



### **Oxidic Surfaces and interfaces**

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The ability to predict material properties is a fundamental requirement for scientific and technological advancement. Thereby computational material science is an important powerful tool being used in the development of advanced materials and their device applications. The properties of these materials, such as electronic and magnetic behavior, can be changed in a controlled way by varying external parameters, such as the pressure, their chemical composition, the valency or the temperature. In this manner one can learn how to improve mechanical, optical and electronic properties of known materials, or one can predict properties of new materials, which are not found in nature but are designed and synthesized in the laboratory. This is a main research field of our group in the Theory department at the Max Planck Institute of Microstructure Physics in Halle.

One of our most important research fields is the computational material design of oxidic materials. This activity is mainly accomplished within the Collaborative Research Center 762 „Functionality of oxidic interfaces“, which is a joint initiative of the universities Halle-Wittenberg, Leipzig and the Max Planck Institute of Microstructure Physics. First-principles design of oxides is one of the most ambitious challenges in modern computational physics. The electronic and magnetic properties of these materials are substantially affected by strongly localized electrons, complex crystalline structures, and mixed valencies of magnetic ions. To describe these specific features of oxides we develop ab-initio concepts that are put in state-of-the-art computer codes. Using efficient numerical algorithms and modern supercomputers we can simulate experiments and study properties of realistic systems.

More specifically, our research on oxides is currently focused on

- (I) Crystalline structures of complex oxidic systems
- (II) Magneto-electric coupling in two-component multiferroics.

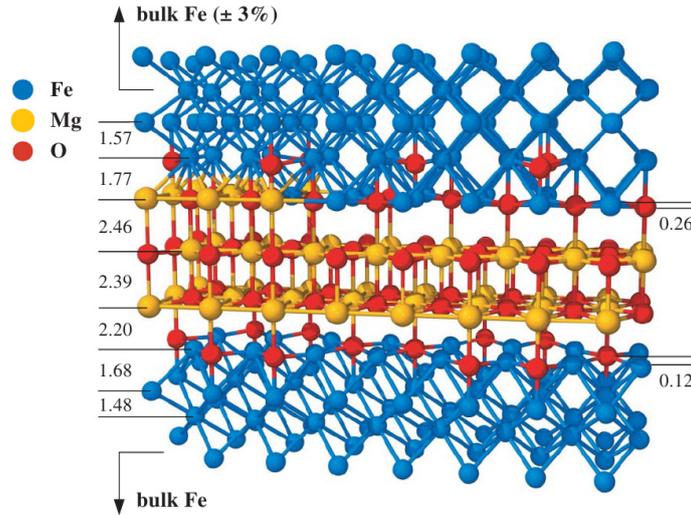
A detailed description of these systems often involves a large number of degrees of freedom, especially when periodic surfaces or interfaces with large unit cells result from surface instabilities or misfits at interfaces. For our first-principles simulations of oxides we use a so called multi-code approach. The real structure of bulk materials and layered systems containing vacancies, impurities or more complicated defect complexes are investigated by means of the Vienna Ab Initio Simulation Package (VASP) [1]. The electronic and magnetic properties in detail are studied with an ab initio multiple scattering code based on the KKR (Korringa Kohn Rostoker) Green's function method [2]. The Green function method allows efficiently describe disorder using the coherent potential approximation [3]. Correlation effects in systems with strongly localized electrons are included via self-interaction corrections [4]. Information from the ab initio calculations are used to investigate the temperature dependence of the magnetic effects by means of Monte Carlo methods. The theoretical calculations are performed in strong interaction with the experimental investigations.

### **Crystalline structures of complex oxidic systems**

Surfaces and interfaces are known to affect strongly electronic, magnetic and transport properties of solids. Broken symmetry, reduced dimensionality, atomic relaxations and intermixing of atoms at their boundaries can substantially modify the electronic structure of the constituent materials. Thereby, oxidic surfaces and interfaces exhibit more specific features arising from the complex electronic structures of oxides, strong reactivity and the richness of stable or metastable configurations that oxide surfaces and interfaces may display depending upon their environment.

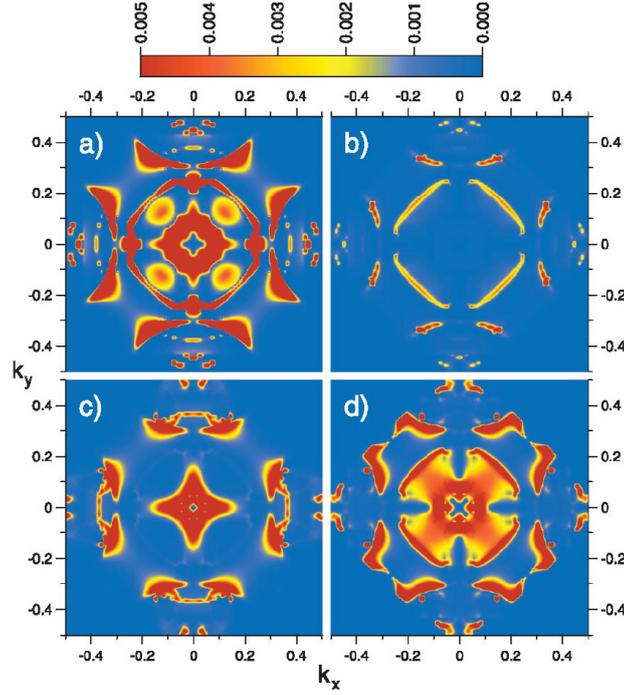
Our particular research interests include interfaces between oxides and metals, which exhibit important functional behavior. A prototype of such interfaces is the Fe/MgO/Fe(001) magnetic tunnel junction (MTJ), which was intensively studied by our group in a close cooperation with the Experimental Department I of our institute. The experimentalists were able to synthesize Fe/MgO/Fe(001) samples and investigate their structural properties using a surface x-ray diffraction method [5,6]. One of the main achievements of this study is the evidence for oxidation of the first iron layer at the Fe/MgO interface. Thereby, it was found that at usual conditions, the Fe electrode on top

of the MgO surface was strongly disordered (see Fig. 1). Only with oxygen-assisted deposition, it was possible to achieve a coherent growth of Fe electrodes, leading to symmetric MTJ structure characterized by FeO layers at both Fe/MgO interfaces. In our theoretical study we investigated impact of various growth conditions and the role of the interfacial FeO layer on the transport properties in Fe/MgO/Fe(001) magnetic tunnel junction.



**Fig. 1.**

Using a multiple scattering Green function method, we evaluated the ballistic conduction for parallel and anti-parallel alignments of magnetic electrodes within the Landauer-Büttiker theory. The most striking result of our simulations is that the sign of the tunnel magnetoresistance (TMR) depends on the symmetry of the structure: the symmetric structure results in a large positive TMR, which increases with MgO thickness, while the TMR is negative for the asymmetric structures. The difference in behavior is explained by interface resonance states induced by the FeO layer, which in the case of a symmetric MTJ are present on both sides of the spacer. This leads to a strong enhancement of the conductance through these states (“hot spots”). Absence of one FeO layer as in the asymmetric case reduces the density of states of the interface resonances and consequently results in less efficient tunneling. This effect can be clearly seen in Fig. 2, where  $k$ -resolved transmissions in the full two-dimensional Brillouin zone (2BZ) are presented for Fe/MgO4/Fe(001) MTJ .



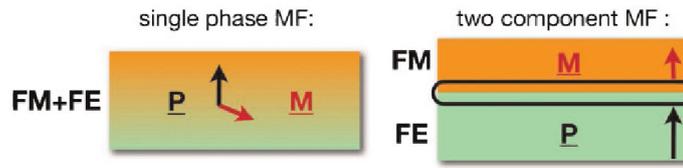
**Fig. 2**

The conductance of the tunnel junction is proportional to the 2BZ integral of the transmission. With the ideal symmetric interfaces (upper panels) the conductance in the parallel (P) configuration (panel a) is strongly enhanced, and in the antiparallel (AP) configuration (panel b) it is reduced, explaining thereby the huge TMR ratio. In the case of asymmetric interfaces, the conductance in the P configuration decreases dramatically (panel c), while the conductance in the AP case (panel d) increases, so leading to a negative TMR ratio. Thus, in the parallel configuration a huge magnetoresistance (MR) occurs if interface resonances are present at both interfaces at the same energy and at the same wave vector. Hence, a mismatch in either energy or wave vector destroys this “handshake” and can reduce the MR considerably. Therefore, the MR typically drops when applying a bias voltage or upon structural disorder, the latter introducing diffusive scattering.

### **Magneto-electric coupling in two-component multiferroics**

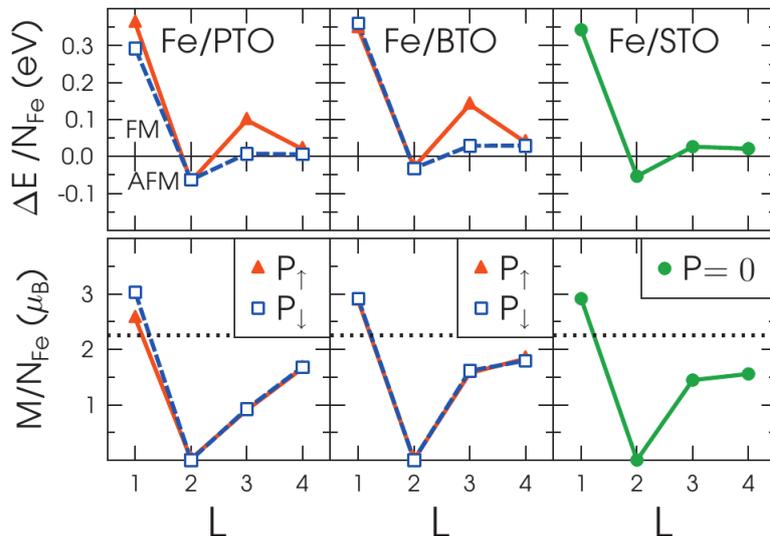
The coexistence of magnetism and ferroelectricity in the same crystalline phase of a so-called multiferroic (MF) material involves the opportunity of magnetoelectric (ME) coupling. ME coupling, in principle, offers magnetization switching by an electric field or polarization switching by a magnetic field. Since this phenomenon allows to store

information in nanometer-sized memories with four logic states, the issues of MFs are of prime interest. In the single-phase MFs, however, the electric polarization and magnetization interact weakly with each other while ferromagnetism disappears far below room temperature. A more robust scenario of magnetoelectricity might occur in artificial MFs composed of ferromagnetic (FM) thin films which are grown epitaxially on a ferroelectric substrate (Fig.3). In the study of composite MFs, the results of ab initio calculations have shown an extremely promising direction for the next years. Although these calculations go ahead of experiment they explore the trends and basic physics of ME.



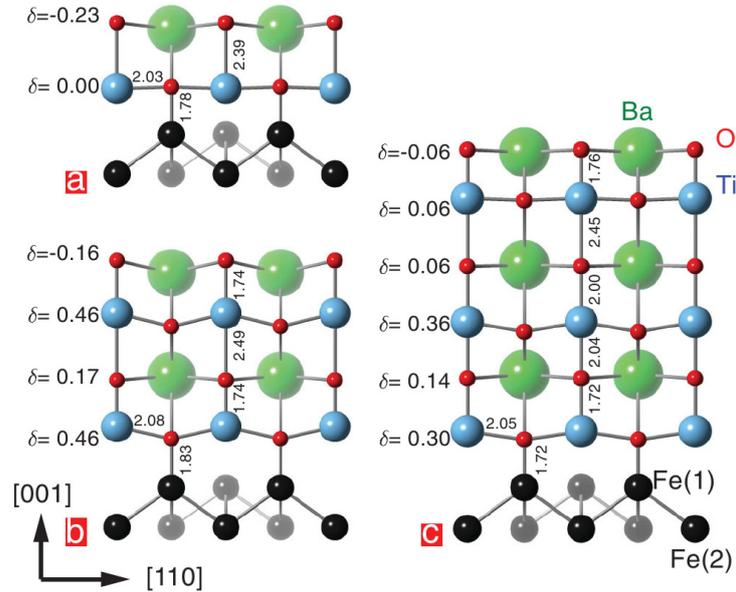
**Fig. 3**

On the basis of first-principles calculations we predicted that epitaxial ultrathin Fe films deposited on TiO<sub>2</sub>-terminated (001) surface of ATiO<sub>3</sub> perovskites (A = Pb, Ba, Sr) exhibit an unexpected change in their magnetic structure with increasing Fe-film thickness (Fig. 4) [7,8]. The magnetic order (upper panels in Fig.4) changes from strongly FM for the single-monolayer Fe system to ferrimagnetic with almost vanishing magnetization upon deposition of a second Fe layer (see magnetic moments in the low panels in Fig 4). FM order is restored for thicker Fe films [7]. This effect can be understood in terms of hybridization of electronic states and structural relaxation.



**Fig. 4**

In a close cooperation with the Experimental Department I we investigated magneto-electric coupling in ultra-thin BaTiO<sub>3</sub> films grown on Fe(001) [9]. Based on the quantitative atomic positions we have shown that the BaTiO<sub>3</sub>/Fe(001) heterojunction is multiferroic in nature. We found a significant multiferroic effect as a result of the substantial polarizations as measured by the relative Ti-O displacements in the  $\delta \approx 0.3\text{--}0.4$  Å range. The multiferroic interface properties were investigated by calculating the dependence of the total energy change ( $\Delta E$ ) and the magnetic moments at the interface for different polarizations ( $P\uparrow$ ,  $P\downarrow$ ) as outlined in Fig. 6. The inset shows  $\Delta E$  for  $\delta\text{Ti-O}=0.30$  Å,  $0.00$  Å and  $-0.30$  Å, corresponding to a simulated switching from  $P\uparrow$  via  $P=0$  to  $P\downarrow$  based on the experimentally derived atomic coordinates (see Fig. 5). Displacements  $\delta$  for  $P\uparrow$  and  $P\downarrow$  are shown for all atoms in Fig. 6 as blue triangles and squares, respectively. A change in polarization from  $P\uparrow$  to  $P\downarrow$  goes in parallel with an energy gain of  $\Delta E \approx 2$  eV via a barrier indicating the possibility of switching the polarization permanently. The induced magnetic moment in the first layer Ti atom increases from  $m_{\text{Ti}}=0.03$   $\mu\text{B}$  to  $m_{\text{Ti}}=-0.35$   $\mu\text{B}$ , in the latter case corresponding to antiferromagnetic coupling. The results open a pathway to the experimental realization of magnetoelectric coupling via multiferroic interfaces, a new tool to control magnetism by electric fields.



**Fig. 5**

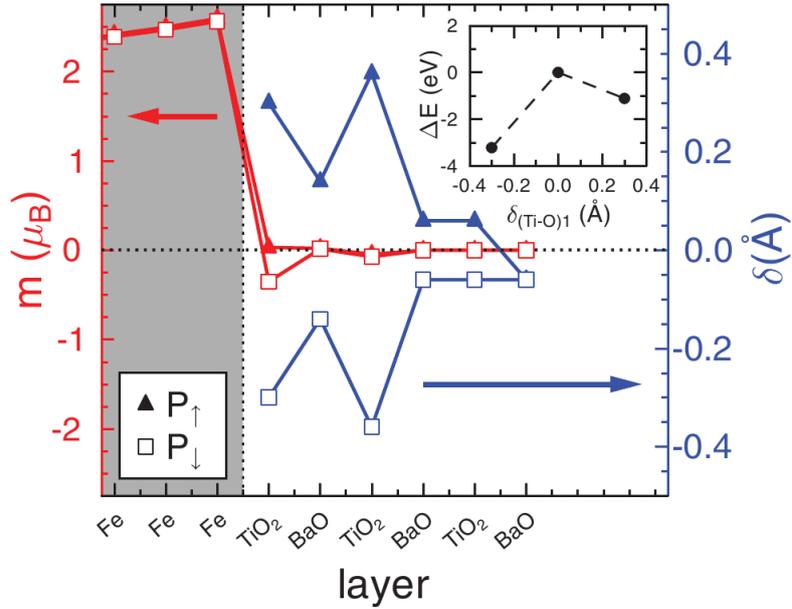


Fig. 6

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