Thermodynamic modeling with uncertainty quantification in the Nb-Ni system using the upgraded PyCalphad and ESPEI

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Abstract

The Nb-Ni system has been remodeled with uncertainty quantification (UQ) by using the presently upgraded software tools of PyCalphad and ESPEI that contain the new capability to model site occupancy of Wyckoff position for the phases of interest. Specifically, the five- and three-sublattice models are used to model the topologically close pack (TCP) phases of $\mu$-Nb$_7$Ni$_6$ and $\delta$-NbNi$_3$, respectively, according to exactly their Wyckoff positions; where the inputs for CALPHAD-based modeling include the presently predicted thermochemical data as a function of temperature by density functional theory (DFT) based first-principles and phonon calculations together with both phase equilibrium and site occupancy data in the literature. Besides phase diagram and thermodynamic properties, the present CALPHAD predictions of site occupancies are also agreed well with experimental data such as the measured Nb sites in $\mu$-Nb$_7$Ni$_6$. In addition, the predicted UQ values using the Markov Chain Monte Carlo (MCMC) method as implemented in ESPEI make it possible to quantify uncertainties in the Nb-Ni system, such as site occupancies in $\mu$-Nb$_7$Ni$_6$ and enthalpy of mixing in liquid.

Highlights

- New capability implemented into PyCalphad and ESPEI to model site occupancy
- TCP phases ($\mu$-Nb$_7$Ni$_6$ and $\delta$-NbNi$_3$) modeled well using sublattice models according exactly to their Wyckoff positions
- The Nb-Ni system remodeled well with uncertainty quantification
- Finite-temperature thermochemical properties predicted by DFT-based phonon calculations

Keywords: CALPHAD modeling; Nb-Ni; PyCalphad and ESPEI; First-principles calculations; Site occupancy; TCP phases; Uncertainty quantification.
1 Introduction

The topologically close pack (TCP) phases, also known as the Frank-Kasper phases [1], are intermetallic compounds with complex crystalline structures, which are frequently observed in Ni-based superalloys, including such as the $\sigma, \chi, P, R, \delta, \mu, M, A15$, and Laves phases [2]. TCP phases are usually brittle and detrimental, and hence, their type, amount, and distribution are of great importance for the performance of Ni-based superalloys [3]. For example, when Ni-based superalloys are highly alloyed with refractory elements (Cr, Mo, Nb, Ta, W, and Re) to achieve better strengths at high temperatures, the TCP phases will be formed and produce detrimental effects on the properties of superalloys by draining refractory elements from the matrix phase like the $\gamma$ phase with the FCC lattice in Ni-based superalloys [4] or the strengthening phase like $\gamma'$ phase with the L1$_2$ lattice in Co-based superalloys [5].

Relevant to the present work, the TCP phases in the Nb-Ni system are $\delta$-NbNi$_3$ and $\mu$-Nb$_7$Ni$_6$, which are deleterious to the performance of Ni-based superalloys since their formations will drain alloying element Nb from the matrix [6]. For example, the formation of 10% area fraction $\delta$-NbNi$_3$ can lower 40% of elongation in Ni superalloy of Inconel 718 [7]. The formation of around 10 vol.% of $\delta$-NbNi$_3$ after stress relief heat treatment resulted in a 9% increase of the ultimate tensile strength but a 45% decrease in the fracture strain in Inconel 625 [8]. Similarly, the $\mu$-Nb$_7$Ni$_6$ also shows undesirable influences on mechanical properties, for example, the precipitation of $\mu$-Nb$_7$Ni$_6$ in the Ni-Mo-Cr system decreased the room temperature impact roughness by 100 joules in the Charpy test [9]. Therefore, an accurate thermodynamic description of the TCP phases in the Nb-Ni system is critical for a better understanding of their formations through thermodynamic calculations, so that the TCP phases can be avoided by designing chemistry and/or process of Ni-based superalloys.

In general, the TCP compounds are complex solution phases with partially occupied Wyckoff sites and/or disordered elements in one or more Wyckoff sites. For example, $\delta$-NbNi$_3$ includes three Wyckoff sites (2a, 2b, and 4e) with space group $Pmmn$ (No. 59) as shown in Table 1a, while $\mu$-Nb$_7$Ni$_6$ has five Wyckoff sites (3a, 6c(1), 6c(2), 6c(3), and 18h) with space group $R\bar{3}m$ (No. 166) as shown in Table 1b. The crystallographic information of Wyckoff sites indicates that a three-
sublattice model is expected for a complete description of δ-NbNi$_3$ and a five-sublattice model for μ-Nb$_7$Ni$_6$. However, the previous CALPHAD modeling of Nb-Ni [10–13] cannot capture well the change of site occupancies in TCP phases, i.e., the occurrence of a given kind of atoms (or vacancy) in a given Wyckoff position of study; for example, Nb in Wyckoff sites of μ-Nb$_7$Ni$_6$ measured by Joubert et al. [14], since μ-Nb$_7$Ni$_6$ was described by the simplified sublattice models like (Ni)$_{0.47}$(Nb)$_{0.53}$, (Nb, Ni)$_7$(Nb)$_6$, and (Nb, Ni)$_3$(Ni)(Nb, Ni)$_2$Nb$_6$; see details in Table 2, which summarizes the previous thermodynamic models for μ-Nb$_7$Ni$_6$ and δ-NbNi$_3$. It shows that Kaufman and Nesor [10] modeled μ-Nb$_7$Ni$_6$ and δ-NbNi$_3$ as stoichiometric compounds (Ni)$_{0.47}$ (Nb)$_{0.53}$ for μ-Nb$_7$Ni$_6$, (Ni)$_{0.75}$ (Nb)$_{0.25}$ for δ-NbNi$_3$, while Kejun et al. [12] used a four-sublattice model (Nb, Ni)$_3$Ni$_4$(Nb, Ni)$_2$Nb$_6$ for μ-Nb$_7$Ni$_6$ and a two-sublattice model (Nb, Ni)$_3$(Nb, Ni)$_1$ for δ-NbNi$_3$. Bolcavage and Kattner [11] used (Nb, Ni)$_7$(Nb)$_6$ for μ-Nb$_7$Ni$_6$. Note that Joubert et al. [15] adopted a five-sublattice model for μ-Nb$_7$Ni$_6$, i.e., (Nb, Ni)$_3$Nb$_2$Nb$_2$(Nb, Ni)$_2$2(Nb, Ni)$_6$, which gives a better description of solubility and site occupancy in μ-Nb$_7$Ni$_6$. However, two sublattices in Joubert et al.’s model [15] include only one element Nb instead of two elements of Nb and Ni. Most recently, Chen et al. [13] remodeled the Nb-Ni system with the (Nb, Ni)$_3$Nb$_4$(Nb, Ni)$_2$(Nb, Ni)$_6$ model for μ-Nb$_7$Ni$_6$ and the (Nb, Ni)$_3$(Nb, Ni)$_1$ model for δ-NbNi$_3$. Table 2 shows that none of the previous thermodynamic models of μ-Nb$_7$Ni$_6$ were based exactly on its Wyckoff sites, resulting in a discrepancy in values of site occupancy between CALPHAD modeling and experiments. The less accurate descriptions of TCP phases, especially their site occupancies, in the Nb-Ni system motivate the present CALPHAD remodeling.

Meanwhile, an arbitrary value of 5000 J/mol-atom was assigned as the enthalpy of formation for nonstable endmember compounds for TCP phases [16], which is less reliable than theoretical predictions. To address this issue, in the present work, density functional theory (DFT) based first-principles and phonon calculations are used to determine thermodynamic properties as a function of temperature for all endmembers of μ-Nb$_7$Ni$_6$ and δ-NbNi$_3$.

The present work aims to remodel the Nb-Ni system in terms of the CALPHAD approach with UQ in terms of the open-source tools of ESPEI (the Extensible, Self-optimizing Phase Equilibria Infrastructure) for database development [17], and PyCalphad for equilibrium thermodynamic
calculations [18]. Here, the input for CALPHAD modeling includes the present first-principles calculations and experimental data in the literature with an emphasis on the site occupancy data. It is worth mentioning that ESPEI has been upgraded in the present work making it possible modeling of site occupancies with UQ for the Wyckoff sites of study.

2 Literature Review of Thermodynamic properties in Nb-Ni

2.1 Review of the previous CALPHAD modeling works

The Nb-Ni system has six phases including three solution phases (BCC, FCC, and liquid) and three intermetallic compounds (\(\mu\)-Nb\(_7\)Ni\(_6\), \(\delta\)-NbNi\(_3\), and NbNi\(_8\)) based on the summary by Chen et al. [16]. The Nb-Ni system has been modeled several times in terms of the CALPHAD approach [10–13]. Kaufman and Nesor [10] provided a modeled Nb-Ni phase diagram by considering \(\mu\)-Nb\(_7\)Ni\(_6\) and \(\delta\)-NbNi\(_3\) as stoichiometric compounds as shown in Table 2, which didn’t match with experimental observations of Nb solubilities in these two phases by Murametsu et al. [19], Duerden et al. [20], and Chen et al. [21].

Kejun et al.’s modeling work [12] adopted the model of \((\text{Nb, Ni})_1\text{Ni}_4(\text{Nb, Ni})_2\text{Nb}_6\) for \(\mu\)-Nb\(_7\)Ni\(_6\), which cannot describe well the solubilities of Nb in the composition range 50 – 54 at. % Nb around 1100°C measured by Duerden et al. [20]. In addition, the enthalpies of formation of \(\mu\)-Nb\(_7\)Ni\(_6\) show a large discrepancy around 13 kJ/mol-atom compared with experiments by Argent et al. [22].

In the modeling work by Bolcavage and Kattner [11], they did not consider the NbNi\(_8\) compound because of the lacking of experimental data at that time. The predicted liquidus in the Nb-rich region is higher around 200 – 300 K than experimental data from Wicker et al [23].

Joubert et al. [15] considered NbNi\(_8\) in their modeling work. However, an arbitrary value of 5000 J/mol-atom was used to describe the enthalpy of formation for the pure element endmembers in the TCP phases. This value is too positive to describe correctly the partially occupied Wyckoff sites in \(\mu\)-Nb\(_7\)Ni\(_6\) in comparison with experimental data from Joubert et al. [14].
The most recent modeling work was done by Chen et al. [16], which was widely used in the modeling of ternary systems such as Fe-Nb-Ni [24], Nb-Ni-Zr [25], and Nb-Ni-Ti [26]. Chen et al.’s work [16] contains the NbNi$_8$ phase but fails to depict phase boundaries between μ-Nb$_7$Ni$_6$ and δ-NbNi$_3$ and between μ-Nb$_7$Ni$_6$ and BCC by Murametsu et al. [19] at 48.6 - 56.2 at. % Nb. It is worth mentioning that the experimental temperatures of phase boundary of liquid with respect to BCC from Wicker et al. [23] and the enthalpies of mixing for the liquid at 1823K from Chistyakov et al. [27] which shows around 10 kJ/mol-atom difference at 50 at. % Nb with Chen et al. [16]’s model was not considered in the modeling by Chen et al. [16].

The sublattice models used before including (Ni)$_{0.75}$ (Nb)$_{0.25}$, (Nb, Ni)$_3$ (Nb, Ni)$_1$ for δ-NbNi$_3$ and (Ni)$_{0.47}$ (Nb)$_{0.53}$, (Nb, Ni)$_1$Ni$_4$(Nb, Ni)$_2$Nb$_6$, (Nb, Ni)$_7$(Nb)$_6$, (Nb, Ni)$_1$Nb$_2$Nb$_2$(Nb, Ni)$_2$(Nb, Ni)$_6$ for μ-Nb$_7$Ni$_6$ cannot match well with both the phase boundary data and thermochemical data together. Therefore, an appropriate sublattice model derived from the crystal structure is needed to precisely describe the behavior of the TCP phases which will also benefit future extrapolations into higher-order systems. In the present work, the sublattice model (Nb, Ni)$_1$(Nb, Ni)$_1$(Nb, Ni)$_2$ is used to model the δ-NbNi$_3$ while (Nb, Ni)$_1$(Nb, Ni)$_2$(Nb, Ni)$_2$ (Nb, Ni)$_2$(Nb, Ni)$_6$ is used to describe the μ-Nb$_7$Ni$_6$, corresponding to their Wyckoff position as shown in Table 1.

2.1 Thermodynamic data

2.1.1 Phase diagram data

Phase boundaries between FCC and Liquid (0 – 15 at. % Nb) were measured using thermal analysis from heating curves by Duerden et al. [20], Pogodin et al. [28], and Grube et al. [29], using differential thermal analysis (DTA) by Chen et al. [21] and Kajikawa [30] and using the solid-liquid diffusion couple method (DCM) by Kajikawa [30]. All these measurements show good agreement, e.g., the temperature differences are less than 40 K with each other. All these data are hence used in the present CALPHAD modeling of the Nb-Ni system.

Phase boundaries of FCC between FCC and δ-NbNi$_3$ (0 – 15 at. % Nb) were measured by Pogodin et al. [28] and Grube et al. [29] by thermal analysis from heating curves. Chen et al. [21] used DFT to analyze the FCC to δ-NbNi$_3$ transition at 1322K, while Guseva et al. [31] detect the FCC to δ-
NbNi₃ phase change using X-ray powder diffraction (XRD) at 1073 – 1473 K. Joubert et al. [15] assessed the homogeneity regions of δ-NbNi₃ using electron probe micro-analysis (EPMA). All these measurements show good agreement with each other, e.g., the composition change from 1000 K to 1500 K is 5 at. % Nb and are used in present modeling.

The NbNis phase was first observed using transmission electron microscopy (TEM) by Quist et al. in 1969 [32]. It was confirmed by Joubert et al. [15] that NbNis is a stable phase with an X-ray diffraction method to test the annealing sample at 723 K for 76 days. Wekken et al. [33] used the changes in the electrical resistivity to detect the existence of NbNis, showing that NbNis will form at 10.3 at. % Nb at 853 K. Chen et al. [21] also detected NbNis with differential scanning calorimetry (DSC). Therefore, NbNis is considered a stable phase in the present work.

The Nb2Ni phase was observed by Zhao et al. [34] by using the transmission electron microscopy (TEM) method for sample annealing at 1523 K for 5h. However, this phase was not confirmed further using samples with long anneal time. The Nb2Ni phase is hence excluded in the present modeling work.

Regarding solubility of Nb in δ-NbNi₃, Murametsu et al. [19] observed 24.0 – 26.6 at. % Nb in δ-NbNi₃ in the temperature range 1023 K – 1303 K by electron probe microanalyzer (EPMA). Chen et al. [21] reported the phase boundary around 23.4 – 25.7 at. % Nb by DTA at 1323 K for 336h. Duerden et al. [20] estimated the phase boundary around 23.5 – 26.5 at. % Nb used XRD at 1273 K. The phase boundary of δ-NbNi₃ between δ-NbNi₃ and the liquid phase was measured by both Grube et al. [29], Duerden et al. [20], and Svechnikov et al. [35] using the heating curves of thermal analysis and Chen et al. [21] using differential thermal analysis (DTA). All these data are included in the present CALPHAD modeling.

Regarding solubility of Nb in μ-Nb₇Ni₆, Duerden et al. [20] estimated 50 – 54 at. % Nb in μ-Nb₇Ni₆ around 1373K using the optical microscopy method. Svechnikov et al. [35] reported 49.8 - 58.3 at. % Nb in μ-Nb₇Ni₆ by using the heating curves of thermal analysis. Murametsu et al. [19] reported 48.6 - 56.2 at. % Nb in μ-Nb₇Ni₆ around 1023 K – 1303 K by electron probe microanalyzer (EPMA). Joubert et al. [14] reported 49.6 - 56.9 at. % Nb in μ-Nb₇Ni₆ at 1273 K by
EPMA. Chen et al. [21] estimated 49.5 – 56.3 at. % Nb in $\mu$-Nb$_7$Ni$_6$ around 1273 K – 1303 K by EPMA. The phase boundary of $\mu$-Nb$_7$Ni$_6$ between $\mu$-Nb$_7$Ni$_6$ and the liquid phase was measured by both Duerden et al. [20] and Svechnikov et al. [35] using the heating curves of thermal analysis and Chen et al. [21] using differential thermal analysis (DTA). All these data are included in the present CALPHAD modeling.

The measured invariant reaction temperatures between liquid, $\delta$-NbNi$_3$, and FCC phase agreed well with each other from 1170 K to 1175 K by Chen et al. [21] using DTA, and Duerden et al. [28] and Svechnikov et al. [36] using the heating curves of thermal analysis. However, the invariant reaction temperatures between liquid, $\delta$-NbNi$_3$, and $\mu$-Nb$_7$Ni$_6$ phases have large uncertainties from 1290 K to 1320 K measured by Duerden et al. [28] and Wicker et al. [23]. All these data are included in the present CALPHAD modeling.

For phase boundaries between liquid and BCC, Svechnikov et al. [36] and Wicker et al. [23] measured them by quenching and thermal analysis, and Duerden et al. [20] measured them by heating, cooling, and quenching. These measurements exhibit noticeable discrepancies up to 300 K. The present modeling work considers all these experimental data.

2.1.2 Thermochemical data

The enthalpies of formation for the Nb-Ni system were measured by Argent et al. [22] through the calorimetry method with an error around 4 kJ/mol-atom. On the other hand, electromotive force (emf) measurements were adopted by Sokolovsky et al. [37], Alekseev et al. [34], and Lyakishev et al. [39] to determine the enthalpies of formation for intermediate phases. However, the results from Alekseev et al. [38] and Sokolovsky et al. [37] show great discrepancies around 8 kJ/mole-atom with respect to those from Argent et al. [22] as shown in Fig. 1Error! Reference source not found.. Compared with the DFT results from the Materials Project [40] and the Open Quantum Materials Database (OQMD) [41] as shown in Fig. 1Error! Reference source not found., general GGA prediction from DFT calculations is higher than the experiments data according to the comparisons of enthalpies of formation (H) for 81 binary sulfides predicted from DFT calculations to those from experimental measurements [42]. The enthalpies of formation data from Argent et al. [22] are higher but still compatible with the results from the DFT predictions [42]. Therefore,
the data from Argent et al. [22] are considered more reliable than those from Sokolvskaya et al. [37] and hence adopted in the present CALPHAD modeling.

Two sets of measurements about enthalpy of mixing were available for the Ni-rich liquid phase. As shown in Fig. 2, the data from Schaefers et al. [43] at 1927 K and 2000 K show a larger difference around 15 kJ/mol-atom compared with those from Chistyakov et al. [27] at 2096 K and Sudavtsova et al. [37] at 2148 K. In general, the enthalpies of mixing for liquids and solids should be compatible with each other like in Al-Cu [44] the difference between the enthalpy of mixing in liquid and the enthalpy of formation of solid is around 4 kJ/mole-atom at 40.0 – 60.0 at. % Cu, and Fe-Ni [45] the difference between the enthalpy of mixing in liquid and the enthalpy of formation of solid is around 5 kJ/mole-atom at 50.0 – 75.0 at. % Ni. The enthalpies of formation of solids in the Nb-Ni system are around 30 kJ/mole-atom at 25.0 at. % Nb, which is closer to the data (around 25 kJ/mole-atom) measured by Chistyakov et al. [27] and Sudavtsova et al. [37]. Since all the experiments were performed using the calorimetry method, the results from Chistyakov et al. [27] and Sudavtsova et al. [37] are adopted in the present work, while the experimental data from Schaefers et al. [43] is not considered due to far away (the difference is 15 kJ/mole-atom at 25.0 at. % Nb) from the enthalpies of formation of solids in the Nb-Ni system. Experimental data of site occupancy are only available for Nb in µ-Nb7Ni6 by Joubert et al. [14] using by electron probe microanalyzer (EPMA) at 1273 K. With the present upgrade for the ESPEI tools (see details in Sec. xx), these data can be included in the present CALPHAD modeling work.

3 Methodology

3.1 First-principles thermodynamics

DFT-based first-principles calculations can be used to predict Helmholtz or Gibbs energy of solid phases as a function of temperature. The expression for Gibbs energy under zero external pressure (i.e., the Helmholtz energy) in the quasiharmonic approach is [46]

\[ G = F(V, T) + PV|_{P=0} = E_0(V) + F_{vib}(V, T) + F_{el}(V, T) \]  

Eq. 1

where \( F \) is the Helmholtz energy, \( V \) the volume, \( T \) the absolute temperature, and \( P \) the pressure. \( E_0(V) \) is the static energy of 0 K without vibrational contribution. \( F_{vib} \) is the contribution of lattice vibrations and \( F_{el} \) the contribution by thermal electrons, and both are a function of \( V \) and \( T \).
The energy versus volume (E-V) data points for each phase (or endmember) at 0 K were predicted by DFT-based first-principles calculations, usually resulting in 7 data points. The \( E_0(V) \) curves were fitted by the following 4-parameter Birch-Murnaghan (BM4) equation of state [46],

\[
E_0(V) = k_1 + k_2 V^{-2/3} + k_3 V^{-4/3} + k_4 V^{-2}
\]

Eq. 2

where \( k_1, k_2, k_3, \) and \( k_4 \) are fitting parameters. This BM4 equation of state will result in four equilibrium properties at \( P = 0 \text{ GPa} \), including equilibrium energy \( E_0 \), equilibrium volume \( V_0 \), bulk modulus \( B_0 \), and the pressure derivative of bulk modulus \( B' \). The vibrational contribution \( F_{vib} \) can be predicted by the frequency-dependent phonon density of states (DOS) [47],

\[
F_{vib}(T, V) = k_B T \int_0^\infty \ln \left[ 2 \sinh \frac{\hbar \omega}{2k_B T} \right] g(\omega) \, d\omega
\]

Eq. 3

where \( g(\omega) \) is the phonon DOS as a function of volume \( V \) and frequency \( \omega \). The thermal electronic contribution \( F_{el} = E_{el} - TS_{el} \), where \( E_{el} \) is the internal energy at the volume \( V \) and temperature \( T \), and \( S_{el} \) is the bare electronic entropy.

3.2 Details of first-principles calculations

The Vienna ab initio Simulation Package (VASP) [48] was adopted for DFT-based first-principles and phonon calculations in the present work. The projector augmented wave (PAW) method was used to describe the electron-ion interactions [49], while the generalized gradient approximation (GGA) by Perdew, Burke, and Ernzerhof (PBE) was used to describe the exchange-correlation functional [50]. The plane-wave basis cutoff energy was set to be 367.945 eV for structural relaxations and phonon calculations, and 520 eV was used for the final static calculations to get accurate E-V data points and electron DOS’s. The convergence criterion of the electronic self-consistency was set as \( 6 \times 10^{-5} \text{ eV/atom} \) for relaxations, static calculations, and phonon calculations, while k-points \((8 \times 8 \times 7)\) is used for relaxations, static calculations of \( \delta \)-NbNi\(_3\) phase and \((5 \times 5 \times 1)\) is used for relaxations, static calculations of \( \mu \)-Nb\(_7\)Ni\(_6\). For phonon calculations, k-points \((2 \times 2 \times 2)\) is adopted during phonon calculations of \( \delta \)-NbNi\(_3\), and k-points \((1 \times 1 \times 1)\) is adopted during phonon calculations of \( \mu \)-Nb\(_7\)Ni\(_6\). The selected electronic configurations include 5 valences for Nb and 10 for Ni, which are the same as those in the Materials Project [40].
DFT-based first principles were performed for the BCC Nb and FCC Ni as reference states and two TCP phases of δ-NbNi₃ and μ-Nb₇Ni₆ in the Nb-Ni system. δ-NbNi₃ will be modeled by a three-sublattice model with a total of 8 configurations; and μ-Nb₇Ni₆ will be modeled by a five-sublattice model with 32 configurations. Phonon calculations were done for BCC Nb and FCC Ni and the most stable configurations of δ-NbNi₃ and μ-Nb₇Ni₆ including Nb₂Ni₂Ni₄, Nb₂Ni₂Ni₄ in δ-NbNi₃ structure, Nb₆Ni₆Nb₆Ni₁₈Nb₃, Nb₆Nb₆Nb₆Ni₁₈Nb₃, Nb₆Nb₆Nb₆Ni₁₈Ni₁₃, and Nb₆Nb₆Ni₆Ni₁₈Ni₁₃ in of μ-Nb₇Ni₆ structure. Structural of μ-Nb₇Ni₆ and δ-NbNi₃ phase of the Nb-Ni system are referred to the entries in Materials Project [40].

3.2 CALPHAD modeling

3.2.1 Thermodynamic models

There are three types of phases in the Nb-Ni system, i.e., the solution phases of BCC, FCC, and liquid; the stoichiometric compound of NbNi₈, and the non-stoichiometric TCP phases of δ-NbNi₃ and μ-Nb₇Ni₆. For the solution phases, the Redlich-Kister polynomial [51] is adopted to describe the Gibbs energy,

\[ G_m^\alpha = x_{Nb} G_{Nb}^\alpha + x_{Ni} G_{Ni}^\alpha + RT \left( x_{Nb} \ln x_{Nb} + x_{Ni} \ln x_{Ni} \right) + x_{Nb} x_{Ni} \sum_{k=0}^3 k L_{Nb,Ni} (x_{Nb} - x_{Ni})^k \]

where \( x_{Nb} \) and \( x_{Ni} \) are the mole fractions of Nb and Ni in phase \( \alpha \). \( G_{Nb}^\alpha \) and \( G_{Ni}^\alpha \) are the Gibbs energies of pure elements, Ni and Nb, with respect to their standard element reference (SER) states at \( P = 1 \) bar and \( T = 298.15 \) K, obtained from the Scientific Group Thermodata Europe (SGTE) database [52]. \( R \) is the gas constant, \( T \) the temperature, and \( k L_{Nb,Ni} \) the \( k \)th interaction parameters.

\[ k L_{Nb,Ni} = a + bT \]

where \( a \) and \( b \) are modeling parameters.

NbNi₈ is treated as a stoichiometric compound with its Gibbs energy described by,

\[ G_{NbNi_8}^{NbNi_8} = 0 G_{Nb}^{BCC} + 0 G_{Ni}^{FCC} + A + BT \]

where \( A \) and \( B \) are model parameters, \( 0 G_{Nb}^{BCC} \) and \( 0 G_{Ni}^{FCC} \) are the Gibbs energies of pure Nb and Ni in their stable structures, i.e., BCC and FCC, respectively. The values of \( 0 G_{Nb}^{BCC} \) and \( 0 G_{Ni}^{FCC} \) are taken from the SGTE database [52].
For non-stoichiometric compounds, the compound energy formalism is used to describe this phase with sublattices that correspond to its Wyckoff sites in the crystal structure [53]. In the compound energy formalism, the Gibbs energy for the phase of interest is described as follows,

\[ G_{mf} = \sum a^t \sum y_i^t ln y_i^t + E_{mf} \]  

where \( a^t \) represents the Gibbs energy contribution of each endmember, \( y_i^t \) the site fraction, and \( E_{mf} \) the excess Gibbs energy which contains the contributions from the mixing in one sublattice where all other sublattices only contain one component; and from the mixing in more than one sublattice where more than one sublattices contain two or more components. As shown in Table 3, in the present work the three-sublattice model (Nb, Ni)\(_1\)(Nb, Ni)\(_2\)(Nb, Ni)\(_3\) is used for \( \delta \)-NbNi\(_3\), corresponding to its Wyckoff positions (2a, 2b, 4f) [54]; and the five-sublattice model (Nb, Ni)\(_2\)(Nb, Ni)\(_2\)(Nb, Ni)\(_2\)(Nb, Ni)\(_6\)(Nb, Ni)\(_1\) is used for \( \mu \)-Nb\(_7\)Ni\(_6\), corresponding to its Wyckoff positions (3a, 6c\(_1\), 6c\(_2\), 6c\(_3\), 18h) [55].

### 3.2.2 CALPHAD modeling by the upgraded ESPEI and PyCalphad

The open-source software tools, and PyCalphd [18] and ESPEI [56], were employed in the present work to remodel the Nb-Ni system. PyCalphad is a Python-based codes for computational thermodynamics using the CALPHAD method, focusing on calculating phase diagrams, investigating thermodynamic properties, and designing new materials [56]. ESPEI, or Extensible Self-optimizing Phase Equilibria Infrastructure, is a tool for thermodynamic database development using the CALPHAD modeling approach [56], which uses PyCalphad as a computational engine to do thermodynamic calculations. ESPEI has two major features. First, ESPEI uses thermochemical data to choose and evaluate parameters to model Gibbs energy of individual phases. Second, ESPEI optimizes model parameters using phase equilibrium data through Bayesian parameter estimation using the Markov Chain Monte Carlo (MCMC) method and quantifies uncertainties of model parameters using the possible values during MCMC [57]. However, in the previous versions of ESPEI before the present work, the site occupancy data cannot be used as input for CALPHAD modeling in ESPEI which also limits the UQ of the site.
occupancy, although the modeling of site occupancies can provide a better description of how the atoms occur in a specific site.

In the present work, a new function that uses site occupancy data to optimize model parameters and quantify their uncertainties will be implemented in ESPEI. The flowchart of the present implementation is illustrated in Fig. 3, showing that ESPEI can take site occupancy as input by JavaScript Object Notation (JSON) format data, then proposes new parameter values from the MCMC method, calculates the site occupancy from fixed conditions, and the proposed parameter values, then compare the error and probability from fixed conditions and the old parameters to decide which parameter is more appreciate based on the Metropolis-Hastings criteria [57]. The format of JSON that contains data about site occupancy is created and the codes to calculate the error and probability of site occupancy are implemented into the error functions of ESPEI. Therefore, the site occupancy data can be considered together with all the available thermochemical and phase equilibrium data to fit all model parameters simultaneously, making the UQ analysis of site occupancy possible. For example, the experimental data of site occupancy by Joubert et al. [14] were used to remodel \( \mu \)-Nb\(_7\)Ni\(_6\) in the Nb-Ni system as shown in Sec. 4.2.

Uncertainty quantification (UQ) in ESPEI can quantify uncertainties of model parameters using the possible values during the MCMC sampling process [57]. The UQ in ESPEI adopts the samples from different Markov chains in the MCMC optimization and leverages them to estimate the uncertainties for thermodynamic properties of interest. In the present work, the UQ of site occupancy is implemented into ESPEI, which allows the quantified analyze the impact of site occupancy from modeling parameters. The uncertainties of site occupancy and enthalpy of mixing were used to show the possible range from the MCMC optimization during CALPHAD modeling of the Nb-Ni system. Note that four chains for each parameter were used during MCMC optimization for 10 steps which is converged, and the standard deviation was set to be 0.01 in the initialization of the chains using Gaussian distributions.

4 Results and discussion

4.1 Thermodynamic properties by first-principles calculations
Table 4 shows the space group, equilibrium volume ($V_0$, Å$^3$/atom), bulk modulus $B_0$ (GPa), and the derivative of bulk modulus $B'_0$ for all phases fitted at 0 K using Eq. 2, in comparison with available experiments [54,55,58,59], proving that DFT calculations from present works are reliable.

The differences in equilibrium volume ($V_0$, Å$^3$/atom) between calculations and experiments are less than 1.72%, which is due to the vibrational contribution in Eq. 1 is not considered during the DFT calculations and the exchange-correlation functions in DFT also bring some uncertainty in DFT predictions. That may lead to the equilibrium volume from experiments higher than the one from calculations, with the difference usually around 10% (from 15 calculations of the transition-metal disulfide compared with the experimental data [42]). For the bulk modulus $B_0$ (GPa) predicted from DFT, bcc-Nb shows a 1.00% difference and FCC-Ni has a 5.03% difference when compared with the experiments. Error! Reference source not found. Fig. 4 shows the predicted phonon DOS curves at equilibrium volumes for the BCC Nb, FCC Ni, δ-NbNi$_3$, and µ-Nb$_7$Ni$_6$ phase. The phonon DOS of BCC Nb, FCC Ni show good agreement with the experimental data as shown in Fig. S1. BCC Nb exhibits a higher phonon DOS at the lowest frequency region (< 5 THz) compared with the FCC-Ni phase, the µ -Nb$_7$Ni$_6$, and the δ-NbNi$_3$ phase, leading to a larger vibrational contribution to Helmholtz energy due to the vibrational entropy which increases with the decrease of logarithmic moment of phonon DOS [60]. While the phonon DOS of the µ-Nb$_7$Ni$_6$ phase is higher at the highest frequency region (>8 THz), which causes the smaller contribution to Helmholtz energy. This can be confirmed by the bulk modulus $B_0$ (GPa) predicted from the DFT of each phase, the bulk modulus $B_0$ (GPa) of BCC Nb is 173.540 GPa, while the bulk modulus $B_0$ (GPa) of the fcc-Ni phase is 195.852 GPa, the bulk modulus $B_0$ (GPa) of µ-Nb$_7$Ni$_6$ phase is 199.960 GPa, and the bulk modulus $B_0$ (GPa) of δ-NbNi$_3$ phase is 207.676 GPa, as shown in Table 4.

Fig. 5 shows the predicted entropy (Fig. 5 (a)) and enthalpy (Fig. 5 (b)) of BCC Nb as a function of temperature from the present calculations using Eq. 1, which are in good agreement with the SGTE data [52] with the average difference of 4.83% and stand deviation 0.49 for entropy; and the average difference of 5.79% and stand deviation 0.97 for enthalpy. Fig. 6 presents the predicted entropy (Fig. 6 (a)) and enthalpy (Fig. 6 (a)) of FCC Ni as a function of temperature from present calculations using Eq. 1, showing good agreement with the SGTE database [52] with the average
difference of 3.24%, and stand deviation of 1.21 for entropy; and the average difference of 6.44%, and stand deviation 2.42 for enthalpy.

Table 5 exhibits the enthalpy of formation ($\Delta H_{\text{form}}$) values of $\delta$-NbNi$_3$ and $\mu$-Nb$_7$Ni$_6$ from DFT-based first-principles calculations at both 0 K and room temperature compared with the experiments [22]. The configurations at the convex hull around the compositions (25 at. % Nb and 50 at. % Nb) in the experiments were chosen to represent the $\Delta H_{\text{form}}$ for $\delta$-NbNi$_3$ (Ni$_1$Nb$_1$Ni$_{12}$) and $\mu$-Nb$_7$Ni$_6$ (Nb$_2$Nb$_2$Nb$_2$Ni$_6$Ni$_1$). The predicted $\Delta H_{\text{form}}$ value of $\delta$-NbNi$_3$ (Ni$_1$Nb$_1$Ni$_{12}$) is -28.4 kJ/mol-atom at 0K and -28.5 kJ/mol-atom at room temperature. The difference between the predicted $\Delta H_{\text{form}}$ value and the experimental data (-31.8 kJ) is 3.2 kJ/mol-atom at 0K and 3.3 kJ/mol-atom at room temperature, which is in the error bar (4.73 kJ/mol-atom) of the experimental data Argent et al. [22] using the calorimetry method during three testing at 25 at. % Nb. While the predicted $\Delta H_{\text{form}}$ value of $\mu$-Nb$_7$Ni$_6$ (Nb$_2$Nb$_2$Nb$_2$Ni$_6$Ni$_1$) is -20.6 kJ/mol-atom at 0K and -20.4 kJ/mol-atom at room temperature. The difference between the predicted $\Delta H_{\text{form}}$ value and the experimental data (-22.6 kJ) is 2 kJ/mol-atom at 0K and 2.2 kJ/mol-atom at room temperature, which is in the error bar (6.82 kJ/mol-atom) of the experimental data Argent et al. [22] using the calorimetry method during six testing at 50 at. % Nb.

4.2 Thermodynamic modeling by ESPEI/PyCalphad

Error! Reference source not found.Fig. 1 illustrates the predicted $\Delta H_{\text{form}}$ values for the stable compounds in the Nb-Ni system at 298 K from the present CALPHAD modeling, in comparison with the present first-principles calculations and first-principles calculations from other work (Materials Project [40] and OQMD [41]) and experimental data from Argent et al. [22]. From Table 5, the predicted $\Delta H_{\text{form}}$ values at 25.0 at. % Nb from both 0K and room temperature shows a good agreement with experimental data [22] for $\delta$-NbNi$_3$ (at 25 at. % Nb) with a difference of less than 3.4 kJ/mol-atom while the error bar from three experiments is 4.73 kJ/mol-atom. For $\mu$-Nb$_7$Ni$_6$, the predicted $\Delta H_{\text{form}}$ values at 46.0 at. % Nb from both 0K and room temperature shows a good agreement with experimental data [22] for $\mu$-Nb$_7$Ni$_6$ (at 50 at. % Nb) with a difference of less than 2.2 kJ/mol-atom while the error bar from three experiments is 6.82 kJ/mol-atom. As shown in Fig. 1, predicted $\Delta H_{\text{form}}$ values from the present modeling by CALPHAD show less than
6.5 kJ/mol-atom difference with Argent et al. [22]’s data from 12.2 – 75.0 at. % Nb, which is slightly higher than the error bar (around 4 kJ/mol-atom) given by Argent et al. [22]. However, Argent et al. [22]’s ΔH\text{\text{form}} value at 50 at. % Nb (-22.4 kJ/mol-atom) has a difference of 6.8 kJ/mol-atom during six experiments. While the predicted ΔH\text{\text{form}} value from the present modeling is -28.9 kJ/mol-atom at 50 at. % Nb, causing a 6.5 kJ/mol-atom difference in ΔH\text{\text{form}} value that is less than the error bar (6.8 kJ/mol-atom) value when compared with the data from Argent et al. [22]’s experiments. Although Sokolvskaya et al. [37]’s data were not considered in the present modeling, the ΔH\text{\text{form}} values (-41.6 kJ/mol-atom) at 50 at. % Nb from Sokolvskaya et al. [37] show 19.2 kJ/mol-atom lower than the one (-22.4 kJ/mol-atom) from Argent et al. [22]. Therefore, the enthalpies of formation at 50 at. % Nb (28.9 kJ/mol-atom) is a reasonably good match with the experiments (-22.4 kJ/mol-atom) from Argent et al. [22].

Fig. 2 plots the presently predicted enthalpy of mixing (ΔH\text{\text{mix}}) curve of liquid at 1823 K in comparison with experiments data measured by Schaefer et al. [43] at 1927K and 2000K, Chistyakov et al. [27] at 2096K and Sudavtsova et al. [37] at 2148K. As mentioned in Sec. 2, experimental data from Chistyakov et al. [27] and Sudavtsova et al. [37] were used during CALPHAD modeling, while Schaefer et al. [43]’s data was excluded due to its far away (the difference is 15 kJ/mole-atom at 25.0 at. % Nb) from the enthalpies of formation of solids in the Nb-Ni system. Fig. 2 shows that the presently calculated results show a good agreement with Chistyakov et al. [27] and Sudavtsova et al. [37] with an average difference of less than 2 kJ/mol-atom.

Fig. 7 shows the calculated phase diagram based on the present CALPHAD modeling in comparison with experimental data [16,19–21,23,35]. The compassion between the present modeling and the previous modeling work by Chen et al. [16] is shown in Fig. S2. The detailed model parameters are summarized in the thermodynamic database (TDB) file in the Supplemental Material. As shown in Table 6, the invariant reactions from the present modeling show good agreements with data from experiments [20,61] with the difference in reaction compositions less than 2.3 at. % Nb, and the variance of the reaction temperature is less than 46 K. Phase boundaries between liquid and BCC measured by Wicker et al. [23] were considered in the present work besides the heating, cooling, and quenching measurements by Duerden et al. [20]. Therefore, the
phase boundaries of liquid and BCC from the present work show around 200 K temperature lower than those from Chen et al.’s modeling work [16] at 50.0 – 85.0 at. % Nb, which gave a better match (with an average difference of around 100 K) with the measured data by Wicker et al. [23]. The phase boundaries of δ-NbNi3 between the FCC phase and δ-NbNi3 are predicted from 23.8 to 23.3 at. % Nb at 790 K – 1547 K from the present modeling, matching well with experimental data including around 23.5 at. % Nb from Chen et al. [21] at 1323 K, 23.6 at. % Nb from Joubert et al. [15] at 1280 K, 23.6 – 23.6 at. % Nb from Duerden et al. [20] at 1273 K - 1420K, and 24.1 – 24.1 at. % Nb from Murametsu et al. [19] from 1070 - 1240 K. The phase boundaries of δ-NbNi3 between the μ-Nb7Ni6 phase and δ-NbNi3 are predicted from 25.7 to 28.4 at. % Nb at 1000 K – 1494 K from the present modeling, matching well with experimental data including around 25.6 at. % Nb from Chen et al. [21] at 1323 K, 26.5 to 26.6 at. % Nb from Duerden et al. [20] at 1273 K - 1420K, and 26.5 at. % Nb from Murametsu et al. [19] at 1170 K. The phase boundaries of μ-Nb7Ni6 between the μ-Nb7Ni6 phase and δ-NbNi3 are predicted around 48.3 – 49.3 at. % Nb at 1000 K – 1494 K from the present modeling. The experimental data included 48.6 at. % Nb from Murametsu et al. [19] at 1240K, 49.7 - 51.8 at. % Nb reported by Svechnikov et al. [35] at 1074 - 1276 K and 49.5 at. % Nb from Chen et al. [21] at 1273K. Phase boundaries of μ-Nb7Ni6 between the μ-Nb7Ni6 phase and BCC were measured by Duerden et al. [20] (54.0 at. % Nb at 1273K), Chen et al. [21] (56.3 at. % Nb at 1323K), Murametsu et al. [19] (56.2 – 56.2 at. % Nb at 1070 - 1240 K), Svechnikov et al. [35] (58.2 – 58.2 at. % Nb at 1074 - 1276 K), and Joubert et al. [14] (56.9 at. % Nb at 1273K). The experimental data shows a difference of 4.2 at. % Nb around 1273K. All the experimental data is considered into the present modeling combing with other thermochemical data like entropy, enthalpy, and site occupancy, which gives the predictions (57.2 – 56.6 at. % Nb at 1000 -1400 K) of the phase boundaries of μ-Nb7Ni6 between the μ-Nb7Ni6 phase and BCC from the present work.

Fig. 8 shows the predicted site occupancy curve of Nb in the μ-Nb7Ni6 phase from the present modeling work compared with the measured data from Joubert et al. [14]. It can be seen that the present CALPHAD predictions of site occupancy regarding Nb in μ-Nb7Ni6 agree with experiments with an absolute error less than 0.062, especially when compared with the site occupancy of Nb in μ-Nb7Ni6 phase predicted by Chen et al. [16] using a four-sublattice model combining the 6c2 and 6c3 sites in five Wyckoff sites of μ-Nb7Ni6 (3a, 6c1, 6c2, 6c3, 18h), cf. Table
Therefore, the sites 6c₂ and 6c₃ have the same site occupancy values from Chen et al. [16]’s model, causing the mean absolute error (MAE) with experiments [14] to 0.044 in site 6c₂ which is much higher than that from the present model (0.008 in site 6c₂). At the same time, the MAE compared with experiments is 0.128 at site 6c₁, 0.032 at site 6c₃, 0.088 at site 18h, and 0.086 at site 3a from Chen et al. [16] modeling while the MAE from the present model is 0.006 at site 6c₁, 0.032 at site 6c₃, 0.024 at site 18h, and 0.002 at site 3a. The stand deviation from the present work is also smaller than the one from Chen et al. [16]’s modeling, with the difference of stand deviation being 0.151 at site 6c₁, 0.043 at site 6c₂, 0.00 at site 6c₃, 0.094 at site 18h, and 0.112 at site 3a. Therefore, with the present sublattice models built according to Wyckoff sites of µ-Nb₇Ni₆ and δ-NbNi₃ and the new functions in ESPEI to consider site occupancy data into modeling, these two TCP phases can be modeled well, making a foundation for generating an accurate thermodynamic database for the multicomponent system.

Fig. 9a shows the UQ regions of site occupancy of each site concerning Nb in µ-Nb₇Ni₆ during CALPHAD modeling using the MCMC method as implemented in ESPEI. It is seen that the uncertainty ranges of Nb in the first sublattice are around 0.2, corresponding to Wyckoff position 6c₁. The shadow region in Fig. 9a covers all the experimental data [14] except the one at 49.6 at. % Nb that has 0.2 difference with the data at 51.8 at. % Nb, which means the uncertainty of site occupancy at site 6c₁ includes most of the uncertainty of the experiments at site 6c₁. Similarly, at the second, fourth, and fifth sublattice corresponding to Wyckoff position 6c₂, 18h, and 3a, the uncertainty ranges of Nb are around 0.2 for both, which also cover most of the experimental data except the one at 49.6 at. % Nb at 6c₁ site that has 0.06 (the average difference is 0.03) difference with the data at 51.8 at. % Nb. For the third sublattice corresponding to Wyckoff position 6c₃, the uncertainty ranges of Nb do not appear due to the third sublattice of stable endmembers is all occupied by Nb around 49.6 -56.9 at. % Nb. The UQ ranges of site occupancy of Nb in µ-Nb₇Ni₆ cover 80% of all experiments, which shows a good match with experimental data considering that the stand deviation of experimental data is around 0.35. The good agreement between UQ and the experimental data shows that the uncertainty during the modeling reflects the uncertainty of the experiments.
Fig. 9b shows the UQ ranges of ΔH_{mix} in liquid, indicating that the uncertainty increases from 0.0 – 40.0 at. % Nb and a slight increase from 40.0 – 80.0 at. % Nb then decreases from 80.0 – 100.0 at. % Nb, with the largest uncertainty around 3 kJ/mol-atom around 80.0 at. % Nb. It shows that a larger increase in ΔH_{mix} uncertainty of liquid appears at the Nb rich region due to the parameters of the liquid phase being more sensitive at the Nb rich region in the present CALPHAD modeling.

4 Conclusions

The present work combines thermodynamic data from DFT-based first-principles calculations and experiments, and the uncertainty quantification (UQ) method in CALPHAD modeling to model the Gibbs energy expressions of the Nb-Ni system.

- Here, first-principles calculations are used to predict thermochemical properties as a function of temperature for the TCP phases of δ-NbNi$_3$ and μ-Nb$_7$Ni$_6$, which provide the predicted ΔH$_{form}$ as input for CALPHAD modeling. The difference between the predicted ΔH$_{form}$ and the experimental data (-22.6 kJ) is 2 kJ/mol-atom at 0K and 2.2 kJ/mol-atom at room temperature.

- The present thermodynamic models of the δ-NbNi$_3$ and μ-Nb$_7$Ni$_6$ phases are built on their Wyckoff positions combined with the site occupancy as input for modeling in ESPEI, making precise descriptions for both the phase diagram and the distribution of site occupancies compared with available experimental data. For the phase diagram, the invariant reactions from the present modeling agree well with data from experiments [20,61] with the difference in reaction compositions less than 2.3 at. % Nb, and the variance of the reaction temperature is less than 46 K. For the predicted site occupancy curve of Nb in the μ-Nb$_7$Ni$_6$ phase, the average MAE for five sites is 0.0144 which is less than 0.0756 from Chen et al. [16]’s modeling.

- The UQ method has been employed to show uncertainties of enthalpy of mixing, and site fraction of Nb in the μ-Nb$_7$Ni$_6$ phase. The UQ regions of site occupancy of Nb in μ-Nb$_7$Ni$_6$ include 80% of the experimental data [14], indicating that the uncertainty during the modeling mirrors the uncertainty of the experiments.
Acknowledgements:
Table 1 (a): The position of Wyckoff position and the site occupancy factors (SOF) of δ phase in Nb-Ni, with Space group Pmmn (no. 59), Pearson symbol oP8, Strukturbericht Designation D0a, Model βCu₃Ti [54]

| Wyckoff position | x  | y  | z     | SOF |
|------------------|----|----|-------|-----|
| 2a               | 0  | 0  | 0.318 | 1.0 |
| 2b               | 0  | 0.5| 0.651 | 1.0 |
| 4f               | 0.75 | 0  | 0.841 | 1.0 |

Table 1 (b): The position of Wyckoff position and the site occupancy factors (SOF) of µ phase in Nb-Ni, with Space group R3m (no. 166), Pearson symbol hR13, Strukturbericht Designation D8s, Model Fe7W6 [55]

| Wyckoff position | x  | y  | z     | SOF |
|------------------|----|----|-------|-----|
| 3a               | 0  | 0  | 0     | 0.5 |
| 6c (1)           | 0  | 0  | 0.167 | 1.0 |
| 6c (2)           | 0  | 0  | 0.346 | 1.0 |
| 6c (3)           | 0  | 0  | 0.448 | 1.0 |
| 18h              | 0.5| 0.5| 0.590 | 1.0 |

Table 2: The sublattice models used from previous assessments

| Sources          | Phase model for δ-NbNi₃ | Phase model for µ-Nb₇Ni₆ |
|------------------|--------------------------|-------------------------|
| Kaufman and Nesor [10] | (Ni)₀.⁷₅(Nb)₀.₂₅ | (Ni)₀.⁴₇(Nb)₀.₅₃ |
| Kejun et al. [12] | (Nb, Ni)₃(Nb, Ni)₁ | (Nb, Ni)₁(Nb, Ni)₂(Nb, Ni)₆ |
| Bolcavage and Kattner [11] | (Nb, Ni)₃(Nb, Ni)₁ | (Nb, Ni)₇(Nb)₆ |
| Joubert et al. [15] | (Nb, Ni)₃(Nb, Ni)₁ | (Nb, Ni)₁(Nb, Ni)₂(Nb, Ni)₆ |
| Chen et al [13] | (Nb, Ni)₃(Nb, Ni)₁ | (Nb, Ni)₁(Nb, Ni)₂(Nb, Ni)₆ |

Table 3: Phase model used for all phases in the present work of Nb-Ni system

| Phase name       | Strukturbericht | Space group | Pearson symbol | Model          |
|------------------|-----------------|-------------|----------------|----------------|
| Liquid(L)        | A1              | Fm3m        | cF4            | (Nb, Ni)       |
| FCC              |                 |             |                | (Nb, Ni)₁(Va)₀ |
| HCP              | A3              | P6₃/mmc     | hP2            | (Nb, Ni)₁(Va)₀ |
| BCC-A2           | A2              | Im3m        | cI2            | (Nb, Ni)₁(Va)₃ |
| δ-NbNi₃          | D0a             | Pmmn        | oP8            | (Nb, Ni)(Nb, Ni)(Nb, Ni)₂ |
| µ-Nb₇Ni₆         | D8s             | R3m         | hR13           | (Nb, Ni)(Nb, Ni)(Nb, Ni)₂(Nb, Ni)₆ |
| NbNi₈             |                 |             |                | (Nb)₈          |

Table 4: Space group, equilibrium volume ($V_0$, Å³/atom), bulk modulus $B_0$ (GPa), and the derivative of bulk modulus $B'_0$ from both DFT calculations and experimental data [54,55,58,59]
| Phase      | Space Group | $V_0$ (Å³/atom) | % Difference | $B_0$ (GPa) | % Difference | $B'/_0$ | Source     |
|------------|-------------|----------------|--------------|-------------|--------------|---------|------------|
| BCC-Nb     | Im3m        | 36.675         | 0.221        | 173.540     | 1.00         | 3.857   | This work  |
|            |             | 36.594         |              | 171.8       |              |         | Expt. [58] |
| FCC-Ni     | Fm3m        | 43.719         | 0.217        | 195.852     | 5.03         | 4.808   | This work  |
|            |             | 43.614         |              | 186.0       |              |         | Expt. [59] |
| $\delta$-NbNi₃ | Pmmn       | 96.707         | 1.714        | 207.676     |              | 4.647   | This work  |
|            |             | 98.365         |              |             |              |         | Expt. [54] |
| $\mu$-Nb₇Ni₆ | R3m        | 549.502        | 0.964        | 199.960     |              | 4.477   | This work  |
|            |             | 554.800        |              |             |              |         | Expt. [55] |

Table 5: The enthalpy of formations of the $\delta$-NbNi₃ phase and $\mu$-Nb₇Ni₆ phase from present first-principle calculations at both 0K and room temperature (RT) compared with experiments [22].

| Phase      | $x_{Nb}$ | $\Delta_fH$ (kJ/mol-atom) at 0K | Difference (kJ/mol-atom) | $\Delta_fH$ (kJ/mol-atom) at RT | Difference (kJ/mol-atom) | Source     |
|------------|----------|---------------------------------|--------------------------|---------------------------------|--------------------------|------------|
| $\delta$-NbNi₃ | 0.25     | -28.4                           | 3.4                      | -28.5                           | 3.3                      | This work  |
|            | 0.25     | -31.8                           |                          | -31.8                           |                         | Expt. [22] |
| $\mu$-Nb₇Ni₆ | 0.46     | -20.6                           | 2.0                      | -20.4                           | 2.2                      | This work  |
|            | 0.50     | -22.6                           |                          | -22.6                           |                         | Expt. [22] |

Table 6: Comparison of temperatures and compositions of invariant reactions from present calculations and experimental measurements [20,61] in the Nb-Ni system.

| Reaction type | Reaction compositions (at. % Nb) | Temperature (K) | Source     |
|---------------|---------------------------------|----------------|------------|
| Eutectic      | Liquid ↔ fcc + $\delta$-NbNi₃    | 14.7           | This work  |
|               | 12.8                            | 23.3           |            |
|               | 16                              | 22.6           | 1547       |            |
|               | 12.7                            | 22.6           | 1555       |            |
|               |                                 | 1675           |            |            |
| Congruent     | Liquid ↔ $\delta$-NbNi₃         | 25.0           | This work  |
|               |                                 | 25.0           |            |            |
|               |                                 | 25.0           | 1675       |            |            |
| Eutectic      | Liquid ↔ $\delta$-NbNi₃ + $\mu$-Nb₇Ni₆ | 41.7          | This work  |
|               |                                 | 28.4           | 49.3       | 1494       |            |
|               | 27.5                            | 50             | 1448       |            |            |
| Peritectic    | Liquid + bcc ↔ $\mu$-Nb₇Ni₆      | 47.9           | This work  |
|               |                                 | 94.8           | 56.3       | 1542       |            |
|               | 95.5                            | 54             | 1568       |            |            |
| Peritectic    | fcc + $\delta$-NbNi₃ ↔ NbNi₈     | 8.5            | This work  |
|               |                                 | 23.8           | 11.1       | 790        |            |
|               |                                 |                | 808        |            |            |

Table 7. The site occupancies of Nb in $\mu$-Nb₇Ni₆ from calculations compared with the predictions from Chen et al. [16]'s work and experimental values [14], with its mean absolute error (MAE), and standard deviation (STD)
| Composition | Type of results | $6c_1$ | $6c_2$ | $6c_3$ | 18h | 3a |
|-------------|-----------------|--------|--------|--------|-----|----|
| $x_{\text{Nb}} = 0.496$ | Calc. from present work | 0.77 | 0.94 | 1.00 | 0.04 | 0.79 |
| | Calc. from Chen | 0.91 | 1.00 | 1.00 | 0.00 | 0.86 |
| | Expt. | 0.67 | 0.85 | 0.95 | 0.13 | 0.74 |
| | Calc. from present work | 0.79 | 0.96 | 1.00 | 0.07 | 0.79 |
| $x_{\text{Nb}} = 0.518$ | Calc. from Chen | 0.91 | 1.00 | 1.00 | 0.01 | 0.87 |
| | Expt. | 0.89 | 1.00 | 0.89 | 0.07 | 0.77 |
| | Calc. from present work | 0.81 | 0.97 | 1.00 | 0.09 | 0.80 |
| $x_{\text{Nb}} = 0.530$ | Calc. from Chen | 0.93 | 1.00 | 1.00 | 0.02 | 0.88 |
| | Expt. | 0.78 | 0.94 | 1.00 | 0.10 | 0.84 |
| | Calc. from present work | 0.81 | 0.97 | 1.00 | 0.10 | 0.80 |
| $x_{\text{Nb}} = 0.533$ | Calc. from Chen | 0.94 | 1.00 | 1.00 | 0.03 | 0.89 |
| | Expt. | 0.85 | 0.99 | 1.00 | 0.12 | 0.81 |
| | Calc. from present work | 0.85 | 0.98 | 1.00 | 0.16 | 0.80 |
| $x_{\text{Nb}} = 0.569$ | Calc. from Chen | 0.95 | 1.00 | 1.00 | 0.08 | 0.90 |
| | Expt. | 0.81 | 1.00 | 1.00 | 0.16 | 0.81 |
| | MAE from present work | 0.006 | 0.008 | 0.032 | -0.024 | 0.002 |
| | MAE from Chen | 0.128 | 0.044 | 0.032 | -0.088 | 0.086 |
| | STD from present work | 0.070 | 0.049 | 0.068 | 0.052 | 0.031 |
| | STD from Chen | 0.221 | 0.092 | 0.068 | 0.146 | 0.143 |

Figures will be replotted
Fig. 1. Enthalpies of formation of the intermetallic compounds in the Nb-Ni system at 298 K
Fig. 2. Calculated enthalpy of mixing of Nb/Ni in the liquid phase in comparison with experimental data.

Fig. 3. Workflow of ESPEI MCMC process (during changed)
Fig. 4. Predicted phonon density of states of the BCC-Nb phase (blue line), the FCC-Ni phase (orange line), the $\delta$-NbNi$_3$ phase (red line), and the $\mu$-Nb$_7$Ni$_6$ (green line) using first-principles calculations.
Fig. 5. (a) Entropy, (b) Enthalpy of BCC-Nb as a function of temperature calculated from present work using phonon calculations, compared with the SGTE database[52].
Fig. 6. (a) Entropy, (b) Enthalpy of FCC-Ni as a function of temperature calculated from present work using phonon calculations, compared with the SGTE database[52].
Fig. 7. Calculated phase diagram of the Nb-Ni system from the present thermodynamic modeling
Fig. 8. Site occupancies of Nb in $\mu$-Nb$_7$Ni$_6$ phase at 1273K with experimental data from Joubert [14].
Fig. 9. The PDUQ result of Site occupancies of Nb in the $\mu$-Nb$_7$Ni$_6$ phase, and the enthalpy of mixing in the liquid phase.
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Supplement