MM 15: Phase Transformations I

Time: Tuesday 14:00–15:45 Location: SCH/A215

MM 15.1 Tue 14:00 SCH/A215

Quantum Geometric Injection and Shift Optical Forces Drive Coherent Phonons — •Luke Pimlott and Habib Rostami — University of Bath, Bath, United Kingdom

We identify injection and shift rectified Raman forces, which are phononic counterparts of the photogalvanic effect, that drive lattice vibrations and trigger transient emergent properties. These forces are governed by the quantum geometric tensor, a phononic shift vector, and interband asymmetries in the electron-phonon coupling. As a response to pulsed light, the injection force induces displacive atomic motion, while, unlike conventional impulsive mechanisms, the shift force produces impulsive atomic displacement in the resonant interband absorbing regime when time-reversal symmetry is broken. Using the bilayer Haldane model, we quantify the injection and shift forces acting on interlayer shear phonons through both analytical and numerical methods. Strikingly, we reveal strong tunability, both in magnitude and direction, of the rectified forces by varying the driving frequency and magnetic flux, uncovering a distinct quantum geometric mechanism for ultrafast and coherent manipulation of quantum materials.

MM 15.2 Tue 14:15 SCH/A215

Charge Density Wave Transition in ZrTe$_3$ from First Principles — •Josu Diego López and Matteo Calandra Buonaura — University of Trento, Trento, Italy

ZrTe$_3$ is a quasi-one-dimensional compound that undergoes a charge density wave (CDW) transition at 63 K with a propagation vector of $\mathbf{q}_{\mathrm{CDW}}$ =(0.07, 0, 0.33) in reciprocal-lattice units and characterized by a very sharp Kohn anomaly in reciprocal space. Although Fermi surface nesting between the quasi-1D bands has been widely invoked to explain this instability, a complete first-principles characterization of the lattice dynamics is still lacking. In particular, the phonon modes at the CDW wavevector have never been computed, even within the harmonic approximation, leaving open fundamental questions regarding the role of the electron-phonon interaction in this material.

In this work, we analyze from first principles the electronic and vibrational properties of the high-temperature phase of ZrTe$_3$. We show that only the correct characterization of the Fermi surface yields an imaginary harmonic phonon mode consistent with the observed CDW. Having access to the harmonic phonons at the critical wavevector also enables the calculation of the electron-phonon interaction at $\mathbf{q}_{\mathrm{CDW}}$, providing a framework to directly compare the electron-phonon mechanism with the nesting scenario in driving the CDW formation.

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MM 15.3 Tue 14:30 SCH/A215

Coupled phase transition and valence fluctuations in Fe-doped *BaTiO$_3$*: a combined DFT and DMFT study — •Zhiyuan Li, Ruiwen Xie, and Hongbin Zhang — Institute of Materials Science, TU Darmstadt, 64287 Darmstadt Germany

Rational control of structural phase transitions in perovskites is a key challenge in materials design. In Fe-doped *BaTiO$_3$*(BTO), experiments observe a tetragonal-to-hexagonal transition, yet the governing microscopic mechanisms remain unclear. A critical control parameter is the Goldschmidt tolerance factor, which relies intimately on the dopant ionic radius and, consequently, the valence state. However, the valence of Fe in BTO remains a long-standing open question, with conflicting reports necessitating a treatment beyond standard DFT. Here, we employ Density Functional Theory (DFT) combined with Dynamical Mean-Field Theory (DMFT) to investigate this interplay. DMFT reveals that the Fe dopant exhibits strong valence and spin fluctuations, which are significantly suppressed by oxygen vacancies to stabilize a high-spin state. Integrating these electronic insights, our total-energy calculations identify three cooperative mechanisms driving the phase transition: tolerance factor variations, Jahn-Teller distortions, and oxygen vacancy formation. Then a systematic quantitative analysis was performed on these three factors. These findings provide a unified microscopic understanding of defect-mediated phase control.

MM 15.4 Tue 14:45 SCH/A215

Interface structure and migration in phase transformations between Fe$_3$O$_4$ and Fe$_2$O$_3$ — •Martina Ruffino[1], Baptiste Bienvenu[1], Xuyang Zhou[2], Guangyi Guo[1], Barak Ratzker[1], Dierk Raabe[1], and Yan Ma[3] — [1]Max Planck Institute for Sustainable Materials, Düsseldorf, Germany — [2]Xi'an Jiaotong University, Xi'an, China — [3]TU Delft, The Netherlands

Although redox phase transformations between hematite (Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$) entail long-range diffusion, they are known to occur on well-defined $(111)_{\mathrm{mag}}||(0001)_{\mathrm{hem}}$ habit planes, and to maintain the oxygen sublattice fixed up to a change in stacking sequence (fcc and hcp arrangement for Fe$_3$O$_4$ and Fe$_2$O$_3$, respectively). Moreover, hematite formations during magnetite oxidation, as well as magnetite formations in hematite during reduction, are often observed to be of lenticular shape. In this study, we propose interfacial disconnections (i. e. steps with dislocation character) suitable for the accomplishment of these phase transformations. Using atomistic simulations with an atomic cluster expansion (ACE) potential developed for iron and its oxides, we calculate the equilibrium structures of the disconnections and we study their motion as a means to transform magnetite into hematite and vice-versa. We then validate theoretical calculations experimentally by investigating i) partially oxidised magnetite and ii) partially reduced polycrystalline hematite. Using transmission electron microscopy, we analyse the hematite/magnetite interfaces, characterising them as faceted interfaces containing steps; we observe good agreement with the simulated disconnection structures.

MM 15.5 Tue 15:00 SCH/A215

Grain boundary thermodynamics away from idealized boundaries: How line defects affect stability — •Tobias Brink[1], Swetha Pemma[1,2], Lena Langenohl[1], Saba Saood[1], Yoonji Choi[1], Rebecca Janisch[2], Christian H. Liebscher[2], and Gerhard Dehm[1] — [1]MPI for Sustainable Materials, Düsseldorf, Germany — [2]Ruhr-Universität Bochum, Germany

The concept of grain boundary (GB) phases (or "complexions") was developed to describe how the atomic structure and/or chemistry of GBs depend on external conditions, such as temperature or chemical potential. Analogous to bulk phases, GB phases also affect material properties. Even in the case of pure metals, structural GB transformations impact diffusivity and GB mobility. Simulation studies often concentrate on special, symmetric boundaries, which are easy to describe. It is unlikely, however, that their behavior can be generalized to the variety of imperfect GBs in a real polycrystal.

Here, we use atomistic simulations with empirical potentials to investigate thermodynamics of asymmetric GBs in Cu. Symmetric $\langle 111 \rangle$ tilt boundaries exhibit two GB phases. These also exist in asymmetric GBs, but contain multiple line defects (disconnections) that enable the deviation from the symmetric GB plane. We found the same defects in thin film samples using scanning electron transmission microscopy. Most importantly, their presence alters the thermodynamic stability of the two GB phases, even for very small deviations from the symmetric GB. We conclude that defects of defects have to be considered in interface thermodynamics.

MM 15.6 Tue 15:15 SCH/A215

Size effects on phase change: solid-state wetting vs. coherency stress — •Yong Li[1] and Jörg Weissmüller[2,1] — [1]Institute of Hydrogen Technology, Helmholtz-Zentrum Hereon, Geesthacht, Germany — [2]Institute of Materials Physics and Technology, Hamburg University of Technology, Hamburg, Germany

Coherent phase transformations in interstitial solid solutions or intercalation compounds with miscibility gaps are crucial to the behavior of energy storage materials, particularly metal hydride and lithium-ion compounds nanoparticles. Prior studies often attribute size-dependent phase transformation behavior either to solid-state critical-point wetting at particle surfaces or to coherent stresses from solute-saturated surface layers. We introduce a hybrid numerical approach that couples atomistic grand canonical Monte Carlo simulations with continuum mechanics analysis of coherency-stress, allowing wetting and mechanical constraints to be simulated simultaneously or independently, thereby decoupling their respective contributions. For material parameters representative of realistic interstitial solutions, we find that solid-state wetting has only a minor influence, whereas coherency stress dominates the size dependence. Mechanical interactions reduce phase-transformation hysteresis at small sizes and increase solute binding in the solid, thereby lowering the chemical potential 'plateau' at the phase coexistence.

MM 15.7 Tue 15:30 SCH/A215

Critical-point wetting at crystal surfaces: Cahn-Hilliard residuum and occurence of first-order wetting transition

— •Marine Bossert[1], Yong Li[2], and Jörg Weissmüller[1,2] — [1]Institute of Materials Physics and Technology, Hamburg University of Technology, Hamburg, Germany — [2]Institute of Hydrogen Technology, Helmholtz Center Hereon, Geesthacht, Germany

Since its publication in 1958, the work by J.W. Cahn and J.E. Hilliard on the free energy of non-uniform systems [1] has been the basis for numerous studies, such as phase-field simulation of microstructure evolution or solute segregation to lattice defects. Cahn and Hilliard found that the second derivative (Laplacian) of the composition field governs the excess energy of systems with conserved networks of sites - such as crystals. A partial integration of the excess energy gives the gradient-square representation, which has been used in all follow-up works in an approximate form that neglects the partial integration residuum. Inspecting critical-point wetting at the surface of an Ising-type FCC crystal with a miscibility gap, this study shows that the solutions obtained with the (exact) second derivative or with the (approximate) gradient-square expressions for the free energy are in fact qualitatively different: the first-order wetting transition predicted by the gradient-square approach is not confirmed by the second-derivative one. Moreover, atomistic Monte-Carlo simulations confirm the absence of a first-order transition. [1] Cahn, J. W., & Hilliard, J. E. (1958).The Journal of Chemical Physics, 28(2), 258-267.