

## MM 31: Computational Materials Modelling - Diffusion &amp; Kinetics II

Time: Wednesday 10:15–11:30

Location: H24

MM 31.1 Wed 10:15 H24

**AKMC simulations of solid-solid phase transformations in molybdenum** — ●ARI HARJUNMAA, JUTTA ROGAL, and RALF DRAUTZ — ICAMS – Ruhr University Bochum, 44789 Bochum, Germany

Molybdenum is a refractory metal used as an alloying element to improve the properties of high-performance materials such as Ni-base superalloys. A common problem in these materials is the formation of topologically close-packed (TCP) phases, which deprive the bulk matrix of the alloying elements and cause the material to become brittle. It is therefore of utmost importance to understand the atomistic processes at work in solid-solid phase transitions leading to the formation of TCP phases. We begin this task by investigating interfaces between the TCP A15 and the cubic BCC phases in molybdenum. We use adaptive kinetic Monte Carlo simulations to discover atomistic processes at the interfaces and to model the time evolution of the systems in question. We also investigate the energetics and stability of the interface structures, and we evaluate the reliability of the employed interatomic potentials by comparing results obtained from density functional theory to those from bond-order and empirical potential simulations.

MM 31.2 Wed 10:30 H24

**A first-principles study of energetics of As, Sb and Bi along selected deformation paths and its application to structure of epitaxial thin films** — ●MARTIN ZOUHAR<sup>1</sup> and MOJMÍR ŠOB<sup>1,2,3</sup> — <sup>1</sup>Central European Institute of Technology, CEITEC MU, Brno, Czech Republic — <sup>2</sup>Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Brno, Czech Republic — <sup>3</sup>Department of Chemistry, Faculty of Science, Masaryk University, Brno, Czech Republic

We present a comprehensive density-functional-theory study of total energy and structural properties of As, Sb and Bi in their A7 ground state and three cubic modifications. All the structures studied are newly described on equal footing with the help of a hexagonal unit cell and can be represented as points in a 3-dimensional parameter space spanned by atomic volume, trigonal distortion and an internal parameter  $u$  of the A7 structure (for cubic structures,  $u=0.25$ ). We calculated the total energies along selected deformation paths by pseudopotential VASP code, displayed them in contour plots as functions of the above-mentioned parameters, identified energy extrema corresponding to the four basic structures and found minimum energy paths connecting selected structures. The calculated energy profiles are employed to determine the structure parameters of As, Sb and Bi thin films on various substrates with the (111) cubic or (0001) hexagonal geometry. Overall good agreement with available experimental data has been found, but we also provide many theoretical predictions which may motivate experimentalists for a deeper study of these systems.

MM 31.3 Wed 10:45 H24

**Phase-field modeling of anisotropically diffusional growth during solid solid transformation: Li-insertion in LiFePO<sub>4</sub>-cathodes for rechargeable Li-ion battery applications** — ●HOLGER FEDERMANN, MICHAEL FLECK, and HEIKE EMMERICH — Material and Process Simulation, University of Bayreuth, Germany

The delithiation process in LiFePO<sub>4</sub> is considered to be a first-order transformation process, where a Li-rich phase transforms into an Li-depleted one. In order to shed light on the delithiation process in LiFePO<sub>4</sub>-cathodes, a continuum phase field model was developed to describe the dynamics of Li-intercalation there. The cathode consists of nanoscale olivine particles and the model describes the phase transformation through Li-insertion. Within the phase-field method, moving phase boundaries between different phases are treated as diffuse inter-

faces of finite width. Then, the evolution of the diffuse phase boundary is driven by the mechanics and the thermodynamics of the adjacent bulk phases. In turn, the motion of the diffuse interface strongly influences the bulk properties such as mechanical or thermodynamical degrees of freedom. Generally, such a diffuse interface approach provides an elegant way to incorporate the complicated effects that occur in these materials, such as the highly anisotropic ionic mobility of the Li-ions in the olivine bulk crystal, the electrochemical reactions at the phase boundary, stress and strain effects due to density differences between the phases. Finally, this model at hand, it could be shown that the interpolation on level of eigenstrains should be preferred for the calculation of the elastic free energy densities of the system.

MM 31.4 Wed 11:00 H24

**Defect-domain wall interactions in ferroelectric materials** — ●ANAND CHANDRASEKARAN<sup>1,2</sup>, DRAGAN DAMJANOVIC<sup>2</sup>, NAVA SETTER<sup>2</sup>, and NICOLA MARZARI<sup>1</sup> — <sup>1</sup>Theory and Simulation of Materials, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland — <sup>2</sup>Ceramics Laboratory, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

Hardening and softening of ferroelectric materials can be engineered through the addition of dopants, and is a key technique to tailor dielectric and piezoelectric properties. Hardening is typically driven by the addition of acceptor dopants, and leads to small electromechanical coefficients and pinched hysteresis loops. Softening can be induced by the addition of donor dopants, which leads to large electromechanical coefficients and open hysteresis loops. Doping results in the formation of defects which interact with the domain walls present in the material. We use here first-principles calculations to show how acceptor dopants lead to the formation of defect complexes which align with the polarization axis and stabilize the ferroelectric domains. We corroborate the AC and DC conductivity data obtained in acceptor-doped materials with first-principles activation energies for the hopping of oxygen vacancies, obtained through nudged elastic-band calculations (NEB). We also calculate the NEB barrier energies for the movement of domain walls in the presence of various defects. As a result, we show how defects and defect associates can influence the mobility of domain walls leading to hardening or softening.

MM 31.5 Wed 11:15 H24

**First-principles thermodynamics of paramagnetic fcc iron** — ●FRITZ KÖRMANN, BLAZEJ GRABOWSKI, BISWANATH DUTTA, TILMANN HICKEL, and JÖRG NEUGEBAUER — Max-Planck-Institut für Eisenforschung GmbH, D-40237, Düsseldorf, Germany

A key issue of thermodynamic first-principles modeling of paramagnetic materials is the interplay of magnetic and atomic degrees of freedom. Practical approaches allowing the computation of atomic forces at finite magnetic temperatures are up to now only rarely available, but are decisive for an accurate description of the thermodynamics in many material systems. For example, first-principles predictions for paramagnetic iron are typically based on empirical approximations, e.g., the 2-states spin model. For this reason, we have recently developed an ab initio approach to obtain effective paramagnetic atomic forces [1]. They are obtained from SQS structures for the magnetic disorder combined with a spin-space averaging procedure. Employing this method we calculate the paramagnetic quasi-harmonic (vibrational) free energy for fcc iron. Adding electronic and magnetic contributions we obtain the complete free energy surface. The derived thermodynamic properties such as phonon spectrum, expansion coefficient, and bulk modulus are in good agreement with experiment.

[1] F. Körmann, A. Dick, B. Grabowski, T. Hickel, and J. Neugebauer, Phys. Rev. B 85, 125104 (2012).