Theory of Complex Disorder in Materials (TCDM2019)

September 16-18, 2019
Linköping University, Linköping, Sweden

Abstracts

LINKÖPING
UNIVERSITY

Psi-k Network

LINKÖPINGS UNIVERSITET
ADVANCED FUNCTIONAL MATERIALS

Theoretical treatment of interstitial impurities in paramagnetic alloy hosts: C in Fe-Mn

A. V. Ponomareva[a], B. O. Mukhamedov[a], I.A. Abrikosov[b]

[a]Materials Modeling and Development Laboratory, National University of Science and Technology 'MISIS', Moscow, Russia, 119049

[b]Department of Physics, Chemistry, and Biology (IFM), Linköpings University, Linköping, Sweden, SE-581 83

We present a generalization of a model that takes into account the magnetic disorder of paramagnetic host with interstitial point defects towards the case of alloy hosts. In the framework of disordered local moment approach combined with magnetic sampling method, we calculate solution enthalpy of carbon impurity in the paramagnetic fcc Fe-Mn steels. First, we use the magnetic special quasirandom structure (M-SQS) method for simulation of the paramagnetic state in Fe-Mn alloys without impurity. Here, Fe and Mn atoms are randomly distributed at the sites of a supercell following the chemical SQS method. Next, to calculate the energies for various magnetic realizations around the interstitial carbon impurity, we vary the position of the impurity within the SQS. Our calculations show that in alloys containing ~ 20 at. % Mn, the solution enthalpy of carbon reduces compared to the pure fcc-Fe. By analyzing the local and global effects of impurity on the properties of the matrix, we discuss various factors that could increase the carbon solubility in high-manganese austenitic steels.

Combined Atomistic Spin Dynamics and Ab Initio Molecular Dynamics: revelation of dynamic spin-lattice coupling in paramgnetic CrN

Björn Alling, LiU

We have developed a new method, the combined atomistic spin dynamics - ab-initio molecular dynamics (ASD-AIMD) to investigate magnetic materials at high temperature. We apply the method to study the mutual coupling of spin fluctuations and lattice vibrations in paramagnetic CrN. The two degrees of freedom are dynamically coupled, leading to nonadiabatic effects. Those effects suppress the phonon lifetimes at low temperature compared to an adiabatic, fast-magnetism approach. The dynamic coupling identified here provides an explanation for the experimentally observed unexpected temperature dependence of the thermal conductivity of magnetic semiconductors above the magnetic ordering temperature.

Our method is based on an alternating scheme of ASD and AIMD steps. In every step of AIMD, constrained non-collinear magnetic moments are used in the density functional theory calculations. The obtained forces are used to update the atomic positions by a single-step propagation of the atoms by 1 fs. With the new atomic positions, new distance dependent magnetic exchange interactions are obtained and used to propagate the magnetic state for 1 fs in the ASD simulation together giving a coupled ASD-AIMD step that are repeated until convergence of studied quantaties.

The dynamics of the spin system impacts atomic lattice vibrations and the quantities related to it, in particular phonon lifetimes. The magnetic state and its dynamics are influenced by the lattice vibrations. Slightly above the transition temperature (300K), the dynamical coupling, is found to significantly reduce the phonon lifetimes of the acoustic modes. In contrast, at high temperatures (1000 K) the dynamical coupling and its impact on phonon lifetimes are largely reduced.

Our ASD-AIMD method provides access to magnetic materials at high temperature with AIMD-level accuracy previously only existing for non-magnetic materials. Dynamical coupling effects between spin and lattice can explain experimentally observed anomolous thermal conductivity in the paramagnetic state of magnetic semiconductors.

Anomalous Phonon Lifetime Shortening in Paramagnetic CrN Caused by Spin-Lattice Coupling: A Combined Spin and Ab Initio Molecular Dynamics Study
Irina Stockem, Anders Bergman, Albert Glensk, Tilmann Hickel, Fritz Körmann, Blazej Grabowski, Jörg Neugebauer, and Björn Alling
Physical Review Letters **121**, 125902 (2018)

A supercell study of longitudinal spin fluctuations and vibrations in bcc-Fe under earth-core conditions

Marian Brännvall, Davide Gambino, Björn Alling
Department of Physics, Chemistry, and Biology
Linköping University, Sweden

With a super cell approach, the coupling of vibrations with longitudinal spin fluctuations (LSFs) and their effects on properties in body-centered cubic iron under Earth’s core conditions has been investigated. We used a snapshot of a constant pressure-temperature ab-initio molecular dynamics simulation at 6000 K and 300 GPa, modelled the paramagnetic phase by using a non-collinear magnetic disorder with local moment size obtained from supercell LSF simulations. In these fixed-spin moment calculations are used to obtain energy landscapes for local moments of each site that depends on the local magnetic environment. The process is stepwise calculations of energy landscapes iterated until self- consistency. We have shown that this methodology can be used to investigate the effect of vibrations on the LSF energy landscapes. This study also demonstrates that there is entropy-induced magnetic moments at Earth’s core conditions in bcc-Fe and that, due to the vibrations, we have a spread in the magnitude of the magnetic moments for the atoms in the super cell. However, looking at the average magnitude gives a similar result to that obtained when vibrations have not been included in previous studies by Ruban et al. The presence of local moments give a 30 GPa change in the obtained pressure as compared to non-magnetic simulations. Magnetism also influence the local forces and the electronic density of states.

Influence of configurational and magnetic disorder on Screw dislocations from first principle calculations

Luis Casillas, Björn Alling

Department of Physics, Chemistry and Biology (IFM), Linköping University, Linköping, Sweden.

Abstract

In this work we have studied the effect of magnetic and configurational disorder on the 1/2<111> screw dislocation core structure in paramagnetic bcc Fe and disordered $Mo_{1-x}W_x$ alloys. Dislocation cores control the mechanical properties of materials, influencing the selection of glide planes, cross slip and dislocation nucleation. Magnetic and configurational disorder can change the structure of the core and impact dislocation mobility. For our calculations, we have employed a quadrupolar periodic array of screw dislocation dipoles [1]. For the magnetic part, we studied the core properties of a screw dislocations in paramagnetic bcc iron using the non-collinear disordered local moment approximation (DLM) and performed structural relaxations with density functional theory (DFT)[2]. We have obtained the dislocation core structure for the easy and hard core configurations in the paramagnetic state, and compared them with their ferromagnetic counterparts. For the configurational disorder part, we have obtained a first principle cluster expansion of a $Mo_{1-x}W_x$ solid solution containing a dislocation. We have obtained the energetics of substitutional solutes as a function of position to respect of the dislocation to asses segregation towards the core and compared with the ordering tendencies in the bulk.

[1] Clouet, Emmanuel, Lisa Ventelon, and F. Willaime. "Dislocation core field. II. Screw dislocation in iron." *Physical Review B* 84.22 (2011): 224107.

[2] Gambino, Davide, and Björn Alling. "Lattice relaxations in disordered Fe-based materials in the paramagnetic state from first principles." *Physical Review B* 98.6 (2018): 064105.

Titel:
High-throughput identification of point defects in SiC
Joel Davidsson

Abstract:
Qubits and single photon emitters are examples of point defects applications. Before a point defect can be utilized in these applications, an important step is to identify and understand both the defect type and its different configurations. A promising way to identify a defect is to combine experimental data with ab initio calculations which include zero-phonon lines and hyperfine coupling parameters. In earlier work, we made a convergence study for divacancies in 4H-SiC. Due to the size of the supercell and the number of calculations needed, we restrict us to the PBE exchange functional. Based on our understanding of the convergence of these calculations, we made an automatic workflow that can calculate zero-phonon lines for many different defects. Each defect is calculated for a range of different configurations, charges, spins, and possible excitations. Currently, we are running these calculations in a high-throughput manner and producing a database for an array of different defects. We present the results from the workflow for various vacancy configurations in 4H-SiC. Our preliminary results suggest that with this choice of methodology, useful data are obtained at a feasible computational cost for a large number of defect types and configurations available in SiC.

Davidsson, J., Ivády, V., Armiento, R., Son, N. T., Gali, A., & Abrikosov, I. A. (2018). First principles predictions of magneto-optical data for
semiconductor point defect identification: the case of divacancy defects in 4H–SiC. New Journal of Physics, 20(2), 023035.
Ivády, V., Davidsson, J., Son, N. T., Ohshima, T., Abrikosov, I. A., & Gali, A. (2017). Identification of Si-vacancy related room-temperature qubits in 4 H
silicon carbide. Physical Review B, 96(16), 161114.
Davidsson, J., Ivády, V., Armiento, R., Ohshima, T., Son, N. T., Gali, A., & Abrikosov, I. A. (2019). Identification of divacancy and silicon vacancy qubits in 6H-SiC. *Applied Physics Letters*, *114*(11), 112107.

Magnetic ordering in high entropy alloys: A combined theoretical and experimental study

Biswanath Dutta[1], Yuji Ikeda[2], Ziyuan Rao[2], Xiaoxiang Wu[2], Zhiming Li[2], Dierk Raabe[2], Jörg Neugebauer[2], Fritz Körmann[1,2]

[1]*Department of Materials Science and Engineering, Delft University of Technology, 2628 CD Delft, Netherlands*

[2]*Max-Planck-Institut für Eisenforschung GmbH, D-40237 Düsseldorf, Germany*

High entropy alloys (HEAs) have become a topic of extensive research in the last few years. Of particular interest are subtleties in the magnetic properties. An in-depth understanding of magnetism is a key step towards improving the structural and functional properties of magnetic HEAs. Using ab initio calculations, we investigate the magnetic properties for several fcc multicomponent alloys, ranging from medium to high entropy alloys. The coherent potential approximation is employed to address the chemical disorder while the high temperature paramagnetic state is treated within the disordered local moment approach. Among the considered magnetic states, our calculations reveal an antiferromagnetic sublattice order for Mn atoms in the lowest energy magnetic state. We also predict an anomalous increase in the Curie temperature and saturation magnetization due to substitution of non-magnetic Cu. The obtained compositional trends are discussed in the light of varying concentration of magnetic elements and volume changes due to Cu substitution. The computationally predicted trends of the magnetic properties show good agreement with the experimental results. We also demonstrate the impact of magnetism on stacking fault energy calculations for CrMnFeCoNi-based HEAs, which can have significant impact on mechanical properties.

Surface properties of cubic (Ti,Al)N alloys by first principle methods

Axel Forslund [1], Andrei Ruban [1,2]
1. KTH Royal Institute of Technology
2. Materials Center Leoben Forschung GmbH

(Ti,Al)N-alloy coatings have since the 80s been used as wear protective coatings [1]. A high Al content is usually preferred to improve the mechanical properties, but the alloy is meta stable and exhibits a miscibility gap with the most unfavourable compositions at the Al rich side [2]. Typical PVD coatings have been able to reach Al contents on the metalloid sublattice around 0.66 [3]. Recently, TiAlN coatings have been deposited with chemical vapour deposition, acquiring higher Al contents, while retaining a cubic structure [4]. Modelling and simulations are an important part of understanding the metastable coating and its formation. The formation of stable surfaces and possible alloy modifications close to the surface are influenced by surface and segregation energies. Such properties can be calculated in a random alloy Ti1-xAlxN by first-principle methods, but the calculations of surface properties is complicated by the many configurational possibilities that are unavoidable with a supercell model of a random alloy. We present weighted averages of configuration dependent segregation energies, and compare the results with mean-field methods. Moreover, we consider implications about the temperature dependence of the surface free energy.

1. Jehn, H. A., Hofmann, S., Rückborn, V.-E. & Münz, W.-D. Morphology and Properties of Sputtered (Ti,Al)N Layers on High Speed Steel Substrates as a Function of Deposition Temperature and Sputtering Atmosphere. Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films 4, 2701–2705. issn: 0734-2101, 1520-8559 (Nov. 1986).

2. Alling, B. et al. Mixing and Decomposition Thermodynamics of c-Ti1-xAlxN from First-Principles Calculations. Physical Review B 75. issn: 1098-0121, 1550-235X. doi:10.1103/PhysRevB.75.045123 (Jan. 2007).

3. Hörling, A., Hultman, L., Odén, M., Sjölén, J. & Karlsson, L. Thermal Stability of Arc Evaporated High Aluminum-Content Ti1-xAlxN Thin Films. Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films 20, 1815–1823. issn: 0734-2101, 1520-8559 (Sept. 2002).

4. Endler, I. et al. Novel Aluminum-Rich Ti1-xAlxN Coatings by LPCVD. Surface and Coatings Technology 203, 530–533. issn: 02578972 (Dec. 2008).

Elasticity of phases in Fe-Al-Ti superalloys: impact of atomic order and anti-phase boundaries

M. Friák[1], V. Buršíková[2], N. Pizúrová[1], J. Pavlů[3,4,1], Y. Jirásková[1], V. Homola[2], I. Miháliková[1,5], A. Slávik[1,5], D. Holec[6], M. Všianská[3,1,4], N. Koutná[5,7], J. Fikar[1], D. Janičkovič[8], M. Šob[4,1,3] and J. Neugebauer[9]

[1]Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Žižkova 22, CZ-616 62 Brno, Czech Republic

[2]Department of Physical Electronics Condensed Matter Physics, Faculty of Science, Masaryk University, Kotlářská 2, Brno, Czech Republic

[3]Central European Institute of Technology, CEITEC MU, Masaryk University, Kamenice 5,

CZ-625 00 Brno, Czech Republic

[4]Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2,

CZ-611 37 Brno, Czech Republic

[5]Department of Condensed Matter Physics, Faculty of Science, Masaryk University, Kotlářská 2, Brno, Czech Republic

[6]Department of Physical Metallurgy and Materials Testing, Franz-Josef-Strasse 18, A-8700 Leoben, Austria

[7]Institute of Materials Science and Technology, TU Wien, Getreidemarkt 9, A-1060 Vienna, Austria

[8]Institute of Physics, Slovak Academy of Sciences, Dubravska cesta 9, 845 11 Bratislava, Slovakia

[9]Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Str. 1, 40237 Düsseldorf, Germany

Keywords: Fe-Al-Ti; superalloys; disorder; magnetism; ab initio; stability; elasticity.

We combine theoretical and experimental tools to study elastic properties of Fe-Al-Ti superalloys. Focusing on samples with chemical composition $Fe_{71}Al_{22}Ti_7$, we use transmission electron microscopy (TEM) to detect their two-phase superalloy nano-structure (consisting of cuboids embedded into a matrix). The chemical composition of both phases, $Fe_{66.2}Al_{23.3}Ti_{10.5}$ for cuboids and $Fe_{81}Al_{19}$ (with about 1 % or less of Ti) for the matrix, was determined from an Energy-Dispersive X-ray Spectroscopy (EDS) analysis. The phase of cuboids is found to be a rather strongly off-stoichiometric (Fe-rich and Ti-lean) variant of Heusler Fe_2TiAl intermetallic compound with the $L2_1$ structure. The phase of the matrix is a solid solution of Al atoms in a ferromagnetic body-centered cubic (bcc) Fe. Quantum-mechanical calculations were employed to obtain an insight into elastic properties of the two phases. Three distributions of chemical species (special quasi-random structures, SQS) were simulated for the phase of cuboids (A2, B2 and $L2_1$) in order to determine a sublattice preference of the excess Fe atoms. The lowest formation energy was obtained when the excess Fe atoms form a solid solution with the Ti atoms at the Ti-sublattice within the Heusler $L2_1$ phase ($L2_1$ variant). Similarly, three SQS configurations of Al atoms in the phase of the matrix with different level of order (A2, B2 and $D0_3$) were simulated. The computed formation energy is the lowest when all the 1st and 2nd nearest-neighbor Al-Al pairs are eliminated (the $D0_3$ variant). Next, the elastic tensors of all phases were calculated. The maximum Young's modulus is found to increase with increasing chemical order. Further we simulated an anti-phase boundary (APB) in the $L2_1$ phase of cuboids and an elastic softening is observed. Finally, to validate these predicted trends, a nano-scale dynamical mechanical analysis (nanoDMA) was used to probe elasticity of phases. Consistent with the prediction, the cuboids were found stiffer. The authors acknowledge the Czech Science Foundation for the financial support received under the Project No. 17-22139S (M.F., J.P., I.M., A.S., V.B., V.H., Y.J., N.P.,J.F.). Additional resources were provided by the Ministry of Education, Youth and Sports of the Czech Republic under the Project CEITEC 2020, LQ1601 (M.Š, M.F., M.V., J.P.).

An *ab initio* study of thermodynamic and mechanical stability of stoichiometric and off-stoichiometric Fe_2CoAl polymorphs

Martin Friák[1,*], Sabina Oweisová[2,1], Jana Pavlů[3,2,1], David Holec[4]
and Mojmír Šob[3,1,2]

[1]Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Žižkova 22,
CZ-616 62 Brno, Czech Republic

[2]Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2,

CZ-611 37 Brno, Czech Republic

[3]Central European Institute of Technology, CEITEC MU, Masaryk University, Kamenice 5,

CZ-625 00 Brno, Czech Republic

[4]Department of Physical Metallurgy and Materials Testing, Franz-Josef-Strasse 18, A-8700
Leoben, Austria

[*] friak@ipm.cz

Keywords: Fe_2CoAl; Heusler; disorder; ab initio; stability; elasticity.

Abstract

We use quantum-mechanical calculations to test a hypothesis of Grover *et al.* (J. Mag. Mag. Mater. 15 (1980) 699) that Co atoms in the Fe_2CoAl compound have on average 3 Fe and 3 Co atoms in their second nearest neighbor shell. We have simulated four structural configurations of Fe_2CoAl including the full Heusler structure, inverse Heusler polymorph and two less-ordered phases matching this idea. The highest thermodynamic stability at T = 0 K is indeed predicted for one of the phases with the distribution of atoms according to Grover and co-workers. However, small energy differences among three of the studied polymorphs lead to a disordered B2-like phase at elevated temperatures. The fourth variant, the full Heusler phase, is predicted to be mechanically unstable. The global magnetic states are predicted to be ferromagnetic but local magnetic moments of Fe and Co atoms sensitively depend on the composition of the first and second coordination shells. For details see Materials 11 (2018) 1543, doi:10.3390/ma11091543.

Acknowledgment

The authors acknowledge the Czech Science Foundation for the financial support received under the Project No. 17-22139S (M.F., J.P.). Additional resources were provided by the Ministry of Education, Youth and Sports of the Czech Republic under the Project CEITEC 2020, LQ1601 (M.Š, M.F., J.P.). Computational resources were made available by the Ministry of Education, Youth and Sports of the Czech Republic under the Projects CESNET (Project No. LM2015042), CERIT-Scientific Cloud (Project No. LM2015085) and IT4Innovations National Supercomputer Center (Project No. LM2015070) within the program Projects of Large Research, Development and Innovations Infrastructures. We also acknowledge very fruitfull discussions with Yvonna Jirásková from IPM in Brno.

Study of the interplay between magnetic and vibrational degrees of freedom in bcc Fe from first principles

Davide Gambino
Department of Physics, Chemistry and Biology (IFM), Linköping University

Proper account of thermal disorder on different degrees of freedom (DOFs) in the modeling of materials at finite temperatures represents a great challenge in investigations by means of first-principles methods. As an example, an accurate and realistic modeling of magnetic materials at elevated temperatures requires to take into account vibrational, magnetic, and electronic DOFs, as well as their interplay. So far, studies that try to address this problem have been performed assuming an adiabatic decoupling of excitations and disorder of the different DOFs, accounting separately for, e.g., the interplay between vibrations and transverse magnetic DOFs, or between transverse and longitudinal magnetic DOFs. An investigation that includes the effect of all these degrees of freedom on each other at the same time is still missing.

As a pre-step towards the closing of this gap, we perform coupled atomistic spin dynamics-ab initio molecular dynamics simulations (ASD-AIMD) [Stockem *et al.*, Physical Review Letters 121, 125902 (2018)] of bcc Fe at its Curie temperature. We initially carry out the simulation neglecting longitudinal spin fluctuations (LSF) in the system, and then we perform fixed-spin moment calculations on one atomic-magnetic configuration by varying the size of each moment in the supercell one at a time, so that we obtain energy landscapes for each atom as a function of moment size. We assess the effect of vibrational and transverse magnetic disorder on the LSF landscapes, considered here in a semiclassical framework based on Landau theory, by comparing the results with corresponding calculations in the ferromagnetic (FM) and disordered local moment (DLM) state on ideal lattice positions and on an atomic configuration taken from FM ab initio molecular dynamics simulation at the same temperature. We find that the landscapes become shallower and shallower with increasing degree of disorder in both DOFs.

The present results pave the way for atomistic simulations from first principles of magnetic materials at high temperature including vibrational, magnetic and electronic degrees of freedom and their interplay.

Accelerating ab-initio studies of alloys properties with active learning of interatomic potentials

Konstantin Gubaev[1], Evgeny Podryabinkin[1], Alexander Shapeev[1],

Gus Hart[2], Ferenc Tasnadi[3], Igor Abrikosov[3]

[1]*Skolkovo Institute of Science and Technology, Russia*

[2]*Brigham Young University, USA*

[3]*Linköping University, Sweden*

We propose an approach to atomistic simulation that uses machine-learning interatomic potentials to approximate quantum-mechanical potential energy surface and an active learning algorithm for the automatic composition of the training dataset.

Our approach significantly reduces the amount of density functional theory (DFT) calculations needed, resorting to DFT only to produce the training data, while calculation of energies/forces/stresses in simulation is performed using interatomic potentials.

We demonstrate the effectiveness of our algorithm by predicting the convex hulls for the following three systems: Cu-Pd, Co-Nb-V, and Al-Ni-Ti; as well we apply our method to predict elastic constants of the fcc TiN for a range of temperatures.

Modeling of longitudinal spin fluctuations at high temperature in bcc-Cr using a supercell methodology

Ylva Hedström, Davide Gambino, Björn Alling
Department of Physics, Chemistry, and Biology
Linköping University, Sweden

Some experimental studies have shown peculiarities in measurements of, for instance, specific heat capacity in chromium at high temperature, above 1400 K but below the melting temperature. It has been suggested that there could be a transition between weak and strong magnetic coupling that causes such an effect. We have investigated theoretically if there are any magnetic effects that can cause these peculiarities. We used a a supercell approach to simulate both longitudinal spin fluctuations and the magnetic exchange coupling between local moments. A snapshot of constant temperature *ab-initio* molecular dynamics simulation at 1600 K has been used to include vibrational effects and perform fixed-spin moment calculations as well as magnetic coupling calculations. We have shown that the magnetic moments in chromium are maintained at such high temperature mostly, but not only, due to magnetic entropy contributions. We find no para-to-diamagnetic transition or any coupling between vibrations and local moments that could justify a peculiarity. The exchange coupling between local moments are also discussed.

Impact of magnetic excitations on the energetics of point and extended defects in Fe-Mn alloys

Omkar Hegde[1], O. Waseda[1], T. Hickel[1], C. Freysoldt[1], J. Neugebauer[1]

[1] *Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany;*

Understanding the impact of paramagnetism on defect energetics and kinetics is, though conceptually and computationally challenging, important for designing Fe-based alloys. Since magnetic degrees of freedom change faster than atomic degrees of freedom in the paramagnetic state, the atoms move according to an averaged force instead of instantaneous forces attained from each spin configuration. Therefore, a new computationally efficient method based on spin-space averaging[1] (SSA) has been developed to handle magnetic disorder next to defects. The method uses the spin constraint tool developed and implemented in the DFT code S/PHI/nX[2]. The performance of the method is demonstrated for local atomic relaxations next to point defects. For α-Fe, we show that both magnetic disorder and local relaxations significantly affect vacancy formation and migration energies. Next, we focus on the FeMn system, for which the vacancy formation energy as a function of Mn concentration for both ferromagnetic and paramagnetic cases is presented. We demonstrate that paramagnetism significantly affects atomic relaxations as well as diffusion barriers and thereby explain why Mn diffusion shows a different temperature dependence than Fe-self diffusion in α-Fe. We have further extended our method to understand grain boundary energetics and present some interesting results.

[1] F Körmann, A Dick, B Grabowski, T Hickel, and J Neugebauer, Phys. Rev. B 85(12):125104, (2012).

[2] S Boeck, C Freysoldt, A Dick, L Ismer, and J Neugebauer, Computer Physics Communications, 182(3):543554, (2011).

Impact of Mo and disorder on diffusion-less transformations in TiAl intermetallic alloys

David Holec[1], Neda Abdoshahi[1], Mohammad Dehghani[2], Andrei V. Ruban[2,3],
Martin Friák[4,5,6], Mojmír Šob[5,6,7] and Jürgen Spitaler [2]

[1]Department of Materials Science, Montanuniversität Leoben, Franz-Josef-Strasse 18, A-8700 Leoben, Austria, david.holec@unileoben.ac.at

[2]Materials Center Leoben Forschung GmbH, Roseggerstrasse 12, A-8700 Leoben, Austria

[3]Royal Institute of Technology, Department of Materials Science, SE 10044 Stockholm, Sweden

[4]Department of Condensed Matter Physics, Faculty of Science, Masaryk University, Kotlářská 2, Brno CZ-611 37, Czech Republic

[5]Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Žižkova 22, Brno CZ-616 62, Czech Republic

[6]Central European Institute of Technology, CEITEC MU, Masaryk University, Kamenice 5, Brno CZ-625 00, Czech Republic

[7]Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, Brno CZ-611 37, Czech Republic

Titanium aluminides have become widely popular for aerospace and automotive applications due to their light weight, favorable mechanical properties and excellent oxidation resistance. To tune the alloy properties to fulfill industrial requirements, many alloying elements are used. In this sense, Mo and Nb are prominent elements as they stabilize the bcc-based phase which allows for hot temperature workability. Recently, a model Ti-Al-Mo alloy has been reported to exhibit martensitic transformation upon rapid cooling.

We employ Density Functional Theory (DFT) as implemented in Vienna Ab initio Simulation Package to perform our first principles calculations. The impact of Mo and chemical disorder was studied using a supercell approach and complemented with Green's functions based DFT calculations, using the coherent potential approximation implemented in the Exact Muffin-Tin Orbitals (EMTO) code.

The base structure of interest is bcc-based disordered β-TiAl and its ordered variant β_o-TiAl (B2 structure). Based on the experimentally reported martensitic hexagonal structure, we have considered also the hcp based α-TiAl structure and an ordered hexagonal variant B19-TiAl. Finally, we have included the γ-TiAl (layered, tetragonally distorted fcc structure).

The β_o-TiAl structure was shown to be mechanically as well as dynamically unstable. The tetragonal transformation path (so called Bain's path) connects the β_o-TiAl with the most stable γ-TiAl structure with no barrier. Similarly, the transformation from β_o to B19 can also proceed without any barrier. The disordered β-TiAl is still unstable, however, the phonon density of states corresponding to imaginary frequencies is significantly reduced as compared with the ordered variant. This may be interpreted as a stabilizing effect of structural disorder. Also the related energy difference between β and α is significantly reduced signifying stabilizing by disorder.

Finally, we have also studied the impact of Mo alloying. Replacing Al with Mo (hence leading to Ti-rich compositions) leads to relative stabilization of the β_o with respect to the γ structure . In this contribution, we will present details of these transformation paths, interplay between Mo alloying and structural disorder and a detailed comparison with available experimental data.

Tuning stacking-fault energies and local lattice distortions in high-entropy alloys

Yuji Ikeda[1], Biswanath Dutta[2], Jörg Neugebauer[1], Fritz Körmann[1,2]

[1]*Computational Materials Design, Max-Planck-Institut für Eisenforschung GmbH, 40237 Düsseldorf, Germany*
[2]*Materials Science and Engineering, Delft University of Technology, 2628 CD Delft, The Netherlands*

Mechanical properties of 3d-transition-element high-entropy alloys (HEAs) have received enormous attention recently. Transition-induced plasticity (TRIP) and twinning-induced plasticity (TWIP) are well-known mechanisms in metallurgy, which could further improve the ductility of HEAs. For this, the stacking-fault energy (SFE) is a key factor to determine the deformation behavior. Alternatively, mechanical strength can be also enhanced by modifying the composition of HEAs such that local lattice distortions, empirically found to correlate with solid solution strengthening, are maximized. Due to the huge phase space spanned by their chemical degrees of freedom, however, it is impractical to tune the mechanical properties solely by an experimental trial-and-error approach. Complementary first-principles calculations are useful for this purpose and are also helpful to better understand how the chemical and magnetic complexity in HEAs affects the mechanical properties on an atomistic level.

In this study, we focus on the impact of composition and interstitial alloying on mechanical properties of HEAs. First, we screen CrMnFeCoNi-based HEAs employing the coherent-potential approximation (CPA) to find promising compositions showing TRIP/TWIP in terms of low SFEs. We find that the Mn content and particularly its impact on magnetism largely modifies the chemical trends of SFEs. Second, we investigate the impact of C interstitial alloying in CrMnFeCoNi Cantor HEA on its phase stability using a supercell approach. We show that the C solution energy substantially fluctuates due to the large variety of different local environments. Third, we demonstrate a high degree of local lattice distortions in fcc VCoNi. This alloy also shows much higher strength than CrCoNi or CrMnFeCoNi. The present study reveals how chemical and magnetic complexity impacts SFEs as well as local lattice distortions. This insight will allow to further explore and optimize the mechanical properties of HEAs.

Ab initio study of local atomic stress, charge and volume distributions in disordered equiatomic multicomponent bcc alloys

Shoji Ishibashi[1,2], Fritz Körmann[1,3], Yuji Ikeda[1], Blazej Grabowski[4] and Jörg Neugebauer[1]

[1]Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany
[2]Research Center for Computational Design of Advanced Functional Materials, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan
[3]Materials Science and Engineering, Delft University of Technology, Delft, The Netherlands
[4]Institute of Materials Science, University of Stuttgart, Stuttgart, Germany

Disordered equiatomic multicomponent alloys, especially those called high-entropy alloys, have been attracting considerable attention from experiment and theory [1] because of their extraordinary properties such as high temperature strength. We investigate properties closely related to mechanical strength, i.e., local atomic stress, charge and volume distributions in various disordered equiatomic multicomponent bcc alloys (binary: MoTa, VW, ternary: HfNbZr, MoNbTa, NbVW, TaVW, quaternary: MoNbTaV, MoNbTaW, NbTaTiV, NbTaVW, quinary: HfMoTaTiZr, MoNbTaTiV, MoNbTaVW, NbTaTiVW) applying the Bader charge analysis on the results obtained by *ab initio* calculations [2].

In each alloy, the three quantities (stress, charge and volume) show finite distributions reflecting variations of local atomic arrangements due to the disordered nature. Their values have good linear correlations with each other, especially for the stress-charge pair. The linear coefficient of the correlation differs from element to element as well as from alloy to alloy, and it can be related to the amplitude of partial density of states of the element in each alloy.

It is also found that the local atomic stress for each atom can be well predicted by linear regression using elemental compositions on the first and second nearest-neighbor-atom shells as descriptors.

[1] Y. Ikeda, B. Grabowski, and F. Körmann, Mater. Charact. **147**, 464 (2019). https://doi.org/10.1016/j.matchar.2018.06.019.
[2] Y. Shiihara, M. Kohyama, and S. Ishibashi, Phys. Rev. B **81**, 075441 (2010). https://doi.org/10.1103/PhysRevB.81.075441.

TCDM 2019, Linköping-Sweden

Crystal structure, vacancy ordering effects and lattice dynamics in metal deficient AlB_2

Erik Johansson, Fredrik Eriksson, Annop Ektarawong, Johanna Rosén, and Björn Alling

Department of Physics, Chemistry and Biology (IFM), Linköping University, Sweden

erik.johansson@liu.se

It is known in the literature that there is an inherent metal deficiency present in AlB_2. It is the name holder of the P6/*mmm* structure type that many (transition) metal diborides crystallize in, for instance Ti, Sc, V, Y, Hf, Zr, Cr, Mn, Nb, Mo and Ta. Another example is Mg, forming MgB_2, a compound that is superconducting up to 39 K. Curiously enough, AlB_2 itself is not fully stoichiometric in this structure that it names. Furthermore, initial calculations of the thermal expansion of stoichiometric AlB_2 indicated that it does not follow experimental measurements as well as TiB_2. Therefore, this project investigates from first-principles density functional theory the configurational thermodynamics of metal vacancies, their origin in the electronic structure and their interplay with lattice vibrations.

By studying the electronic density of states, it is revealed that stoichiometric AlB_2 pushes the Fermi energy into the conduction band, introducing occupied anti-bonding orbitals. In contrast, metal deficient AlB_2 can deplete these states and shift the Fermi energy into the middle of the pseudo-gap between the bands. The exact configuration of vacancies at different compositions is studied in detail. Through the use of cluster expansion, effective cluster interactions are obtained and used in Monte Carlo simulations in order to study vacancy order-disorder transition temperature and to derive a phase diagram. For a subset of vacancy structures, phonon vibrational contributions in the quasiharmonic approximation are calculated to obtain volume expansion for metal deficient AlB_2, and are compared with experimental measurements performed by our partners.

Johan Klarbring
Theoretical Physics Division,
Department of Physics, Chemistry and Biology (IFM),
Linköping University, SE-581 83, Linköping, Sweden

Dynamic disorder, anharmonicity and phase transformations in perovskite-structured materials from first-principles

The perovskite crystal structure, and structures derived from it, hosts a very large range of chemistries and, as a result, a broad range of attractive properties. Common subclasses include the oxide and halide perovskites. While oxide perovskites have been studied intensively for decades, the interest in halide perovskites have surged in recent years owing to their great promise in optoelectronic devices, where, in particular, hybrid organic-inorganic lead halide perovskites and lead-free double halide perovskites are intensively studied.

Perovskite structured materials have a set of distinct features making them challenging to model by standard first-principles methods. These include high degrees of anharmonicity, complicated sequences of phase transformations and large electron-phonon coupling.

The most common class of phase transformations in these materials are the so called antiferrodistortive (AFD) transitions, which are related to the cooperative tilting of the octahedral network that makes up the perovskite structure. At low temperature, the octahedra are found in several different types of tilt configurations, depending on the type of constituent atoms, but are almost always found in the “tilt-less” ideal perovskite at high temperature.

In this talk, I will present results on our first-principles investigations of phase transformations and anharmonicity in single [1, 2] and double perovskite We use static DFT calculations to map out the potential energy surfaces (PES) of combinations of the unstable octahedral tilting phonon modes in the oxide $CaMnO_3$ and the halides $CsPbI_3$ and $CsSnI_3$. Based on the results it is pointed out that the phase transformations in these single perovskites are not well described as standard soft-mode driven displacive transitions. Instead, the results in agreement with a model in which the octahedral tilts “disappear” through dynamic disorder. This entails that, even at temperatures above the transition to the ideal cubic perovskite, the octahedral tilts are locally present in the material on the timescale of thermal vibrations. At high temperature anharmonic thermal excitations cause the system to hop between different tilt configurations in such a way that the ideal cubic perovskite emerges as a time average. This behavior is explicitly observed in our ab inito molecular dynamics (AIMD) simulations of $CaMnO_3$.

Finally, we investigate the lead-free halide double perovskite $Cs_2AgBiBr_6$. We show that while the single perovskites mentioned above have octahedral tilting PES with deep minima offset from the cubic “tilt-less” structure, the octahedral tilting PES of $Cs_2AgBiBr_6$ is instead extremely flat. This results in a qualitatively different type of anharmonicity. We further show how the cubic-to-tetragonal phase transformation observed in $Cs_2AgBiBr_6$ on cooling can be qualitatively reproduced using an energy and temperature dependent phonon spectral function, constructed by mapping out an effective third order Hamiltionian from AIMD, in the framework of the temperature dependent effective potential (TDEP) method [3].

[1] J. Klarbring, S.I. Simak. Phys. Rev. B **97**, 024108 (2018).
[2] J. Klarbring Phys. Rev. B **99,** 104105 (2019)
[3] O. Hellman et al. Phys. Rev. B **84**, 180301(R) (2011); O. Hellman et al. Phys. Rev. B. **87**, 104111 (2013); O. Hellman et al. Phys. Rev. B **88**, 144301 (2013)

Electronic Structure and Lattice Stability of Correlated Oxides under High Pressure

Ivan Leonov

M. N. Miheev Institute of Metal Physics, Russian Academy of Sciences, 620108 Yekaterinburg, Russia

Materials Modeling and Development Laboratory, National University of Science and Technology 'MISIS', 119049 Moscow, Russia

The theoretical understanding of the electronic, magnetic, and structural properties of strongly correlated materials is one of the most fundamental problems in condensed matter physics. In spite of intensive research over several past decades, an explanation of this mutual influence of the electronic structure, magnetism, and phase stability near the Mott metal-insulator transition (MIT) is still missing. Usually, the changes of the electronic structure at the MIT are intimately linked with an abrupt change of the lattice. As a result, the MIT is often accompanied by a structural transition complicated by the appearance of spin and/or charge ordering near to the Mott insulating state. Here, I will focus on this particular problem and discuss an application of the DFT+DMFT computational scheme to explore the electronic structure, magnetic moments, and lattice properties of a series of correlated systems, such as wüstite FeO, hematite Fe_2O_3, and nickelate oxide $BiNiO_3$ at high pressures. Our results reveal a complex interplay between electronic correlations and lattice in the above-mentioned compounds under pressure. In particular, in the vicinity of a pressure-induced MIT FeO and Fe_2O_3 are found to exhibit a series of complicated electronic, magnetic, and structural transformations, which are accompanied by a (site-selective or orbital-selective) collapse of local magnetic moments and delocalization of the Fe *3d* electrons under pressure [1]. Our results show a complex variety of different crystallographic structures in the vicinity of the MIT in these materials. $BiNiO_3$ exhibits an anomalous negative-charge-transfer insulating state characterized by charge disproportionation of the Bi 6s states, with Ni^{2+} ions [2]. Under pressure it exhibits the MIT associated with the melting of charge disproportionation of the Bi ions due to a charge transfer between the Bi *6s* and O *2p* states. Our results demonstrate that electronic correlations are critically important to explain the electronic state and the lattice stability of the above-mentioned oxides under pressure.

[1] E. Greenberg *et al.*, Phys. Rev. X **8**, 031059 (2018); I. Leonov, G. Kh. Rozenberg, I. A. Abrikosov, to appear in npj. Comput. Mater.

[2] I. Leonov, A. S. Belozerov, S. L. Skornyakov, arXiv:1907.1317

Title: Data-guided approach for multi-principal element alloys discovery

Authors: Y. Lysogorskiy, A. Ferrari, R. Drautz
ICAMS, Ruhr University Bochum, Bochum, Germany

Multiple principal element alloys nominally consist of five or more elements at near-equal compositions in a single crystalline phase. Considering fifty chemical elements, more than two millions possible equiatomic compositions with five constituent species can be easily reached. The experimental study of such a large number of combinations is prohibitive. Standard ab-initio simulations, even in the high-throughput regime, are limited in a similar way by high computational costs. Thus, preliminary filtering and reduction to a feasible number of candidate materials systems are necessary.

In the given work we present a data-guided approach that tackles the combinatorial complexity of element combinations in high-entropy alloy by exploiting surrogate machine learning models that estimate the mechanical properties (i.e. via bulk and shear modulus as proxies) together with other criteria, such as solid solution strengthening, solid-solution forming ability and also novelty and cost. With this pre-selection the best candidate multi-principal element alloys can be shortlisted for subsequent studying by ab-initio methods, experimental synthesis and characterisation. As an example, we present the investigation of the phase stability in one of the alloys selected by our approach.

Coexistence of complex phases in Ni(Ti,Zr)(Sn,Sb) and Co(Ti,Zr)(Sn,Sb) half-Heuslers.

Joaquín Miranda Mena and Thomas Gruhn

Biomaterials, Universität Bayreuth, Universitätsstraße 30, D-95447 Bayreuth, Germany

Half-Heuslers, such as NiTiSn and CoTiSb, present excellent electronical properties to be considered as high-efficiency thermoelectrics, provided their lattice heat conductivity is diminished. In this regard, selective alloying can reduce lattice vibrations in two ways: by disorder scattering and by phase separation. In this work with the help of a cluster expansion in Ni(Ti,Zr)(Sn,Sb) and Co(Ti,Zr)(Sn,Sb) alloys, we couple three computational methods, which can capture the relevant physics at different length-scales, namely density functional theory, Monte Carlo simulations and a mean-field model. We found that the transition from a disordered state to a phase separation is indeed possible and controlled by two very different mechanisms. One is the lattice's mismatched created by the shorter(longer) atomic radius of Ti(Zr); the second mechanism is given by the bond's covalency whose strength is regulated by the change in the Sb/Sn electron counting, which at the same time triggers the formation of magnetic domains. We provide phase diagrams that could guide the synthetization of materials with a suitable morphology for efficient phonon scattering.

Structure of metastable cubic SiNx tissue phase in nanocomposites with TiN from ELNES spectroscopy.

W. Olovsson (1), B. Alling (1), M.P. Belov (2), I.A. Abrikosov (1), A. Fallqvist (1), J. Palisaitis (1), L. Hultman (1), and P.O.Å. Persson (1)

(1) Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-58183 Linköping, Sweden
(2) Materials Modeling and Development Laboratory, National University of Science and Technology MISIS, Leninskii pr 4, Moscow 119049, Russia

By using electron energy loss near edge structure (ELNES) spectroscopy together with first-principles density functional theory (DFT) calculations, starting from the highly accurate all electron full potential linearized augmented plane wave (FPLAPW) method as implemented

in the WIEN2k program package [1], we investigate the structure of the much debated metastable cubic SiNx tissue phase in nanocomposites with TiN. The calculations are performed by using the TELNES3 package within WIEN2k. The studied material belongs to the hardest known and are therefore of very high interest for hard and superhard applications, such as cutting tools. From the study, we infer that SiNx hosts vacancies on the Si site [2].

[1] http://www.wien2k.at/
[2] A. Fallqvist et al. Phys. Rev. Mat. 2, 093608 (2018)

A DMFT insight into the Earth's core: electronic correlations in iron under extreme conditions

L. V. Pourovskii

CPHT, CNRS, Ecole Polytechnique, IP Paris, F-91128 Palaiseau, France
Collège de France, 11 place Marcelin Berthelot, 75005 Paris, France

The Earth's inner core (EIC) formed by a solid iron-rich alloy is subjected to extreme conditions with the pressure of 330÷370 GPa and temperature of 5200÷6500 K. The composition, crystal structure, elastic and transport properties of the EIC matter remain actively debated. During the last decade the EIC pressure-temperature conditions have been reached in laser-heated diamond anvil cells, however, experimental measurements at such conditions are still challenging. In this talk we review recent theoretical studies of iron and iron-rich alloys under the EIC conditions focusing on the impact of many-body effects on their electronic structure, phase stability and transport. These studies have been carried out using a beyond-DFT approach based on the dynamical mean-field theory (DMFT). The strength of correlation effects is found to vary significantly between the three known phases of pure Fe. In particular, a good-metal Fermi liquid behavior is predicted for the hexagonal close-packed (hcp) ε-phase, while body-centered-cubic (bcc) α-Fe exhibits a non-Fermi-liquid electron-electron scattering (EES) and a Curie-Weiss magnetic susceptibility [1]. The impact of alloying with Ni on electronic correlations in these 3 phases is also analyzed [2]. The Fermi-liquid state of ε-Fe is shown to result in a significant suppression of its Lorenz number leading to a relatively high contribution of the ESS to the thermal resistivity that is comparable to the electron-phonon one [3]. The impact of lattice vibrations on many-electron effects is studied for the bcc α-phase; the loss of perfect crystalline order is predicted to suppress the non-Fermi-liquid state. The transport in this phase is found to be determined by intertwined effects due to the electron-lattice and electron-electron scattering.

References:

[1] Pourovskii , Miyake, Simak, Ruban, Dubrovinsky, Abrikosov PRB 87, 115130 (2013)
[2] Vekilova, Pourovskii, Abrikosov, Simak, PRB 91, 245116 (2015)
[3] Pourovskii, Mravlje, Georges, Simak, Abrikosov, New J. Phys. 19, 073022 (2017)

SCALE-BRIDGING STUDY OF MAGNETISM FOR IRON-SILICON STEELS

M. Rinaldi[1], M. Mrovec[1], R. Drautz[1]
ICAMS, Ruhr-Universitaet Bochum, Germany

Magnetic steels containing small amounts of silicon have been used extensively as soft magnetic materials in various technological applications. These materials are characterized by low magnetocrystalline anisotropy and magnetostriction constants. The addition of silicon is crucial for improvement of intrinsic magnetic properties as well as low core losses, small saturation induction and high electrical resistivity. From a theoretical point of view, the behavior of magnetic materials can be simulated using a suitable micromagnetic model to obtain relevant mesoscopic quantities, such as the coercive field and the magnetic permeability, and to establish a link between the microstructure and magnetic properties. In our work, we employ first-principles electronic structure calculations to investigate the dependence of micromagnetic parameters (i.e., magnetic anisotropy, exchange stiffness constant and magnetostriction) on the Si concentration in the Fe-Si system. The obtained parameters are used as input into a micromagnetic model that can provide equilibrium distribution of magnetization, the coercive field and the magnetic permeability as a function of the microstructure (e.g., grain size and orientation, free surfaces).

High temperature magnetism and phase stability of 3-d metal and their alloys from DFT-based modeling

Andrei Ruban[1,2]

[1] *Department of Materials Science and Engineering, Royal Institute of Technology, 10044 Stockholm, Sweden;*
[2] *Materials Center Leoben Forschung GmbH, 8700 Leoben, Austria*

The talk will present different density functional theory based models of the finite temperature itinerant and localized magnetism including magnetic short- and long-range order as well as longitudinal spin fluctuations in the paramagnetic state and their applications to the description of thermodynamic properties of the corresponding systems. Several examples of 3d-metals and their alloys will be given demonstrating their seeming success and limitations.

Superionic-like diffusion in an elemental crystal: bcc Titanium

D.G. Sangiovanni,[1,2] J. Klarbring,[1] D. Smirnova,[2,3] N. Skripniak,[1] D. Gambino,[1]
M. Mrovec,[2] S. Simak,[1] I.A. Abrikosov[1,4]

[1]Department of Physics, Chemistry and Biology (IFM) Linköping University,
SE-581 83, Linköping, Sweden

[2]ICAMS, Ruhr-Universität Bochum, D-44780 Bochum, Germany

[3]Joint Institute for High Temperatures, Russian Academy of Sciences, Moscow,
Russia

[4]Materials Modeling and Development Laboratory, NUST "MISIS", 119049 Moscow,
Russia

Recent theoretical investigations [Belonoshko et al. Nature Geoscience 10 (2017) 312] revealed that concerted migration of several atoms occurs in bcc Fe at earth inner-core temperatures, >6000 K, and pressures, ~360 GPa. We combine first-principles and semi-empirical atomistic simulations to show that a liquid-like diffusion, a dynamical disorder analogous to the one predicted for bcc iron at extreme conditions, is also operative and of relevance for the high-temperature bcc phase of pure Ti at ambient pressure. The mechanism entails a rapid collective movement of numerous (from two to tens) neighbors along tangled closed-loop paths in a defect-free crystal lattice. We argue that this phenomenon is fundamentally different from formation, followed by fast recombination, of vacancy/self-interstitial pairs, and closely resembles the diffusion behavior observed in superionics. Our results show that concerted migration underlies the anomalously large and markedly non-Arrhenius atomic self-diffusivities of bcc Ti in relation to Group-VB and Group-VIB metals and that the occurrence of liquid-like diffusion in bcc Ti is the atomistic manifestation of vanishingly small ω-mode phonon frequencies previously detected via neutron scattering measurements.

Title: Active learning of interatomic potentials

Abstract:

Molecular modelling relies, typically, on two classes of models of interatomic interaction, namely (1) quantum-mechanical (QM) models that are very accurate but very computationally expensive, and (2) empirical interatomic potentials that typically offer only qualitative accuracy but are very computationally efficient. There has been a number of successful applications of machine learning to constructing interatomic potentials that combine the efficiency of empirical potentials and the accuracy of QM models. A harder challenge, however, is to make such potentials reliable - it requires fitting hundreds to thousands of parameters and making sure that they produce reasonable results in the entire region of interest in the phase space (which could be given only implicitly, e.g., all configurations with energy below a certain threshold).

In my talk I will give a mathematician's perspective on the field of machine learning interatomic potentials. I will then present an example of accurate and computationally efficient machine learning interatomic potentials, and finally I will show how active learning can ensure reliability of such potentials. I will conclude by illustrating how these potentials can be used to treat disorder, defects, and vibrations in materials.

Sergei I. Simak; IFM, Linköping University, SE-581 83, Linköping, Sweden

Phase stability of dynamically disordered solids from first principles
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 Bi_2O_3, 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).

Study of electronic topological transitions in Ir-Os, Ir-Pt, Os-Re, Os-Rh disordered alloys under high pressure.

E.A.Smirnova[1], K.V.Karavaev[1], I.A.Abrikosov[1,2]

[1] NUST "MISIS", Moscow
[2] IFM, Linköping University, Linköping

We present a systematic study of the electronic structure of disordered alloys of Ir-Os, Ir-Pt, Os-Re, and Os-Rh system. For the calculations of the total energy of the disordered alloys we used the Exact Muffin-Tin Orbitals (EMTO) method in combination with the coherent potential approximation [1]. We investigated the Fermi surfaces topology with increasing the pressure in alloys with different concentrations. It was shown that the electronic topological transitions (ETTs), associated with changes in pressure, exist in hcp alloys of Os-Re, Os-Rh, Ir-Os. In fcc alloys of these systems there are no pressure induced changes of the Fermi surface topology. At the same time, in all the systems there are ETTs associated with changes of the concentration of the alloy. We investigated the effect of ETTs on the thermodynamic and elastic properties of the considered disordered alloys.

[1] L. Vitos, I.A. Abrikosov, and B. Johansson, Phys. Rev. Lett. 87, 156401 (2001).

Using machine-learning potentials for vibrational free energy calculations of multicomponent alloys

P. Srinivasan[1], Y. Ikeda[2], B. Grabowski[2,3], J. Janssen[2], A. Shapeev[4], J. Neugebauer[2], and F. Körmann[1,2]

[1]*Delft University of Technology, Delft, Netherlands*
[2]*Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany*
[3]*University of Stuttgart, Stuttgart, Germany*
[4]*Skolkovo Institute of Science and Technology, Moscow, Russia*

Abstract

High entropy alloys have gained widespread attention in recent times owing to their superior mechanical properties. *Ab inito* modeling is a powerful tool to analyze and predict their thermodynamic properties. In combination with statistical sampling techniques, free energy surfaces *F(T,V)* are accessible from which properties such as thermal expansion coefficient and heat capacity can be derived and directly compared to experiments. At higher temperatures, the vibrational free energy — including anharmonic contributions — is a major contributor. But as the number of components in the alloy increases, *ab initio* calculations to obtain accurate values of the free energy become very expensive and infeasible. In this work, we present a density-functional-theory based approach to accurately and efficiently calculate vibrational free energies for such chemically complex materials [1]. The method combines two techniques – firstly, a machine learnt potential (moment tensor potential [2]) is built based on *ab initio* data, the validity of which is tested by comparing its results to DFT, and secondly, the MTP is used as a part of a thermodynamic integration [3] to get accurate vibrational free energies. The approach is applied to 5 unaries and 12 refractory alloys having two to five components to study the impact of configurational entropy on the vibrational free energies. The workflow is implemented in pyiron [4] (http://pyiron.org) to enhance its dissemination and reuse.

References

[1] B. Grabowski, Y. Ikeda, P. Srinivasan. F. Körmann, C. Freysoldt, A. I. Duff, A. Shapeev and J. Neugebauer. *submitted*, (2019)

[2] A. V. Shapeev. *Multiscale Model. Simul.*, 14, 1153, (2016)

[3] A. I. Duff, T. Davey, D. Korbmacher, A. Glensk, B. Grabowski, J. Neugebauer and M. W. Finnis. *Phys. Rev. B*, 91, 214311 (2015)

[4] J. Janssen, S. Surendralal, Y. Lysogorskiy, M. Todorova, T. Hickel, R. Drautz and J. Neugebauer. *Comp. Mat. Sci*, 163, 24 (2019)

---

submitted to TCDM 2019, Linköping, Sweden

Development of interatomic potential for atomistic simulation of Fe-Cr-H system

S. Starikov, D. Smirnova, M. Mrovec, R. Drautz

Interdisciplinary Centre for Advanced Materials Simulation, Ruhr-University, Bochum, Germany

The atomistic simulation with classical potential is a powerful tool for study of mechanical and transport properties in material. The choice of interatomic potential plays key role at such simulations. In this work, we have developed a new interatomic potential for Fe-Cr-H system that have several strong advantages in comparison with the existing interatomic models. To construct the potential functions, we applied the force-matching method. It gives a way to construct physically justified interatomic potentials from the fitting database containing no experimental data. The idea is to adjust the interatomic potential to optimally reproduce per-atom forces (together with total energies and stresses) computed at the ab initio level for a fine-tuned set of reference structures. The reported potential has an angular-dependent form and can be used for simulation of pure iron or pure chromium, as well as for consideration of ternary cases including Fe, Cr and H. The results of classical molecular dynamics were compared with the results of DFT calculations and the available experimental data. Summary of the performed tests on elastic, thermophysical, defects and diffusional properties proves that the potential has a wide range of applicability.

Thermal expansion of quaternary nitride coatings

Ferenc Tasnádi,[1] Magnus Odén,[1] and Igor A. Abrikosov[1, 2]
[1] *Department of Physics, Chemistry, and Biology (IFM),*
Linköping University, SE-581 83, Linköping, Sweden.
[2] *Materials Modeling and Development Laboratory, NUST "MISIS", 119049 Moscow, Russia.*

(Dated: May 31, 2019)

Abstract

Pseudoternary $\mathrm{Ti}_{(1-x)}\mathrm{X}_x\mathrm{N}$ (X = Zr, Hf, Nb, V, Ta) coatings (without Al content) have gained attention as alternatives of TiN for cutting and machining tools because of improved wear, oxidation resistance or lubricating effects. Motivated by the superior properties of $\mathrm{Ti}_{(1-x)}\mathrm{Al}_x\mathrm{N}$ alloy thermodynamic properties of quaternary nitrides are of industrial interests.

The thermal expansion coefficient of technologically relevant multicomponent cubic nitride alloys are analysed using the quasi-harmonic Debye model with ab initio elastic constants calculated at 0 K and an isotropic approximation for the Grüneisen parameter. Our linear approximation approach is benchmarked against measured thermal expansion of TiN and $\mathrm{Ti}_{(1-x)}\mathrm{Al}_x\mathrm{N}$ as well as against results of ab-inito molecular dynamics simulations and a recently developed machine learning approach. We show that the thermal expansion coefficients of $\mathrm{Ti}_{(1-x-y)}\mathrm{X}_y\mathrm{Al}_x\mathrm{N}$ (X = Zr, Hf, Nb, V, Ta) solid solutions monotonously increase with the amount of alloying element X at all temperatures except for Zr and Hf, for which they instead decrease for $y \gtrsim 0.5$. Moreover we discuss an extension of the applied linear approximation.

Extended theoretical investigation of high pressure polymorphs of silica

Johan Tidholm,[1] Olle Hellman,[2, 1] Sergei I. Simak,[1] Ferenc Tasnádi,[1] and Igor A. Abrikosov[1]
[1]*Department of Physics, Chemistry, and Biology (IFM),*
Linköping University, SE-581 83, Linköping, Sweden.
[2]*Division of Engineering and Applied Science, California Institute of Technology, Pasadena, California 91125.*

One of the most common materials known is silica (SiO_2), its large number of polymorphs have been studied to increase the insight of the interior's behaviour of our planet. Two newly discovered high pressure phases of silica, coesite-IV and coesite-V, have been reported.[1] For these two new phases together with the two competing ones (stishovite and seifertite), we have calculated, from ab initio simulations, equation of states (EOS), bulk moduli, enthalpies, Bader charges, elastic constants, and electronic structure in the form of band structures and density of states (DOS). Additional for the two new phases, phonon calculations were also preformed. The enthalpy of coesite-IV and coesite-V where approximately 0.4 eV per atom higher than stishovite and seifertite in the relevant pressure range, together with the results of the phonon calculations, indicating that these two new phases are dynamical stable within these pressures, we make the conclusion that coesite-IV and coesite-V are metastable and could exist in nature. The bulk moduli for the two new phases were also lower than the two competing phases. These results suggest that the lower mantle could be more compressible than previously thought. By comparing the electronic structure of the two new phases and the competing ones we hope to find additional information that could explain the large differences of enthalpy. And by calculating the elastic constants extend the information of the mechanical properties of these two new phases of silica.

---

[1] E. Bykova, M. Bykov, A. Černok, J. Tidholm, S. I. Simak, O. Hellman, M. P. Belov, I. A. Abrikosov, H. P. Liermann, M. Hanfland, V. B. Prakapenka, C. Prescher, N. Dubrovinskaia, and L. Dubrovinsky, Nature communications **9**, 4789.

Lattice Green function calculations in presence of a dislocation

Dallas R. Trinkle, Materials Science and Engineering, University of Illinois, Urbana-Champaign

Mechanical behavior, specifically plastic deformation at low and high temperatures in metal alloys is governed by the motion of dislocations: topological line defects in a crystal. Dislocations in crystalline materials were hypothesized nearly eighty years ago, and their experimental and theoretical study has provided powerful tools for modern materials engineering. While the long-range elastic field of a dislocation is known and straight-forward to compute, many of the strongest effects of dislocations occur in the "core"--the center of the dislocation--where elasticity breaks down, and new chemical bonding environments can often make even empirical potential descriptions suspect. Hence, there is much effort to use the accuracy of modern quantum mechanical methods (like density-functional theory) to study dislocation cores accurately, as well as their interaction with other defects, such as solutes and boundaries. While there are a variety of possible coupling or "multiscale" techniques available, I will focus on flexible boundary conditions, which use the lattice Green function to couple electronic structure to an infinite harmonic bulk; this approach greatly simplifies many "hand-shaking" problems, and generally provides a computationally efficient approach. The latest developments include a new numerical approach that accounts for the topology change of a dislocation. This same methodology can also be used to compute a dislocation core in a random alloy, which requires new considerations beyond that of a ordered crystal.

Temperature dependent elastic properties and stacking fault energy of nickel from first principles

Jing Zhang, Pavel A. Korzhavyi

Materials Science and Engineering, KTH Royal institute of Technology, SE-100 44 Stockholm, Sweden

Abstract

Nickel-based superalloys are an important group of high-temperature materials. Since nickel is the main component of the matrix in nickel-based superalloys, understanding the temperature behavior of the physical properties of pure nickel is of fundamental interest. Temperature-dependent elastic properties (bulk modulus B, shear modulus G and single crystal elastic constants) and stacking fault energies (SFEs) are very useful in modeling the effect of temperature on the properties of nickel-based alloys. Thus, the generalized stacking fault energy (so-called γ-surface) is the key to the mechanisms of plastic deformation in metallic materials. In this work, temperature-dependent elastic properties and SFEs are investigated using the exact muffin-tin orbitals (EMTO) method based on density functional theory. The exchange-correlation energy is treated within the GGA using the PBE formalism. The disordered local moment (DLM) model was employed for the description of magnetic degrees of freedom in the paramagnetic state of nickel. The free energy contributions due to lattice vibrations at finite temperatures have been taken into account in the quasi-harmonic Debye model. The SFEs have been calculated according to three different methodologies, i.e. the axial-next-nearest-neighbor-Ising (ANNNI) model, the tilted supercell approach, and the slab supercell approach. The results show that the elastic constants and SFEs decrease dramatically with increasing temperature. This “softening” effect on the mechanical properties of nickel mainly results from the thermal expansion of the lattice as well as from the magnetic entropy contribution.

Keywords: Nickel; elastic properties; stacking fault energy; temperature dependence.

Description of Paramagnetism, gap formation and atomic displacements in 3d oxide perovskites in polymorphous DFT

Alex Zunger

Energy Institute, University of Colorado, Boulder, Colorado 80309, USA

ABO_3 perovskite oxides with a *3d* transition metal element on the B site ("Mott Insulators") have held the solid-state physics community in constant fascination ever since Mott and Peirles have characterized them as failures of band theory. These compounds are usually insulators in their high temperature spin-disordered paramagnetic phase, and insulators (or rarely metals) in their low temperature spin-ordered phases. The failure of Naïve DFT to describe their basic ground state properties has led to a community mass migration to explicitly correlated approaches, implemented through time fluctuation of spins via *symmetry-conserving* approaches codified by the on-site repulsion energy U. Structural distortions such as bond disproportionation in $RNiO_3$ or Jahn-Teller motions in $LaMnO_3$ appears as secondary effects, not related to gapping.

Band theory was assumed for long to fail to describe Mott insulators, in particular in the PM phase. However, this failure occurred under rather restrictive assumptions, such as using in band theory a primitive unit cell containing but a single, ABO_3 formula unit (a monomorphous description with a single local motif , so structural symmetry breaking could not be accommodated), along with a non-spin polarized description. Under such restrictions, a system with an odd number of electrons, unable to form magnetic states, must have a Fermi level that intersects a band, in contradiction with experiment.

However, such naïve (N) Density Functional Theory (N-DFT) does not represent what band theory can do. Indeed, recent work, to be discussed here, had shown that when the PM phase is described by a supercell, where different transition metal sites can 'see' different local environments (a polymorphous description) with local moments that add up to zero globally, but not necessarily locally, the system could lower its total energy by coupling to atomic displacements and magnetic moments. This can open gaps when such coupling exist (most ABO3), but leaves the system metallic when such coupling is negligible (e.g SrVO3). In conjunction with exchange-correlation functionals that distinguish occupied from unoccupied states, such a polymorphous DFT applied to all ABO_3 3d perovskites as well as 3d binary oxides NiO, MnO, FeO, CoO has shown that the observed trends in LT vs HT magnetism and gaping can be systematically accounted for by considering *symmetry breaking* modes that simultaneously lower the systems total energy. This is true whether one uses "U" as in in DFT+U, or even without U, using a functional that better cancels the self- interaction error (SCAN).This illustrates how the basic trends in Mott insulator ground state properties can be accounted for using single-determinant DFT, and exemplifies Mott Insulators without Mott-Hubbard U. We conclude that the allegation of the failure of DFT was premature, and that the migration to dynamic time fluctuations methods (instead of spatial fluctuations used here) represents merely a choice and a viewpoint, not forced by the physics.

- In collaboration with G. Trimarchi, J.Varignon, and Z.Wang

Julien Varignon , Manuel Bibes & Alex Zunger Nature Commun volume 10,
Article number: 1658 (2019)
Origin of band gaps in 3d perovskite oxides

Julien Varignon, Manuel Bibes, and Alex Zunger PHYSICAL REVIEW B 100, 035119 (2019)
Mott gapping in 3d ABO3 perovskites without Mott-Hubbard inter-electronic repulsion energy U

G. M. Dalpian, Q. Liu, J. Varignon, M. Bibes, and Alex Zunger, "Bond disproportionation, charge self-regulation, and ligand holes in s-p and in d-electron ABX3 perovskites by density functional theory" Phys. Rev. B 98, 075135 (2018).

Giancarlo Trimarchi, Zhi Wang, and Alex Zunger, PHYSICAL REVIEW B 97, 035107 (2018) “Polymorphous band structure model of gapping in the antiferromagnetic and paramagnetic phases of the Mott insulators MnO, FeO, CoO, and NiO”

Qihang Liu, Gustavo M. Dalpian and Alex Zunger, "Antidoping in Insulators and Semiconductors Having Intermediate Bands with Trapped Carriers" Phys. Rev. Lett. 122, 106403 (2019).

Julien Varignon and Manuel Bibes and Alex Zunger “Origins Vs. fingerprints of the Jahn-Teller effect in d-electron ABX3 perovskites” http://arxiv.org/abs/1906.07587

icet – A Python library for constructing and sampling alloy cluster expansions

Mattias Ångqvist[1], William A. Muñoz[1], J. Magnus Rahm[1], Erik Fransson[1], Céline Durniak[2], Piotr Rozyczko[2], Thomas Holm Rod[2], and Paul Erhart[1]

[1] Chalmers University of Technology, Department of Physics, Gothenburg, Sweden
[2] Data Management and Software Centre, European Spallation Source, Copenhagen, Denmark

May 15, 2019

Abstract

Many materials exhibit some form of chemical ordering, which can have a crucial impact on their macroscopic properties. Here, atomic scale modeling based on the so-called alloy cluster expansion (CE) technique can yield very valuable information. In this contribution, we present the open-source icet package that provides an efficient implementation of this methodology. It takes advantage of state-of-the-art machine learning techniques to generate accurate and predictive models based on quantum mechanical calculations. The icet package features a Python interface that enables seamless integration with other Python libraries including for example SciPy or scikit-learn. Yet, all computationally demanding parts are written in C++ providing performance while maintaining portability. We demonstrate the application of icet by (1) studying chemical ordering and associated properties in a series of intermetallic clathrates as a function of composition and temperature and (2) by predicting the phase diagrams of bulk and surface alloys.

Correlated electronic structure with uncorrelated disorder

Andreas Östlin

We introduce a computational scheme for calculating the electronic structure of random alloys that includes electronic correlations within the framework of the combined density functional and dynamical mean-field theory. By making use of the particularly simple parametrization of the electron Green's function within the linearized muffin-tin orbitals method, we show that it is possible to greatly simplify the embedding of the self-energy. This in turn facilitates the implementation of the coherent potential approximation, which is used to model the substitutional disorder. The computational technique is tested on the Cu-Pd binary alloy system, and for disordered Mn-Ni interchange in the half-metallic NiMnSb [1].

[1] A. Östlin, L. Vitos, and L. Chioncel, Phys. Rev. B 98, 235135 (2018)