrt{A\,K}$ of walls that are oriented in different crystallographic directions differ due to the spin stiffness, the value of A depends on the propagation direction. However, the values obtained for A by electronic-structure calculations do not change much for different propagation direction (cf. figure 22 left panel). A further indication of the relevance of the DM interaction in the studied system is the fact, that all domain walls that are observed within one sample show the same rotational direction [57], this cannot be explained on the basis of symmetric exchange interactions. In the following we take the DM term into account, but we restrict our investigations to planar domain walls that can be described with the equations (22) and (26). If the propagation direction and the spin-rotation axis are both oriented along a high-symmetry line, we have to consider eight different walls that depend on six parameters. The walls are listed in table 1 and their energies are given by equation (26).

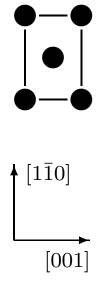
	K_{001}		$K_{1\bar{1}0}$		
walls normal to [001] A_{001}	⊙ → ⊗ ⊙ → ⊗ ⊙ → ⊗ $+D_{001}$	⊙ ← ⊗ ⊙ ← ⊗ ⊙ ← ⊗ $-D_{001}$	⊙ ↑ ⊗ ⊙ ↑ ⊗ ⊙ ↑ ⊗ $D=0$	⊙ ↓ ⊗ ⊙ ↓ ⊗ ⊙ ↓ ⊗ $D=0$	
walls normal to [1$\bar{1}$0] $A_{1\bar{1}0}$	⊗ ⊗ ⊗ → → → ⊙ ⊙ ⊙ $D=0$	⊗ ⊗ ⊗ ← ← ← ⊙ ⊙ ⊙ $D=0$	⊗ ⊗ ⊗ ↑ ↑ ↑ ⊙ ⊙ ⊙ $+D_{1\bar{1}0}$	⊗ ⊗ ⊗ ↓ ↓ ↓ ⊙ ⊙ ⊙ $-D_{1\bar{1}0}$	

Table 1: Planar rotation paths and corresponding model parameters. In the domains, the magnetization points out-of-plane.

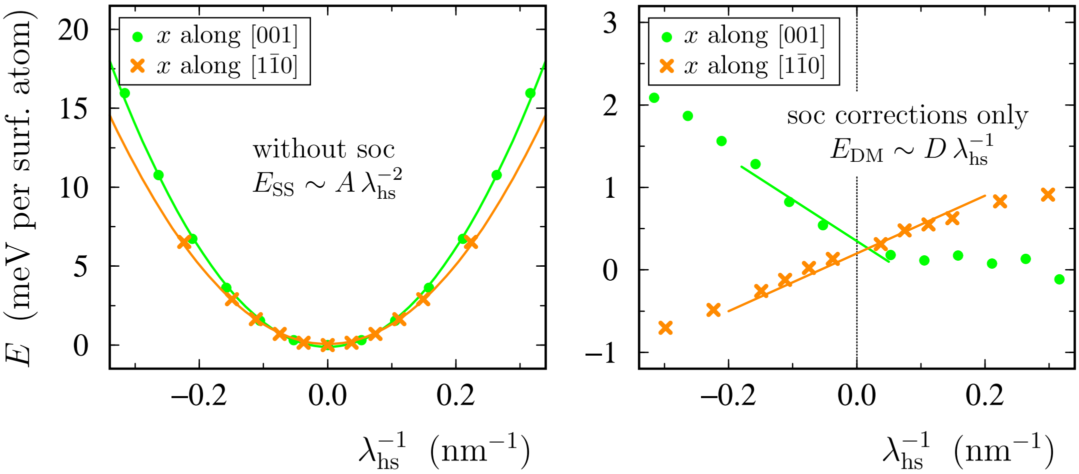


Figure 22: Energies of homogeneous spin spirals obtained from electronic-structure calculations. $|\lambda_{\mathrm{hs}}|$ denotes the spirals period length and the sign of λ_{hs} depends on the rotational direction. The left panel shows the energies obtained by neglecting spin-orbit coupling, quadratic fits to these curves yield the values for A. The right panel shows the effect of the spin-orbit coupling, here we plotted the energy differences between the results obtained by including and neglecting spin-orbit coupling. The spin-rotation axis is chosen in-plane and orthogonal to the propagation direction. The slopes of the curves at $\lambda_{\mathrm{hs}}^{-1} = 0$ correspond to D. The fits are indicated with solid lines.

We estimate values for the model parameters by electronic-structure calculations. These calculations are performed with the FLAPW method implemented in the FLEUR code [12]. A and D are obtained by using a generalized Bloch theorem [51, 52] and the approach introduced in section 5.2. The results of these calculations are shown in figure 22. The anisotropy constant K consists of two main contributions, a term due to the anisotropic electronic energy and a term due to the magnetostatic interactions. The first term can be estimated directly from the electronic energies of collinear configurations with different spin quantization axes, the second term can be estimated from the magnetic (dipole) moments $\mathbf{M}_j$ by applying the well-known formula

$$E^{(\mathrm{dip})} = \frac{\mu_{\mathrm{B}}^2}{2} \sum_{j \neq 0} \frac{(\mathbf{M}_j \cdot \mathbf{M}_0)(\mathbf{R}_j - \mathbf{R}_0)^2 - 3\big((\mathbf{R}_j - \mathbf{R}_0) \cdot \mathbf{M}_j\big)\big((\mathbf{R}_j - \mathbf{R}_0) \cdot \mathbf{M}_0\big)}{|\mathbf{R}_j - \mathbf{R}_0|^5} \,. \tag{60}$$

This sum converges fast, since we are considering a two-dimensional ultrathin magnetic film and not a magnetic bulk system. The results our calculations are summarized in table 2 (for computational details cf. [45]). The values given for the spin-stiffness constants A are fairly accurate, since they are obtained from an unambiguous fitting procedure on a curve on a large energy scale (cf. figure 22). The values given for D are less accurate, but they tell us the order of magnitude of the Dzyaloshinskii vector. The accuracy of the anisotropy constants K is not satisfactory, these calculations reach the limit of our computational method and we cannot rule out an error of a few meV nm^{-1} (note that 1 meV nm^{-2} $\widehat{=}$ 0.035 meV per Fe atom).

Inserting the values given in table 2 in equation (26) yields the wall energies

$$\begin{aligned}
4\sqrt{A_{001}\,K_{001}} - \pi\,|D_{001}| &= -1.2\,\mathrm{meV\,nm}^{-1} \,, \\
4\sqrt{A_{001}\,K_{1\bar{1}0}} &= 45.6\,\mathrm{meV\,nm}^{-1} \,, \\
4\sqrt{A_{1\bar{1}0}\,K_{001}} &= 28.1\,\mathrm{meV\,nm}^{-1} \,, \\
4\sqrt{A_{1\bar{1}0}\,K_{1\bar{1}0}} - \pi\,|D_{1\bar{1}0}| &= 17.7\,\mathrm{meV\,nm}^{-1} \,.
\end{aligned} \tag{61}$$

A negative wall energy indicates that a rotating spin structure is energetically more favorable than a

		001	$1\bar{1}0$
spin stiffness	A / (meV)	56.4	44.8
DM interaction	D / (meV nm^{-1})	−10.4	7.3
anisotropy energy	K / (meV nm^{-2})	1.1	2.3

Table 2: Theoretically predicted model parameters converted into areal densities. The crystallographic directions refer to the indices used in table 1.

collinear state. From the results (61) we would predict a spiral propagating along the [001]-direction, thus we would not only explain the experimentally observed domain-wall orientation but also the formation of the regular domain pattern. However, due to the large uncertainties in the values and the restriction to planar spin structures, the good agreement with the experiment may be supported by an accidental cancellation of errors. Nevertheless, the calculations clearly show two points: The observed wall orientation cannot be explained by the spin stiffness alone, and the DM interaction is strong enough to compete with the other quantities. Keeping in mind that all domain walls show the same rotational direction, the DM interaction presents the most plausible explanation for the observed mesoscale magnetic structure. The studied system nicely illustrates the relevance of the Dzyaloshinskii-Moriya interactions for magnetic surfaces.

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