

# High-Throughput Thermodynamic Modeling and Uncertainty Quantification for ICME

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One foundational component of the integrated computational materials engineering (ICME) and Materials Genome Initiative is the computational thermodynamics based on the calculation of phase diagrams (CALPHAD) method. The CALPHAD method pioneered by Kaufman has enabled the development of thermodynamic, atomic mobility, and molar volume databases of individual phases in the full space of temperature, composition, and sometimes pressure for technologically important multicomponent engineering materials, along with sophisticated computational tools for using the databases. In this article, our recent efforts will be presented in terms of developing new computational tools for high-throughput modeling and uncertainty quantification based on high-throughput, first-principles calculations and the CALPHAD method along with their potential propagations to downstream ICME modeling and simulations.

## INTRODUCTION

Thermodynamics is at the core of every physical description of nature. In recognition of this fact, and coincident with the rise of modern computing, the development of the calculation of phase diagrams (CALPHAD) method was pioneered by Kaufman<sup>1,2</sup> and institutionalized in 1973 to rationalize and systematize alloy chemistry through the use of computer calculations.<sup>3</sup> In the decades since, there has been a tremendous effort by the scientific community to collect data to build thermodynamic descriptions for both metallic and nonmetallic systems with increased sophistication and accuracy as our understanding of the underlying physical phenomena has improved.<sup>4–6</sup> As pointed out in the integrated computational materials engineering (ICME) report<sup>7</sup> and practiced in our research activities,<sup>8,9</sup> “current CALPHAD development efforts include establishment of linkages with physics-based tools such as density functional theory for calculating the energetics required to assess phase stability and linkage with and development of diffusion databases and models that are in turn linked to microstructural evolution prediction tools”. The ICME report further emphasizes that

“the enabling factors that led to the CALPHAD capability of today will also be critical enablers for the development of a widespread ICME capability”. Similarly, the Materials Genome Initiative<sup>10</sup> focuses on integration of computational and experimental toolsets in data creation, management, and sharing along with data analysis tools with the CALPHAD modeling as one key component.<sup>11–13</sup>

The CALPHAD modeling of thermodynamics is based on mathematically formulated models describing the thermodynamic properties of individual phases. The model parameters are evaluated from the thermochemical data of the individual phases and phase equilibrium data between phases, starting from pure elements, binary systems, and ternary systems. The most commonly used thermodynamic descriptions of pure elements in common structures were compiled by Dinsdale<sup>14</sup> as recommended by the consortium Scientific Group Thermodata Europe (SGTE). The evaluations of binary model parameters have been based on these pure element model parameters, and the values of ternary model parameters are thus related to both pure element and binary model parameters. Therefore, any modification of a constitutive subsystem has a compounding effect on the description of a

multicomponent system because it affects every description of systems, making remodeling of higher component subsystems necessary.<sup>15</sup> This situation is particularly pressing when more and more atomic interacting energetics predicted from first-principles calculations based on density functional theory (DFT) become available, which have the potential to improve the modeling of subsystems in multicomponent systems.<sup>8,16,17</sup>

In addressing this challenge, Shang et al.<sup>18</sup> developed the extensible self-optimizing phase equilibrium infrastructure (ESPEI) for CALPHAD modeling of thermodynamics. In ESPEI, a two-step automated procedure determines the model parameters of individual phases, first exclusively using thermochemical data from DFT-based first-principles calculations, and then using experimental phase equilibrium data. In this article, the further development of ESPEI is discussed along with its new capability for uncertainty quantification of computational thermodynamics. The quantification of uncertainty reinforces the notion of CALPHAD as the premier method for integrating heterogeneous thermophysical data into self-consistent models as part of an ICME design pipeline.

Recently, we have further proposed a robust optimization approach to uncertainty quantification of thermodynamic calculations from the uncertainties of Gibbs energy model parameters,<sup>19,20</sup> with the latter discussed in this article being the starting point of the ICME supply chain and playing a central role in the development of ICME.<sup>7,21,22</sup> It may be mentioned that the robust optimization is a different research field from sensitivity analysis. Sensitivity analysis is the study of how the uncertainty in the output of a mathematical model or system can be apportioned to different sources of uncertainty in its inputs. It can be considered to be the postoptimization tool for quantifying the change of final results with small perturbations in condition or input. Nevertheless, the goal of robust optimization is to find the optimal solution with prior ensured feasibility when the problem parameters vary within the prescribed uncertainty set. That means regardless of what the exact parameter values are, the estimated phase boundary must be located in the fluctuation area as long as the parameters come from the uncertainty set. Together with the approaches discussed in the current article, the robust optimization can be a powerful tool in determining materials and processing tolerance in ICME.

## HIGH-THROUGHPUT CALPHAD MODELING

Mathematically speaking, CALPHAD modeling is multivariate regression of the Gibbs energy functions of individual phases. Because the semiempirical nature of regression admits fitting against heterogeneous data types from both experimental and theoretical sources, the CALPHAD method is an excellent approach for quantifying the state of

knowledge for the thermodynamic behavior of known physical systems and for extrapolating to predict the behavior of new systems. In the development of a CALPHAD model for a phase, there are three key decisions: first, the sublattice model<sup>23</sup> including the number of sublattices, their site ratios, and component occupancies; second, the optimal set of parameters; and finally, the optimal values of the optimal set. Because of the large number of parameter degrees of freedom, the last two are particularly challenging, and much of the expert knowledge in CALPHAD modeling relates to how one determines which model parameters to evaluate and which model parameters to leave at zero. Our high-throughput approach aims to document and quantify subjective judgment rather than seeking absolute objectivity in parameter selection.

With the development of pycalphad,<sup>24</sup> our high-throughput CALPHAD modeling is rebuilt following the same two-step automation procedure as in the previous version of ESPEI.<sup>18</sup> In the CALPHAD method, a crystalline phase is divided into sublattices based on Wyckoff positions corresponding to the phase's symmetry with the maximum number of sublattices for a crystalline phase equal to the number of Wyckoff positions with the end-members denoting stoichiometric compounds with one constituent in each sublattice. The energy of a phase is partitioned into a mixture of end-members and constituent interactions in and across sublattices, which is commonly referred to as the compound energy formalism (CEF).<sup>23</sup> In practice, usually fewer sublattices are used because some Wyckoff positions are energetically degenerate.

As mentioned in the Introduction, the Gibbs energies of pure elements in several common structures were compiled<sup>14</sup> and used for most CALPHAD modeling in the literature, enabling the development of multicomponent databases. Nonetheless, generally the scientific community has not standardized on Gibbs energies for most structures, particularly for the CEF's end-members, and these must be obtained from DFT-based first-principles calculations.<sup>8,16</sup> New and improved standards for pure-element reference data are an active discussion area within the community.<sup>25</sup> Furthermore, the atomic interaction energetics in individual sublattices cannot be directly measured experimentally and have been largely relied on expert knowledge in the CALPHAD modeling. In the past decade, we have exerted significant efforts to predict those interaction energetics from DFT-based first-principles calculations through the special quasirandom structures (SQS) that mimic the random mixing in individual sublattices.<sup>26–29</sup>

In the first step of the two-step high-throughput CALPHAD modeling, the model parameters of pure elements, stoichiometric compounds, and end-members in CEF models are evaluated in the order of heat capacity and entropy because they represent the second and first derivatives of Gibbs energy,

respectively, and the model parameter for the enthalpy is evaluated at last. The last question is how to choose an appropriate number of parameters for each model. A high-quality fit reproduces the data without “overfitting”. This selection problem is discussed within the context of uncertainty quantification in the next section.

The procedure for evaluating interaction parameters for mixing in each sublattice is similar but with two key differences. The first difference is that the reference state is now shifted from “of formation” to “of mixing,” meaning all parameter evaluations are performed relative to the “surface of reference” defined by the end-members. The second difference is that the system of equations gets more complicated with the introduction of mixing terms. In our approach, mixing parameters are evaluated in the order of one-sublattice binary interactions, two-sublattice binary interactions, and so on followed by the same sequence for ternary interactions. For each interaction, the procedure analogous to the end-member case is used.

This modeling procedure exclusively relies on the thermochemical data from DFT-based first-principles calculations. As a result of the intrinsic uncertainties of these theoretical data, the model parameter thus obtained must be refined by considering correlations between model parameters of different phases, represented by phase equilibrium data such as phase stability, phase boundary, and phase compositions. Although phase boundary data allow for straightforward visual comparison, it is significantly less useful than thermochemical data for model parameter evaluations. There are several reasons for this. First, even though the phase diagram is, in principle, a function of all phases’ energies, in practice, only a small portion of a phase’s temperature and composition domain is relevant to depicting stability on the phase diagram; phase boundaries provide no information about the energy in regions where a phase is metastable. Second, measured phase regions only provide information about the stability of the present phases *relative to* the others. At best this only provides information on lower bounds of energy differences between phases under certain conditions. Finally, there is no closed-form expression for the residual of a predicted phase boundary. In fact, many sets of model parameters could yield equivalent phase boundaries. All of these factors complicate the use of phase boundary data in our automation procedure.

In the present work, the following procedure is developed, which is conceptually similar to the “Rough Search” approach in the literature:<sup>30</sup>

1. Perform an equilibrium calculation including *all phases in the system* at each measured temperature and phase compositions using the model from the first step.

2. Define a mean chemical potential of each component based on the arithmetic mean of the corresponding chemical potentials as a mean equilibrium hyperplane.
3. Perform another set of equilibrium calculations with *only the desired phase* at each composition, and calculate the residual driving force with respect to the mean equilibrium hyperplane.
4. Choose new model parameters to approximately reduce the residual driving force at each data point to zero.
5. Repeat until stopping criteria are satisfied.

The refinement of model parameters based on the residual thus defined will be discussed within the context of uncertainty quantification in the next section. It should be pointed out that the key contribution of the high-throughput CALPHAD modeling is to write down an algorithm describing how to build a CALPHAD model so a computer can follow the procedure many times efficiently in parallel for different systems. Nevertheless, it is not only the issue of efficiency, but also the massive data from DFT-based first-principles calculations, that make the CALPHAD modeling more robust and more accurate.<sup>8</sup>

## UNCERTAINTY QUANTIFICATION OF THE CALPHAD METHOD

By *quantified uncertainty*, we are referring to uncertainty in the free parameters, e.g., excess mixing, in our models. *Propagated uncertainty* refers to “flowing” the quantified parameter uncertainty through our models to a predicted quantity of interest, e.g., the heat capacity or a phase transition temperature. Previous work in uncertainty analysis for CALPHAD modeling is limited. The seminal work by Jansson describing the PARROT software<sup>31</sup> for thermodynamic model optimization mentioned the model parameter uncertainty but was quick to shift the discussion to considering the covariance in the prediction error as more of an empirical weighting matrix for different datasets. The first software package to incorporate Bayesian methods into CALPHAD modeling introduced the capability of iteratively updating parameter probability distributions using estimates of the parameter covariance matrix.<sup>32</sup> An earlier paper by one author discussed a conceptually similar sequential Bayes algorithm for efficiently fitting excess parameters in thermodynamic models.<sup>33</sup> Stan and Reardon discussed implementing Bayesian model optimization using a genetic algorithm,<sup>34</sup> although there does not appear to be a public implementation of their approach.

The uncertainty quantification is closely related to the models and model parameters. In determining the number of model parameters in modeling of pure elements, stoichiometric compounds, and CEF end-members, a scoring criterion similar to the standard mean-squared error criterion with an additional factor that penalizes overfitting is



developed. Given the requirement that the scoring method be fast to compute, penalize overfitting, and be based in sound statistical theory, the well-known Akaike Information Criterion (AIC) is selected in the present work.<sup>35,36</sup> The AIC is defined as  $2m + d\ln\text{RSS}$  with RSS being the sum of the squared values of the residuals,  $m$  the number of parameters, and  $d$  the number of data points. For interaction parameters in sublattices, there is a large number of possible mixing terms to consider in a general, multiphase case. A multivariate model scoring criterion such as AIC cannot be reliably applied due to the large number of parameter combinations. A univariate parameter scoring technique is thus developed. One complication is that a univariate scoring method necessarily relies on statistics about the parameter values, but each parameter has distinct units and scale. Here it is necessary to appeal to our domain-specific knowledge about what a typical range for these parameters can be and to assign subjective variances to rescale the model parameters. Once a scaling approach is determined, a univariate scoring method can be chosen such as the well-known  $F$  test<sup>37, 38</sup> to determine a suitable set of parameters to evaluate.

The statistical distribution of values of the chosen set of parameters is then investigated. In the present work, a scheme for regularization is applied, which is the process of modifying a regression strategy to increase its robustness to ill-posed problems. In a Bayesian context, it means assumptions about the prior probability distribution of model parameter values, and the prior probability distribution is updated to the posterior probability distribution through likelihood (information) and evidence (normalizing quantity). In the present work, the posterior probability distribution is determined by the Markov chain Monte Carlo (MCMC) sampling method<sup>39</sup> as detailed in Ref. 40.

In benchmarking the approach, a model case of a binary solution is tested with 10 synthetic datasets and Gaussian noise, i.e., five values for enthalpy and entropy of mixing with one “bad” dataset of systematic bias. All of them have equal values for prior dataset variance with the true values of excess enthalpy and excess entropy being 7000 J/mol and 5 J/mol/K, respectively. The excess Gibbs energy is represented by the following equation:

$${}^E G_{mf} = x_A x_B (H_{ex} - T S_{ex} + L_{ex} T^2) \quad (1)$$

with the true value of  $L_{ex}$  being zero. The MCMC simulation results are shown in Fig. 1 with the true values in solid blue and the dashed lines for 95% credible interval. It is worth noting that in Bayesian analysis, parameters are random variables, whereas in frequentist analysis, data are random variables. Therefore, the frequentist  $x\%$  confidence interval, when repeated on multiple samples, would contain the true parameter value

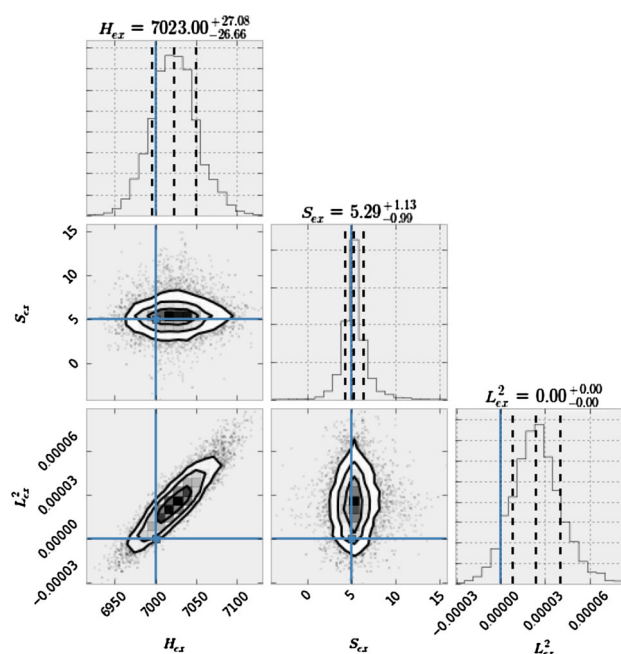


Fig. 1. MCMC simulation results for a model case with true values in solid blue and the dashed lines for 95% credible interval.

$x\%$  of the time; while, the Bayesian  $x\%$  credible interval indicates that there is an  $x\%$  probability that the true parameter value is in this range, given the data and the prior beliefs. More results on all thermodynamic quantities as a function of temperature and composition can be shown.

The approach thus programmed and benchmarked is then used for UQ analysis in the Al-Ni binary system with magnetic properties and heat capacity of Ni3Al shown in Fig. 2.

## APPLICATION TO THE Al-Ni BINARY SYSTEM

The Al-Ni binary system is the most important system in Ni-based superalloys. In this article, we report the results on the modeling of FCC and BCC phases in the binary system. A four-sublattice model is used for the FCC lattice to enable the description of the A1/L1<sub>2</sub>/L1<sub>0</sub> ordering, and a two-sublattice model is used for the BCC lattice to describe the A2/B2 ordering as in the work by Dupin et al.<sup>41</sup> The model parameters for the end-members are evaluated from the energetics from DFT-based first-principles calculations and the SGTE pure element database.<sup>14</sup> The interaction parameters in each sublattice are evaluated using the mixing properties of SQS supercells from DFT-based first-principles calculations.<sup>42–47</sup> The detailed procedure and results can be found online at the Jupyter Notebook.<sup>48</sup> For example, Fig. 3 shows the negative enthalpy of mixing between Al and Ni in the second sublattice of the two-sublattice model with the first sublattice occupied by Ni for the BCC lattice with the symbols denoting the results from DFT-based

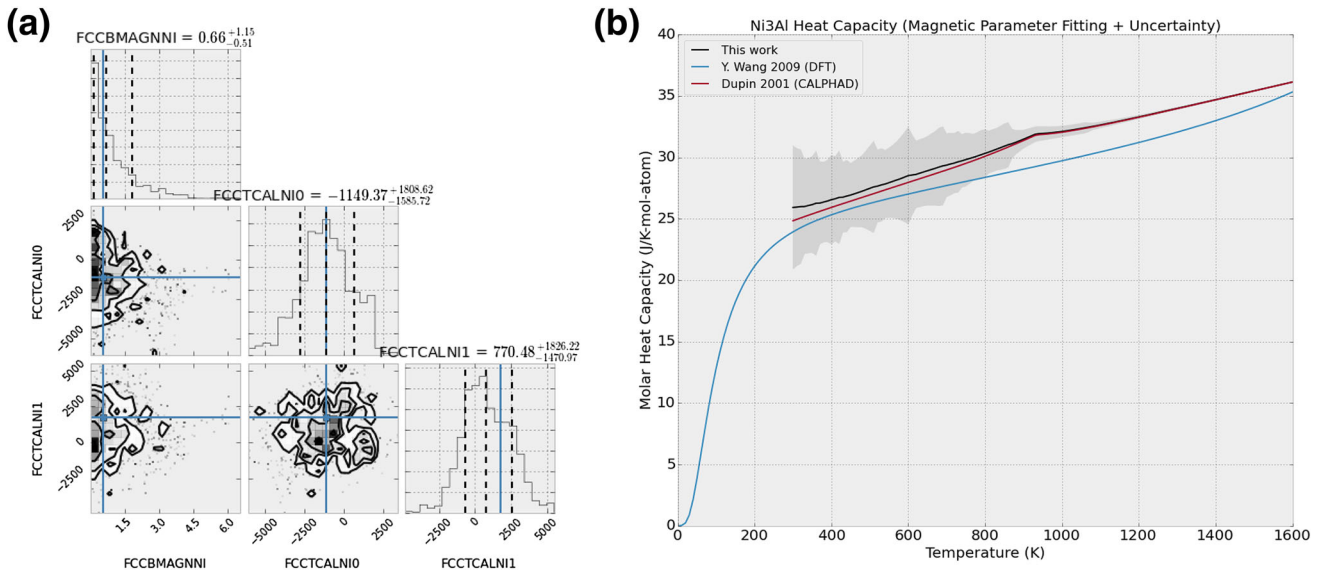


Fig. 2. UQ analysis of (a) magnetic properties in terms magnetic moment (FCCBMAGNI) and interaction parameters (FCCTCALNIO and FCCTCALN1), and (b) heat capacity of  $\text{Ni}_3\text{Al}$ .

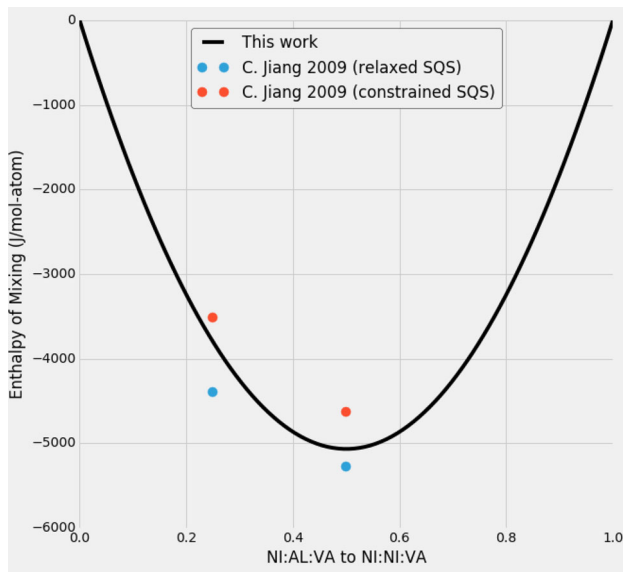


Fig. 3. Enthalpy of mixing between Al and Ni in the second sublattice of the two-sublattice model for the BCC lattice with the symbols from DFT-based first-principles calculations and the curve from current CALPHAD modeling.

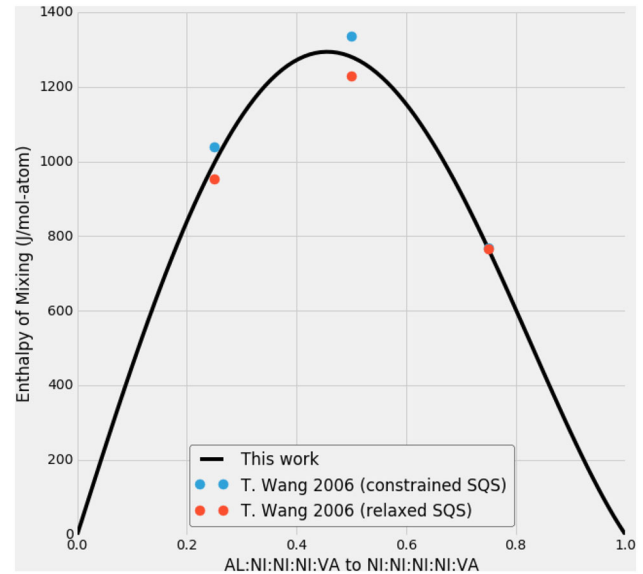


Fig. 4. Enthalpy of mixing between Al and Ni in the first sublattice of the four-sublattice model for FCC lattice with the symbols from DFT-based first-principles calculations and the curve from current CALPHAD modeling.

first-principles calculations in the literature<sup>49</sup> and the curve from the current automation procedure. Figure 4 depicts the positive enthalpy of mixing between Al and Ni in the first sublattice of the four-sublattice model with the other sublattices occupied by Ni for the FCC lattice with the symbols denoting the results from DFT-based first-principles calculations in the literature<sup>46</sup> and the curve from the current automation procedure. As an example, this TDB file is used in Thermo-Calc<sup>50</sup> to calculate the FCC–BCC phase diagram fully based on the data from first-principles calculations as shown in Fig. 5.

## SUMMARY AND FUTURE DIRECTIONS

It is maximally beneficial for CALPHAD models to communicate about the uncertainty of their predictions. With good estimates of the uncertainty of model predictions, one can begin to judge when prediction errors are a result of insufficient data or whether they are a result of systematic biases in our model. This is valuable for realizing the ICME vision of quantitative prediction of material behavior: Through quantified uncertainty, models communicate confidence in their ability to be applied to materials design.

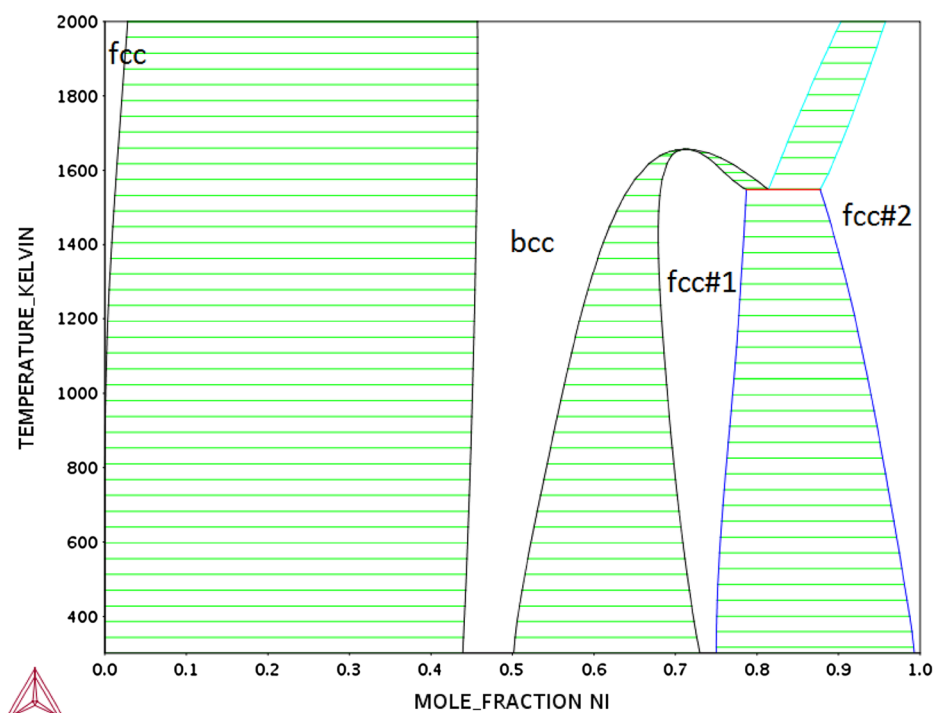


Fig. 5. Predicted metastable FCC-BCC Al-Ni phase diagram based on the high-throughput modeling procedure described in this work.

A new class of CALPHAD databases can be rapidly constructed using the automated parameter selection and uncertainty quantification procedure described in this work. Because these new databases will be semantically linked to the underlying structured experimental and first-principles data by an automated workflow, the inevitable future requirement to update them will be significantly easier to resolve. By improving the accuracy of these types of predictions, high-throughput modeling, powered by pycalphad, has the potential to expand the CALPHAD modeling into more aspects of ICME.

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