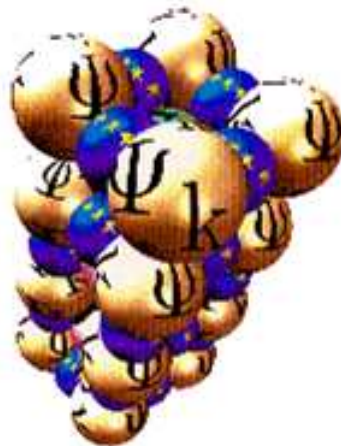

AB INITIO (FROM ELECTRONIC STRUCTURE) CALCULATION OF COMPLEX PROCESSES IN MATERIALS

Number 95

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1 Editorial

In this first autumn issue of the Psi-k Newsletter, in the General News section, we repeat the information on the Psi-k2010 Conference by its chairman Matthias Scheffler. Following this, we have three reports on recent Psi-k supported workshops and a number of job announcements and abstracts of newly submitted or recent papers.

The scientific highlight of this issue is by Rossitza Pentcheva (Munich, Germany) and Warren Pickett (Davis, USA) on "Electronic Phenomena at Complex Oxide Interfaces: Insights from First Principles".

For further details on this newsletter, please check the table of content.

The *Uniform Resource Locator* (URL) for the Psi-k webpage is:

<http://www.psi-k.org.uk/>

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2 General News

2.1 Psi-k2010 Conference

Berlin, Germany, September 12 - 16, 2010

http://www.fhi-berlin.mpg.de/th/Meetings/psik_2010/

Dear colleagues,

Please note this in your calendar!

The next big "Psi-k conference" will take place in Berlin in September 2010. Some information can be found on the above noted web site.

The abstract submission deadline will be May 1, 2010.

As the three previous Psi-k conferences (1996, 2000, 2005), Psi-k2010 will cover theoretical and computational research of electronic structure and properties of matter, ranging from novel basic concepts and methods to applications for condensed matter and real functional materials to systems of biological interest.

We will have about 5 plenary talks, about 100 invited talks, and many contributed talks and posters. We will create an atmosphere for hard and enjoyable work, but we will also make sure that you get an impression of the vibrant city and night life in Berlin.

Looking forward to seeing you in Berlin in September next year.

With best wishes,

Matthias Scheffler (conference chair)

3 Psi-k Activities

”Towards Atomistic Materials Design”

3.1 Reports on the Workshops supported by Psi-k

3.1.1 Report on CECAM Workshop: Orbital Magnetization in Condensed Matter

Lausanne

Jun 15, 2009 - Jun 17, 2009

Sponsored by: CECAM, Intelbiomat, and Ψ_k

Organized by: F. Mauri, R. Resta, and Ph. Sainctavit

<http://www.cecama.org/workshop-303.html>

Report

Macroscopic magnetization is a fundamental concept that all undergraduates learn about in elementary courses. In view of this, it is truly extraordinary that before 2005 there was no generally accepted formula for the macroscopic orbital magnetization in condensed matter. This workshop has been intended a very timely forum for discussing the many open issues.

Orbital magnetization—as opposed to spin magnetization—occurs whenever time-reversal symmetry is broken in the spatial wavefunction. For instance, in a ferromagnet the spin-orbit interaction transmits the symmetry breaking from the spin degrees of freedom to the spatial (orbital) ones; the two contributions to the total magnetization can be resolved experimentally. Other examples include the induced magnetization in applied magnetic fields, or in any other time-reversal-symmetry breaking perturbations. Whenever the unperturbed system is nonmagnetic, the induced magnetization is 100% of the orbital kind.

Sweeping advances are occurring at the time of the workshop in the field of orbital magnetization, and a “modern theory” is in development. The key formulas are resemblant of (but more complex than) the Berry-phase formulas of the modern theory of electric polarization, developed in the 1990s, and by now famous. Formulas for orbital magnetization discussed at the workshop are: (1) for crystalline solids, either metallic or insulating, at the mean field level (HF or Kohn-Sham); (2) for noncrystalline insulators at a the mean-field level (such as for Car-Parrinello simulations). Some progress has been achieved even in the case of a correlated wavefunction, but the ultimate theory has not yet been developed.

Mostly model Hamiltonians have been addressed before 2009; the first results from a first-principle implementation were just submitted in preprint form, and discussed at the workshop

([5] by Ceresoli et al.). Concerning applications of the novel theory, a promising novel scheme for evaluating NMR shielding tensors has been proposed ([8] by Thonhauser et al.); its first-principle implementation was also just submitted in preprint form at the workshop time.

Another open issue relates orbital magnetization (which is a ground state property) to magnetic circular dichroism, by means of magneto-optical sum rules widely used by X-ray spectroscopists at synchrotron facilities. This was discussed by the leading specialists, also in relationship to Ref. [6] below.

Key references:

- [1] D. Xiao, J. Shi, and Q. Niu, *Phys. Rev. Lett.* 95, 137204 (2005).
- [2] T. Thonhauser, D. Ceresoli, D. Vanderbilt, and R. Resta, *Phys. Rev. Lett.* 95, 137205 (2005).
- [3] D. Ceresoli, T. Thonhauser, D. Vanderbilt, and R. Resta, *Phys. Rev. B* 74, 024408 (2006).
- [4] J. Shi, G. Vignale, D. Xiao, and Q. Niu, *Phys. Rev. Lett.* 99, 197202 (2007).
- [5] D. Ceresoli, U. Gerstmann, A.P. Seitsonen, and F. Mauri,
<http://arxiv.org/abs/0904.1988>.
- [6] I. Souza and D. Vanderbilt, *Phys. Rev. B* 77, 054438 (2008).
- [7] D. Xiao, J. Shi, D.P. Clougherty and Qian Niu, *Phys. Rev. Lett.* 102, 087602 (2009)
- [8] T. Thonhauser, D. Ceresoli, A.A. Mostofi, N. Marzari, D. Vanderbilt, and R. Resta,
<http://arxiv.org/abs/cond-mat/0709.4429>.
- [9] D. Ceresoli and R. Resta, *Phys. Rev. B* 76, 012405 (2007).

Programme

Day 1 - June, 15th 2009

09:20 to 09:30 - Welcome

09:30 to 10:00 - Raffaele Resta

Macroscopic magnetization: Analogies to and differences from the case of electrical polarization

10:00 to 10:15 - Discussion

10:15 to 10:45 - David Vanderbilt

Theory of orbital magnetization in crystalline systems

10:45 to 11:00 - Discussion

11:00 to 11:30 - Coffee Break

11:30 to 12:00 - Qian Niu

Theory of Orbital Magnetization and its Generalization to Interacting Systems

12:00 to 12:15 - Discussion

12:15 to 14:00 - Lunch Break

14:00 to 14:30 - Patrick Bruno

Hall Effect, Generalized Einstein Relation, and Berry Phase

14:30 to 14:45 - Discussion

14:45 to 15:15 - Gerrit van der Laan

Sum rules for E1-E1 x-ray absorption

15:15 to 15:30 - Discussion

15:30 to 15:55 - Andrei Rogalev

X-ray Magnetic Circular Dichroism Studies of Paramagnetics

15:55 to 16:00 - Discussion

16:00 to 16:15 - Coffee Break

16:15 to 16:45 - Fabrice Wilhelm

Induced orbital magnetism of 5d transition metals studied with XMCD

16:45 to 17:00 - Discussion

17:00 to 17:20 - Davide Ceresoli

First principles theory of the orbital magnetization: ferromagnetic metals and organometallic complexes

17:20 to 17:30 - Discussion

17:30 to 17:45 - Yugui Yao

First principles calculations of orbital magnetization: Preliminary Results

17:45 to 17:50 - Discussion

Day 2 - June, 16th 2009

09:00 to 09:30 - E.K.U. Gross

Exact Born-Oppenheimer decomposition of the complete electron-nuclear wave function

09:30 to 09:45 - Discussion

09:45 to 10:15 - Paolo Lazzeretti

Induced orbital paramagnetism in BH, CH⁺, C₄H₄, and C₈H₈ systems

10:15 to 10:30 - Discussion

10:30 to 10:50 - Uwe Gerstmann

Ab initio calculation of the electronic g-tensor beyond perturbation theory: diatomic molecules and defects in semiconductors

10:50 to 11:00 - Discussion

11:00 to 11:15 - Coffee Break

11:15 to 11:40 - Philippe Sainctavit

Is there a relation between the magnetic anisotropy of a single molecule magnet and the orbital magnetic moments of its ions?

11:40 to 11:45 - Discussion

11:45 to 12:15 - Guang-Yu Guo

Orbital magnetization, XMCD and magnetic hyperfine field

12:15 to 12:30 - Discussion

12:30 to 14:00 - Lunch Break

14:00 to 14:30 - Ivo Souza

What is the most physical way of dividing up the orbital magnetization into two gauge-invariant parts?

14:30 to 14:45 - Discussion

14:45 to 15:05 - Raffaele Resta

Single \mathbf{k} -point formulas for the electrical and magnetic cases

15:05 to 15:15 - Discussion

15:15 to 15:45 - Sergej Savrasov

Calculations of Magnetic Exchange Interactions in d- and f- Electron Systems

15:45 to 16:00 - Discussion

16:00 to 16:15 - Coffee Break

16:15 to 16:45 - David Vanderbilt

Orbital magnetoelectric effects and topological insulators

16:45 to 17:00 - Discussion

17:00 to 17:20 - Ming-Che Chang

Optical properties of topological insulator

17:20 to 17:30 - Discussion

19:30 to 21:30 - Dinner

Day 3 - June, 17th 2009

09:00 to 09:30 - Jonathan Yates

Spin-spin coupling in the solid state

09:30 to 09:45 - Discussion

09:45 to 11:05 - Anne-Christine Uldry

Spin and orbital moments in the Fe-Cr alloy

10:05 to 10:15 - Discussion

10:15 to 10:45 - Timo Thonhauser

Orbital Magnetization and its Connection to NMR Chemical Shifts

10:45 to 11:00 - Discussion

11:00 to 11:30 - Coffee Break

12:00 to 12:15 - Discussion

11:30 to 12:00 - Junren Shi

Polarization Induced by Inhomogeneity

12:00 to 12:15 - Discussion

12:15 to 14:00 - Lunch Break

Abstracts of the presentations

Calculations of Magnetic Exchange Interactions in d- and f-Electron Systems

Sergej Savrasov, University of California

The use of linear response based magnetic force theorem for calculating exchange interactions in magnetic materials is well established. In this talk several recent applications of this method to extract exchange couplings in systems such as Mott insulators, high temperature superconductors and novel iron based superconductors will be given together with its shortcomings when applying the method to 4f systems (such, e.g., as Gd) and to systems exhibiting orbital moments such, e.g, as Ce and Ce compounds. Possible ways to improve the approach will be discussed.

Ab initio calculation of the electronic g-tensor beyond perturbation theory: diatomic molecules and defects in semiconductors

Uwe Gerstmann, University of Paderborn

We show how a recently developed formula for the orbital magnetization can be used to calculate the elements of the electronic g-tensor in an ab-initio pseudopotential scheme whereby the spin-orbit coupling enters explicitly the self-consistent cycle [*]. In comparison with linear response approaches, the new method allows an improved calculation of the g-tensor of paramagnetic systems containing heavy elements (e.g. the XeF molecule) or systems with large deviations of the g-tensor from the free electron value. The latter situation is encountered in paramagnetic centers in solids, such as those exhibiting a moderate Jahn-Teller distortion.

[*] work done in collaboration with D. Ceresoli, A.P. Seitsonen, F. Mauri

X-ray Magnetic Circular Dichroism Studies of Paramagnetics

Andrei Rogalev ESRF-Grenoble.

Coauthors : F. Wilhelm, J. Goulon, N. Jaouen, J.P. Kappler

X-ray Magnetic Circular Dichroism (XMCD) spectroscopy is a well-established experimental tool to study the microscopic origin of magnetism allowing one to determine separately spin and orbital magnetic moments. So far, XMCD has been extensively used to investigate mainly ferro- or ferrimagnetic materials and only very few studies have been performed on paramagnetic compounds. In this presentation, we wish to report the results of thorough XMCD studies of orbital magnetization in a variety of paramagnetic systems: - Paramagnetic Curie insulators (salts of rare earth elements and of 5d transition metals) give rise to an intense XMCD signal in the hard X-ray range under high magnetic field and at low temperature; - Spin and orbital moments in Pauli paramagnets has been investigated on a pure Pd single crystal with enhanced temperature-independent paramagnetic susceptibility. Using magneto-optical sum rules we were able to determine the spin moment (0.012B) and the orbital moment (0.003 B) induced in the Pd 4d shell by a magnetic field of 7 Tesla. The latter was decomposed into two contributions: the Kubo-Obata term and the one arising from the spin-orbit interaction - Very weak XMCD signals due to a field induced orbital magnetization have been detected at the L-edges of Eu³⁺ Van Vleck Paramagnetic compounds.

Sum rules for E1-E1 x-ray absorption

Gerrit van der Laan, Diamond Light Source

Sum rules relating the integrated intensity of the spin-orbit split manifolds of the core to valence shell transitions in x-ray absorption spectroscopy have been well established [1]. The sum rules for XMCD have become powerful tools to obtain the element-specific spin and orbital part of the magnetic moments in materials. The sum rule for XMLD relates the integrated intensity to the anisotropic part of the spin-orbit interaction, which is proportional to the magnetocrystalline anisotropy energy of the material [2]. The spin-orbit sum rule for the isotropic XAS (or EELS) gives us the type of angular momentum coupling in e.g. actinide metals [3]. However, the derivation of the sum rules contains many assumptions and the most important ones will be discussed here. There is a large discrepancy in the angular dependence of the orbital moment as assessed by the XMCD sum rule compared to experimental results obtained by macroscopic techniques [4], which is so far not well understood.

[1] G. van der Laan Angular momentum sum rules for x-ray absorption Phys. Rev. B 57, 112 - 115 (1998).

[2] G. van der Laan Magnetic linear x-ray dichroism as a probe of the magnetocrystalline anisotropy Phys. Rev. Lett. 82, 640 - 643 (1999).

[3] K.T. Moore and G. van der Laan Nature of the 5f states in actinide metals Rev. Mod. Phys. 81, 235 - 298 (2009).

[4] G. van der Laan Microscopic origin of magnetocrystalline anisotropy in transition metal thin films J. Phys.: Condens. Matter 10, 3239 - 3253 (1998).

Optical properties of topological insulator

Ming-Che Chang, National Taiwan Normal University

The axion coupling in topological insulator couples electric polarization with magnetic field, and magnetization with electric field. As a result, the usual laws of electromagnetic (EM) wave propagation are modified. We report on some preliminary, classical results regarding the reflection and refraction of EM wave at the surface of a topological insulator. Based on these results, possible ways to determine the axion coupling by optical measurement are suggested.

Orbital magnetization, XMCD and magnetic hyperfine field

Guang-Yu Guo, National Taiwan University, Department of Physics, Taipei 106

X-ray magnetic circular dichroism (XMCD) is measured as the difference in the absorption rate between left and right circularly polarized x rays. In the early 1990's, Thole et al. discovered that the integrated XMCD signals for a given spin-orbit split absorption edge are related to the local spin and orbital magnetic moments (XMCD sum rules) [1,2]. This discovery initiated an exciting period for the synchrotron radiation-based x-ray spectroscopy because XMCD became a powerful probe of magnetism in solids. [3] Nevertheless, these XMCD sum rules were derived based on a single-ion model. Thus, the validity of these sum rules was subsequently analyzed by a number of research groups worldwide by both using the results of explicit ab initio band-structure calculations and rederiving the sum rules within the framework of itinerant electron

theory. In this talk, I will report my own attempts to verify the XMCD sum rules through both numerical [4,5] and analytical [6,7] calculations. The magnetic hyperfine field of an ion in a solid is the magnetic field at the site of the atomic nucleus produced by the electrons in the solid and may be measured by the nuclear methods such as the Moesbauer effect and the nuclear magnetic resonance (NMR). It is another useful probe of the local magnetization in, e.g., magnetic multilayers and thin films. In this talk, I will present our ab initio studies of the hyperfine field in various magnetic metals [8,9,10] which demonstrated that the hyperfine field contains not only the main Fermi contact (spin) contribution but also the significant contribution from the orbital magnetization. Furthermore, the orbital hyperfine field is shown to be linearly related to the local orbital magnetic moment of the ion concerned.

- [1] B. T. Thole et al., Phys. Rev. Lett. 68, 1943 (1992).
- [2] P. Carra et al., Phys. Rev. Lett. 70, 694 (1993).
- [3] C. T. Chen et al., Phys. Rev. Lett. 75, 152 (1995).
- [4] G. Y. Guo et al., Phys. Rev. B 50, 3861 (1994).
- [5] G. Y. Guo et al., J. Magn. Magn. Mater. 148, 66 (1995).
- [6] G. Y. Guo, J. Phys.: Cond. Matter. 8, L747 (1996).
- [7] G. Y. Guo, Phys. Rev. B 57, 10295 (1998).
- [8] G. Y. Guo and H. Ebert, Phys. Rev. B 53, 2492 (1996).
- [9] G. Y. Guo and H. Ebert, J. Magn. Magn. Mater. 156, 289 (1996).
- [10] G. Y. Guo and H. Ebert, Hyperfine Interactions 97/98, 11 (1996).

What is the most physical way of dividing up the orbital magnetization into two gauge-invariant parts?

Ivo Souza, University of California, Berkeley

Coauthor: David Vanderbilt

An intriguing feature of the modern theory of orbital magnetization in crystals is that it identifies two separately gauge-invariant - and hence potentially separately measurable - contributions to \mathbf{M}_{orb} [1,2,3]. Intuitively, one is associated with the “self-rotation”, and the other with the “itinerant circulation” part of the electron motion. Unfortunately this appealing physical picture becomes blurry upon closer inspection. Already in the simplest case of an insulator with a single valence band subtly different partitions of \mathbf{M}_{orb} were obtained in the two original derivations of the bulk orbital magnetization formula[1,2]. Matters are complicated further when it comes to multiband insulators, Chern insulators, and metals. For example, it is not clear how to extend the semiclassical derivation of the two terms in Ref. 1 to a multiband gauge-invariant framework. A multiband gauge-invariant partition of \mathbf{M}_{orb} was proposed in Ref. 3, but it remained unclear how to separate experimentally the two resulting terms. I will discuss how the f-sum rule for the magnetic circular dichroism spectrum provides a natural way of dividing up \mathbf{M}_{orb} into two parts[4]. The sum rule yields a contribution to \mathbf{M}_{orb} whose relation to the various terms defined in Refs. [1-3] is as follows: in the single-band case it reduces to the self-rotation term of Ref. 1. In the multiband case it equals the difference between the gauge-invariant local and itinerant

circulations defined in Ref. 3 (which for a single band reduce to the ones in Ref. 2). In the case of ordinary band insulators it can be thought of as the gauge-invariant part of the self-rotation of the Wannier functions, in complete analogy with the gauge-invariant part of the Wannier spread [5]. Like \mathbf{M}_{orb} itself, the sum rule remains well-defined in metals and Chern insulators, even though the simple Wannier-based interpretation is lost.

[1] D. Xiao, J. Shi, and Q. Niu, *Phys. Rev. Lett.* 95, 137204 (2005).

[2] T. Thonhauser, D. Ceresoli, D. Vanderbilt, and R. Resta, *Phys. Rev. Lett.* 95, 137205 (2005).

[3] D. Ceresoli, T. Thonhauser, D. Vanderbilt, and R. Resta, *Phys. Rev. B* 74, 024408 (2006).

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Spin-spin coupling in the solid state

Jonathan Yates, Oxford University

Sin-spin (or J) coupling is an indirect interaction of the nuclear magnetic moments mediated by bonding electrons, and provides a direct map of the atomic connectivities in a material. In solution-state NMR, J-coupling measurements can often be obtained from one dimensional spectra where the multiplet splitting in the peaks is clearly resolved. However, in the solid-state, this is often not the case as these splittings are typically obscured by the broadenings from anisotropic interactions. In recent years, bond correlation experiments, in particular, those employing spin-echo magic angle spinning techniques, have resulted in accurate measurements of J-coupling in both inorganic and organic systems. To complement and support these advances in experimental technique we have developed a first principles method to calculate J-coupling in solid-state systems. We have applied this technique, in combination with experimental work undertaken by several groups, to a range of solid-state systems. Examples include both organic and inorganic crystals (ordered and disordered), and couplings which involve a range of nuclei and bond types (regular, hydrogen bonds, and also non-bonding interactions).

Orbital magnetoelectric effects and topological insulators

David Vanderbilt, Rutgers University

I will first briefly review the theory of the intrinsic (Karplus-Luttinger) contribution to the anomalous Hall conductivity of a metal, which essentially involves integrating the Berry curvature over the occupied Fermi sea. If one looks at the limit as a band is filled and the Fermi surfaces disappear, the integrated Berry curvature takes an integer value (“Chern number”) that is normally zero. By definition, a “Chern insulator” is one in which this integer is non-zero. Strangely, the orbital magnetization is linear in the Fermi energy in this case, because of contributions from chiral edge states at the surface of the crystal. Such a system is also known as a “quantum Hall insulator” because it would exhibit a quantum Hall effect in the absence of a magnetic field. While no examples are known to exist in nature, theoretical models of Chern insulators are readily constructed (Haldane first did so two decades ago [1]), and there is no known reason why they should not exist. I shall briefly discuss some of our theoretical work on the properties of such prospective Chern insulators [2-3], and speculate about prospects for

discovering experimental realizations. There has been a great deal of interest recently in another kind of topological insulator, the "Z2" or "quantum spin Hall" insulator. Such a system can be conceptualized by imagining that a spin-up system of electrons having Chern number +1 coexists with a spin-down system having Chern number -1 in such a way that the system as a whole has total Chern number zero and obeys time-reversal (T) symmetry. Even when the spin-orbit interaction is turned on, the system carries a topological "even-odd" (Z2) label that distinguishes it from a normal insulator. Again, chiral edge states are required, provided that T symmetry also remains unbroken at the surfaces. Some of the recent excitement about this subject is due to the discovery of experimental realizations in the Bi[x]Sb[1-x] [4], Bi[2]Te[3] [5], and related systems. Third, I will try to give a flavor of our recent theory of the orbital contribution to the linear magnetoelectric effect (or equivalently, to the surface Hall conductivity) in magnetoelectric insulators [6]. The theory exhibits many attractive analogies to the theory of polarization, and involves a higher-order kind of Chern index than was introduced above. Interestingly, our theory predicts that the surface of a Z2 topological insulator, if it is gapped by a T-breaking perturbation, will exhibit a half-integer quantum Hall effect.

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[4] D. Hsieh et al., Nature 452, 970 (2008).

[5] Y.L. Chen et al., <http://arxiv.org/abs/0904.1829>.

[6] A.M. Essin, J.E. Moore, and D. Vanderbilt, Phys. Rev. Lett. 102, 146805 (2009).

Theory of orbital magnetization in crystalline systems

David Vanderbilt, Rutgers University

There are subtleties associated with the proper definition of orbital magnetization in a crystalline solid that are similar to those that arise in the theory of electrical polarization, related to the fact that matrix elements of the position operator are ill-defined in the Bloch representation. Standard methods for computing the orbital magnetization have been based on integrating orbital currents inside muffin-tin spheres, and while this may be a very good approximation in some contexts, it fails to capture a possible "interstitial" or "itinerant" contribution to the orbital magnetization. In 2005, two groups independently solved this long-standing problem, using quite different methods: a semiclassical wavepacket approach in one case [1], and a derivation based on the Wannier representation in the other [2-3]. More recently, a third independent derivation of the same formula has been given based on the long-wave limit [4]. In this talk I will review our Wannier-based derivation [2-3]. The orbital magnetization of a periodic insulator was shown to be comprised of two contributions, an obvious one associated with the internal circulation of bulk-like Wannier functions in the interior and an itinerant one arising from net currents carried by Wannier functions near the surface. Our final expression for the orbital magnetization can be rewritten as a bulk property in terms of Bloch functions, making it simple to implement in modern code packages. The correctness of the expression was tested by evaluating it for model two-dimensional tight-binding systems. Recently, Ceresoli et al. have computed the orbital magnetization for Fe, Ni, and Co using the new approach [5]. An interesting aspect of the theory

is that the orbital magnetization can be decomposed into two contributions, corresponding roughly to the internal-circulation and itinerant pieces, each of which is independently gauge-invariant (i.e., invariant with respect to k-dependent unitary rotations among the occupied Bloch states). The physical meaning of these terms and their connections with the static limits of dynamical phenomena are discussed in Ref. [6].

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[2] T. Thonhauser, D. Ceresoli, D. Vanderbilt, and R. Resta, Phys. Rev. Lett. 95, 137205 (2005).

[3] D. Ceresoli, T. Thonhauser, D. Vanderbilt, and R. Resta, Phys. Rev. B 74, 024408 (2006).

[4] J. Shi, G. Vignale, D. Xiao, and Q. Niu, Phys. Rev. Lett. 99, 197202 (2007).

[5] D. Ceresoli, U. Gerstmann, A.P. Seitsonen, and F. Mauri, <http://arxiv.org/abs/0904.1988>.

[6] I. Souza and D. Vanderbilt, Phys. Rev. B 77, 054438 (2008).

Theory of Orbital Magnetization and its Generalization to Interacting Systems

Qian Niu, University of Texas at Austin

Recently, a new formula for the orbital magnetization was proposed. In this talk, I will review the original derivation of the formula based on the semi-classical wave-packet dynamics, as well as a general derivation based on the standard perturbation theory of quantum mechanics. The quantum derivation clarifies the origin of the novel aspects of the semi-classical derivation, such as the Berry phase correction to the density of states. It is valid for general systems including insulators with or without a Chern number, metals at zero or finite temperatures. More importantly, we are able to combine the quantum derivation with the exact current and spin density functional theory (SCDFT), proving the validity of the formula for interacting systems. With this development, the new magnetization formula, in combination with the recent advances in the construction of optimized effective potential for SCDFT, will turn out to be a powerful practical tool for the study of systems that have long defied traditional ab-initio methods.

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Polarization Induced by Inhomogeneity

Junren Shi, Institute of Physics, Chinese Academy of Sciences

We develop a new formula for calculating the electric polarization of an inhomogeneous system. It is shown that the electric polarization induced by the inhomogeneity can be expressed as a difference of a Chern-Simons field between the final and initial state. This is a generalization to the geometric formula of King-Smith and Vanderbilt, which is only applicable for the homogeneous system. The new formula demonstrates a new application of the semi-classical approach, besides that on the orbital magnetization.

Di Xiao, Junren Shi, Dennis P. Clougherty and Qian Niu, Phys. Rev. Lett. 102, 087602 (2009)

Macroscopic magnetization: Analogies to and differences from the case of electrical

polarization

Raffaele Resta, CNR-INFM Democritos and University of Trieste

In this introductory talk, I will start with some basic considerations of macroscopic electrostatics and magnetostatics, including the relationship between macroscopic polarization/magnetization and macroscopic fields as a function of the shape of a finite sample. The limiting cases of purely either longitudinal or transverse polarization/magnetization will be illustrated. Switching then to microscopics, I will focus on the position operator r , which is unbound and "forbidden" in the Hilbert space of the wavefunctions obeying periodic Born-von-Karman boundary conditions (PBC), while it is trivial within "open" boundary conditions (OBC). This feature has hampered a microscopic theory of macroscopic polarization until the early 1990s (see Ref. [1] for a review), and of macroscopic orbital magnetization until 2005 (see next talk). Notice that the r operator enters the textbook definition of both electrical polarization and orbital magnetization, while it is harmless about spin magnetization. It also enters the definition of (spin) toroidal moment [2]. For crystalline systems within an independent-electron scheme (e.g. Kohn-Sham), our macroscopic observables are expressed as Brillouin-zone (BZ) integrals, where the key ingredients are k -derivatives of (the periodic part of) the Bloch orbitals. In the case of electrical polarization, the BZ integral can be equivalently expressed—perhaps more intuitively—in terms of the electrical dipoles of the Wannier charge distributions in the unit cell. The analogous tempting assumption—namely, that orbital magnetization can be expressed in terms of the magnetic dipoles of the Wannier orbitals in the unit cell—turns out to be incorrect. To understand the reason for the difference, one has to consider a finite sample within OBC, where the counterpart of the Wannier orbitals are still well defined localized orbitals. In a finite sample, due to the unbound nature of the r operator, surface charges/currents give a nonvanishing contribution to macroscopic polarization/magnetization. The charge of Wannier orbitals, even in the surface region, is quantized (equal to one) and neutralized by the classical nuclear charge: ergo, there cannot be any surface contribution to electrical polarization. Instead, in the magnetic case, the current carried by the Wannier orbitals is not quantized, and the surface region contributes nontrivially to orbital magnetization. However, as shown in the next talk, even this contribution can be expressed in terms of bulk quantities within PBC.

[1] D. Vanderbilt and R. Resta, in: "Conceptual foundations of materials: A standard model for ground- and excited-state properties", S.G. Louie and M.L. Cohen, eds. (Elsevier, 2006), p. 139.

[2] C.D. Batista, G. Ortiz, and A.A. Aligia, Phys. Rev. Lett. 101, 077203 (2008).

Induced orbital paramagnetism in BH, CH⁺, C₄H₄, and C₈H₈ systems

Paolo Lazzeretti, Department of Chemistry, University of Modena and Reggio Emilia

Concise information on the general features of the quantum-mechanical current density induced in the electrons of a molecule by a spatially uniform, time-independent magnetic field is obtained via a stagnation graph that shows the isolated singularities and the lines at which the current density vector field vanishes. Stagnation graphs provide a compact description of current density vector fields and help the interpretation of molecular magnetic response, e.g., magnetic susceptibility and nuclear magnetic shielding. A few noticeable examples are discussed. The stagnation

graph of cyclopropane, obtained at the Hartree-Fock level via a procedure based on continuous transformation of the origin of the current density formally annihilating the diamagnetic contribution, shows that the current interpretation of this molecule as an archetypal sigma-aromatic system should be revised. The stagnation graphs of lithium hydride, acetylene, carbon dioxide, and azulene provide the first evidence of the existence of electronic toroidal currents inducing orbital anapole moments. The induced orbital paramagnetism of boron monohydride, cyclobutadiene and clamped cyclooctatetraene are explained via stagnation graphs showing that vortical lines occur at the intersection of nodal surfaces of real and imaginary components of the the electronic wave function.

Single k-point formulas for the electrical and magnetic cases

Raffaele Resta, CNR-INFM Democritos and University of Trieste

Coauthor: Davide Ceresoli

For crystalline systems within an independent-electron scheme (e.g. Kohn-Sham), both electrical polarization [1] and orbital magnetization [2] are expressed as a Brillouin-zone integral. For disordered systems most Car-Parrinello simulations are performed in a large supercell within a single k-point framework. The single-point polarization formula exists since a long time [3], and has been widely used, e.g. in the computation of infrared spectra. It is worth stressing that the single-point polarization formula can be regarded as the special case of a more general many-body formula, expressed in terms of an explicitly correlated wavefunction, well beyond independent-electron schemes. The analogous single-point orbital magnetization formula has been established in 2007 [4]; as a corollary, even the Chern number can be evaluated—somewhat counterintuitively—from a single Hamiltonian diagonalization. However, at variance with the electrical case, the single-point formula does not seem to lead towards a many-body theory, allowing the computation of orbital magnetization in terms of an explicitly correlated wavefunction.

[1] D. Vanderbilt and R. Resta, in: "Conceptual foundations of materials: A standard model for ground- and excited-state properties", S.G. Louie and M.L. Cohen, eds. (Elsevier, 2006), p. 139.

[2] D. Ceresoli, T. Thonhauser, D. Vanderbilt, and R. Resta, *Phys. Rev. B* 74, 024408 (2006).

[3] R. Resta, *Phys. Rev. Lett.* 80, 1800 (1998).

[4] D. Ceresoli and R. Resta, *Phys. Rev. B* 76, 012405 (2007).

First principles calculations of orbital magnetization: Preliminary Results

Yugui Yao,

Institute of Physics, Chinese Academy of Sciences

The recent discovered formula about the orbital magnetization for periodic solid can include contribution from the interstitial regions, which are usually ignored in the past calculations. Using this formula, we calculate the orbital magnetizations in the ferromagnetic transition metals Fe, Co, Ni by FLAPW method. However, we have not obtained improved results compared with experimental ones.

First principles theory of the orbital magnetization: ferromagnetic metals and organometallic complexes

Davide Ceresoli, MIT

We present first principles calculations of the orbital magnetization in real materials by evaluating a recently discovered formula for periodic systems, within density functional theory. We obtain improved values of the orbital magnetization in the ferromagnetic metals Fe, Co, and Ni, by taking into account the contribution of the interstitial regions neglected so far in literature. [*] We also use the orbital magnetization to compute the EPR g -tensor in transition metal complexes. In these systems, the main issue is spurious self-interaction in most exchange-correlation functionals, often leading to the electrons being over-delocalized, and even resulting in unphysical fractional occupation numbers. I will show that the DFT + Hubbard U approach improves the agreement with respect to experiment, of the EPR g -tensor and hyperfine couplings in high-spin Mn-oxo complexes. [**]

[*] work done in collaboration with: U. Gerstmann, A. P. Seitsonen and F. Mauri

[**] work done in collaboration with: E. Li and N. Marzari

Is there a relation between the magnetic anisotropy of a single molecule magnet and the orbital magnetic moments of its ions?

Philippe Saintavrit, CNRS-IMPMC and Pierre and Marie Curie University, Paris 6

Coauthors: Matteo Mannini, Francesco Pineider, Marie-Anne Arrio, Ricardo Moroni, Christophe Cartier dit Moulin, Andrea Cornia, Dante Gatteschi and Roberta Sessoli.

Single Molecule Magnets (SMM) are new molecules developed by coordination chemistry that present at low temperature magnetic properties similar to those of nanomagnets: blocking temperature, opening of the magnetic cycle, magnetic anisotropy. In order to understand the parameters governing these properties we have applied X-ray Magnetic Circular Dichroism (XMCD). The technique is well suited to give information on the magnetic structure of the individual ions present in one molecule and it gives direct information on the orbital magnetic moment. The molecules for which the opening of the magnetic cycle is the largest are Mn₁₂ and Fe₄ SMM. For both molecules we measured 3d ions L_{2,3} edges and we obtained that the orbital magnetic moments on the ions of the molecules (Mn(IV) and Mn(III) in Mn₁₂ SMM and Fe(III) in Fe₄ SMM) are very close to zero (always below 0.05 Bohr magneton with —/— below 0.02) [1,2,3]. On the contrary we measured on another molecule, Cr[(CN)Ni]₆ an orbital magnetic moment on Ni(II) ions as large as 0,15 mB (with —/— = 0.07) but for which no opening of the magnetic cycle could be detected down to temperatures as low as 20 mK [4]. These findings tend to show that the orbital magnetic moment of the individual ions is not governing the SMM hysteresis.

[1] Matteo Mannini, Francesco Pineider, Philippe Saintavrit, Chiara Danieli, Edwige Otero, Corrado Sciancalepore, Anna Maria Talarico, Marie-Anne Arrio, Andrea Cornia, Dante Gatteschi and Roberta Sessoli. Magnetic memory of a single-molecule quantum magnet wired to a gold surface. *Nature Materials* 8, 194-197 (2009).

[2] Matteo Mannini, Francesco Pineider, Philippe Saintavrit, Loic Joly, Arantxa Fraile-Rodriguez, Marie-Anne Arrio, Christophe Cartier dit Moulin, Wolfgang Wernsdorfer, Andrea Cornia,

Dante Gatteschi, and Roberta Sessoli. X-Ray Magnetic Circular Dichroism Picks out Single-Molecule Magnets Suitable for Nanodevices. *Advanced Materials*, 21, 167-171 (2009)

[3] Matteo Mannini, Philippe Sainctavit, [Roberta Sessoli, Christophe Cartier dit Moulin, Francesco Pineider, Marie-Anne Arrio, Andrea Cornia, and Dante Gatteschi. XAS and XMCD Investigation of Mn Monolayers on Gold. *Chemistry : a European Journal*, 14, 7530-7535 (2008)

[4] M.-A. Arrio, A. Sculler, Ph. Sainctavit, Ch. Cartier dit Moulin, T. Mallah, and M. Verdager. Soft X-ray Magnetic Circular Dichroism in Paramagnetic Systems: Element-Specific Magnetization of Two Heptanuclear CrIII MII6 High-Spin Molecules. *Journal of the American Chemical Society* 121, 6414-6420 (1999)

Orbital Magnetization and its Connection to NMR Chemical Shifts

Timo Thonhauser, Wake Forest University

We propose an alternative approach for computing the NMR response in periodic solids that is based on the recently developed theory of orbital magnetization [1-4]. Instead of obtaining the shielding tensor from the response to an external magnetic field, we derive it directly from the orbital magnetization appearing in response to a microscopic magnetic dipole [5]. Our new approach is very general, and it can be applied to either isolated or periodic systems. The converse procedure has an established parallel in the case of electric fields, where Born effective charges are often obtained from the polarization induced by a sublattice displacement instead of the force induced by an electric field. Our novel approach is simple and straightforward to implement since all complexities concerning the choice of the gauge origin are avoided and the need for a linear-response implementation is circumvented. We have demonstrated its correctness and viability by calculating chemical shieldings in simple molecules, crystalline diamond, and liquid water, finding excellent agreement with previous theoretical and experimental results. Applications to more complex systems are currently in progress.

[1] D. Xiao, J. Shi, and Q. Niu, *Phys. Rev. Lett.* 95, 137204 (2005).

[2] T. Thonhauser, D. Ceresoli, D. Vanderbilt, and R. Resta, *Phys. Rev. Lett.* 95, 137205 (2005).

[3] D. Ceresoli, T. Thonhauser, D. Vanderbilt, and R. Resta, *Phys. Rev. B* 74, 024408 (2006).

[4] J. Shi, G. Vignale, D. Xiao, and Q. Niu, *Phys. Rev. Lett.* 99, 197202 (2007).

[5] T. Thonhauser, D. Ceresoli, A. Mostofi, N. Marzari, R. Resta, D. Vanderbilt, arxiv: 0709.4429.

Spin and orbital moments in the Fe-Cr alloy

Anne-Christine Uldry, Paul Scherrer Institute

Coauthors: M. Samaras, R. Iglesias, M. Victoria and W. Hoffelner

The Fe-Cr system exhibits an interesting phase diagram where short-range order and frustration are suspected to play a key role in the formation of microstructures. The Fe-Cr alloys have recently come under scrutiny for their potential role as structural materials for the next generation of nuclear reactors. A crucial issue in this context is the behaviour of the material over a long period of time and intense irradiation, which has to be tackled by both experiments and modelling. As the modelling of ferritic alloys beyond the quantum mechanical scale is often

validated against the results obtained from DFT, it seems important to establish as well a one-to-one experimental validation of the DFT predictions. Spectroscopic measurements obtained at synchrotron irradiation facilities present such a possibility. In particular, the orbital-to-spin moment ratios of Fe can be both calculated and measured by X-ray Magnetic Circular Dichroism (XMCD). A series of calculations with Wien2k through a range of Cr concentration is under way. While the orbital moments in these compounds are weak, they are nonetheless sensitive to changes of the local atomic environment and their role as probe for different microstructures are being investigated.

PInduced orbital magnetism of 5d transition metals studied with XMCD

Fabrice Wilhelm, ESRF

Many current and anticipated applications for magnetic materials involve heterostructures or alloys containing magnetic and non-magnetic components. The experimental technique that allows one to study the induced magnetism in non magnetic elements is the X-Ray Magnetic Circular Dichroism (XMCD). It provides quantitative information on spin and orbital magnetic moments of atoms in both amplitude and direction. Since X-ray absorption spectra are related to the density of unoccupied states at the absorbing atom for a given angular momentum, the XMCD is an appropriate tool to study hybridization effects and magnetic interactions. In the first part of the talk, I will present XMCD studies performed at the L_{3,2}-edges of the 5d TM element in 3d-5d magnetic systems which reveal a strong polarization of the 5d band induced by a large 3d/5d hybridisation. I will show that in certain materials such as Fe/W multilayers and VAu₄ compounds, the induced orbital moment of W and Au is breaking the Hunds third rules. In the second part of the talk, I will present XMCD studies performed at the L_{3,2}-edges of the 5d TM element in 4f-5d and even 5f-5d magnetic systems. I will show that in RE-5d compounds, such as NdPt₂, GdPt₂ and HoPt₂, despite the strongly localized character of the 4f shells, the shape of the XMCD signal at the L-edges of 5d elements are directly related to the nature of 4f elements and that the sizeable orbital magnetic polarization at the Pt atom is found to depend strongly on the spin-orbit coupling of the RE elements.

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3.1.2 Report on The International School of Crystallography, 41st Course
”From Novel Experimental Approaches to Applications in
Cutting-Edge Technologies”

Erice- Sicily, Italy

4 - 14 June 2009

Organizers : E.V. Boldyreva (Novosibirsk State University and the Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the RAS, ul. Kutateladze, 18, Novosibirsk, 630128, Russian Federation; Tel: +7-383-363-4272, Fax: +7-383-363-4132, e-mail: boldyrev@nsu.ru)

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N. Dubrovinskaia served as a coordinator for the theoretical session of the School (Institute of Earth Sciences, Heidelberg University, Im Neuenheimer Feld 236 D-69120 Heidelberg Germany, Tel: +49-6221/54-85 33; Fax: +49-6221/54-48 05; E-mail: Natalia.Dubrovinskaia@min.uni-heidelberg.de)

<http://www.crystalleric.org/erice2009/2009.htm>

Summary

As a thermodynamic parameter, pressure is remarkable in many ways. It spans in the visible universe over sixty orders of magnitude, from the non-equilibrium pressure of hydrogen in intergalactic space, to the kind of pressure encountered within neutron stars. In the laboratory, it provides unique possibility to control structure and properties of materials, dramatically alter electronic properties, break existing, or form new chemical bonds by reaching compressions in excess of an order of magnitude for molecular materials. High-pressure science finds direct or indirect application in several fields of modern European technology, such as mechanical engineering (strain/stress analysis), optoelectronics and spintronics, nanotechnology, pharmaceutical industry, food processing, petroleum industry, seismic data interpretation, etc.

The School was devoted to the theme of crystallographic studies at high pressure with emphasis on the phenomena characteristic to the compressed state of matter, as well as experimental and theoretical techniques, used to study these phenomena. The agenda of the School naturally encompassed elements of physics (properties and structure), chemistry (chemical reactions, transport), materials science (new materials) and engineering (mechanical properties); in addition it covered direct applications and implications for geology (minerals in their natural, deep earth environments), planetary sciences, biology and medicine (deep sea ecosystems, mem-

branes, protein and nucleic acid folding, the role of high-pressure in the origin of prebiotic forms of matter and the origin of life, des-activation of viruses and toxins). More detailed information can be found on the meeting website <http://crystalerice.org>. The Erice Schools had a program of 10 days of intensive training and interaction, and was attended by one hundred twenty two participants (56 lectures were given by 46 speakers). The school had a unique format, truly focused on education, which emphasized direct hands-on exercises and stimulated active interaction between the instructors and the students.

The field of theoretical studies at high pressure is dynamically expanding and the School gave an up-date of the state of affairs in this field for young scientists and students. **Theoretical methods for high-pressure science** was one of the main topics of the School that reinforced theoretical aspects of the meeting.

S. Scandolo (Italy) gave a review of some fundamental aspects of atomistic simulations in high pressure research, including the construction of the interatomic potentials and the basic methods to sample the constant-pressure and constant-temperature statistical ensemble. I.A. Abrikosov (Sweden) outlined recent developments of theoretical methodology for first-principles simulations of alloys at high pressure. Particular attention was paid to the techniques for a treatment of solution phases. B. Winkler (Germany) spoke about both experimental and theoretical approaches to studies of the role of hydrogen bonding in minerals at high pressure. P. Macchi (Switzerland) gave a comprehensive introduction into the semi-empirical & ab initio quantum chemistry description of solid state phases under high pressures with a special emphasis on the systems with hydrogen bonds, stacking interactions, etc. A Workshop on theoretical calculations of organic, organometallic, coordination compounds at high pressures was given by P. Macchi.

Full lectures are available at:

<http://cars9.uchicago.edu/surfacewiki/HPCrystallography/Erice2009/LecturePresentations>

Scientific program:

Full scientific program for the school is available at:

<http://www.crystalerice.org/erice2009/2009PreliminaryProgram.doc>

3.1.3 Report on Workshop Superconductors by the Mediterranean Sea: Classic and Novel Materials, Electronic States and Critical Properties



Hotel Porte Conto, Alghero, Sardinia, Italy

7-11 September 2009

Psi-k, ESF (INTELBIOMAT), CCP9, SLACS (CNR-INFN, Cagliari)

James Annett and Sandro Massidda

<http://www.phy.bris.ac.uk/groups/theory/psi-k-superconductivity.html>

The theme of the workshop is ab initio theory of superconductivity, particularly based upon the recent developments of functionals for superconducting DFT. We also address exotic superconducting materials, and nanoscale devices in which normal state DFT calculations are used as the input for constructing models of the superconducting state and transport properties.

The main topics were, Electron-phonon coupling in low temperatures superconductors, Methodological improvements for calculating SC properties, Superconductivity at the nanoscale, Normal and superconducting state of HTS cuprates, Role of electron-phonon coupling in SC compounds and Unconventional superconductivity. In addition the workshop brought together theorists and experimentalists working on superconducting materials. The main experimental themes were electronic quasiparticle states, as measured in ARPES, transport and Fermi surface geometries, as measured in de Hass van Alphen and related experiments, and probes of the superconducting gap in μ SR, tunnelling and Andreev point contact experiments.

The first day of the conference focussed on high temperature superconductors and the recently discovered pnictide family of superconducting materials. Lilia Boeri gave an excellent presen-

tation on the work of the Stuttgart group. She started by reviewing the phase diagrams and structures of the various pnictide materials. She then presented the results of DFT calculations, including calculation of electron-phonon coupling constants, magnetic moments and the exchange gap as a function of the antiferromagnetic moment. The work demonstrated that electron-phonon coupling cannot account for the high transition temperatures observed in the Fe based pnictide materials. Furthermore the Stoner exchange parameter estimated from LDA was found to be too large to account for the experimental moment. Dr Patrick Rourke presented the first experimental talk, reviewing the angle dependent magnetoresistance measurements of the Bristol group on high T_c superconductors. He showed that in the Tl2201 materials there is clear evidence for a large cylindrical Fermi surface, in agreement with ARPES and band structure calculations. A detailed analysis of the data suggested a strongly k dependent electron scattering rate, which has both Fermi liquid-like T^2 temperature dependent components as well as k dependent components having a non Fermi-liquid linear in T temperature dependence. Experimental results on the LSCO family of superconductors suggested a similar k and temperature dependence, however it was also necessary to include a term to account for resistivity saturation. The temperature-doping phase diagram shows broad regions of Fermi liquid T^2 and non Fermi-liquid T temperature dependencies, but no evidence for a quantum critical point as a function of doping underneath the superconducting ‘dome’ region. The magnetism in the pnictide materials was also the subject of the talk given jointly by Christophe Bersier, John Kay Dewhurst and Sangeeta Sharma. The key point was that existing density functionals, such as GGA, do a bad job of structural optimization in these materials, and that the precise structural parameters are very closely linked to the magnetic states. Using a full potential LAPW method, they studied the various non-collinear magnetic states, such as checkerboard, stripe, and 2K antiferromagnetism, and their dependence on doping and Fermi level in the materials.

In the afternoon session Dr Samuele Sanna discussed both pnictides and cuprate materials as studied in μ SR experiments. In the cuprates the experiments were able to establish two types of magnetic behaviour once the antiferromagnetic order is destroyed by doping, these are a ‘frozen spin fluctuation’ regime and a spin-glass regime. A small coexistence region of these two states was also observed. In the pnictide materials the μ SR experiments indicate that superconductivity and antiferromagnetism coexists only for a very small part of the phase diagram, and that the nature of the coexistence could be in nanoscale magnetic clusters consistent with scanning tunnelling microscopy experiments. Sergey Borisenko provided a very impressive overview of ARPES experiments in superconductors and related compounds, including investigations of the charge density wave material TaSe₂. For BSCO he showed that the kink in the band dispersion near to the Fermi level can be used to deduce both the bosonic mode energy and electron-bosonic mode coupling parameter λ . These appeared consistent with interpreting the mode as spin fluctuation derived, but not as a phonon. Other experiments were shown for the ruthenate Sr₂RuO₄, and the CDW materials TaSe₂ and NbSe₂. For the latter the measured Fermi surface appears to be inconsistent with the predictions from LDA. He also presented very exciting prospects for the science that will be achieved with the new 1-cubed instrument, which should obtain spectra at 1K with 1meV resolution. Finally Prof Wysokinski described the spin-triplet superconductor Sr₂RuO₄ and the proposed gap function and three band model for chiral p-wave superconductivity in this material. He showed that orbital dependent superconductivity leads to

distinct features in the NMR spectra for Ru and O nuclei, which can be used to help determine the structure of the gap function. A spin-flop type rotation of the superconducting d-vector was also found for a c-axis oriented field.

On the second day A. Floris began with a very clear summary of the achievements of the ab initio superconducting DFT theory, especially its predictions for T_c and gap values in classic superconductors and in MgB_2 . As a novel example of the theory Dr Floris presented results for Cmca phase of high pressure molecular hydrogen, which led to the prediction of $T_c = 242\text{K}$ at a pressure of 450GPa. In the next talk Prof M. Calandra described first principles calculations on the CDW compound 2H-NbSe_2 . He predicted that both bilayer and single-layer NbSe_2 undergo a CDW instability. However in the bilayer, as in the bulk, the instability leads to a metallic state, while in the single-layer material it leads to a semimetallic ground state, in agreement with recent experimental data. Claudia Ambrosch-Draxl presented the results of electron-phonon coupling calculations obtained in the LAPW method. The results compare well with the classic work of Engelsberg and Schrieffer, 1963, and shows a complex dispersion of models and subbands as the electron band dispersion crosses the phonon frequency. This was illustrated explicitly for calculations of H vibrational modes on $\text{W}(001)$. For the high T_c cuprates the lattice instabilities and structural phase transitions in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ led to imaginary phonon frequencies in the ideal tetragonal structure. An analysis of the Hubbard U led to the suggestion that GGA+ U calculations were able to get an estimate of U as a function of doping, x , which in turn, led to a reasonable magnetic moment per Cu of $\sim 0.6\mu_B$ per copper.

In the afternoon of the second day Rolf Heid reported his extensive first principles study of the electron-phonon coupling in $\text{YBa}_2\text{Cu}_3\text{O}_7$ in the framework of the local density approximation (LDA). From this analysis he reported that the phonon-induced self-energy is about a factor 5 too small compared to the one estimated from experiments on the ‘kink’ in the ARPES quasiparticle dispersion curves. The phonon-induced pairing potential was calculated for both s and d-wave pairing channels and was found to be especially weak for pairing in the d-wave channel, strongly implying that this is not the source of the high T_c superconductivity. Marina Putti reported results for experimental measurements of the upper critical field, H_{c2} in pnictide superconductors. The anisotropy parameter H_{c2}^{ab}/H_{c2}^c was determined in several families of pnictide superconductors, including 1111, 122, and 11 materials, based on Fe layers have been discovered. It was found that the 1111 family shows larger T_c and anisotropic upper critical field, while the 122 family is less anisotropic. Finally the 11 family has the lowest T_c , it is nearly isotropic, but with a huge H_{c2} slope.

On the final day Prof Gonnelli described Andreev point contact experiments to elucidate the multiple gap structures in the Fe-As superconductors. The experiments seem to point clearly to two gaps, each of which is nodeless. Interestingly the larger gap can be as large at $2\Delta/k_B T_c \sim 9$, while the smaller one has $2\Delta/k_B T_c \sim 5$. Fitting the detailed temperature dependence to a three band Eliashberg theory can be obtained, but required very large values of the coupling constants λ . Prof Zwicky described the complex phase diagrams of layered organic superconductors exhibit. In particular she argued that the phase which separates the homogeneous superconducting state from the normal state is a realization of an inhomogeneous Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) state, based upon the upturn of the B_{c2} phase transition, which exceeds the paramagnetic limiting field, at low temperatures.

The session on nanoscale and non-equilibrium superconductivity was limited to just a single talk, by E. Perfetto. He described a new approach to calculations of non-equilibrium transport in a model S-N-S junction, designed to model a nanoscale device with superconducting quantum point contacts. The Andreev states and their contribution to the total current was determined, as was the Josephson effect current as a function of external phase difference between the superconducting leads. A novel time evolution of the time-dependent Bogoliubov-deGennes equations was used to obtain the non-equilibrium Green's function, from which one could see both transient and steady state regimes, the latter agreeing with the Landauer formalism results. The transient effects clearly showed the effects of multiple Andreev reflections.

The final talk of the workshop was given by another experimentalist, Prof Andy Mackenzie. He reviewed experiments on Fermi surface and superconductivity in Sr_2RuO_4 , and in particular on the effort to use the experimental de Haas - van Alphen effect is being used to measure the influence of spin-orbit coupling on its Fermi surface. He also described the metamagnetic phase diagram and search for a quantum critical point in $\text{Sr}_3\text{Ru}_2\text{O}_7$. In this material recent STM results in collaboration with J.C. Davis have produced the first real-space imaging of a Wannier function in a very strongly renormalized 'heavy' d-electron Fermi liquid as well as a field-induced transition to an electronic liquid-crystalline nematic like phase.

Altogether the workshop had an excellent mix of experimental and theoretical talks, and provided a very useful 'snapshot' of the state of electronic structure research in the field of superconductivity. It is clear that future progress will rely on methods which go beyond simple LDA/GGA functionals, and include both LDA+U approaches as well as realistic treatments of electron-phonon coupling.

Programme

7 September 2009

Arrival and registration

8 September 2009

9.15, L. Boeri

10.00, P. Rourke

11.15 C. Bersier, JK Dewhurst and S. Sharma

14.30 S. Sanna

15.15 A. Borisenko

16.00 K. Wysokinski

9 September 2009

9.15, A. Floris

10.00, M. Calandra

11.15 C. Ambrosch-Draxl

14.30 R. Heid

15.15 M. Putti

16.00 short introductions to posters

20.30 Poster session

10 September 2009

9.15, R. Gonelli

10.00, G. Zwicknagl

11.15 E. Perfetto

14.30 A. Mackenzie

15.15 Closing remarks

18.15 musical evening with traditional sardinian instruments and voice

11 September 2009 Departure and optional excursion to The National Park of Asinara

Abstracts of presented papers

Iron-based superconductors: what can we learn from DFT?

L. Boeri, MPI-FKF Stuttgart, Germany

The discovery of superconductivity with a critical temperature T_c of 26 K in fluorine-doped LaOFeAs in early 2008 has initiated a so-called "iron age" in the field of superconductivity. In a few months, several new iron-based superconductors, with T_c 's as high as 55 K, have been found. Their crystal structures show a common motive, characterized by a square Fe lattice, surrounded by distorted tetrahedra of pnictogen or chalcogen atoms. Besides superconductivity, iron-based superconductors show a spin density wave (SDW) transition accompanied by a lattice distortion. This points to a possible unconventional origin of superconductivity, in analogy with the high- T_c cuprates, although there is no general consensus on the pairing mechanism. In this talk, I will first review and discuss the main experimental findings concerning iron-based superconductors. I will then use Density Functional theory to describe the electronic and vibrational properties of LaOFeAs, which is a prototype compound for iron pnictides. Using linear response calculations, I will show that the standard Migdal-Eliashberg theory fails to account for the observed critical temperature.[1] Using an ab-initio effective tight-binding Hamiltonian, based on Fe d and As p Wannier orbitals, derived from NMTO downfolding, I will then analyze in detail the origin of the complicated band structure of iron pnictides, and use this tight-binding model to discuss the origin of magnetism in Fe-based superconductors and its itinerant nature[2], which is probably at the basis of the observed failure of LDA in the description of their magnetic properties.[3].

1. L. Boeri, O. V. Dolgov, and A. A. Golubov, Phys. Rev. Lett. 101, 026403 (2008) and cond mat/0902.0288.
2. O.K. Andersen and L. Boeri, in preparation.
3. I. I. Mazin, M. D. Johannes, L. Boeri, K. Koepnick, and D. J. Singh, Phys. Rev. B 78, 085104 (2008).

A transport perspective on scattering in the cuprates: the pseudogap, quantum criticality, and superconductivity

P. Rourke, University of Bristol, UK

An overview of the Hussey group's recent work to unravel the temperature dependence, momentum dependence, and doping dependence of scattering in the high temperature cuprate superconductors, via magnetoresistance measurements. Our results point to an anisotropic scattering rate, with implications on possible pseudogap physics, quantum criticality, and superconductivity in these compounds.

Why magnetism in $\text{CeO}_{1-x}\text{F}_x\text{FeAs}$ and $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ is different

C. Bersier, JK Dewhurst and S. Sharma, Institut für Theoretische Physik, Freie University Berlin

Using state-of-the-art first-principles calculations we study the magnetic behaviour of CeOFeAs. We find the Ce layer moments oriented perpendicular to those of the Fe layers. An analysis of incommensurate magnetic structures reveals that the Ce-Ce magnetic coupling is rather weak with, however, a strong Fe-Ce coupling. Comparison of the origin of the tetragonal to orthorhombic structural distortion in CeOFeAs and LaOFeAs show marked differences; in CeOFeAs the distortion is stabilized by a lowering of spectral weight at the Fermi level, while in LaOFeAs by a reduction in magnetic frustration. Finally, we investigate the impact of electron doping upon CeOFeAs and show that while the ground state Fe moment remains largely unchanged by doping, the stability of magnetic order goes to zero at a doping that corresponds well to the vanishing of the Néel temperature.

Competition of magnetism and superconductivity in high T_c superconductors: from cuprates to pnictides

Samuele Sanna, Physics Department "A.Volta" University of Pavia, Pavia, ITALY

The recent discovery of the Fe-based superconductors open new chances to unravel the puzzle of the High T_c superconductivity. In particular the proximity between the superconducting and magnetic phases, like in cuprates, renovates the issue of whether they compete or cooperate to produce a high transition temperature. I will talk about the phenomenological behavior at the magnetic-superconducting crossover, where the two states often coexist nanoscopically. In particular, results from several μSR experiments on cuprates and pnictides will be discussed.

ARPES of superconductors

Sergey Borisenko, IFW-Dresden, Germany

I will overview our most recent results on high-temperature cuprate and pnictide superconductors as well as other density waves systems. The progress from the instrumental point of view will be demonstrated on the example of "1-cubed ARPES" end-station at BESSY which allows

to collect photoemission data at temperatures below 1K.

Orbital dependent pairing effects in Sr_2RuO_4 : NMR relaxation rate

Karol Wysokiski, Institute of Physics, M. Curie-Skłodowska University, Lublin, Poland

The p-wave chiral superconductor Sr_2RuO_4 is a quasi-two dimensional, highly anisotropic system with three bands crossing the Fermi energy. Low temperature power law behaviour is observed in temperature dependent physical properties, including specific heat, penetration depth and NMR relaxation rate, which is consistent with the existence of a line of nodes in the quasiparticle gap. However the interpretation of these experiments is complicated by possible temperature dependencies arising from the multi-band or orbital dependent pairing. The calculations of the the NMR relaxation rate $1/T_1$ on the basis of realistic orbital specific, three orbital, three dimensional model with phenomenological coupling constants will be presented. The model leads to the ground state with chiral - gapless order parameter on the γ sheet of the Fermi level and with nodes on the remaining two sheets. Our results compare well with existing experimental ^{101}Ru NQR data showing a relaxation rate $1/T_1 \sim T^3$, and no visible Hebel-Slichter like peak below T_c . On the other hand the diagonal d_{xy} orbital projected components of the relaxation rate show a more complex behaviour, including a Hebel-Slichter like peak below T_c . We speculate that these orbital dependencies might be related to the differences observed between spin relaxation rates for ^{17}O and ^{101}Ru nuclei in this material.

Applications of density functional theory for the superconducting state

A. Floris, Institut für Theoretische Physik, Freie University Berlin

In this contribution we will review the basic theory of Superconducting Density Functional Theory (SCDFT) and some recent applications to some of the most relevant electron-phonon based superconductors, with particular emphasis to molecular hydrogen under high pressure.

Origin of charge density wave behavior in bulk and few layers 2H-NbSe2

Matteo Calandra, Paris, France

We investigate the charge density wave (CDW) instability in 2H-NbSe₂ as a function of the number of layers. We demonstrate that density functional theory is able to describe the metallic charge density wave behaviour in bulk 2H-NbSe₂. We predict that both bilayer and single-layer NbSe₂ undergo a CDW instability. However, while in the bilayer, as in the bulk, the instability occurs at momentum $\mathbf{q}_{cdw} \approx \frac{2}{3}\mathbf{GM}$ and leads to a metallic state, in the single-layer occurs at $\mathbf{q}_{cdw} \approx \frac{1}{4}\mathbf{GM}$ and leads to a semimetallic ground state, in agreement with recent experimental data. Finally we attribute the origin of the CDW behaviour to a large enhancement of the electron-phonon matrix element at momenta close to \mathbf{q}_{cdw} .

Electron-phonon coupling in (un)conventional superconductors: the role of doping

I will discuss the impact on electron-phonon coupling (EPC) on the electronic structure, the traces of which can clearly be seen in photoemission experiments. To this extent the GW approach is employed, solving the complex Dyson equation with the bare electronic bands as well as the Eliashberg function calculated from first principles. It will be shown that the EPC gives rise to complicated temperature-dependent band-splitting in the order of the phonon frequencies. This effect, which in general does not only show up in superconductors, will be demonstrated for MgB₂. To tackle the question of whether kinks seen in photoemission data of high-temperature superconductors are arising from the EPC, the phonon band structure of Ba doped La₂CuO₄ is investigated. Here the strong correlations as well as structural phase transitions are challenging issues which need to be further explored before final conclusions can be drawn.

Electron-phonon coupling, self-energy effects and pairing interaction in YBa₂Cu₃O₇ within the local density approximation.

Rolf Heid, Forschungszentrum Karlsruhe, Institut für Festkörperphysik, Germany

Recent observations of kinks in the electronic dispersion and of phonon anomalies for several members of the cuprates have been suggestive of a strong interaction between electronic and lattice degrees of freedom in the high-T_c superconductors. In this talk, I discuss a first principles study of the electron-phonon coupling in YBa₂Cu₃O₇ in the framework of the local density approximation (LDA). Using a realistic phonon spectrum the momentum and frequency dependence of the coupling is calculated and its consequences for the electronic self-energy in the normal state and for the phonon-induced pairing interaction is analyzed. It is found that for electronic states close to the Fermi energy the phonon-induced self-energy is about a factor 5 too small compared to the experiment [1]. In addition, the phonon-induced pairing potential, relevant for superconductivity, exhibits a momentum dependence which is not favorable for pairing in the d-wave channel, leading to a coupling constant of only 0.022, which is even ten times smaller than the small value of the s-wave channel [2]. I will address implications for the above mentioned experimental observations as well as potential corrections due to strong correlations.

1. R. Heid, K.-P. Bohnen, R. Zeyher, D. Manske, Phys. Rev. Lett. **100**, 137001 (2008).
2. R. Heid, R. Zeyher, D. Manske, K.-P. Bohnen, Phys. Rev. B **100**, 024507 (2009).

New Fe-based superconductor: huge upper critical fields, low coherence length, thermal fluctuation, paramagnetic limit

Marina Putti , University di Genova, Italy

In 2008 the Hosono group discovered high temperature superconductivity in oxipnictide. After that several distinct families of superconductors (1111, 122, 11,111) based on Fe layers have been discovered. They share several characteristics with cuprate superconductors, like layered structure, small coherence length, non conventional pairing, that had been shown to make prac-

tical applications difficult, especially large thermal fluctuations. On the other hand pnictides are more metallic, anisotropy is generally smaller and does not strongly depend on the level of doping, the order parameter symmetry is supposed to be different. Despite the several similarities the different families exhibit important difference. The 1111 family, indeed, shows larger T_c , huge but also anisotropic upper critical field and in field fan-shaped resistive transition reminiscent of those of cuprates, while the 122 family is less anisotropic and presents sharper resistive transitions which are displaced in field like in low temperature superconductors. Finally 11 family has the lowest T_c , it is nearly isotropic, presents huge H_{c2} slope and not negligible thermal fluctuations. Upper critical field, H_{c2} , the electronic anisotropy parameter $\hat{I}^3 = H_{c2}^{ab}/H_{c2}^c$, will be discussed and compared across the pnictide family.

Point-contact Andreev-reflection spectroscopy in iron pnictides of the 1111 and 122 families: Evidence for two-gap nodeless superconductivity and strong electron-boson coupling Renato S. Gonnelli, Dipartimento di Fisica and CNISM, Politecnico di Torino, Italy

The number, symmetry and amplitude of the gaps in the Fe-As superconductors are still open issues, as well as the origin of the electron pairing in these compounds. Here, we review our recent point-contact Andreev-reflection measurements in $\text{SmFeAsO}_{0.8}\text{F}_{0.2}$ ($T_c^{on}=53$ K) and $\text{LaFeAsO}_{0.9}\text{F}_{0.1}$ ($T_c^{on}=27$ K) polycrystals and present new results in $\text{Ba}(\text{Fe}_{0.9}\text{Co}_{0.1})_2\text{As}_2$ single crystals. In all the cases, the low-temperature conductance curves clearly indicate the presence of two gaps in the superconducting state. No zero-bias peaks were observed, which rules out the d-wave symmetry. The gap amplitudes can be extracted from a generalized two-band BTK fit of the normalized conductance curves. The resulting values of the gaps, Δ_1 and Δ_2 , lie slightly below and well above the BCS value, respectively. In Sm-1111, their low-T values are $\Delta_1(0) = 6.15 \pm 0.45$ meV and $\Delta_2(0) = 18 \pm 3$ meV, which give gap ratios ($2\Delta/k_B T_c$) of 2.5 – 3 and 7 – 9, respectively. Both Δ_1 and Δ_2 show a BCS-like temperature dependence and close at the bulk T_c . In La-1111 we obtained similar gap ratios but the experimental situation is more complex, depending also on the different local T_c shown by the contacts in crystallites with slightly different doping. At T_c , the normal-state conductance shows unusual features at zero bias (a depression in La-1111 and a hump in Sm-1111) that are progressively washed out on increasing temperature, to finally disappear at $T^* 140$ K, close to the Néel temperature of the parent compound. The experimental T_c and the gap values of the superconducting pnictides of both the families can be simultaneously reproduced within the Eliashberg theory by using a three-band model where the dominant role is played by interband interactions and the order parameter shows a $s\pm$ -wave symmetry. High values of the electron-boson coupling constants and small typical boson energies (in agreement with experiments) are necessary to obtain the values of all the gaps and to correctly reproduce their temperature dependence. The presence of high-energy features (at $E > \Delta_2$) in the conductance curves of $\text{Ba}(\text{Fe}_{0.9}\text{Co}_{0.1})_2\text{As}_2$ single crystals, which can be related to a very strong electron-boson coupling is also presented and discussed.

Co-authors: D. Daghero, M. Tortello, G.A. Ummarino, V.A. Stepanov, J.S. Kim, R.K. Kremer,

Layered organic metals: Novel superconducting states in high magnetic fields

G. Zwicknagl, Braunschweig, Germany

Layered organic superconductors exhibit complex phase diagrams. Of particular interest is the fact that the upper critical fields separating normal and superconducting phases are unusually high. For field direction parallel to the conducting layers, they may exceed the estimated paramagnetic limit. In addition, there are indications for transitions between different superconducting states slightly below H_{c2} .

In this talk, I argue that the phase which separates the homogeneous superconducting state from the normal state is a realization of an inhomogeneous Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) state. The latter arises due to the population imbalance of the paired fermions. I shall give a brief introduction into the quasiclassical theory of inhomogeneous superconductors which is adopted to calculate the critical fields using realistic band structure information. I shall discuss how electronic properties affect the formation and stability of the inhomogeneous superconducting states

Equilibrium and time-dependent Josephson currents in one-dimensional superconducting junctions Enrico Perfetto, CNISM Roma "Tor Vergata"

We investigate the transport properties of a one-dimensional superconductor-normal metal-superconductor (S-N-S) system described within the tight-binding approximation. We compute the equilibrium dc Josephson current and the time-dependent oscillating current generated after the switch-on of a constant bias. In the first case an exact embedding procedure to calculate the Nambu-Gorkov Keldysh Green's function is employed and used to derive the continuum and bound states contributions to the dc current. A general formalism to obtain the Andreev bound states (ABS) of a normal chain connected to superconducting leads is also presented. We identify a regime in which all Josephson current is carried by the ABS and obtain an analytic formula for the current-phase relation in the limit of long chains. In the latter case the condition for perfect Andreev reflections is expressed in terms of the microscopic parameters of the model. When a finite bias is applied to the S-N-S junction we compute the exact time-evolution of the system by solving numerically the time-dependent Bogoliubov-deGennes equations. Our scheme allows us to describe the ac regime as well as the transient dynamics whose characteristic time-scale is dictated by the velocity of multiple Andreev reflections.

Sr_2RuO_4 and the physics of triplet pairing Andy Mackenzie University of St Andrews, Scotland

In this talk I will review the body of experimental knowledge that has been accumulated about the unconventional superconductor Sr_2RuO_4 , and then discuss a recent project in which the de Haas - van Alphen effect is being used to measure the influence of spin-orbit coupling on its

Fermi surface.

Orbital magnetic moment in a chiral p-wave superconductor

James Annett, University of Bristol, UK

The problem is the orbital angular momentum carried by the ^3He A phase is a famous paradox. Naively a condensate of $L_z = 1\hbar$ Cooper pairs will carry a corresponding macroscopic angular momentum, possibly entirely carried by a single chiral edge state. However in the case of the p-wave superconductor Sr_2RuO_4 the condensate is also of $L_z = 1\hbar$ Cooper pairs, and so should possess a finite ground state orbital magnetic moment. We discuss the calculation of this bulk moment in a realistic three band description of the superconductor, and compare our predicted moment with experiments including recent optical Kerr effect measurements.

Doping dependence of electron phonon interaction in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ Ali Tavana, University of Leoben (Austria) and Sharif University of Technology (Iran)

Density functional theory (DFT) calculations have been performed for the high- T_c superconductor $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ (LBCO) in order to study the role of electron phonon (e-ph) interaction and lattice distortions. Using the virtual crystal approximation, calculations are performed for the entire doping range, i.e. for the undoped non-superconducting ($x=0, 0.002$), for the superconducting ($x=0.05, 0.075, 0.10$), for the overdoped region ($x=0.20$), and for the “1/8 anomaly” ($x=0.125$). The electronic ground states of LBCO for different Ba concentrations are also investigated using the LDA+U approximation to account for the strong electronic correlations. We study the interplay between antiferromagnetic (AF) order and nature of the ground state.

Phonon frequencies and e-ph interaction parameters $\lambda(q, \nu)$ are calculated based on the linear response theory. We find two degenerated strongly anharmonic phonon modes which soften around the M point and two other branches which exhibit softening around the Z point of Brillouin zone. Structural distortions related to those phonons are in accordance with the HTT to LTO and LTO to LTT phase transitions. We investigate the origin of the major contributions to the overall coupling parameter. The later quantity is also analyzed in terms of the doping dependence. We discuss the results with respect to related experimental data.

On the possible secondary component of the order parameter observed in London penetration depth measurements Angelo Valli, Vienna University of Technology

Recent experiments show a low-temperature deviation from the pure d-wave behavior in the temperature dependence of the in-plane magnetic field penetration length in optimally doped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ compounds. This peculiar behaviour can reflect the presence of a secondary component of the superconducting order parameter, which has been proposed to be an isotropic s-wave. We show that a much more sensible description of the experimental results can be obtained assuming a time reversal breaking $d_{x^2-y^2} + id_{xy}$ order parameters within

a BCS approach for an effective low-energy model.

Static and Dynamical Susceptibility of pure and doped LaOFeAs Marco Monni, SLACS (INFN-CNR) and Department of Physics - University of Cagliari

The mechanism of superconductivity in pnictides is still under debate. The magnetic properties of these compounds suggest a possible role of spin fluctuations in the pairing mechanism. The effective interaction among electrons can be expressed in terms of the susceptibility χ . The latter is therefore a key quantity in the determination of both the magnetic properties of the system in the normal state, and of the contribution of spin fluctuations to the pairing potential. A basic ingredient to obtain χ is the independent-electron susceptibility χ_0 . Using $\text{LaO}_{(1-x)}\text{F}(x)\text{FeAs}$ as a prototype material, in this work we present a detailed ab-initio study of χ_0 , as a function of doping and of the internal atomic positions, starting from accurate electronic structures calculations within density functional theory.

Magnetic properties of $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ John Kay Dewhurst, Institut für Theoretische Physik, Freie University Berlin

Using state-of-the-art first-principles calculations we have elucidated the complex magnetic and structural dependence of LaOFeAs upon doping. Our key findings are that (i) doping results in an orthorhombic ground state and (ii) there is a commensurate to incommensurate transition in the magnetic structure between $x = 0.025$ and $x = 0.04$. Our calculations further imply that in this system magnetic order persists up to the onset of superconductivity at the critical doping of $x = 0.05$. Finally, our investigations of the undoped parent compound reveal an unusually pronounced dependence of the magnetic moment on details of the exchange-correlation (xc) functional used in the calculation. However, for all choices of xc functional an orthorhombic structure is found.

Scaling relations and virial theorems in density functional theory Cesar R. Proetto, Freie Universitaet, Berlin

Scaling relations and virial theorems are derived for the relevant quantities of the density functional description of many-electron systems at thermodynamic equilibrium.

Workshop Participants

1. Claudia Ambrosch-Draxl, Leoben, Austria
2. James Annett, University of Bristol
3. Fabio Bernardini, Dept. of Physics, Univ. of Cagliari
4. Christophe Bersier, Fu Berlin

5. Lilia Boeri, MPI-FKF Stuttgart
6. Sergey Borisenko, IFW-Dresden
7. Paolo Brotto, University degli studi di Genova - DIFI
8. Matteo Calandra, Paris, France
9. Giorgio Concas, Dipartimento di Fisica, Universita' di Cagliari
10. John Kay Dewhurst, Institut fur Theoretische Physik, FU Berlin
11. Frank Essenberg, Institut fur Theoretische Physik
12. Renato S. Gonnelli, Dipartimento di Fisica and CNISM, Politecnico di Torino
13. Eberhard Gross, Berlin, Germany
14. Andrea Floris, Freie Universitaet Berlin
15. Henning Glawe, Institut fur Theoretische Physik
16. Thomas Haynes, University of Bristol
17. Rolf Heid, Forschungszentrum Karlsruhe
18. Andreas Linscheid, Free University, Berlin
19. Andy Mackenzie, University of St Andrews
20. Sandro Massidda, Cagliari, Italy
21. Marco Monni, SLACS (INFN-CNR) and Department of Physics - University of Cagliari
22. Enrico Perfetto CNISM Roma "Tor Vergata"
23. Cesar R. Proetto, Freie Universitaet Berlin
24. Marina Putti, University di Genova
25. Patrick Rourke, Bristol, UK
26. Antonio Sanna, Free University Berlin
27. Samuele Sanna, Physics Department "A.Volta" University of Pavia
28. Sangeeta Sharma, Institut fur Theoretische Physik, Freie University Berlin
29. Ali Tavana, University of Leoben (Austria) and Sharif University of Technology (Iran)
30. Angelo Valli, Vienna University of Technology
31. Karol Wysokiski, Institute of Physics, M. Curie-Sklodowska University
32. Gertrude Zwicknagl, Braunschweig, Germany

4 General Job Announcements

Postdoctoral Research Position

**Department of Physics, Applied Physics & Astronomy
Rensselaer Polytechnic Institute, Troy, NY 12180, USA**

We invite applicants for post-doctoral position in computational physics and applied mathematics. Our newly established project involves the development of computational defect theory beyond the current density functional methods and the corresponding codes development. We also invite applicants for the application of currently available first-principles approaches to the study of extended defects in photovoltaic materials, van der Waals systems, and hydrogen release from nanostructured metal hydrides. Candidate should send curriculum vitae, list of publications (including preprints of unpublished papers, if possible) and list of three references to

Prof. Shengbai Zhang
Department of Physics, Applied Physics & Astronomy
Rensselaer Polytechnic Institute (RPI)
110 Eighth Street
Troy, NY 12180, USA

RPI is an equal opportunity/affirmative action employer. Clarifications or further details can be obtained via e-mail to zhangs9@rpi.edu.

PhD Position

Computational Materials Physics - Faculty of Physics, University of Vienna, Vienna, Austria

The University of Vienna (Austria) and the Center for Computational Materials Science (CMS, <http://www.cms.tuwien.ac.at/>) invites applications for a PhD studentship in Computational Materials Science.

The CMS in Vienna is a research center and graduate school based on a collaboration of research groups from the Faculties of Physics and Chemistry from the University of Vienna and the Technical University of Vienna. The activities of the CMS concentrate on the development of methods for multiscale simulations in condensed materials. The techniques being actively developed by the members of the CMS range from ab-initio density functional calculations (VASP, WIEN2k) to statistical-mechanical approaches for the description of liquids, amorphous materials and soft matter. The simulation tools developed by the members of the CMS are applied to a wide range of research projects: structural materials, magnetic materials, surfaces, interfaces, ultrathin films and nanomaterials, semiconductors and insulators, chemical reactions and catalysis, liquids and soft matter. Within its Graduate school the CMS invites applications for a PhD studentships in Computational Materials Science to be led in the Vienna ab-initio Simulations Package (VASP) group. The VASP group, directed by J. Hafner and G. Kresse, is one of the world leading groups in computational material science. The VASP package is recognized as one of the most flexible and robust ab initio packages and is presently used by about 1000 academic institutions and industrial research centers.

The PhD student will be part of a multidisciplinary research team within a collaborative EU-INDIA FP7-funded project involving other two European theoretical groups (Trinity College Dublin and University of Cagliari) and three Indian theoretical groups (S.N. Bose national Center for Basic Sciences Kolkata, Harish-Chandra Research Institute Allahabad, and Jawaharlal Nehru Center for Advanced Scientific Research Bangalore). The overall aim of the project is the investigation, through a synergy of advanced First-Principles, density-functional based methods, and Model Hamiltonian calculations suited for strong-correlated systems, of the properties and functionalities of transition metal oxides that may be viable candidates as building blocks of future micro- and nanoelectronic devices with enhanced capabilities.

We are looking for outstanding candidates with a degree in physics, chemistry or materials science, a strong background in quantum mechanics, statistical mechanics, mathematics and computing and a strong personal commitment to research. You will join a lively community performing frontline research. Applications with the usual credentials (CV, eventually also publications) and two letters of recommendation should be sent to cesare.franchini@univie.ac.at. For the successful applicant, the appointment to the PhD Studentship can become effective from September-October 2009 on. The salary will be about 25300 Euro/year before taxes, the contract will be for three years. Female students are particularly encouraged to apply.

PhD position “DFT+DMFT for complex transition metal oxides”

School of Physics, Trinity College Dublin, Ireland

A PhD studentship is available in the Computational Materials Theory group within the School of Physics at Trinity College Dublin, Ireland. The PhD project aims at combining electronic structure calculations using density functional theory with dynamical mean-field theory, and applying this method to study the properties of complex transition metal oxides, in particular manganites, ruthenates, and cuprates.

Candidates must have a strong overall motivation and a keen interest in theory and computation, as well as in addressing specific materials science problems. In addition, candidates are required to have at least a 2.1 honors degree from an Irish university or better qualification (e.g. MSc, Diplom, Laurea, . . .). Experience in working with UNIX/Linux environments and programming in either Fortran or C/C++ is beneficial. Applicants whose first language is not English will have to provide a TOEFL certificate or equivalent (e.g. IELTS).

Trinity College is located in the heart of Dublin, one of Europe’s most vibrant capital cities. The School of Physics at Trinity College has a very strong research program in computational materials science and maintains close links with several on-campus interdisciplinary research centers, such as CRANN (Center for Research on Adaptive Nanostructures and Nanodevices) or TCHPC (Trinity Center for High Performance Computing), and also with many research groups abroad.

The position is available immediately or at the earliest possible date once a suitable candidate has been identified. All tuition and fees plus an annual stipend of 16,000 euro (tax free) are covered. Applications including cover letter, CV, references, and a short statement of research interests (email and pdf format preferred) should be sent to:

Dr. Claude Ederer,
School of Physics
Trinity College,
Dublin 2, Ireland
email: edererc@tcd.ie

There is no deadline for these positions. Screening of applications will start immediately and will continue until the positions are filled. For further information please contact Dr. Ederer directly.

See also: www.tcd.ie/Physics/People/Claude.Ederer

5 Abstracts

A first-principles study of bulk oxide formation on Pd(100)

N. Seriani, J. Harl, F. Mittendorfer, G. Kresse

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Abstract

The catalytic oxidation activity of palladium is influenced by the oxidation state of the metal. Under technologically relevant conditions, bulk and surface oxides may form and decompose. By employing first-principles calculations based on density functional theory, we have investigated the transition from the surface oxide to the bulk oxide on Pd(100). We show that the most stable orientation of the oxide film is PdO(101)@Pd(100) at any film thickness. The monolayer has unique electronic, chemical, and thermodynamic properties in comparison to thicker oxide films. In particular, carbon monoxide adsorbs by 0.3 eV more strongly on thicker oxides than on the surface oxide, a fact that should influence the catalytical activity. Finally, we show that a simple model employing density functional theory energies predicts a StranskiKrastanov growth mode for the oxide film, with a critical thickness of 1 ML. Our results give a framework for the interpretation of experiments of Pd oxide growth.

(J. Chem. Phys. 131, 054701 (2009))

Contact person: Nicola Seriani (nicola.seriani@univie.ac.at)

Understanding the Clean Interface Between Covalent Si and Ionic Al_2O_3

H. J. Xiang, Juarez L. F. Da Silva, Howard M. Branz, and Su-Huai Wei
National Renewable Energy Laboratory, Golden, Colorado 80401, USA

Abstract

The atomic and electronic structures of the (001)-Si/(001)- γ - Al_2O_3 heterointerface are investigated by first principles total energy calculations combined with a newly developed “modified basin hopping” method. It is found that all interface Si atoms are 4-fold coordinated due to the formation of Si-O and unexpected covalent Si-Al bonds in the new abrupt interface model. And the interface has perfect electronic properties in that the unpassivated interface has a large LDA band gap and no gap levels. These results show that it is possible to have clean semiconductor/oxide interfaces.

(Phys. Rev. Lett. **103**, 116101 (2009))

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Superexchange Interactions in Orthorhombically Distorted Titanates $RTiO_3$ ($R= Y, Gd, Sm, \text{ and } La$)

I. V. Solovyev

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National Institute for Materials Science,
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Abstract

Starting from the multiorbital Hubbard model for the t_{2g} -bands of $RTiO_3$ ($R= Y, Gd, Sm, \text{ and } La$), where all the parameters have been derived from the first-principles electronic structure calculations, we construct an effective superexchange (SE) spin model, by treating transfer integrals as a perturbation. We consider four approximations for the SE interactions: (i) the canonical crystal-field (CF) theory, where the form of the occupied t_{2g} -orbitals is dictated by the CF splitting at each Ti-site and three extensions of the CF theory, namely (ii) the relativistic one, where occupied orbitals are confined within the lowest Kramers doublet obtained from the diagonalization of the crystal field and relativistic spin-orbit (SO) interactions; (iii) the finite-temperature extension, which consider the effect of thermal orbital fluctuations near the CF configuration on interatomic interactions between the spins; (iv) the many-electron extension, which is based on the diagonalization of the full Hamiltonian constructed in the basis of two-electron states separately for each bond of the system. The main results are summarized as follows. (i) Thermal fluctuations of the orbital degrees of freedom can substantially reduce the value of the magnetic transition temperature. (ii) The relativistic SO coupling is generally responsible for anisotropic and antisymmetric Dzyaloshinsky-Moriya interactions. All interactions are rigorously derived and their implications to the magnetic properties of $RTiO_3$ are discussed. (iii) The CF theory, although applicable for $YTiO_3$ and high-temperature structures of $GdTiO_3$ and $SmTiO_3$, breaks down in the case of $LaTiO_3$. In the latter, the CF splitting is small. Therefore, the many-electron effects *in the bonds* as well as the relativistic SO interaction start to play an important role. It is argued that the combination of these two effects can be responsible for the AFM character of interatomic correlations in $LaTiO_3$. (iv) The SE interactions in $YTiO_3$ strongly depend on the details of the crystal structure. Crystal distortions in the low-temperature structure tend to weaken the ferromagnetic interactions.

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Ab-initio theory of the lattice thermal conductivity in diamond

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Abstract

We present a first principles theoretical approach to calculate the lattice thermal conductivity of diamond based on an exact solution of the Boltzmann transport equation. Density-functional perturbation theory is employed to generate the harmonic and third-order anharmonic interatomic force constants that are required as input. A central feature of this approach is that it provides accurate representations of the interatomic forces and at the same time introduces no adjustable parameters. The calculated lattice thermal conductivities for isotopically enriched and naturally occurring diamond are both in very good agreement with experimental data. The role of the scattering of heat-carrying acoustic phonons by optic branch phonons is also investigated. We show that inclusion of this scattering channel is indispensable in properly describing the thermal conductivity of semiconductors and insulators. The accurate adjustable-parameter-free results obtained herein highlight the promise of this approach in providing predictive descriptions of the lattice thermal conductivity of materials.

(Physical Review B **80**, 125203 (2009))

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Measurement of effective electron mass in biaxial tensile strained silicon on insulator

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Abstract

We present measurements of the effective electron mass in biaxial tensile strained silicon on insulator (SSOI) material with 1.2 GPa stress and in unstrained SOI. Hall-bar MOSFETs on 60 nm SSOI and SOI were fabricated, and Shubnikov-de Haas oscillations in the temperature range $T = 0.4\text{--}4\text{ K}$ for magnetic fields of $B = 0\text{--}10\text{ T}$ were measured. The effective electron mass in SSOI and SOI samples was determined as $m_t = (0.20 \pm 0.01)m_0$. This result is in excellent agreement with first-principles calculations of the effective electron mass in the presence of strain.

(Submitted to Appl. Phys. Lett.)

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Electronic structure and effective masses in strained silicon

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Abstract

The structural and electronic properties of strained silicon are investigated quantitatively with *ab initio* computational methods. For this purpose we combine density-functional theory within the local-density approximation and the *GW* approximation for the electronic self-energy. From the variation of the total energy as a function of applied strain we obtain the elastic constants, Poisson ratios and related structural parameters, taking a possible internal relaxation fully into account. For biaxial tensile strain in the (001) and (111) planes we then investigate the effects on the electronic band structure. These strain configurations occur in epitaxial silicon films grown on SiGe templates along different crystallographic directions. The tetragonal deformation resulting from (001) strain induces a valley splitting that removes the sixfold degeneracy of the conduction-band minimum. Furthermore, strain in any direction causes the band structure to warp. We present quantitative results for the electron effective mass, derived from the curvature of the conduction band, as a function of strain and discuss the implications for the mobility of the charge carriers. The inclusion of proper self-energy corrections within the *GW* approximation in our work not only yields band gaps in much better agreement with experimental measurements than the local-density approximation, but also predicts slightly larger electron effective masses.

(Submitted to Phys. Status Solidi C)

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First-principles calculation of electronic excitations in solids with SPEX

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Abstract

We describe the software package SPEX, which allows first-principles calculations of quasiparticle and collective electronic excitations in solids using techniques from many-body perturbation theory. The implementation is based on the full-potential augmented-plane-wave (FLAPW) method, which treats core and valence electrons on an equal footing and can be applied to a wide range of materials, including transition metals and rare earths. After a discussion of essential features that contribute to the high numerical efficiency of the code, we present illustrative results for quasiparticle band structures calculated within the *GW* approximation for the electronic self-energy, electron-energy-loss spectra with inter- and intraband transitions as well as local-field effects, and spin-wave spectra of itinerant ferromagnets. In all cases the inclusion of many-body correlation terms leads to very good quantitative agreement with experimental spectroscopies.

(Submitted to Z. Phys. Chem.)

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First-Principles Approach to Heat and Mass Transfer Effects in Model Catalyst Studies

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Abstract

We assess heat and mass transfer limitations in *in situ* studies of model catalysts with a first-principles based multiscale modeling approach that integrates a detailed description of the surface reaction chemistry and the macro-scale flow structures. Using the CO oxidation at RuO₂(110) as a prototypical example we demonstrate that factors like a suppressed heat conduction at the backside of the thin single-crystal, and the build-up of a product boundary layer above the flat-faced surface play a significant role.

(Catalysis Letters (accepted))

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Structure and excitonic coupling in self-assembled monolayers of azobenzene-functionalized alkanethiols

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Abstract

Optical properties and geometric structure of self-assembled monolayers of azobenzene-functionalized alkanethiols have been investigated by UV/Visible and near-edge X-ray absorption fine structure spectroscopy in combination with density-functional theory. By attaching a trifluoro-methyl endgroup to the chromophore both the molecular tilt and twist angle of the azobenzene moiety are accessible. Based on this detailed structural analysis the energetic shifts observed in optical reflection spectroscopy can be qualitatively described within an extended dipole model. This substantiates sizeable excitonic coupling among the azobenzene chromophores as an important mechanism that strongly suppresses *trans* to *cis* isomerization in densely-packed self-assembled monolayers.

(submitted to: J. Am. Chem. Soc.)

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Azobenzene at Coinage Metal Surfaces: The Role of Dispersive van der Waals Interactions

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Abstract

We use different semi-empirical dispersion correction schemes to assess the role of long-rang van der Waals interactions in the adsorption of the prototypical molecular switch azobenzene ($C_6H_5-N_2-C_6H_5$) at the coinage metal surfaces Cu(111), Ag(111) and Au(111). Compared to preceding density-functional theory results employing a semi-local exchange and correlation functional we obtain partly sizable changes of the computed adsorption geometry and energetics. The discomfoting scatter in the results provided by the different schemes is largely attributed to the unknown form of the damping function in the semi-empirical correction expression. Using the congeneric problem of the adsorption of benzene as a vehicle to connection with experiment, we cautiously conclude that the account of dispersive interactions at the metal surfaces provided by the various schemes is in the right ballpark, with the more recent, general schemes likely to overbind.

(submitted to: Phys. Rev. B)

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Structure and energetics of azobenzene at Ag(111): Benchmarking semi-empirical dispersion correction approaches

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Abstract

We employ normal-incidence x-ray standing wave and temperature programmed desorption spectroscopy to derive the adsorption geometry and energetics of the prototypical molecular switch azobenzene at Ag(111). This allows to assess the accuracy of semi-empirical correction schemes as a computationally efficient means to overcome the deficiency of semi-local density-functional theory with respect to long-range van der Waals (vdW) interactions. The obtained agreement underscores the significant improvement provided by the account of vdW interactions, with remaining differences mainly attributed to the neglect of electronic screening at the metallic surface.

(submitted to: Phys. Rev. Lett.)

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Density functional theory study of the conformational space of an infinitely long polypeptide chain

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Abstract

The backbone conformational space of infinitely long polyalanine is investigated with density-functional theory and mapping the potential-energy surface in terms of (L, θ) cylindrical coordinates. A comparison of the obtained (L, θ) Ramachandran-like plot with results from an extended set of protein structures shows excellent conformity, with the exception of the polyproline II region. It is demonstrated the usefulness of infinitely long polypeptide models for investigating the influence of hydrogen bonding and its cooperative effect on the backbone conformations. The results imply that hydrogen bonding together with long-range electrostatics is the main actuator for most of the structures assumed by protein residues.

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Landauer theory of ballistic torkances in noncollinear spin valves

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Abstract

We present a theory of voltage-induced spin-transfer torques in ballistic noncollinear spin valves. The torkance on one ferromagnetic layer is expressed in terms of scattering coefficients of the whole spin valve, in analogy to the Landauer conductance formula. The theory is applied to Co/Cu/Ni(001)-based systems where long-range oscillations of the Ni torkance as a function of Ni thickness are predicted. The oscillations represent a novel quantum size effect due to the noncollinear magnetic structure. The oscillatory behavior of the torkance contrasts a thickness-independent trend of the conductance.

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Substrate-induced antiferromagnetism of a Fe monolayer on the Ir(001) surface

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Abstract

We present detailed *ab initio* study of structural and magnetic stability of a Fe monolayer on the fcc(001) surface of iridium. The Fe monolayer has a strong tendency to order antiferromagnetically for the true relaxed geometry. On the contrary an unrelaxed Fe/Ir(001) sample has a ferromagnetic ground state. The antiferromagnetism is thus stabilized by the decreased Fe-Ir layer spacing in striking contrast to the recently experimentally observed antiferromagnetism of the Fe/W(001) system which exists also for an ideal bulk-truncated, unrelaxed geometry. The calculated layer relaxations for Fe/Ir(001) agree reasonably well with recent experimental low-energy electron diffraction data. The present study centers around the evaluation of pair exchange interactions between Fe atoms in the Fe overlayer as a function of the Fe/Ir interlayer distance which allows for a detailed understanding of the antiferromagnetism of a Fe/Ir(001) overlayer. Furthermore, our calculations indicate that the nature of the true ground state could be more complex and display a spin spiral like rather than a $c(2 \times 2)$ -antiferromagnetic order. Finally, the magnetic stability of the Fe monolayer on the Ir(001) surface is compared to the closely related Fe/Rh(001) system.

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Effect of strain on the stability and electronic properties of ferrimagnetic $\text{Fe}_{2-x}\text{Ti}_x\text{O}_3$ heterostructures from correlated band theory

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Abstract

Based on density functional theory (DFT) calculations including an on-site Hubbard U term we investigate the effect of substrate-induced strain on the properties of ferrimagnetic Fe_2O_3 - FeTiO_3 solid solutions and heterostructures. While the charge compensation mechanism through formation of a mixed Fe^{2+} , Fe^{3+} -contact layer is unaffected, strain can be used to tune the electronic properties of the system, e.g. by changing the position of impurity levels in the band gap. Straining hematite/ilmenite films at the lateral parameters of $\text{Al}_2\text{O}_3(0001)$, commonly used as a substrate, is found to be energetically unfavorable as compared to films on $\text{Fe}_2\text{O}_3(0001)$ or $\text{FeTiO}_3(0001)$ -substrates.

(Journal of Applied Physics, in press.)

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6 SCIENTIFIC HIGHLIGHT OF THE MONTH: Electronic Phenomena at Complex Oxide Interfaces: Insights from First Principles

Electronic Phenomena at Complex Oxide Interfaces: Insights from First Principles

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Abstract

Oxide interfaces have attracted considerable attention in recent years due to the emerging novel behavior which does not exist in the corresponding bulk parent compounds. This opens possibilities for future applications in oxide based electronics and spintronics devices. Among the different materials combinations, heterostructures containing the two simple band insulators LaAlO_3 and SrTiO_3 have advanced to a model system exhibiting unanticipated properties ranging from conductivity, to magnetism, even to superconductivity. Electronic structure calculations have contributed significantly towards understanding these phenomena and we review here the progress achieved in the past years also showing some future directions and perspectives. A central issue in understanding the novel behavior in these oxide heterostructures is to discover the way (or ways) that these heterostructures deal with the polar discontinuity at the interface. Despite analogies to polar semiconductor interfaces, transition metal oxides offer much richer possibilities to compensate the valence mismatch, including *e.g.* an electronic reconstruction. Moreover, electronic correlations can lead to additional complex behavior like charge disproportionation and order, magnetism, and orbital order. We discuss in some detail the role of finite size effects in ultrathin polar films on a nonpolar substrate leading to another intriguing feature - the thickness dependent insulator-to-metal transition in thin LaAlO_3 films on a $\text{SrTiO}_3(001)$ substrate, driven by the impending polar catastrophe. The strong and uniform lattice polarization that emerges as a response to the potential buildup enables the system to remain insulating up to a few layers. However, beyond a critical thickness there is a crossover from an ionic relaxation to an electronic reconstruction. At this point two bands of electron and hole character, separated both in real and in reciprocal space, have been shifted sufficiently by the internal field in LaAlO_3 to impose the closing of the band gap. We discuss briefly further parameters that allow one to manipulate this behavior *e.g.* via vacancies, adsorbates or an oxide capping layer.

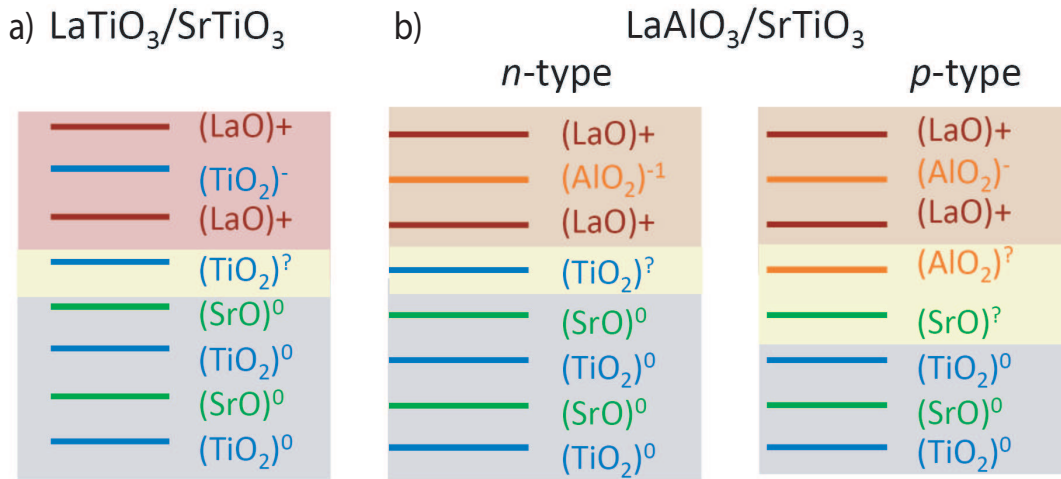


Figure 1: Schematic picture of the charge discontinuity at the a) $\text{LaTiO}_3/\text{SrTiO}_3$, as well as the b) n - and p -type interfaces in $\text{LaAlO}_3/\text{SrTiO}_3$. Due to mismatch of charges, the ions cannot maintain their formal valence at the interface.

1 Introduction to polar oxide surfaces and interfaces

As common as ionic insulators are – your table salt, for example – electronically they are very specific materials. In the band picture of electronic structure, in a conventional (band) insulator the Fermi level falls between two band complexes, and there are *precisely* enough electrons available to fill the lower set of (valence) bands and leave none in the upper set of (conduction) bands. In ionic oxides, it is common for the ions to be closed shell, and the ionic solid is insulating because the individual constituents are nondegenerate and stable. For such a conventional insulator to conduct, carriers must be coerced into otherwise filled or unfilled bands of states *e.g.* through doping.

A different type of oxide insulator arises when ions have partially filled shells. These transition metal compounds are known as Mott insulators, and fail to conduct because (in the classical simplest picture) the energy gain from hopping between the open-shell ions (roughly speaking, proportional to the bandwidth W) is outweighed by the interaction energy cost of putting an extra electron on an ion (the Coulomb repulsion U , also known as the “Hubbard U ”). In practice, there are a number of energy scales and degrees of freedom that make the behavior much more complex and interesting. For these reasons, and because they give rise to the high temperature superconductors, these Mott insulators remain, after 50 years of study, a very active field of research.

Transition metal oxides exhibit both an impressive structural variety and a rich spectrum of functionalities such as high T_c superconductivity, magnetism, ferroelectricity and colossal magnetoresistance, among many others. In a heterostructure such properties can be combined, *e.g.* in the search for multiferroic materials (see for example Ψ_k Highlight 93 by Fechner *et al.*). However, perhaps a more compelling reason to study oxides is that it has become clear that novel electronic states can be realized at oxide interfaces that do not exist in the bulk phases.

Layer-by-layer growth allows synthesis of phases that are not thermodynamically stable. Recent developments of growth techniques like pulsed laser deposition (PLD) and molecular beam epitaxy (MBE) have enabled the synthesis of oxide superlattices with atomic precision [1,2]. These artificial “digital” materials are currently a source of excitement both from a fundamental point of view and for future technological applications in electronics and spintronics devices because of the novel functional properties that arise. Prominent examples are the two-dimensional electron gas measured at the interface between the Mott-insulator LaTiO_3 (LTO) and the band insulator SrTiO_3 (STO) [2], as well as between the two simple band insulators LaAlO_3 (LAO) and STO [3]. Reports of superconductivity [4] and magnetism [5] in the latter system have fueled research both on the theoretical and experimental side. Due to the emerging new functionalities and the underlying fundamental questions, *Science* magazine selected oxide interfaces as one out of ten “runners-up” in the breakthroughs of 2007 [6]. This area of research was also featured in an editors article in *Physics Today* [7].

As we will relate in this article, symmetry breaking and charge neutrality violation at the interface play a central role in the emergence of unexpected behavior. Analogous to oxide surfaces [8–10] the question of polarity arises also at oxide interfaces. In the perovskite structure the ionic charge is modulated along the [001] crystallographic direction, e.g. in LaTiO_3 positively charged $(\text{La}^{3+}\text{O}^{2-})^+$ -layers alternate with negatively charged $(\text{Ti}^{3+}\text{O}_2^-)^-$ -layers, while SrTiO_3 consists of formally neutral $(\text{Sr}^{2+}\text{O}^{2-})^0$ - and $(\text{Ti}^{4+}\text{O}_2^-)^0$ -layers. As shown in Fig. 1 a valence discontinuity arises at the (001)-interface (IF) between the polar LTO and the nonpolar STO, i.e. there is $\frac{1}{2}$ electron per IF cell in excess for the formal charge states of STO to be maintained, or $\frac{1}{2}$ too little for LTO. This excess of charge corresponds to carrier densities around 3.5×10^{14} . The situation is similar in LAO/STO: at the *n*-type IF there is half an electron too much to keep the formal charges, while with a SrO-AlO₂ stacking (*p*-type) there is an extra $\frac{1}{2}$ hole.

During the film growth process of polar materials it is expected that the dipoles lead to a shift of the potential which increases proportional to the number of overlayers (i.e. a constant electric field). [11] This impending “polar catastrophe” has to be accommodated in some way. At first glance polar oxide interfaces bear similarities to polar semiconductor heterostructures. For the latter, compensation is often achieved through the so-called atomic reconstruction, where the surface/interface chemical composition is strongly altered via ordering of defects or roughening. On the other hand, at oxide interfaces an electronic reconstruction involving electron transfer into unoccupied bands can take place. Taking into account the correlated nature of the 3*d*-electrons and the possibility of multiple valence states in transition metal ions, more complex compensation mechanisms can arise leading to the stabilization of novel electronic phases.

Ab initio calculations play a key role in understanding the physics at oxide interfaces, but we note also that the structural complexity, the large system sizes and, last but not least, the treatment of electronic correlations pose high demands on the theoretical description. Rather than providing a full review of all theoretical work done so far, we have selected several cases that exemplify the insight that can be obtained from density functional theory (DFT) calculations, focusing on interfaces between polar and nonpolar materials. Most of the results presented here are obtained using the full-potential linearized augmented plane waves method as implemented in the WIEN2k code [13] and the generalized gradient approximation [14] to the exchange correlation potential also including correlation effects within the LDA/GGA+*U* method [12]

(for more details the reader is referred to the original papers). Specifically, we will compare the compensations mechanisms that arise in heterostructures of the Mott insulator LTO and the band insulator STO to those comprised of the conventional ionic insulators LAO and STO. The latter is chosen both because it shows a striking variety of properties making it by far the most studied system, and also because the remarkably intricate behavior of these rather simple materials ought to be understood before one deals with the additional complexity arising from the “Mott physics” in open shell transition metal oxides. In Section 2 we address the electronic properties of infinitely extended superlattices of LTO/STO and compare them to those at the isolated n - and p -type LAO/STO interfaces (Section 3.1 and Section 3.2, respectively). The latter are contrasted in Section 3.3 to the behavior of thin LAO films on a STO(001) substrate, where we explore finite size effects and the origin of the intriguing thickness-dependent insulator-to-metal transition. In Section 4 we summarize the current state of understanding of these materials and mention some future perspectives.

2 Compensation mechanisms at the $\text{LaTiO}_3/\text{SrTiO}_3$ interface

SrTiO_3 is a band insulator with a band gap of 3.2 eV. Due to the well known problem of the local density approximation (LDA) or GGA to underestimate the band gap, the GGA band gap separating occupied O $2p$ states from unoccupied Ti $3d$ states is 2.0 eV. In contrast, in LaTiO_3 the Ti $3d$ band is singly occupied and a strong intra-atomic Coulomb repulsion on the Ti ion leads to Mott insulating behavior. LaTiO_3 is one of the most studied correlated insulators. In bulk form its perovskite structure is strongly distorted, which narrows the $3d$ bands and thereby contributes to the Mott insulating character. The connection between the Jahn-Teller distortion and strong interaction effects in this compound is still a subject of intense research. [15]

Experiments indicate that LTO grows coherently on STO. The lattice mismatch between LTO ($a = 3.97\text{\AA}$) and STO ($a = 3.905\text{\AA}$) is relatively small (2%) and produces a tetragonal distortion which breaks the t_{2g} degeneracy when LTO is incorporated into superlattices grown on STO substrates. The effect of the pseudocubic structure and the tetragonal distortion is one of the relevant issues that will be discussed in the following.

“Interdiffusion layers” of LTO/STO with sheet carrier densities in the range $10^{13} - 10^{15} \text{ cm}^{-2}$ were grown in 1996 by Yoshida and collaborators [16]. In 2002 Ohtomo *et al.* [2] reported abrupt IFs involving LTO and STO demonstrating atomic control of the number of LTO layers within the STO host during the PLD process. Annular dark field transmission electron microscopy (TEM) images indicated atomically sharp interfaces. The observed conductivity at the interface between two insulators opened up the study of polar IFs with one strongly correlated component. Electron energy loss spectra (EELS) indicated a mixed Ti^{3+} , Ti^{4+} signal close to the interface with a decay length into the STO host of the order of 1 nm, which stimulated and focused some of the early theoretical work. Subsequent studies [17–20] reported more characteristics, including nanostructures with high mobility [19] as well as samples with poor conductivity. [20] Photoemission studies of buried LTO/STO IFs found a sharp Fermi cutoff (itinerant states), becoming sharper after $\text{La} \leftrightarrow \text{Sr}$ interdiffusion due to annealing [21].

2.1 Model Approaches

Before turning to the first principles studies of this system we review briefly the results from model Hamiltonian approaches. The theoretical study of this Mott insulator-band insulator interface was initiated by Okamoto and Millis, using single and then multiple band Hubbard models and a statically screened Coulomb interaction $e^2/|R-R'|$ interaction [22]. This approach results in a complex phase diagram with ferromagnetic, antiferromagnetic, and nonmagnetic solutions, as well as orbitally-ordered phases in certain regimes. Employing a similar approach but an exact diagonalization for a one-dimensional chain and two-leg ladders, Kancharla and Dagotto [23] obtained that the charge disturbance extended over nine or more atomic layers away from the interface even for large interaction strength. Lee and MacDonald considered [24] again a Hubbard model with similar interactions, with new features including a Thomas-Fermi (TF) treatment of the system, and consideration of a finite system (thin film). The TF solution provided a guideline in analytic form for the minimum number of layers required to drive the electronic reconstruction at the IF. More recently, Sigrist and coworkers [25] have addressed similar model Hamiltonians using auxiliary boson (slave boson) mean field theory. For (1) a correlated slab (variable interaction strength) embedded within a band insulating material ("STO"), and (2) multilayers they obtained a metallic (though highly renormalized) quasiparticle behavior even in the strongly interaction limit: a 2D electron gas.

2.2 DFT studies of electronic and orbital reconstruction

The odd number of electrons near the interface will give in the local density approximation (LDA) at least one partially filled band, *i.e.* a metallic IF. This metallicity is likely to persist when spin polarization (LSDA) is included, though insulating solutions are in principle possible in LSDA. The early DFT-based studies of the LTO/STO IF adopted the LSDA (or GGA) description, necessarily obtaining metallic IFs. [26,27] One emphasis was on the degree of confinement of the conducting layer to the IF region, which was attributed to a wedge shaped potential due to the incorporated LaO layer [26]. Both of these studies found a decay length of roughly three unit cells: the charge is spread over several TiO_2 layers away from the interface with intermediate valent $\text{Ti}^{3+\delta}$ ions.

To model superlattices containing a Mott and a band insulator, we have adopted the LDA+ U [12] (GGA+ U) method as a standard approach to describe the Mott insulating nature of LTO. A variety of heterostructures were considered, where the number of LTO (n) and STO (m) layers was varied $1 \leq n, m \leq 9$. In the following we denote these superlattices by $\text{LTO}_n/\text{STO}_m$. To describe the antiferromagnetic (AFM) G-type coupling of LTO (rocksalt arrangement of the Ti-spins), but most importantly to allow more complex electronic reconstructions and magnetic order, the lateral cell was enlarged to $c(2 \times 2)$ or $p(2 \times 2)$.

The initial question that arises is the appropriate value of the on-site repulsion parameter (Hubbard) U to choose. Calculations for an undistorted LTO crystal in a tetragonal setup (to model the magnetic coupling) show that a value of $U = 8$ eV, and intra-atomic Hund's $J = 1$ eV is needed to obtain an AFM-G type insulator. This value is somewhat higher than the one generally used for titanates with a distorted perovskite structure [31].

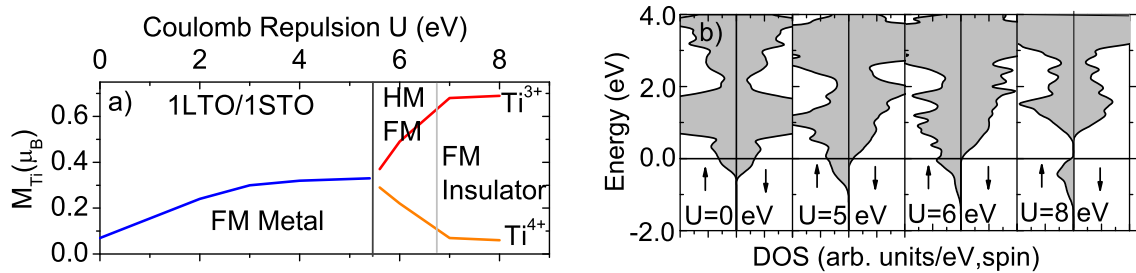


Figure 2: a) Evolution of the magnetic moment of Ti in a $\text{LTO}_1/\text{STO}_1$ superlattice (SL) with a $c(2 \times 2)$ lateral periodicity as a function of the Hubbard U -parameter. b) Density of states (DOS) (arrows denote the majority and minority DOS) (1,1)-SL for different U values. A charge disproportionation occurs beyond $U \approx 5.5$ eV. HM FM denotes the region where the system shows half metallic ferromagnetic behavior, before a Mott-Hubbard band gap forms at around $U \approx 6.5$ eV. [28]

For a $\text{LTO}_1/\text{STO}_1$ superlattice (which in fact corresponds to one type of double perovskite compound), we have investigated how the value of U influences the behavior of the Ti ion. As shown in Fig. 2 for $U=0$ a small moment of $\approx 0.07\mu_B$ moment arises on the Ti ions. With increasing U up to 5 eV the magnetic moments of the two equivalent Ti-ions at the interface increase and saturate at $0.33\mu_B$. In this region the system is a ferromagnetic (FM) metal. However, beyond this value charge disproportionation emerges, making the system a ferromagnetic half-metal for $5 < U < 7$ eV, before a band gap opens up for $U > 7$ eV separating the lower Hubbard band from the unoccupied 3d states. In the strong interaction regime a layer of Ti^{3+} and Ti^{4+} ions ordered in a checkerboard arrangement emerges at the interface. As shown in Fig. 3 the extra electron at the Ti^{3+} sites occupies the d_{xy} -orbital. This is not true orbital ordering because the Ti ion lies at the IF and the lowered symmetry breaks the degeneracy of the t_{2g} orbitals, with d_{xy} lying lowest. The local Ti^{3+} moment, reduced by mixing with oxygen as is common in oxides, is $0.72\mu_B$; the total moment per IF cell including the induced moment on the O ion is enforced by the FM insulating state to be $1\mu_B$. Finally, an antiferromagnetic coupling between Ti^{3+} within the interface layer becomes energetically favored [28].

This $\text{LTO}_1/\text{STO}_1$ heterostructure is however more a synthetic compound than a periodic array of interfaces. To determine the compensation mechanism and relaxation length towards bulk behavior at an isolated interface, we have studied more extended superlattices. The change in the electronic structure across a $\text{LTO}_1/\text{STO}_5$ multilayer with *ideal positions* of the atoms is displayed in Fig. 4a. Within GGA+ U , the charge mismatch is accommodated essentially entirely in the IF layer which contains charge ordered Ti^{4+} and Ti^{3+} . The Ti^{4+} ion in the next layer on the STO side has a projected density of states that is nearly identical to that of bulk STO. Analogously, Ti^{3+} ions one cell away from the IF in a superlattice with a thicker LTO part ($\text{LTO}_5/\text{STO}_5$ - not shown here) is similar to that of bulk LTO. Small differences between Ti^{4+} and Ti^{3+} ions in the IF layer and their counterparts in the bulk can be attributed to the different environment.

Hamann *et al.* [27] and Okamoto *et al.* [29] pointed out the importance of the structural relaxations on the electronic properties. This strong electron-lattice coupling has become essential to understand the behavior near IFs involving polar discontinuities. GGA [27] and LDA+ U [29] calculations within a $p(1 \times 1)$ unit cell predict a strong ferroelectric distortion of 0.15 \AA in the

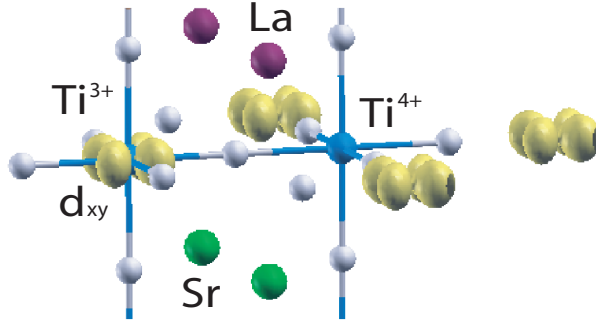


Figure 3: Spatial distribution of the electron density integrated between -2 eV and E_F showing the charge and orbitally ordered state at the LTO/STO interface. For $U = 8$ eV Ti^{3+} and Ti^{4+} order in a checkerboard arrangement with an occupied d_{xy} -orbital at the Ti^{3+} -sites, and no charge at the Ti^{4+} sites.

interface TiO_2 -layer leaving the Ti-Ti distance across the LaO layer larger than the Ti-Ti distances within the STO slab. The lattice distortion quickly decays away from the IF into the STO host. As shown in Fig. 4b these lattice relaxations invoke small but nonetheless important band shifts compared to the ideal structure: the occupied Ti d_{xy} state (the lower Hubbard band) rises by 0.3-0.4 eV, closing the very small gap and leading to partially filled bands and conducting behavior. A small concentration of holes are introduced into the d_{xy} band, with the compensating electrons going into deeper layers in the STO slab in Ti-orbitals of d_{xz} , d_{yz} character. This orbital occupation is sustained even at the GGA level [30]. Within GGA+ U the IF layer of Ti ions remains charge-ordered and magnetically ordered, in spite of the $\sim 30\%$ occupation of holes in the band and a reduction of the magnetic moment at Ti^{3+} to $0.49 \mu_B$. Overall, the lattice polarization obtained within GGA redistributes and smooths the charge profile, resulting in a larger relaxation length towards bulk behavior in the STO host [27, 29].

On the other hand, a structural relaxation within GGA+ U taking into account a larger $c(2 \times 2)$ lateral periodicity results in quite a different electronic behavior. While the vertical relaxations are slightly weaker than within GGA, a lateral relaxation of the oxygen ions away from the Ti^{3+} sites (breathing mode) leads to a further stabilization of the charge and orbitally ordered state. Moreover, the splitting between the occupied Ti d_{xy} orbital and the rest of the t_{2g} states is enhanced leading to a larger band gap as displayed in Fig. 4c.

This charge and orbitally ordered phase at the LTO/STO interface results from the interplay of electronic correlations and additional degrees of freedom and is an example how these can lead to unexpected compensation mechanisms of the interface polarity involving novel electronic states.

Since x-ray diffraction experiments [18] indicate only a tetragonal (and not orthorhombic) distortion for the epitaxial LTO layers in these heterostructures, an important issue is whether LTO can preserve its insulating character without the GdFeO_3 -type distortion of the bulk compound. The question of the (non)conducting character of pseudocubic LTO has been addressed by Ishida and Liebsch. [32] using a LDA+DMFT (dynamical mean field theory) method includ-

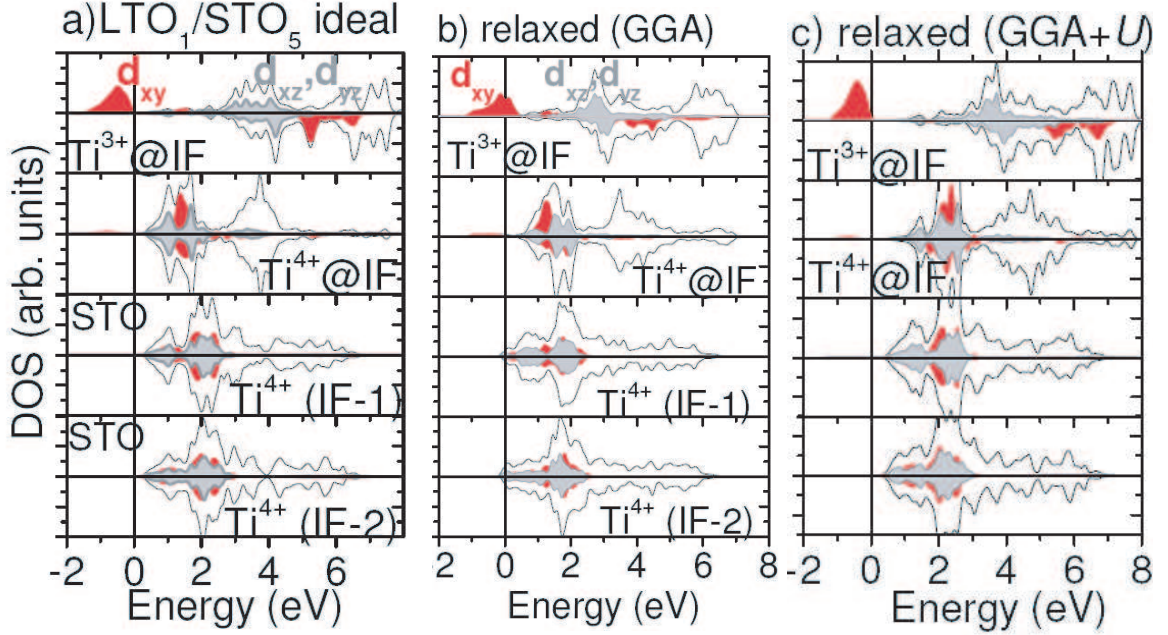


Figure 4: Layer-resolved projected DOS of the Ti 3d-states in the LTO₁/STO₅-heterostructure with ideal (a) and relaxed positions of the ions (b) within GGA and (c) within GGA+ U . For the structure related within GGA the excess charge leaks into the STO host [28], while relaxation within GGA+ U stabilizes further the charge and orbitally ordered state at the interface.

ing the Ti 3d states and treating the on-site interaction with exact diagonalization techniques. For tetragonal LTO appropriate to growth on STO, they obtained a metal-insulator transition in LTO at $U = 6$ eV ($J = 0.65$ eV). This critical value of U is not much different than what we obtained from GGA+ U . However, assuming that $U = 5$ eV is more appropriate for Ti, the authors conclude that tetragonal LTO itself is metallic, and that this accounts for the conducting LTO/STO multilayers that are observed experimentally. Using this value of U and treating (LTO)₃/(STO)₄ multilayers, they find that some of the Ti charge in LTO is transferred into the STO layers. Since the Fermi level of LTO must lie within the STO gap, this leaking of charge into STO would be like the “metal-induced gap states” that are well studied in conventional metal-semiconductor IFs.

2.3 Compensation through La,Sr intermixing

Besides the possibility of an electronic reconstruction, we have also considered an atomic reconstruction through an intermixed (La,Sr) layer. The projected DOS of a superlattice containing two unit cells of LTO and STO with one mixed La, Sr layer at the interface is shown in Fig. 5. While Ti ions on the LTO side of the interface behave nearly as in the Mott insulating bulk material, the Fermi level crosses the d_{xy} band of Ti³⁺ next to the interface. The t_{2g} bands of Ti⁴⁺ on the STO side have also a small occupation, leaving the system conducting. This is possibly related to the fact that solid solutions of LTO and STO (LSTO) are conducting even for small doping concentrations of Sr [33,34] in LTO, or La in STO.

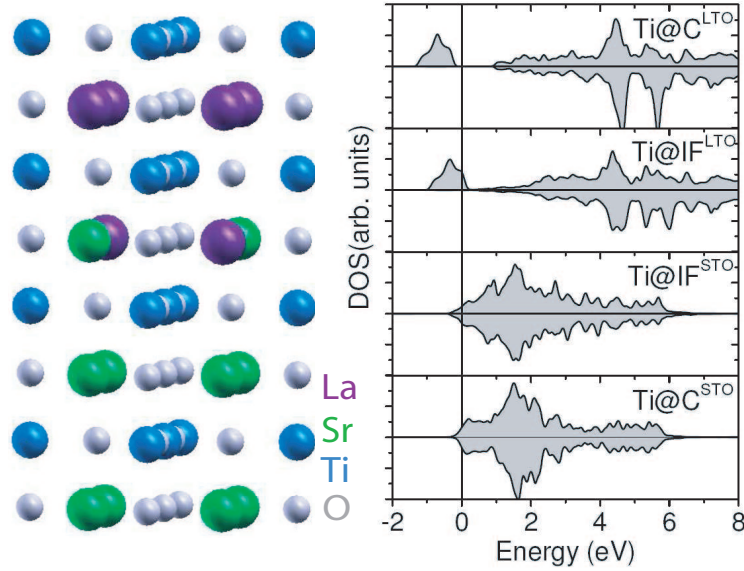


Figure 5: Layer-resolved projected DOS of the Ti $3d$ -states in the $\text{LTO}_2/\text{STO}_2$ -heterostructure with an intermixed La,Sr-layer. In the central Ti layer of the LTO slab, Mott insulating behavior is retained. The LTO side of the interface can be considered as a slightly (hole) doped Mott insulator, and compensating electrons must lie in the conduction bands on the STO side of the interface.

The implications of strong electronic correlations at the LTO/STO IF have certainly not been completely resolved. It is also important that more widely spaced IFs be studied to corroborate the results on the isolated IF. In the meantime, however, the limelight and the effort have both been concentrated on the LAO/STO system, which we will discuss in the next Section.

3 Compensation mechanisms in the $\text{LaAlO}_3/\text{SrTiO}_3$ system

At an LAO/STO interface both the A and the B cations change across the interface, leading to two distinct types of interfaces: the electron doped n -type interface with a LaO-layer next to a TiO_2 layer and the hole doped p -type interface where a SrO-layer lies next to a AlO_2 -layer (see Fig. 1). The interest in this system was triggered by experimental findings that the n -type interface between these two band insulators is conducting, while the p -type interface was reported to be insulating [3]. The high electron mobility ($10^5 \text{ cm}^2/\text{Vs}$) and carrier density¹ ($\sim 10^{17} \text{ cm}^{-2}$) initially reported for the n -type interface suggested possible applications in oxide based electronic devices and invoked a surge in both theoretical and experimental studies. In later studies, however, it became clear that growth conditions during the PLD process play a decisive role and that the unusually high carrier density is rather related to the formation of oxygen vacancies during the deposition process [11, 35–38]. This *extrinsic* conductivity has a predominantly 3D character [39]. Increasing the oxygen partial pressure during growth or subsequent annealing in an oxygen atmosphere leads to an increase in sheet resistance by several orders of magnitude. In fact the three functional properties observed so far can be related to three different regions of

¹Note that the intrinsic carrier density scale of one-half carrier per interface cell equals to $3 \times 10^{14} \text{ cm}^{-2}$.

oxygen pressure [40]: (3D) conductivity at $p_{\text{O}_2} \sim 10^{-6}$ mbar, superconductivity at $p_{\text{O}_2} \sim 10^{-4}$ mbar [4], while magnetic effects [5] are observed at $p_{\text{O}_2} \sim 10^{-3}$ mbar.

Many of the theoretical studies so far have focused on the origin and type of carriers at the interface leading to conductivity. The formal charge mismatch at the polar interface means that there will be too many (*n*-type interface) or too few (*p*-type interface) electrons to satisfy the formal charges, so there must be potential carriers in the interface regions. As just discussed, the initially measured conductivity is extrinsic in nature. Films grown at “high” oxygen pressures, where the effect of oxygen defects is minimized, are (nearly) insulating at low temperature. The fact that carriers seem to become localized at low temperature is a more challenging result to explain than if they were simply free and conducting. We restrict our discussion to this regime of defect-free heterostructures where the influence of oxygen vacancies can be neglected.

3.1 The *n*-type LaAlO₃/SrTiO₃ interface

In order to model the *n*-type interface most studies have adopted multilayers containing two inversion symmetric *n*-type interfaces to avoid the formation of a net dipole in the the slab with its resulting spurious electric field. From electron counting one expects that the odd number of electrons per interface cell must give a metallic result within LDA. This was confirmed for both *n*-type and *p*-type IFs [41–43]. Gemming and Seifert [41] found the “excess” charge for either *n*- or *p*-type interfaces to be rather strongly localized to within a couple of layers of the interface and that the metallic state can be canceled by adding a background charge. The dielectric properties determined from linear response theory show a strong dependence not only on strain but also on the local interface chemistry. Popovic *et al* [44] investigated more extended superlattices with the *n*-type interface and, also after relaxation, concluded that the interfacial charge extended several layers away from the interface layer. This study noted multi-subband occupation, with some electron remaining localized at the interface while other bands contained more delocalized electrons. This aspect will be discussed in more detail below.

Because the LaO-TiO₂ layers at the *n*-type interface constitute the building block of the Mott insulator LTO, we have considered the role of correlation effects also in this case. Indeed, the resulting compensation mechanism is very similar to the one in LTO/STO superlattices with a charge disproportionation into a charge (CO) and orbitally ordered (OO) state with Ti³⁺ and Ti⁴⁺ ordered in a checkerboard arrangement [42].

The role of lattice relaxations has been investigated considering more isolated interfaces in a LAO_{4.5}/STO_{5.5} superlattice (with $a_{\parallel} = a_{\text{STO}} = 3.91\text{\AA}$) shown in Fig. 6 [45]. The lattice relaxation was performed separately within GGA and GGA+*U*. The main characteristic, common to both, is a strong polarization in the layers close to the interface, predominantly in the STO part of the heterostructure, whereas in the LAO layer next to the IF both cations and anions shift by similar amounts. Analogous to the LTO/STO interface (see previous Section) a strong buckling in the interface TiO₂ layer by 0.17 Å (GGA) and 0.12 Å (GGA+*U*) is found. The precise value of lattice polarization at the interface varies slightly with the separation between the interfaces and the lateral lattice parameter [41, 43, 47].

While the atomic displacements within both approaches show similar trends, they have some-

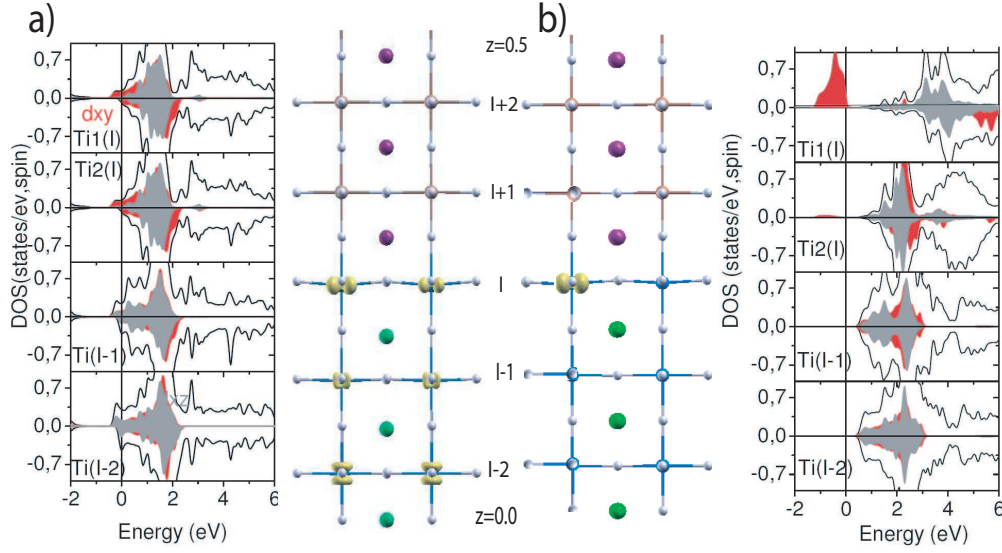


Figure 6: Layer resolved DOS obtained within GGA+ U showing the Ti 3d bands and side views of the LAO_{4.5}/STO_{5.5} superlattice, relaxed within a) GGA and b) GGA+ U . The side views display also the spatial distribution of the occupied 3d-orbital at the Ti-sites. Structural relaxation within GGA+ U leads to two distinct Ti sites at the interface: Ti³⁺ and Ti⁴⁺, while the GGA-geometry results in two identical Ti ions in the IF layer and finite occupation of Ti 3d states in deeper layers [45].

what higher absolute values within GGA. Still, subtle differences (e.g. a small lateral shift of the oxygens away from the Ti³⁺-ions) result in a completely different electronic behavior for the GGA+ U and the GGA geometries. For the former the charge and orbitally ordered state is further stabilized and the charge is strongly confined to the interface layer (see Fig. 6b) [45]. Zhong and Kelly [49] have addressed further symmetry lowering due to rotations/tilting of the octahedra that narrow the Ti 3d band and found that these are energetically favorable even within LDA. Including correlation effects with the LDA+ U method, they obtain a similar charge disproportionation, orbital reconstruction and AFM coupling of the spins in the strong interaction limit.

In contrast, for the GGA geometry the excess charge is redistributed over the STO part of the LAO_{4.5}/STO_{5.5} heterostructure (see Fig. 6a). While CO is nearly suppressed, there is a residual orbital ordering with an occupation of the d_{xy} orbital of Ti in the interface layer, while in more distant layers the d_{xz} , d_{yz} orbitals are occupied. Analyzing the band structure, Popovic, Satpathy, and Martin found [44] that the latter bands have a very small dispersion and lie a bit higher than the bottom of the dispersive d_{xy} band (at $\vec{k}=0$). The authors proposed that only the latter contributes to the transport properties of the system. This gives a possible explanation that the measured carrier densities are one order of magnitude lower than the expected $3.5 \times 10^{14} \text{ cm}^{-2}$.

Still the CO/OO solution corresponds to the ground state (favored by 0.45 eV). For the samples grown at high pressures the sheet resistance is seven orders of magnitude higher and shows an upturn at low temperatures which is consistent with CO or polaronic behavior. Electron delocalization at higher temperatures may lead to the behavior described in Fig. 6a.

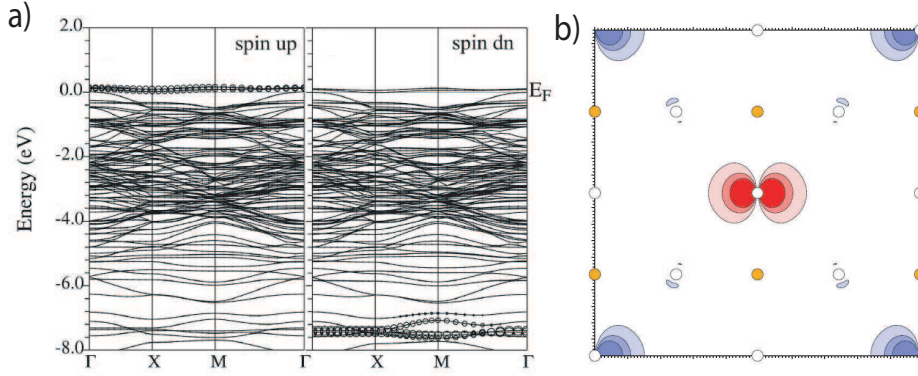


Figure 7: $O\pi$ -holes at the p -type LAO/STO interface in a $p(2 \times 2)$ -cell within GGA+ U : (a) band structure, showing the strongly localized upper Hubbard band at the Fermi level and (b) spatial distribution of the antiferromagnetically coupled holes in the AlO_2 -IF [42].

Several studies have addressed the band offsets at the n -type LAO/STO interface. Depending on the applied method: the reference potential method [63], the $O1s$ core levels [44,45], the local density of states or the macroscopic averaging technique [46] there are notable differences (e.g. the calculated valence band offset varies between 0.1-0.9eV). In general, the STO band gap lies completely within the LAO gap, implying that charge carriers of either sign (electrons or holes) will go into the STO side of the interface.

To determine the confinement of the electron gas at the interface, Janicka *et al.* [50] have considered superlattices containing 23 MLs of STO and 1-5 layers of LAO. These GGA calculations determine a relaxation length of ~ 1 nm. Using the $O2s$ states to probe the band bending and the calculated band gap of bulk STO, these authors conclude that electrons 5 ML away from the interface occupy a classically forbidden region, forming so called metal-induced gap states.

3.2 The p -type $LaAlO_3/SrTiO_3$ Interface

The p -type LAO/STO interface which was found to be insulating despite the charge mismatch has been less studied. The initial reports of Ohtomo and Hwang [3] suggested that the interface is structurally perfect *i.e.* without appreciable defects. For such an interface LDA/GGA gives a metallic solution with the Fermi level crossing the $O2p$ band [42,43]. Since the occupied Sr and Al states lie well below the Fermi level, the only possibility to obtain insulating behavior (assuming a defect-free heterostructure) is to consider correlation effects at the $O2p$ orbitals. Applying a Hubbard repulsion U on the $O2p$ states with a single hole present, amounts to a lifting of the orbital degeneracy of the $O2p$ -band. Considering the charges and geometry of Al and O in the AlO_2 layers, it is likely that the holes will go into π -bonds. Indeed the GGA+ U treatment results in a localization of a significant part of the hole on a central oxygen with some contribution of the nearest neighbors, while the next nearest neighbors are not affected (see Fig. 7b) and have a fully occupied $O2p$ band. The holes are spin-polarized and the degree of localization of charge is enhanced for antiferromagnetic coupling. However, as shown in Fig. 7a, the upper Hubbard band is pinned at the Fermi level with some admixing of O in the next SrO layer. These calculations [42] were performed for superlattices with ideal positions of the atoms

where the two inversion symmetric interfaces are rather close. Including lattice relaxations and a better separation between the interfaces is likely to lead to an insulating polaronic solution.

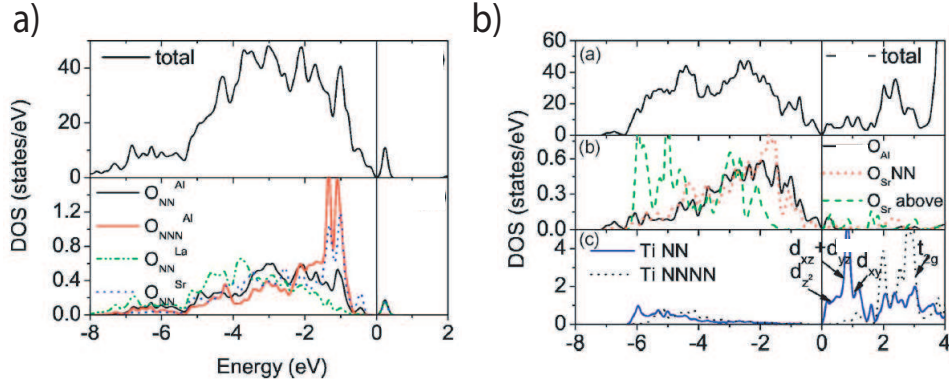


Figure 8: DOS of the p -type LAO/STO IF with an oxygen vacancy in the a) AlO_2 -layer and b) SrO-layer; In a) the unoccupied states above the Fermi level have O $2p$ character and are localized at the neighboring oxygen ions around the vacancy, while in b) they are mainly due to Ti $3d$ bands of the underlying TiO_2 layer. [42]

In later experiments [11] it became clear that oxygen vacancies play a significant role at the p -type interface. We have considered also this more obvious possibility and find that indeed the Fermi level lies in a dip of the DOS both for a vacancy in the AlO_2 and the SrO-layer [42]. However, states are observed immediately above the Fermi level and these have different character for both cases. In the former (Fig. 8a) they result from the neighboring oxygens around the vacancy, while in the latter (Fig. 8b) they are $3d$ states of the Ti ion whose apex oxygen is missing. In both cases the vacancies are likely to lead to F-centers.

Park *et al.* [43] have also addressed the electronic behavior at the p -type as a function of the oxygen vacancy concentration, finding that a system with 25% vacancies in the SrO layer is metallic, while 50% results in a small band gap. We note that the concentration of oxygen vacancies is rather high, but consistent with the 32% estimated from experiment [11].

3.3 Thin LAO Films on a STO(001) substrate

Recent experiments on thin LAO films deposited on an STO(001) substrate revealed a significant thickness dependence of the transport properties [51]: The system switches from insulating to conducting behaviour between 3 and 4 monolayers (MLs). Moreover it was shown that metallic behavior can be induced by an external bias even below the critical thickness of 4 MLs and that conducting and insulating regions can be “written” by an atomic force microscope tip [52]. At a first glance these results do not fit in the picture obtained from the DFT calculations for extended LAO/STO superlattices discussed in Section 3.1. In the latter case the compensation mechanism at the n -type interface is rather local, involving partial occupation of the Ti $3d$ band independent of the thickness of the LAO or STO layer.

In order to explore the effect of the surface on the interfacial properties we have performed DFT calculations within GGA for 1-5 MLs of LAO on a STO(001) substrate. These are modeled

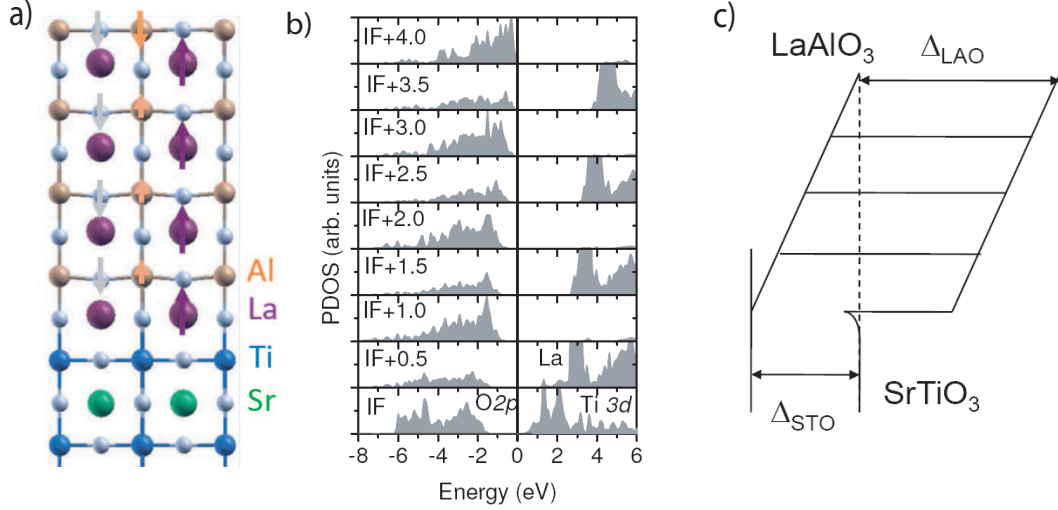


Figure 9: a) Side view of the relaxed structure of 4 MLs LAO/STO(001) showing a strong polar distortion of the LAO film dominated by a 0.2-0.3 Å outward relaxation of La^{3+} (purple atoms) and additional buckling in the subsurface AlO_2 layers; b) layer resolved density of states of 4 ML LAO/STO(001) with relaxed positions of the cations. The strong lattice polarization allows the system to remain insulating (here $E_g = 0.4\text{eV}$) until a crossover to an electronic reconstruction takes place at around 5 MLs of LAO/STO(001) [53]. c) schematic figure of the band bending in LAO/STO(001).

in the supercell geometry with two inversion symmetric surfaces on both sides of the slab to avoid spurious electric fields. The surfaces are separated from their periodic images by a vacuum region of $\sim 10 \text{ \AA}$. In the following we will discuss the role of the lattice relaxations and their implications for the electronic properties.

3.3.1 Ionic screening of the electric field

As discussed in the previous Sections, in the LTO/STO and LAO/STO superlattices the ferroelectric distortion is most pronounced in the SrTiO_3 part of the system with a significant buckling of the interface TiO_2 layer. In contrast, for the thin films the strongest ionic displacements are observed in the LaAlO_3 film. In all cases the surface AlO_2 layer relaxes inward with similar values for oxygen and Al, while the subsurface layers show a strong and uniform lattice polarization, dominated by an outward relaxation of La of 0.2-0.3 Å and buckling in the AlO_2 layers. The relaxation pattern for a 4 ML film is shown in Fig. 9a. Using the formal ionic charges we can make a rough estimate of the dipole shift resulting from the polar distortion. We note that these dipole moments include only the ionic part and no contributions due to electron cloud polarization. Indeed, the obtained trend is surprisingly uniform with a layer-resolved dipole moment of ~ 0.55 and $\sim 0.75 e\text{\AA}$ in the AlO_2 and LaO layers, respectively and a vanishing dipole moment in the surface AlO_2 and interface TiO_2 layers. Adding these contributions for a 4 ML LAO film on $\text{STO}(001)$ results in a total ionic dipole of $4.8 e\text{\AA}$, which is 60 % and of opposite sign to the bare dipole of the polar LAO film. Thus, the lattice relaxation plays an important role in reducing the electric field generated by the polar LAO-film.

3.3.2 Finite Size Effects: Thickness dependent Insulator-to-Metal Transition

The lattice polarization in the LAO film has also a significant impact on the electronic properties: While all systems with bulk positions of the ions show metallic behavior, below the critical thickness the strong lattice polarization allows the system to remain insulating preserving the bulk charge states of the ions. The band gap that opens up upon relaxation of the structure amounts to 1.7 eV for 1 ML LAO/STO(001) but decreases steadily (by ~ 0.4 eV/ML with each added layer). Finally, at a LAO-film thickness of around 5 ML the band gap collapses and a crossover to an electronic reconstruction takes place. In order to gain insight in the underlying mechanisms we have plotted in Fig. 9b the layer-resolved density of states for 4 ML LAO/STO(001). The rigid upward shift of the O2p bands as they approach the surface reflects the strong electric field of the LAO film. In this system, which still has a band gap of 0.4 eV, the valence band maximum is determined by the top of the O2p band in the surface layer, while the conduction band minimum is at the bottom of the Ti 3d states. The electronic reconstruction that emerges beyond 5 MLs of LAO is due to the overlap of these two bands resulting in a finite occupation of the Ti 3d band and some holes in the surface O 2p band. As shown in the schematic picture (Fig. 9c) the potential buildup due to the polar LAO layer causes charge transfer into the narrow band gap STO. This mechanism is intriguing, because it suggests two types of carriers that are spatially separated - holes localized in the surface layer and electrons in the interface layer. Further analysis of the band structure reveals that the band overlap is also indirect in reciprocal space with the bottom of the Ti d_{xy} band at the Γ -point and the top of the valence O 2p band being at the M -point. Recent x-ray adsorption spectroscopy measurements have confirmed that the d_{xy} orbital is the lowest available state for conduction electrons [54]. We note however that the total carrier density just beyond the critical thickness is an order of magnitude lower than the expected $3.5 \times 10^{14} \text{ cm}^{-2}$ as also found from hard x-ray angle resolved photoelectron spectroscopy [55], but increases continuously with each added layer [56, 57].

The thickness dependent insulator-to-metal transition was also addressed by Ishibashi and Terakura [58] exploiting the recently proposed Coulomb cutoff technique [59] for eliminating any direct Coulomb interaction based coupling between supercells and their periodic images. In their calculations the transition to metallic behavior was obtained already at four overlayers of LAO (the same as experiment) instead of five as in our calculations; this may reflect a ~ 0.2 eV difference in potential rise across the LAO slab, part of which may easily be due to small differences in the atomic relaxations. It is worth mentioning that depending on setup (see discussion in next Section), the choice of exchange correlation potential (LDA vs. GGA), differences in the lateral lattice constant and the resulting atomic relaxations, the calculated critical thickness for the insulator-to-metal transition varies from 3 to 6MLs [52, 53, 58, 60–62]. The predicted critical thickness is likely to be affected also by the band gap underestimation typical for LDA/GGA.

Due to the small occupation of the Ti 3d band after electronic reconstruction sets in, the properties are less influenced by correlation effects compared to the isolated interface. Lee and Demkov [63] have studied 3 and 5 ML LAO on STO(001) using LDA+ U with $U_{eff} = 8.5$ eV. They find in the latter case a charge transfer exclusively in a split-off Ti state of d_{xy} character in the interface layer. The pseudo Jahn-Teller effect is discussed as indication of a strong electron-phonon coupling and a possible origin of superconductivity. Breitschaft *et al.* [64] argue that

the shape of scanning tunneling spectroscopy curves is better described using $U = 2$ eV and that the system shows a two-dimensional electron liquid behavior.

An interesting question is whether holes contribute to the conductivity and whether they can survive in the surface layer or whether other mechanisms - *e.g.* oxygen vacancy formation - can eliminate them. Cen *et al.* [52] have addressed surface vacancies in a 3ML LAO/STO(001) film, showing that when the surface AlO_2 layer is compensated by vacancies, the interface layer becomes metallic with a finite occupation of the Ti $3d$ band. Moreover, the compensation of the surface layer through oxygen vacancies removes also the upward shifts of the oxygen $2p$ bands. Willmott *et al.* addressed the possibility of interdiffusion at the interface by including a LTO layer at the n -type interface. [65] This leads also to a metallic state with an enhanced occupation of the Ti $3d$ band at the interface. These results show that the properties at the interface can be affected in important ways by the precise termination, stoichiometry and chemical composition of the surface and interface, thus opening paths to manipulate the electronic behavior of the system.

Thin LAO films with a p -type interface: Ishibashi and Terakura [58] found that five layers of LAO over a p -type IF remain insulating (recall that five layers over the n -type IF is metallic due to band overlap). Thus there is definitely asymmetry for the two types of IFs in this system. They also found that if no atomic relaxation was done (ideal geometries were used), then *every case* was metallic; the electronic system and its screening alone cannot sustain the formal ionic charges in such heterostructures. The analysis of electronic screening in this system, which reveals local response that is virtually impossible to obtain by experiment, initiates an important area of study that needs to be continued and extended to gain fundamental understanding of these heterostructures.

3.4 Superlattices with coupled interfaces

As we have seen in the previous Section, deposition of polar LAO films on nonpolar STO(001) results at some point – around four layers in the LAO/STO system – in an electronic reconstruction, which from theoretical studies so far involves a simultaneous electronic reconstruction at the interface and the surface. Experimental probes have not yet established this scenario with certainty.

There is a (somewhat) larger scale version of this issue that merits attention: One can consider the repeated growth of alternating n - and p -type interfaces [35]. The corresponding supercell has no inversion or mirror symmetry; it is polar and has a dipole. In such a case the *polarization catastrophe* is again an issue, but with an increased distance scale: the repeat distance is the supercell dimension rather than the unit cell dimension. Calculations of such LAO/STO superlattices containing alternating p and n interfaces have been reported, and they show also thickness dependent phenomena: while $\text{LAO}_4/\text{STO}_4$ superlattices were insulating after structural relaxation [41,43], $\text{LAO}_n/\text{STO}_n$ beyond $n = 8$ were conducting [66]. Analogous to the thin films, the reconstruction involves electron carriers at the n -type interface and hole carriers at the p -type interface and transfer between them. These calculations on asymmetric systems/cells raise some conceptual questions about the physical behavior, and also the simulation.

The polar nature of oxides (LAO and LTO in the cases discussed here) led early on to questions about how the experimental heterostructures should be simulated in calculations. To model *isolated* IFs it has been the practice to use (as mentioned above) symmetric supercells, *i.e.* two opposing n -type IFs in the supercell. Then there is, by symmetry, no dipole in the cell and a periodic, supercell treatment is appropriate. In the study of finite overlayers computational practices have varied. Again, the use of symmetric supercells is straightforward; each half of the cell may have a dipole as determined by the geometry and the (self-consistent) response to electric fields while the opposing dipoles leave a slab that can be treated in a periodic supercell.

This approach makes the cells twice as large and enhances significantly ($\sim 2^3=8$) the computational cost, which is an important practical issue. Finite slabs [60] or repeated opposing n - and p -type IFs without inversion symmetry have also been used to model such situations. In such cases the imposition of periodicity on the potential results in an internal electric field in the STO side of the slab that is comparable in magnitude to that in LAO and opposite in sign [66]. Son *et al.* have also modeled asymmetric slabs, [56] employing a “dipole correction” that has been devised [67,68] for finite slabs to correct for the imposed periodicity. The superlattices containing exclusively n -type interfaces and those with alternating n and p -interfaces correspond to two distinct physical situations. Still the question remains as to what extent these can be realized experimentally taking into account possible asymmetry due to roughness and/or defects. The comparison of various methods and comparison with experiment needs further consideration to obtain a reliable physical picture.

4 Modeling Oxide Interfaces: Summary and Perspectives for the Future

In summary, first principles calculations suggest that at an interface between a polar and a nonpolar material different compensation mechanisms may be at work, depending on some rather detailed features. For infinitely extended superlattices of the Mott insulator LTO and the band insulator STO and in superlattices containing n -type LAO/STO interfaces, the ground state is a charge and orbitally ordered Ti^{3+} , Ti^{4+} -layer with an occupied d_{xy} orbital at the Ti^{3+} sites. Structural relaxation within GGA+ U including a larger lateral periodicity leads to a further confinement of the excess electron at the interface. On the other hand, relaxation within GGA within a $p(1 \times 1)$ lateral unit cell leads to a delocalization and redistribution of the charge throughout the STO part of the superlattice (overscreening), significantly increasing the confinement length of the electron gas. This scenario is likely to happen at higher temperatures when electron hopping is possible.

In contrast, a completely different situation arises in thin LAO films on a STO(001) substrate. Here a strong and uniform lattice polarization leads to an insulating behavior for a few LAO layers. However, the potential buildup with each added LAO layer invokes a reduction of the band gap and finally an insulator-to-metal transition and an electronic reconstruction but with a much lower carrier density than expected from formal electron counting. We note that the finite size effects are not restricted to LAO films on STO but has also been reported experimentally for *e.g.* LVO/STO(001) [70, 71].

Recent measurements of Hwang et al. [69] show that thin LAO films (5-10 MLs) exhibit metallic temperature dependence, while thicker films (up to 25 MLs) show an upturn of the sheet resistance at low temperatures. These findings seem to support the DFT results suggesting a coupling of surface and interface in the thinner films and an interface confined compensation mechanism at more isolated interfaces possibly connected with localization and charge ordering.

The electronic behavior in thin LAO is likely to be very sensitive to defects and adsorbates. DFT calculations [52] give indications that oxygen vacancies can cancel the potential buildup observed in shifts of the O $2p$ bands in the non-defective films. Moreover, adsorbates or a nonpolar oxide layer [72] can modify significantly the properties of the system. Thus, finite size effects (film thickness) together with a number of further parameters (e.g. defects, adsorbates, an oxide overlayer or an external bias) can be used to tailor the interfacial properties and need further attention in future.

In this review we have concentrated on systems where the charge mismatch is due to a d^1-d^0 occupation across the interface, and we have seen that electronic correlations can lead to novel compensation mechanisms unanticipated from semiconductor heterostructures. These processes open the possibility of realizing novel charge, orbital and magnetically ordered states. A further degree of complexity arises when both transition metal ions across the interface contain d electrons and e.g. the valence mismatch across the interface is enhanced. The competition between these ions to compensate the charge mismatch at the interface may result in complex orbital physics and promises to lead to a plethora of new electronic phases. Obtaining a fundamental understanding of the phenomena that arise at polar transition metal oxide interfaces could lead to novel concepts for oxide-based electronics devices.

While we have considered here oxide heterostructures with perovskite structure, analogous effects can arise also in other systems. An example for a polar interface where the constituents have a corundum derived structure is the hematite-ilmenite system. A stacking of $2\text{Fe}^{3+}/3\text{O}^{2-}$ layers in hematite and $2\text{Fe}^{2+}/3\text{O}^{2-}/\text{Ti}^{4+}$ in ilmenite results in a polar discontinuity across the Fe_2O_3 - FeTiO_3 -interface. DFT calculations including an on-site Coulomb correction [73,74] give theoretical evidence for the lamellar magnetism hypothesis [75]: a mixed Fe^{2+} , Fe^{3+} contact layer is formed to accommodate the charge mismatch. The uncompensated moments in the interface layer give rise to ferrimagnetism at the interface between the canted antiferromagnet Fe_2O_3 and the room-temperature paramagnet FeTiO_3 . This interface induced magnetism makes this system interesting e.g. for spintronics applications.

Unanticipated phenomena can arise also in heterostructures without a polar discontinuity. For example the confinement of the electrons in a heterostructure and lattice strain have been suggested as a means to control the orbital occupation [76]. So far much of the focus has been on “conducting versus insulating” behavior. However, a recent discovery has illustrated that such a question does not cover all possibilities. Calculations on VO_2/TiO_2 heterostructures, non-polar and seemingly having only the d^1-d^0 aspect to arouse interest, display a previously unknown electronic structure, consisting of point Fermi surfaces as does graphene, but possessing a highly anisotropic behavior: in the 2D plane the electrons have nearly free character, but in the perpendicular direction the dispersion is massless, like the dispersion (in both directions) in graphene. These “semi-Dirac” points so far exist only in two-dimensional oxide heterostructures, and their

study may rival the activity in graphene. The low energy behavior is distinct [78] not only from graphene but also from another point Fermi surface system, the zero-gap semiconductor. The very different physical structure compared to graphene (robust heterostructure versus a flexible monatomic sheet) will likely lead to very different applications. Fundamental understanding of both polar effects, and the characteristics of dispersion, should be important aspects of future studies.

Finally, another complexity should be noted. In the studies of polar interfaces, correlation effects arising from strong intra-atomic interaction have been shown to lead to very different behavior than arises if such effects are neglected. However, so far such interactions have been treated (nearly always) in a static, mean-field manner. It is one of the fundamental precepts of strongly correlated systems that upon doping (which is very likely to occur at some level, perhaps inadvertently) dynamical processes come into play and determine many of the properties of doped correlated insulators. Including such dynamical effects, and especially doing so self-consistently, will be an important part of the next generation of theoretical modeling of oxide heterostructures.

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