

# Search for substitutes of critical materials with targeted properties by scale-bridging and high-throughput modelling and simulation

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In this lecture I will address three case studies on how sustainable substitutes for such materials, which have outstanding functionalities but also constraining criticalities, can be discovered and developed efficiently by employing multi-scale-coupling and high-throughput-screening concepts of ICME.

In the first case, a multi-scale chain from atomic-level first-principles theory to microstructure-level phase-field theory for ferroelectric piezoelectrics is set up for the still best material  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  (PZT), which contains the biomedically health-critical element Pb, and then transferred to  $(\text{K, Na})\text{NbO}_3$  (KNN), which is a potential substitute for PZT. [1]

The second case is on the modelling of structure-property relationships for transparent and conductive oxides (TCO), which are free of the geologically resource-limited element Indium and therefore potential substitutes for the still best TCO material Indium Tin Oxide (ITO) for front electrodes on, e.g., smart phones or solar cells. [2]

In the third case, a combinatorial high-throughput-screening approach is employed to search for crystal structures and chemical compositions of intermetallic phases of transition-metal (TM) and rare-earth (RE) elements, which have sufficiently good intrinsic ferromagnetic properties for permanent magnets but contain less amounts of the geopolitically supply-critical RE elements than, e.g., the still best permanent magnets based on  $(\text{Nd,Dy})_2\text{Fe}_{14}\text{B}$ . [3]

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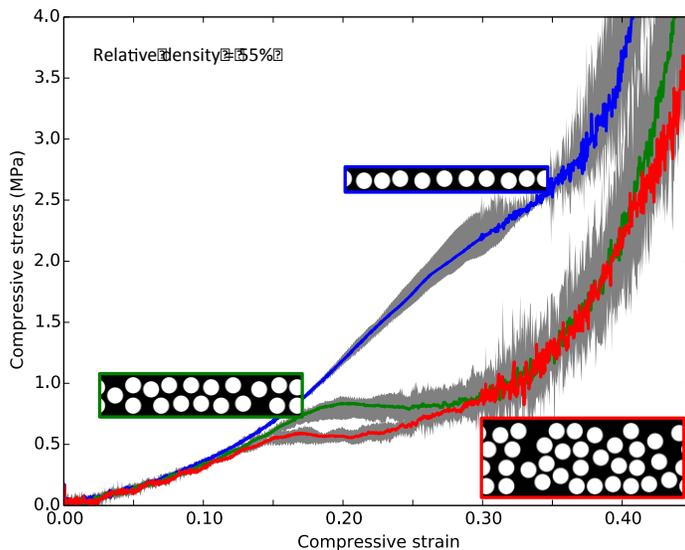
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# Modeling the Behavior of Cellular Silicone Pads in the Structure-Continuum Transition

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Cellular silicone pads have properties that make them excellent materials for applications where components must be protected from the effects of high temperature, intense mechanical loading, and other extremes. These pads can be engineered to have a controlled distribution of pore sizes through a process of adding spherical particles to silicone, curing the mixture, and then washing out the inclusions to form pores. Experiments have shown that when these pads are thin (1-2 pores through the thickness) they are drastically stronger in compression than thicker pads, which exhibit a continuum-like response that is independent of thickness. The goal of this work is to develop models for this behavior to guide material characterization experiments and improve the continuum-based material models. The results of FE simulations, in which pads of varied thickness and with randomly placed pores of uniform size are compressed under periodic boundary conditions, confirm the trend of increasing strength with decreasing thickness (see Figure 1). This behavior is consistent with the stretching and bending of struts/walls in foams, as quantified by Alkhader et al [1], and a similar behavior is seen in periodic structures [2]. The presentation will further explore the underlying mechanics leading to this behavior and compare results with an accompanying experimental study to better predict the behavior of these materials.



**Figure 1:** Finite Element modeling shows thinner cellular silicone pads exhibit a stronger stress-strain response than thicker pads. Each curve is the averaged response of several foams of equal thickness with the shaded region representing the maximum and minimum response. Representative images of the foams are shown for each thickness.

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## **Analysis of electronic subgap states in amorphous semiconductor oxides on the example of Zn-Sn-O systems**

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A molecular dynamics (MD) and density-functional-theory (DFT) study of amorphous Zn-Sn-O (ZTO) with focus on the use as transparent conducting oxides materials is presented. The amorphous structures generated by MD are in the following relaxed using the local-density-approximation (LDA) of DFT. The Zn/Sn ratio, the oxygen content and individual point defects are investigated concerning their thermodynamic and electronic properties and compared to data of crystalline structures. Defect levels in the electronic band structure of ZnO are analysed in terms of densities of states, which are calculated by means of the LDA and with a self-interaction-correction (SIC).

In our study we connect the electronic subgap states, which were observed recently by Nomura et al.[1] and Erslev et al.[2] with structural features of the amorphous samples. According to our analysis the valence band tail, caused by the disordered O 2p orbitals, is superimposed by deep defect states that can be assigned to undercoordinated O atoms which is not in line with the assignment of those states to oxygen vacancies by Kamiya et al.[3]. Our alternative is further supported by the fact that doping with H atoms suppresses these states by creating O--H bonds, which improves the transparency and is consistent with experimental findings [1].

The deep levels below the conduction band arise mainly from undercoordinated Sn atoms or Zn--Sn pairs. The addition of oxygen can be a possible route to reduce such defect levels.

In a similar study on In-Ga-Zn-O (IGZO) we have found essentially the same characteristics. Defect levels due to undercoordinated oxygen atoms create defect levels in the lower half of the band gap whereas metal--metal (In--Zn e.g.) related defects lead to defect levels in the upper half of the band gap. Our work is published in

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## **Materials Design and Discovery: Role of Atomic-Scale Modeling**

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A driving force for much of the research that takes place in many disciplines is the discovery and design of new materials to improve existing technologies or enable new applications. Material modeling methods are now widely applied and show promise for fulfilling the ultimate goal contained within the phrase “materials by design”. This presentation will review the evolution of some common material modeling methods and their integration with cutting-edge experimental methods as well as data informatics. Illustrative applications will be discussed within the context of metal/piezoelectric interfacial systems for electronic devices, new metal alloy design, and the role of strain and dopants in the design of multifunctional materials. A future outlook of materials modeling within the context of material design and discovery will also be provided.

## **Thermodynamics of $\alpha$ -Fe solid solution: interplay between vacancies and interstitial solutes (C, N and O)**

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Carbon (C), nitrogen (N) and oxygen (O) atoms are always present in  $\alpha$ -iron (Fe), either as impurities or as alloying elements. Even the so-called pure Fe usually contains at least 0.1 appm of each impurity.

In this work we show that, despite low solute concentrations and even lower equilibrium vacancy concentrations, their interplay has an important impact on some thermodynamic properties of  $\alpha$ -Fe solid solutions, e.g. vacancy formation energies and solute solubility limits.

For each solute, a generalized Hamiltonian is derived on the perfect body-centered cubic lattice including substitutional and octahedral interstitial sites. It is composed of 2-, 3- and 4-body interactions between vacancies and solutes, up to the 8<sup>th</sup> nearest-neighbour. Interactions are fitted to a whole set of DFT calculations of small vacancy-solute clusters binding energies, and the predictive capability of the Hamiltonian is checked against another set of clusters. The interaction model is included into a Low Temperature Expansion formalism (validated by comparison with Atomic Monte Carlo simulations) from which the free energy of the solid solution is obtained. First, it is shown how solutes (mostly N and O) strongly decrease the vacancy formation energy, even at concentrations below 1 appm. This observation could as well explain the frequent disagreement between experimental and DFT decomposition of Fe self-diffusion activation energy. Then, the Fe-rich part of Fe-X (X = C, N or O) phase diagrams is computed, using a semi-empirical method for the estimation of solute solution entropies. Vacancies are predicted to play a non-negligible role in the phase diagram of Fe-O.

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**OpenKIM.org: Ensuring reliability, reproducibility and transferability in multiscale and atomistic simulations**

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Multiscale and atomistic simulations using empirical interatomic potentials play a key role in realistic scientific and industrial applications. This talk describes a current NSF-CDI funded effort to develop an open source online tool for promoting the use and reliability of interatomic models. The open Knowledgebase of Interatomic Models (<https://OpenKIM.org>) allows users to compare model predictions and reference data using a visualization system, to generate new predictions by uploading simulation test codes, and to download models conforming to an application programming interface (API) standard that has been developed in collaboration with atomistic simulation community. An overview of the KIM project will be given along with recent developments related to the KIM API, a new data structure for representing arbitrary material properties, and metrics for interatomic model transferability.

## **Grain boundary segregation as a route to stabilize nanocrystalline alloys: A phase field study**

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Owing to their nanometer characteristic length scale, nanostructured alloys exhibit a unique combination of properties, which render them an attractive material of choice in many technological sectors. On the other hand, these systems are often unstable against grain growth and coarsening processes even at low service temperatures and/or modest processing schedules. The development of nanostructured materials with increased stability against microstructural evolution processes is necessary in order to increase their competitiveness viz-à-viz other materials systems, especially in applications with harsh operating environments and elevated temperatures.

Recent experimental findings suggest that stable nanostructured alloys can be formed. In such systems, a heterogeneous distribution of solute is reached when the alloying elements preferentially occupy grain boundary regions; a state where bonding preferences are satisfied and a reduction in grain boundary energy is achieved. The design parameters here are the choice of solute and host atoms and their respective compositions, such that the resulting alloy is stable against grain growth and long-range chemical ordering.

In this talk, we present a diffuse-interface model for grain boundary segregation in binary nanostructured alloys and the accompanying solute drag affecting grain growth and phase separation. The model accounts for bulk thermodynamics, interface-driven processes and solute-grain boundary interaction, and is linked with atomistic models through several input parameters, such as diffusivity, boundary mobility and interfacial energy. Simulation results highlight the role of high solute content in grain boundaries on grain growth in these systems. Furthermore, scaling laws for growth dynamics and their dependence on solute concentration, which are extracted from the modeling results, provide further avenues to explore as far as the stability of these systems.

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## **Scale bridging modelling of hydride formation**

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Hydrogen embrittlement is a serious issue for many high strength steels, and still a thorough understanding of this phenomenon is lacking. Among the different suggested models the hydrogen enhanced decohesion picture is based on a change of fracture energy due to hydrogen accumulation. We discuss the role of hydride formation, especially near free surfaces and in the vicinity of crack tips, from a combined ab initio, atomistic, mesoscale and thermodynamic perspective. Here, in particular the presence of elastic deformations can largely influence the hydride phase formation, and we demonstrate how this aspect can be covered in a scale bridging approach.

# **Material and microstructure based design of anisotropic linear elastic properties of cubic crystal aggregates using zeroth-, first- and second-order bounds**

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A simple scheme based on analytical results is presented for the design of the anisotropic linear elastic properties of cubic crystal aggregates. The scheme is based on analytical results of zeroth-, first- and second-order bounds, delivering a total of 12 design variables which span the design space. The first-order bounds are known as the Voigt and Reuss bounds while the considered second-order bounds are the Hashin-Shtrikman bounds derived in Böhlke and Lobos (2014). These first- and second-order bounds are represented in terms of the one-point statistics of the polycrystal, the crystallographic texture, through the usage of a fourth-order texture coefficient. After having chosen which properties are to be designed, a physically suitable material, which fulfills prescribed criteria, is selected. This is achieved by using zeroth-order bounds and material data. Consequently, a homogenization scheme consistent with the considered bounds is chosen as an approximation for the real material behavior. Using the chosen homogenization scheme, the focused properties are analyzed in order to obtain their possibilities and limitations through microstructure adaptation. Finally, the optimal crystallographic texture with the best approximation of the prescribed properties is identified.

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