

MM 34: Methods in Computational Materials Modelling (methodological aspects, numerics)

Sessions: Finite temperature properties and computational spectroscopy

Time: Thursday 10:15–13:00

Location: H44

MM 34.1 Thu 10:15 H44

Tight-binding insight in phase stabilities of magnetic iron — •NING WANG¹, THOMAS HAMMERSCHMIDT¹, TILMANN HICKEL², JUTTA ROGAL¹, and RALF DRAUTZ¹ — ¹ICAMS, Ruhr-Universität Bochum — ²Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf

Although the phase diagram of iron has been well-established, we still lack a consistent and theoretical understanding. The difficulty lies in the modelling of complex thermal excitations including magnetic, vibrational and electronic excitations and their mutual interactions. Here we present a spin-lattice fluctuation theory by combining the spin-fluctuation theory and the semi-empirical tight-binding model. With this model we perform a thorough investigation of magnetic and structural phase transitions in magnetic iron. A thermodynamic-integration calculation shows a bcc-fcc phase transition driven by magnetic fluctuations. We employ the spin-space averaging scheme and obtain strong magnetic phonon softening in bcc iron. We observe a sign change in the calculated vibrational-entropy difference between bcc and fcc iron, which is attributed to the transformation back from fcc to bcc iron and in a good agreement with experimental deduction.

MM 34.2 Thu 10:30 H44

The temperature dependence of surface and grain boundary energies from first principles — •DANIEL SCHEIBER, MAXIM POPOV, and LORENZ ROMANER — Materials Center Leoben Forschung GmbH

Material properties generally depend on temperature. While for many bulk properties, the temperature dependence has been well investigated in experiment and theory, for grain boundary and surface energies the topic has remained largely unexplored. A large gap exists between experimental measurements at elevated temperatures and ab-initio simulations performed at 0K. The explanation for these deviations could also be rooted in the missing temperature treatment in the simulations.

In this study, we investigate the temperature dependence grain boundary energies in tungsten. Within the quasi-harmonic approximation we evaluate the phonons using ab-initio density functional theory for different grain boundaries. With that the Helmholtz free energies for grain boundaries are evaluated as a function of temperature. Our simulations show considerable reduction in interface energy with temperature for all investigated grain boundaries and surfaces. This change in interface energy may be directly related to changes in segregation energy, as it is known that segregation scales with grain boundary energy. Finally, we discuss the limitations of our approach and compare the results to available experimental data.

MM 34.3 Thu 10:45 H44

Ab initio benchmark of anharmonic free energies in naphthalene — •MARCIN KRYNSKI, NATHANIEL RAIMBAULT, and MARIANA ROSSI — Fritz Haber Institute of the Max Planck Society, Berlin, Germany

Organic molecular crystals are a vast group of compounds with undisputed industry importance, known for their ability to form polymorphs with properties tied strongly to their crystallographic structure. A large body of theoretical research is centered on polymorph energy ranking [1], which is impacted by the (often neglected) thermodynamic conditions and anharmonicities of the potential energy surface (PES). We present a study of anharmonic contributions to the free energies of the p21a14 and p21c14 molecular crystal polymorphs of naphthalene. We employ dispersion-corrected density-functional theory and compare full anharmonic free-energy evaluations [2] to more computationally tractable approximate methods, gauging the effect of lattice expansion at different temperatures. We show that at the PES, p21c14 is lower in energy than p21a14 by ca. 3meV/molecule for any combination of PBE/PBE0/B3LYP with pairwise or many-body van der Waals (vdW) corrections. Without vdW corrections, the crystals are not stable. We assess whether temperature and lattice expansion explain the experimentally observed stability of the p21a14 polymorph and extend our methodology to polymorphs of pimelic acid, which shows a puzzling temperature-dependent lattice contraction along one axis. [1] A.

Reilly *et al.*, *Acta Cryst. B* **72**, 439 (2016); [2] M. Rossi, P. Gasparotto, M. Ceriotti, *PRL* **117**, 115702 (2016)

MM 34.4 Thu 11:00 H44

Phase stability of dynamically disordered solids from first principles — JOHAN KLARBRING and •SERGEI SIMAK — IFM, Linköping University, SE-581 83, Linköping, Sweden

Dynamically disordered solid materials show immense potential in applications. In particular, superionic conductors are very promising as solid state electrolytes in batteries and fuel cells. The biggest obstacle in living up to this potential is the limited stability of the dynamically disordered phases. To obtain the free energies of disordered materials has long been a challenge. We outline a method that offers a solution [1]. It is based on a stress-strain thermodynamic integration on a deformation path between a mechanically stable ordered variant of the disordered phase, and the dynamically disordered phase itself. We show that the large entropy contribution associated with the dynamic disorder is captured in the behavior of the stress along the deformation path. We apply the method to Bi₂O₃, whose superionic δ -phase is the fastest known solid oxide ion conductor. We accurately reproduce the experimental transition enthalpy and the critical temperature of the phase transition from the low temperature ground state α phase to the superionic δ phase. The method can be used for a first-principles description of the phase stability of superionic conductors and other materials with dynamic disorder, when the disordered phase can be connected to a stable phase through a continuous deformation path.

[1] J. Klarbring and S. I. Simak, *Phys. Rev. Lett.* **121**, 225702 (2018).

MM 34.5 Thu 11:15 H44

The driving force behind the distortion of 1D monatomic chains - Peierls theorem revisited — •DANIELA KARTOON^{1,2}, URI ARGAMAN¹, and GUY MAKOV¹ — ¹Materials Engineering Department, Ben-Gurion University of the Negev, Beer Sheva 84105, Israel — ²NRCN-Nuclear Research Center Negev, Beer Sheva IL 84190, Israel

The onset of distortion in one-dimensional monatomic chains with partially filled valence bands is considered to be well-established by the Peierls theorem, which associates the distortion with the formation of a band gap and a subsequent gain in energy. Similar mechanism is commonly used to explain the distorted structures in half-filled p-band materials. Employing modern total energy methods on both one-dimensional chains and half-filled p-band materials, we reveal that the distortion is not universal, but conditional upon the balance between distorting and stabilizing forces. Furthermore, in all systems studied, the electrostatic interactions between the electrons and ions act as the main driving force for distortion, rather than the electron band lowering at the Fermi level as is commonly believed. The main stabilizing force which drives the materials toward their symmetric arrangement is derived from the electronic kinetic energy. Both forces are affected by the external conditions, e.g. stress, and consequently the instability of one-dimensional nanowires is conditional upon them. This suggests a more general mechanism of high-to-low symmetry transitions, and may shed new light on the distortion of more complex structures.

15 min. break

MM 34.6 Thu 11:45 H44

Anharmonic Raman Spectra in Polymorphic Crystals from Density-Functional-Perturbation Theory and Machine Learning — NATHANIEL RAIMBAULT and •MARIANA ROSSI — Fritz Haber Institute of the Max Planck Society, Berlin, Germany

Anharmonic contributions to vibrational Raman spectra of molecular crystals can be decisive to identify the structure of different polymorphs. In this work we characterise the low-frequency Raman spectral region of different polymorphs of the flexible aspirin and paracetamol crystals. We include anharmonicities through the time-correlation formalism, combining ab initio molecular dynamics and density-functional perturbation theory (DFPT) implemented in a full-potential, all-electron framework [1]. Lattice expansion and anhar-

monic thermal nuclear motion strongly affect the collective vibrations of the low-frequency region. This effect is much less pronounced at higher frequencies. We obtain excellent agreement with experimental lineshapes at frequencies below 200 cm^{-1} , highlighting the necessity of going beyond the harmonic approximation and providing unambiguous polymorph assignment. In order to bypass the cost of DFPT evaluations of the polarisability tensor, we employ different forms of Kernel Ridge Regression (KRR) and discuss their efficiency. Training our models on several hundreds of points, we reproduce Raman spectra that would otherwise require the calculation of tens of thousands of points. [1] H. Shang, N. Raimbault *et al.*, *New J. Phys.* **20**, 073040 (2018)

MM 34.7 Thu 12:00 H44

Electric Field Gradient in Ca₃Mn₂O₇ — PEDRO RODRIGUES¹, IVAN MIRANDA², SAMUEL SANTOS^{1,2}, ARMANDINA LOPES¹, GONÇALO OLIVEIRA¹, LUCY ASSALI², JOÃO PEDRO ARAUJO¹, and HELENA PETRILLI² — ¹Faculdade de Ciências, Universidade do Porto, Porto, Portugal — ²Instituto de Física, Universidade de São Paulo, São Paulo, Brazil

Naturally layered perovskites, such as the Ruddlesden-Popper phases or A-site ordered double perovskites have appeared as a fascinating route in exploring the design and achievement of nonexpensive room temperature multiferroic materials. In these, distortions of the lattice such as octahedron rotation and tilting modes, couple to polar cation dislocation modes, inducing cation ordering and a spontaneous ferroelectric polarization, a mechanism known as hybrid improper ferroelectricity. Here, several structural, charge and magnetic phase transitions of Ca₃Mn₂O₇ is studied by combining theoretical and experimental methods, in order to provide a tool to unravel its local electronic and magnetic properties. The theoretical approach is performed using ab-initio electronic structure calculations, in the framework of the Density Functional Theory (DFT); measurements are performed for structural characterization as well as magnetic and hyperfine quantities. Through this comparison, a local scenario of the complex behavior of this class of systems is studied. By inspecting electric field gradients at the nuclei obtained via theoretical calculations and inferred from Perturbed Angular Correlations (PAC) measurements at a Cd probe, trends are obtained and the application of the proposed procedure is discussed.

MM 34.8 Thu 12:15 H44

Proton irradiation of ice in space conditions simulated via real-time TDDFT — DANIEL MUÑOZ-SANTIBURCIO — CIC nanoGUNE, San Sebastián, Spain

Proton irradiation of ice is of great importance for a number of astrophysical/chemical processes. Here I will show the results of real-time TDDFT calculations where the irradiation of ice with highly energetic protons is simulated in real time via Ehrenfest MD [1], following the excitations of the electronic subsystem in the ice sample promoted by the passing of the proton projectile at the same time that the change of the trajectory of the projectile is strictly described, going beyond the ‘constant velocity’ approximation that is usually employed when modeling such radiation damage processes. I will also describe the dependence of these effects as a function of the energy and orientation of the incoming proton, helping to fill a gap in the current experimental and theoretical knowledge of this process.

[1] D. Muñoz-Santiburcio and E. Artacho, *in preparation*.

MM 34.9 Thu 12:30 H44

Computation of NMR shifts for paramagnetic solids including zero-field-splitting: significant effects beyond the contact shifts — AROBENDO MONDAL^{1,2} and MARTIN KAUPP¹ — ¹Theoretical Chemistry/Quantum Chemistry, TU Berlin, Germany — ²Theoretical Chemistry, TU Munich, Germany

NMR is a powerful tool for studying the structural and electronic properties of paramagnetic solids. However, the interpretation of paramagnetic NMR spectra is often challenging as a result of the interactions of unpaired electrons with the nuclear spins of interest. Recently, we reported a novel protocol to compute and analyze NMR chemical shifts for extended paramagnetic solids, accounting comprehensively for Fermi-contact (FC), pseudo-contact (PC), and orbital shifts.^[1] We combine periodic DFT computation of hyperfine and orbital-shielding tensors with an incremental cluster model for g- and zero-field-splitting (ZFS) D-tensors. The hyperfine tensors are computed with hybrid DFT functionals using the highly efficient Gaussian-augmented plane-wave implementation of the CP2K code. The incremental cluster model allows the computation of g- and ZFS D-tensors by ab initio complete active space self-consistent field and N-electron valence-state perturbation theory methods. We find that ⁷Li shifts in the high-voltage cathode material LiCoPO₄ are dominated by spin-orbit-induced PC contributions, in contrast to previous assumptions, changing the interpretation of the shifts fundamentally in terms of covalency.

[1] Mondal, A.; Kaupp, M. *J. Phys. Chem. Lett.*, **2018**, *9*, 1480-1484.

MM 34.10 Thu 12:45 H44

Characterization of local structure using a mixed radial, orientational three-body correlation function — MARTIN H. MUESER and SERGEY V. SUKHOMLINOV — Universität des Saarlandes, 66123 Saarbrücken, Germany

Computer simulations of condensed matter systems are often run with the goal to ascertain the degree to which the local structure of a system lacking long-range order resembles that of crystalline reference phases. As a tool for such analysis we propose a mixed radial, orientational three-body correlation function, i.e., $g_{ABC}(r_{BC}, \vartheta_{ABC})$. This function is defined to be proportional to the probability of finding an atom of type C at a distance r_{BC} under an angle of ϑ_{ABC} given that r_{AB} is within 10% of a typical AB bond length or AB nearest-neighbor distance. This correlation function allows the local order in disordered systems to be more easily related to that of reference crystals than with other methods that have so far been conventionally used. This method could also be used to detect and quantify local symmetries.

In order to demonstrate the use of the analysis and its usefulness, a visual library of mono- and two-component crystals is produced and compiled, and then applied to a diverse body of selected liquids and disordered solids. These include the analysis of the extent with which liquid Lennard-Jonesium and liquid copper resemble face-center-cubic or hexagonal close packing, the relative amount of cristobalite in a simple model of liquid silica, the extent of the Peierls deformation in liquid antimony and the identification of the seesaw molecular geometry occurring in zinc-phosphates under pressure.