Commentary: Recent Advances in Ab Initio Thermodynamics of Materials

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The Materials Genome Initiative (MGI)'s goals are to significantly reduce the time and resources necessary to discover, develop, and deploy new materials. Realization of the MGI demands the integration of multiple approaches, spanning advanced simulation, synthesis, and characterization as well as effective informatics approaches. While many initiatives are currently being pursued to address the MGI challenge, the development of new materials solutions to specific technological needs must start by first understanding the phase stability of the material to be developed. This is important not only to assess the feasibility of making the material in the first place but also to understand what changes the material undergoes during processing as well as during operation.

Thermodynamics of materials thus lies at the base of any further material development. For almost a century, the phase stability of materials was mostly explored through empirical means. Fifty years ago, within the inorganic materials community, the advent of the calculation of phase diagrams (CALPHAD) method enabled the systematic organization of information about the thermodynamic properties of phases that in turn made possible the prediction of phase diagrams. Within the CALPHAD approach, the thermodynamics of phases are described through mathematical models that are in turn determined by fitting to experimental data. In the past decades, experimental data (phase equilibria, thermochemistry, calorimetry, etc.) has been supplemented by calculations of thermodynamic properties based on so-called first-principles (ab ini-

tio) calculations, which are basically methods that solve approximations of the Schrödinger's equation in which the only information required—within many approximations and parametrizations—is the identity of the atoms as well as their spatial arrangement.

While there are still many limitations in these methods (for example, typical uncertainties of a few meV result in differences of tens of Kelvin in relevant temperatures in phase diagrams), first-principles thermodynamic approaches have proven to be remarkably useful, particularly in instances when experimental measurements of thermochemical properties are not available (an increasingly common occurrence) or when the phases that need to be described are not truly thermodynamically stable (but whose description is necessary within the CALPHAD formalism) and cannot be characterized through experimental means.

In this technical topic, we have collected a series of articles that illustrate some of the most recent advances in the use of first-principles methods to describe the thermodynamic properties of materials. Examples are presented of recent theoretical and computational techniques to predict thermodynamic properties, to search ground states, and to integrate first-principles thermodynamics to CALPHAD assessments. Also presented are some more specialized examples in which first-principles methods have been used to describe the phase stability of complex materials.

In their article, "Materials Design and Discovery with High-Throughput Density Functional Theory: The Open Quantum Materials Database (OQMD)," James Saal and collaborators present the recent development of the Open Quantum Materials Database (OQMD), which combines highly accurate high-throughput DFT calculations—based on crystal structures reported in the inorganic crystal structure database (ICSD) as well as derived

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structures—with numerical minimization techniques to identify the ground state in multicomponent systems. In fact, the cover image of the current issue is a graphical representation of the ground states of all the systems currently considered in OQMD. In essence, that figure represents a “ground state” of everything. In addition, they report on the use of machine learning techniques for the rapid screening of the ground state of high-order chemical systems. The article describes how this materials informatics approach has already been used to discover potential promising materials in the fields of batteries, strengthening precipitates in Mg alloys, etc. Techniques such as those described in this article are a fundamental tool to bring the MGI to fruition.

In his article “Cluster Variation Method,” Tetsuo Mohri writes a very didactic description of the cluster variation method (CVM), originally developed by Kikuchi and collaborators. This method enables the description of the thermodynamic properties and prediction of phase stability of crystalline phases by considering not only the energetics of atomic arrangements but also the entropic contributions due to configurational degrees of freedom. Since the CVM is formulated on a lattice, the direct connection to first-principles calculations is possible. The article not only describes the traditional CVM approach but also discusses extensions (Continuous Displacement Cluster Variation) to consider instances in which atomic size mismatch is so large that one must consider local atomic relaxations.

The third article of the series is Axel van de Walle’s “Methods for First-Principles Alloy Thermodynamics,” which describes the use of simplified cluster expansion-based Hamiltonians to predict the thermodynamic properties and phase stability of crystalline phases at finite temperatures. The method allows for the explicit incorporation of configurational, electronic, and vibrational degrees of freedom. In his article, Axel describes the basics of the methods used as implemented in his tremendously powerful Alloy Theoretic Automated Toolkit (ATAT) package, which is already widely used by the community to describe the thermodynamic properties of a wide range of materials systems.

As mentioned earlier in this commentary, one of the major drivers for the current advances in the use of *ab initio* methods to predict the thermodynamic

properties of materials is to use this information to refine thermodynamic descriptions based on the CALPHAD method. Once thermodynamic information on phases has been encoded within this formalism, it can later be used in materials design. A major challenge currently facing the CALPHAD community is the need to update thermodynamic descriptions when better information becomes available. In their article, “Density Functional Theory-Based Database Development and CALPHAD Automation,” Yi Wang and collaborators present new advances to predict the thermodynamic properties of materials at elevated temperatures through the incorporation of all thermally excitable degrees of freedom. More impressively, they present a novel software tool, ESPEI (extensible, self-optimizing phase equilibrium computer program), that provides not only the data infrastructure to store thermodynamic property data but also to automate the process of CALPHAD thermodynamic assessment. These and other tools, including OQMD and ATAT, constitute valuable additions to the Materials Genomics Toolkit.

Finally, in their article, “Interaction of Phase Transformation and Magnetic Properties of Heusler Alloys: A Density Functional Theory Study,” Peter Entel and collaborators present a very nice example on how DFT studies can be used to investigate the phase stability of multifunctional materials. Specifically, Entel focuses on magnetic Heusler alloys that have applications as ferromagnetic shape memory materials. Through the use of sophisticated DFT calculations of ground state properties, as well as finite temperature effects due to vibrational and magnetic degrees of freedom as well as through the use of sophisticated Monte Carlo simulations (not unlike those available in the ATAT package), they have been able not only to explain available experimental data but also to gain new insights into the underlying physical principles controlling the transformation behavior of this very important class of materials.

To close, this collection of papers presents some of the most exciting developments in the application of *ab initio* methods for understanding the thermodynamic properties of materials. Looking forward, the techniques and tools presented in this issue (as well as many other very worthy contributions by others) will constitute a strong foundation for materials genomics efforts in the near future.