MM 59: Computational Materials Modelling IX - Ferroelectrics

Time: Thursday 15:45–17:45   Location: IFW D

MM 59.1   Thu 15:45   IFW D

Ferroelastic Switching of Doped Zirconia – First-Principles Insights — •CHRISTIAN CARBOGNO[1,2], CARLOS G. LEVI[1], CHRIS G. VAN DE WALLE[1], and MATTHIAS SCHEFFLER[1,2] — [1]Materials Department, University of California, Santa Barbara, USA — [2]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

ZrO_2 based ceramics play a pivotal role for thermal barrier coatings in gas and propulsion turbines. The phase stability required for these applications is typically achieved by Y-doping, which however also results in an undesirable degradation of toughness. Recently, high phase stability and toughness has been achieved by co-doping such Y-stabilized ZrO_2 (YSZ) with Ti (TiYSZ) [1]. We use density-functional theory to investigate these effects by inspecting the underlying structural dynamics. Our calculations reveal that the minimum-energy path (MEP) for the tetragonal-to-cubic phase transformation differs significantly from the path discussed in literature [2]. We show that the correct MEP involves *ferroelastic switches*, i.e., the realignment of the tetragonality along a different cartesian direction. We inspect how (co-)dopants affect these *ferroelastic switches*, which are typically considered to be the primary toughening mechanism in these compounds [1]. Hence, our calculations shed light on the atomistic mechanisms that determine the dynamics and the high-temperature properties of YSZ and TiYSZ.

[1] T. A. Schaedler, O. Fabrichnaya, and C. G. Levi, *J. Eur. Ceram. Soc.* **28**, 2509 (2008).
[2] S. Fabris, A. T. Paxton, and M. W. Finnis, *Acta Materialia* **50**, 5171 (2002).

MM 59.2   Thu 16:00   IFW D

Microscopic description of $BaTiO_3$ and related materials near the ferroelectric phase transition — •GIOVANNI PIZZI[1], ANDREA CEPELLOTTI[1], SAMED HALILOV[2], BORIS KOZINSKY[3], MARCO FORNARI[4], and NICOLA MARZARI[1] — [1]Theory and Simulation of Materials, EPFL (CH) — [2]Department of Materials Science and Engineering, MIT (USA) — [3]Robert Bosch LCC Research and Technology Center, Cambridge (USA) — [4]Dept. of Physics, Central Michigan University (USA)

Ferroelectric materials like $BaTiO_3$ have been used for decades in a broad range of technological applications (capacitors, gate dielectrics, IR detectors, holographic memories, . . .). However, there is still significant debate in the literature concerning the microscopic behavior of these materials, in particular near the paraelectric–ferroelectric phase transition. In $BaTiO_3$, Ti displacements with respect to the center of the oxygen cage create local dipole moments that are at the origin of the finite polarization in the ferroelectric states. However, these perovskites display a complex energy landscape with multiple local minima. As a result, local finite dipoles exist even in the paraelectric cubic phase, contrary to what is often assumed in simulations. In order to clarify the microscopic behavior of these materials, we perform total-energy calculations to systematically and automatically explore their energy landscape, together with ab-initio molecular dynamics calculations to assess the driving mechanisms for the formation of the different phases and to understand the differences among different structurally similar materials.

MM 59.3   Thu 16:15   IFW D

Polarization rotation at the ferroelectric domain walls of $PbTiO_3$ and PZT — •ANAND CHANDRASEKARAN[1,2], DRAGAN DAMJANOVIC[2], NAVA SETTER[2], and NICOLA MARZARI[1] — [1]Theory and Simulation of Materials, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland — [2]Ceramics Laboratory, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

Polarization rotation and domain wall mobility are two key factors driving the development of state-of-the-art piezoelectric and ferroelectric devices. Ferroelectric domain walls in $PbTiO_3$ (PT) are thought to be predominantly of the 'Ising type', where the polarization does not rotate but diminishes in magnitude close to the domain wall. However, our first-principles calculations show how tensile strains drastically increase polarization rotation in the vicinity of domain walls, that thus acquire both Néel and Bloch character. Large-scale calculations on PT and ordered lead zirconate titanate (PZT) show that the Bloch and Néel components of the polarization are long ranged, while the Ising component is short ranged and decays over 2-3 unit cells. Our analysis points to the possibility of tuning domain wall thickness through strain engineering. Such rotations enhance domain mobility through a reduction in the barrier energy for polarization reversal. Interestingly, the addition of Zr to PT delivers the required tensile strains, thus leading to the enhanced properties observed at the morphotropic phase boundary in PZT.

15 min break

MM 59.4   Thu 16:45   IFW D

Study of nonmagnetic and ferromagnetic fcc cerium with one-electron methods — •FABIEN TRAN, FERENC KARSAI, and PETER BLAHA — Vienna University of Technology, Vienna, Austria

Density functional theory was used to study at low temperature the α and γ phases of cerium which were identified as the nonmagnetic and ferromagnetic solutions, respectively, that we could stabilize in our calculations. Four different levels of approximations for the exchange-correlation energy were used: LDA, PBE, PBE+U, and YS-PBEh. The latter two contain an adjustable parameter, the onsite Coulomb repulsion parameter U for PBE+U and the fraction α_x of Hartree-Fock exchange for YS-PBEh, which were varied in order to study their influence on the results. It is concluded that while a small value of U or α_x leads to the correct trend for the stability ordering of the two phases, larger values are necessary for a better (but still not very satisfying) description of the electronic structure.

MM 59.5   Thu 17:00   IFW D

Comparison of transition path sampling and metadynamics for the study of solid-liquid interface properties — •DANIEL SOPU, XUEYONG PANG, JUTTA ROGAL, REBECCA JANISCH, and RALF DRAUTZ — ICAMS, Ruhr-Universität Bochum, Universitättsstr. 150, 44801, Bochum

During solid-liquid phase transformation the kinetics of nucleation and growth are determined to a large extent by interfacial properties. Of particular interest are the interface free energy, the interface mobility and the anisotropy of these quantities. To extract interface properties from experiment is difficult and likewise atomistic modeling of these properties is challenging and requires sophisticated techniques. Here, we present a comparison of two techniques to study solid-liquid interface properties in Al, namely transition path sampling and metadynamics. Transition path sampling explores transition state regions and generates an ensemble of reactive trajectories that contain the full dynamical information of the phase transformation. Metadynamics is a non-equilibrium molecular dynamics simulation method which reconstructs the free energy surface of the phase transition by adding a time dependent bias potential. We compare and contrast the two methods and for which properties of the solid-liquid transformation each of the methods is most applicable.

MM 59.6   Thu 17:15   IFW D

Crystal structure prediction of materials in the BCNOP system at high pressure — •ZAMAAN RAZA and MARCO SAITTA — Université Pierre et Marie Curie, Paris, France

The structure and properties of crystals containing light elements with no d- and f-electrons is often thought to be well understood, yet they frequently display unexpected characteristics when subjected to high pressures. We study the formation of novel binary and ternary compounds in the BCNOP system, at a wide range of temperatures and pressures. Examples of such systems include the ternary B-N-O, B-C-O and C-N-O systems, which are poorly understood even at ambient conditions.

In this work, we seek a better understanding of the physical and chemical phenomena occurring at high temperatures and pressures in such systems of light elements, and search for novel phases with industrially important properties, such as superhardness, superconductivity and high energy density. This presentation focuses on the theoretical side, and on what is regarded as one of the most difficult problems in the physical sciences, crystal structure prediction. The problem arises from the fact that the configurational space increases exponentially in size with the number of atoms in the system, making searches for the ground state on most potential energy surfaces intractable. To

this end, we use two different approaches towards structure prediction, namely random structure searching using the AIRSS method (*J. Phys. Condens. Mat.* **23**:53201, 2011) and evolutionary algorithms as implemented in the USPEX suite (*Comp. Phys. Comm.* **175**:713, 2006).

MM 59.7   Thu 17:30   IFW D

Localized Resolution of Identity: Accurate and efficient evaluation of the coulomb operator for advanced functionals — •Arvid Conrad Ihrig, Jürgen Wieferink, Igor Ying Zhang, Sergey Levchenko, Matti Ropo, Patrick Rinke, Volker Blum, and Matthias Scheffler — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

A key component for high-level correlation methods is the Coulomb operator, which requires the evaluation of four-center Coulomb integrals. For numeric atom-centered orbitals, as used in the all-electron code FHI-aims [1], the four-center integrals are most efficiently evaluated with the "Resolution of Identity" (RI), which expands basis-function products in an auxiliary basis. In this contribution we show the practical applicability of a localized RI-variant ("RI-LVL"), which expands products of basis functions only in the subset of those auxiliary basis functions which are located at the same atoms as the basis functions. We demonstrate the accuracy of RI-LVL for exact exchange in HF and PBE0, and also for correlation methods like MP2 and RPA for the S22 test set[2] of weakly interacting dimers. The error relative to the established RI can be converged in a systematic way by augmenting the auxiliary basis set with additional basis functions of increasing angular momentum. We also show that RI-LVL exhibits a superior scaling with system size, both in terms of computational time and memory requirements.

[1] V. Blum *et al.*, Comput. Phys. Commun. **180**, 2175 (2009)
[2] P. Jurečka *et al.*, Phys. Chem. Chem. Phys **8**, 1985 (2006)