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Thermodynamic optimization of the Cu–Nd system

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ABSTRACT

The thermodynamic constraints to eliminate artificial phase relations were introduced with the Cu–Nd system as an example. The enthalpies of formation of the compounds Cu_6Nd, Cu_5Nd, Cu_2Nd and αCuNd are calculated using density functional theory. Taking into account all the experimental data and the first-principles calculated enthalpies of formation of these compounds, the thermodynamic optimization of the Cu–Nd system was performed under the proposed thermodynamic constraints. It is demonstrated that the thermodynamic constraints are critical to obtain a set of thermodynamic parameters for the Cu–Nd system, which can avoid the appearance of all the artificial phase relations.

1. Introduction

CALPHAD has been proved to be a useful technique used to calculate multi-component phase diagrams for practical applications [1]. One of the advantages of the CALPHAD is that it can predict phase diagrams and thermodynamic properties of the higher order systems with some certainties by means of thermodynamic extrapolation. However, it is not a rare occurrence that a series of unexpected phase relations, the existence of which is unlikely from a thermodynamics point of view, are found to emerge in the phase regions without experimental data or the phase diagrams of higher order systems, which were calculated with the previously published thermodynamic parameters [2].

The Cu–Nd system has been optimized by Du and Clavaguera [3] and Lysenko [4]. However, a careful test of the published thermodynamic parameters reveals that both calculations yield some artificial phase relations. There are three problems in the calculation [3], as shown in Fig. 1. The first problem is that an inverse liquid miscibility gap emerges at about 1500 K. The second problem is that the liquid phase re-stabilizes at low temperatures. The third issue is that the Cu_6Nd phase decomposes into the (Cu) phase and Cu_5Nd phase at about 300 K. Due to lack of the enthalpy of formation of the compound Cu_5Nd, it is hard to say whether this feature is right or not. Thus, further research on the enthalpies of formation of the compounds is necessary. Lysenko [4] re-optimized this binary system based on the parameters [3]. The inverse miscibility gap is eliminated in the calculated phase diagram [4]. However, the decomposition of the Cu_6Nd phase still occurs at about 300 K. Another problem associated with the optimization by Lysenko [4] is that the invariant reactions associated with Cu_7Nd_2 are not consistent with the experimental ones. According to the experimental data [5], the Cu_7Nd_2 phase was decomposed via the reaction Cu_7Nd_2 = liquid + Cu_4Nd at about 1058 K. In the calculated phase diagram of Lysenko [4], however, this reaction was replaced by a solid-state reaction $Cu_7Nd_2 = Cu_2Nd + Cu_4Nd$. Besides, the calculated phase diagram [4] showed some deviations from the experimental data. The calculated phase diagram of Lysenko [4] is shown in Fig. 2.

The above problems also exist in some other previous optimizations. Due to the development of the thermodynamic software [6] and the increasingly enhanced awareness of these problems, they can be detected by powerful software [7–9]. The purposes of the present work are: (1) to calculate the enthalpies of formation of the compounds Cu_6Nd, Cu_5Nd, Cu_2Nd and αCuNd using density functional theory (DFT) [10], (2) to introduce thermodynamic constraints to solve the above problems and (3) to present a reasonable thermodynamic description of the binary Cu–Nd system taking into account all the experimental data and the calculated enthalpies by first-principles, with a desire to eliminate the artificial phase relations via introduced thermodynamic constraints.

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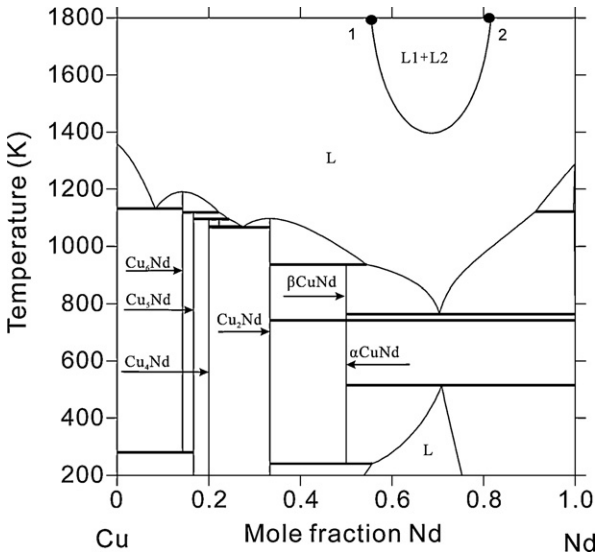

Fig. 1. Calculated Cu–Nd phase diagrams using parameters from [3].

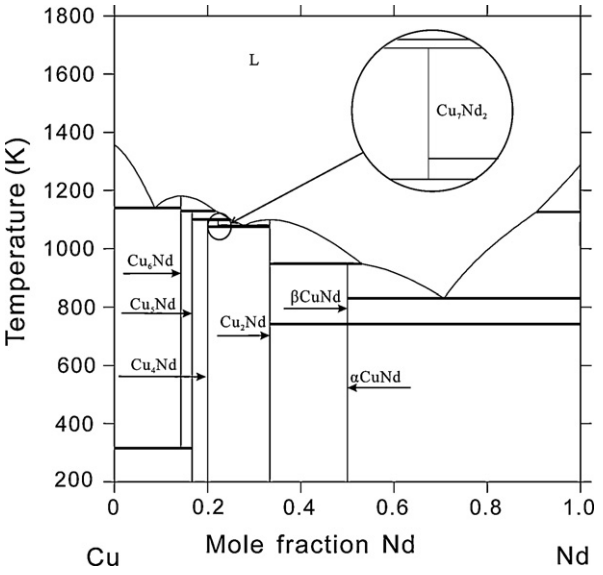

Fig. 2. Calculated Cu–Nd phase diagrams using parameters from [4].

The experimental data, which were used by Du and Clavaguera [3], are employed in the present work. Thus, the phase equilibrium data [5,11] and all the thermodynamic data [12–15] are used in this work. The crystal structure data for Cu_6Nd, Cu_5Nd, Cu_4Nd, Cu_2Nd and αCuNd are listed in Table 1 [5,11].

Table 1
Crystal structure data for the phases in the Cu–Nd system [5,11].

Phase	Person sym-bol/prototype	Space group	Lattice parameter (nm)			Ref.
			a	*b*	*c*	
Cu_6Nd	oP28/$CeCu_6$	Pnma	0.8064	0.5058	1.0113	[11]
Cu_5Nd	mP28/$CaCu_5$	P6/mmm	0.5110	–	0.4107	[11]
Cu_4Nd	Unknown	Unknown	0.527	–	–	[5]
Cu_2Nd	ol12/KHg_2	Imma	0.4387	0.7059	0.7420	[5]
αCuNd	oP8/FeB	Pnma	0.7279	0.4514	0.5636	[11]

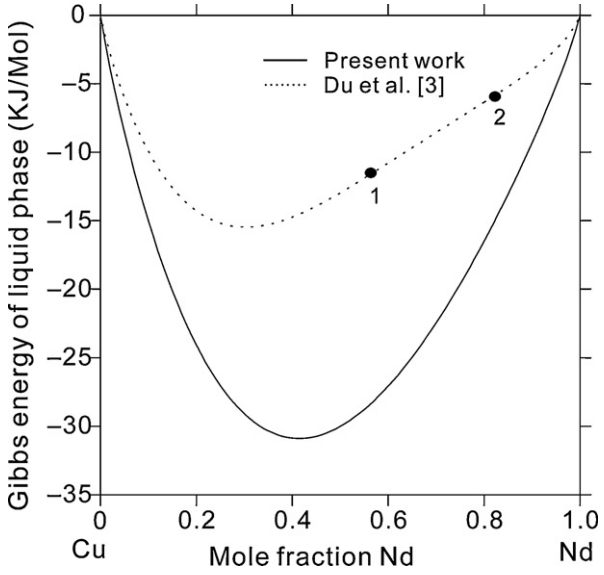

Fig. 3. Molar Gibbs energies of mixing at 1800 K resulting from [3] and present work.

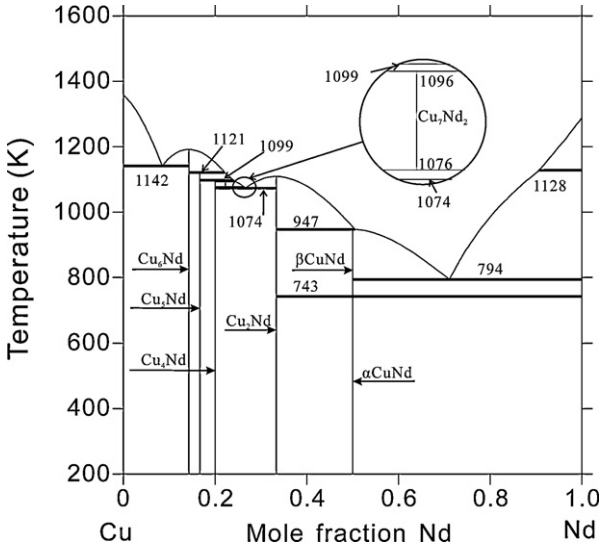

Fig. 4. The presently calculated Cu–Nd phase diagram.

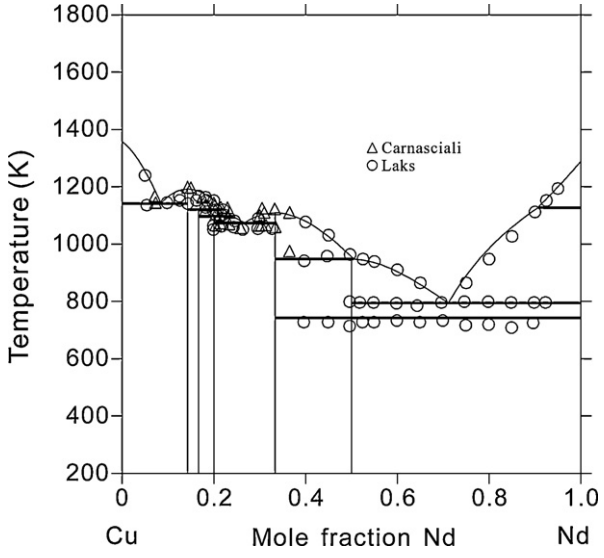

Fig. 5. The presently calculated Cu–Nd phase diagram compared with the experimental data [5,11].

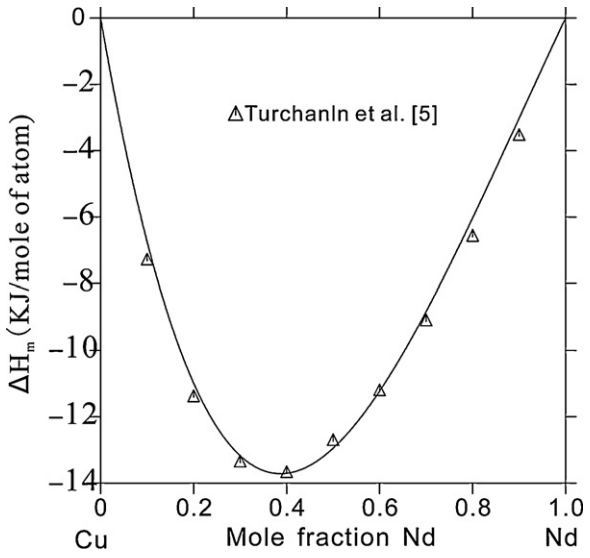

Fig. 6. Calculated enthalpy of mixing of the liquid phase at 1523 K compared with the experimental data [5].

2. First-principles calculation

The enthalpies of formation are critical to the thermodynamic descriptions of the compounds. However, only the enthalpies of formation of the Cu_6Nd and Cu_2Nd have been determined [12]. Thus, the total energies for the Cu_6Nd, Cu_5Nd, Cu_2Nd and αCuNd were calculated using DFT [10] within generalized gradient approximations (GGA) [16] with projector augmented-wave (PAW) pseudo-potentials [17], as implemented in the Vienna *ab* initio simulation package (VASP) [18,19]. The GGA proposed by Perdew et al. of (PBE) [20] was used in the calculation. Brillouin zone integrations were performed using a Monkhorst–Pack mesh [21], i.e. $11 \times 11 \times 13$ for Cu_6Nd and $9 \times 9 \times 5$ for other compounds. The energy cut off 400 eV was used to converge total energy to less than 1 meV/atom. The structure was fully relaxed using the Methfessel–Paxton smearing method [22] and a final self-consistent static calculation via the tetrahedron smearing method with Blochl corrections [23] was performed.

The enthalpy of formation of a compound is defined as the difference between the energy of the compound and the sum of the energies of its constituent elements in their stable states:

$$\Delta H_f = E_{total}^{Cu_xNd_{1-x}} - xE_{total}^{Cu\text{-}fcc} - (1-x)E_{total}^{Nd\text{-}dhcp} \quad (1)$$

where $E_{total}^{Cu_xZr_{1-x}}$ is the total energy of the compound Cu_xNd_{1-x}, and $E_{total}^{Cu\text{-}fcc}$ and $E_{total}^{Nd\text{-}dhcp}$ are the total energies of Cu and Nd in their stable structures, respectively. Since the influence of pressure on the condensed phases was ignored and the energy was calculated at 0 K without any entropic contributions, the calculated energy of formation was taken to be the enthalpy of formation at 298 K. The calculated results are listed in Table 2. The first-principles calculated enthalpies of Cu_6Nd and Cu_2Nd are consistent with the experimental data, as shown in Table 2. Both the experimental data and the first-principles calculated results are taken into account in this work.

Table 2
The enthalpies of formation (ΔH_f) of the compounds.

Compound	ΔH_f (kJ mol^{-1})		
	Experiment	DFT	CALPHAD
Cu_6Nd	−13.300 [13]	−13.939	−13.580
Cu_5Nd	–	−15.846	−15.704
Cu_2Nd	−16.900 [13]	−20.488	−20.250
αCuNd	–	−18.127	−18.280

3. Thermodynamic constraints

To avoid the artificial phase relations in the previous modeling [3,4], it is necessary to impose the thermodynamic constraints. We adopted specific recipes for specific problems so that a more reasonable thermodynamic description can be attained. The specific recipes are described as follows.

3.1. Inverse miscibility gap

The Redlich–Kister (R–K) polynomial [24] is the dominant model that has been utilized for describing the excess Gibbs energy of solution phases. The R–K polynomial is expressed as:

$$^{ex}G_m^L = x(1-x)\sum_{i=0}^{n} {}^iL(1-2x)^i \quad (2)$$

in which ${}^iL = A_i + B_iT + C_iT\ln T$ are the parameters to be optimized.

It has been demonstrated in some publications [7–9] that improper parameters in the R–K polynomial for describing the excess energy of a solution phase may yield the negative value for the second derivative of its Gibbs energy ($\partial^2 G^\phi/\partial x^2$) at certain temperatures and compositions. As shown in Fig. 3, the dash line represents the Gibbs energy of mixing for the liquid phase at 1800 K resulting from Du and Clavaguera [3]. The second derivative of the Gibbs energy ($\partial^2 G^\phi/\partial x^2$) is less than 0 between the point 1 and point 2 in the dash line. Consequently, an unrealistic miscibility gap may appear in the phase diagram, as shown in Fig. 1. To avoid the inverse liquid miscibility gap in the calculated phase diagram, it is necessary to guarantee a positive value of $\partial^2 G^\phi/\partial x^2$ for the whole phase region. In the new version of the thermo-calc software, a quantity QF(liquid), which has the identical sign to the second derivative of the Gibbs energy, was introduced to meet the constraint, $\partial^2 G^\phi/\partial x^2 > 0$.

3.2. Re-stabilization of liquid phase at low temperature

The re-stabilization of the liquid phase at low temperature in the αCuNd + (αNd) two-phase region is rooted in a too negative value of its Gibbs energy at low temperature. One way to avoid this feature is simply to set the constraint that the driving forces (DGM) of the αCuNd and (Nd) phase are positive while that of the liquid phase is negative in this region.

3.3. Decomposition of the Cu_6Nd phase

Since the enthalpy of formation of Cu_5Nd had not been experimentally determined, the enthalpies of formation of the Cu_5Nd and Cu_6Nd calculated by DFT in this work were used to judge whether the Cu_6Nd is stable below 300 K. Our calculation shows that the total enthalpy of mixing for the (Cu) and Cu_5Nd at the composition Cu_6Nd is −13582 J/mol-atom, which is larger than the enthalpy of formation of Cu_6Nd −13939 J/mol-atom. That is to say, according the first-principles calculations, the decomposition $Cu_6Nd = Cu_5Nd + (Cu)$ at about 300 K is unrealistic. The method to solve this problem during optimization is similar to the one for the first problem. We can set the constraint that the driving forces (DGM) of the (Cu) and Cu_6Nd phase are positive while that of the Cu_5Nd phase is negative in this region.

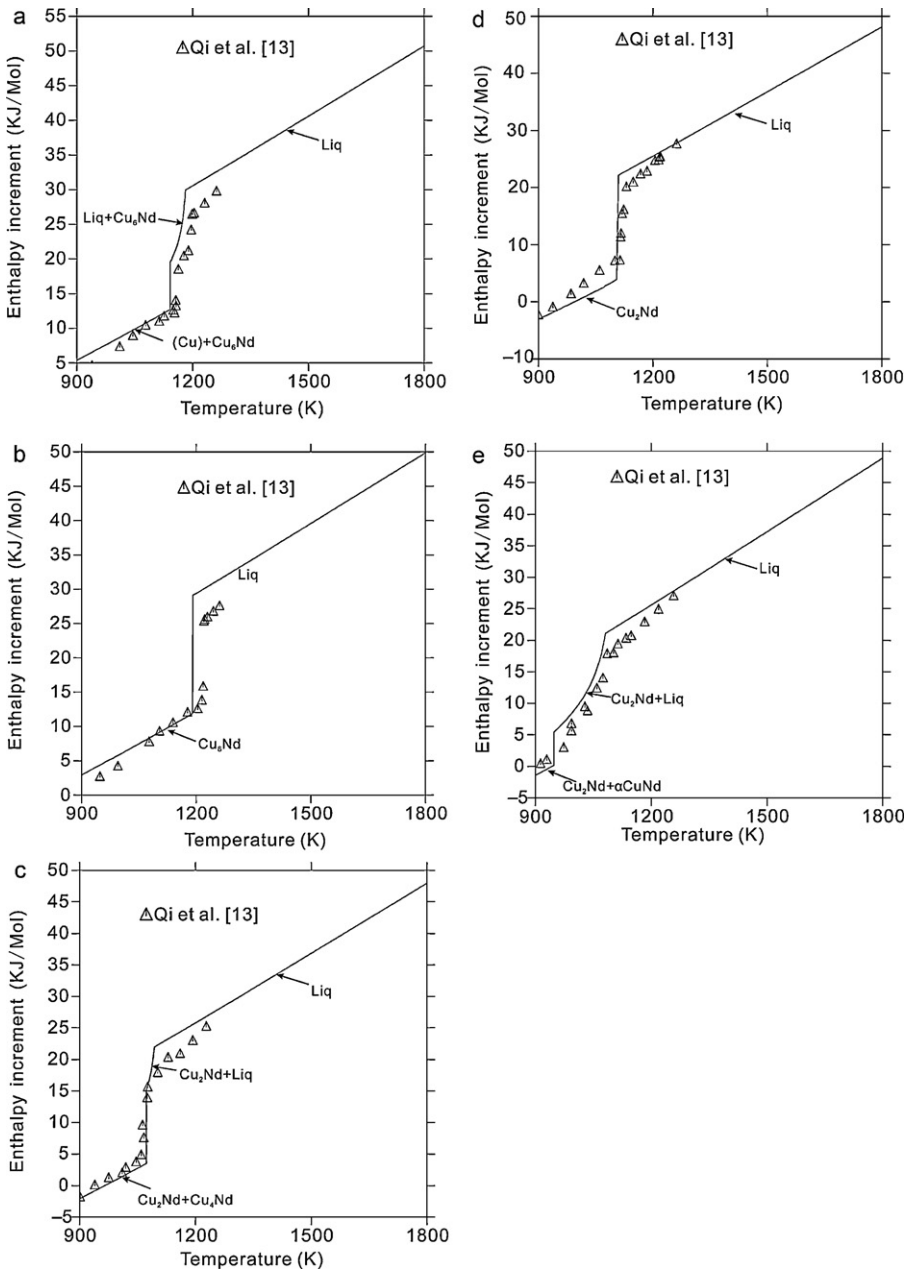

Fig. 7. Calculated enthalpy increments vs. temperature relative to the molar enthalpies of Cu and Nd at 298.15 K. (a) With composition of 11.6 at.% Nd, (b) with composition of 14.3 at.% Nd, (c) with composition of 28.9 at.% Nd, (d) with composition of 33.3 at.% Nd and (e) with composition of 39.8 at.% Nd.

3.4. Equilibria associated with the Cu_7Nd_2 phase

According to the experiment [5], the Cu_7Nd_2 phase is formed by the reaction liquid + Cu_4Nd = Cu_7Nd_2 at 1098 K and decomposes into Liquid phase and Cu_4Nd phase at 1058 K. Since the Cu_7Nd_2 phase exists in a narrow temperature range, a small change of the Gibbs energy for the Cu_7Nd_2 phase may yield wrong results, as shown in the work of Lysenko [4]. Therefore, a preliminary thermodynamic modeling was performed in the first step without taking into account the Cu_7Nd_2 phase. In this step, the thermodynamic parameters for all the other phases could be evaluated. Using these parameters, the enthalpies and entropies of formation were calculated for the composition Cu_7Nd_2 at the eutectoid temperature (1098 K) and the peritectic temperature (1058 K), based on the liquid–Cu_4Nd equilibrium. The parameters A and B of Cu_7Nd_2 can be evaluated through the strategy that the calculated enthalpies of formation at 1098 K and 1058 K give the interval for A, while entropies of formation give the value for B.

4. Results and discussions

Taking into account the thermodynamic constraints proposed above, the thermodynamic modeling of the Cu–Nd system was performed in the present work.

The Gibbs energy of the pure element i in phase ϕ is expressed by the following equation:

$$G_i^{\phi}(T) - H_i^{\mathrm{SER}} = A + BT + CT\ \ln(T) + DT^2 + ET^3 + FT^{-1} + HT^7 + IT^{-9} \quad (3)$$

Table 3
Optimized parameters in the Cu–Nd system.

Liquid: $(Cu,Nd)_1$
$L^{0,liquid}_{Cu,Nd} = -55583.6 + 5.8955T - 2.4901T\ln(T)$
$L^{1,liquid}_{Cu,Nd} = -27795.1 + 3.1830T - 1.2911T\ln(T)$
$L^{2,liquid}_{Cu,Nd} = -3806$
Cu_6Nd: $(Cu)_{6/7}(Nd)_{1/7}$
$\Delta G_f^{Cu_6Nd} = -13581.0 - 0.7253T$
Cu_5Nd: $(Cu)_{5/6}(Nd)_{1/6}$
$\Delta G_f^{Cu_5Nd} = -15704.5 + 0.1205T$
Cu_4Nd: $(Cu)_{4/5}(Nd)_{1/5}$
$\Delta G_f^{Cu_4Nd} = -16826.7 - 0.1695T$
Cu_7Nd_2: $(Cu)_{7/9}(Nd)_{2/9}$
$\Delta G_f = -10046.4 - 7.2194T$
Cu_2Nd: $(Cu)_{2/3}(Nd)_{1/3}$
$\Delta G_f^{Cu_2Nd} = -20250.0 - 1.3786T$
βCuNd: $(Cu)_{1/2}(Nd)_{1/2}$
$\Delta G_f^{\beta CuNd} = -16592.3 - 2.4898T$
αCuNd: $(Cu)_{1/2}(Nd)_{1/2}$
$\Delta G_f^{\alpha CuNd} = -18280.0 - 0.2176T$

in which H_i^{SER} is the molar enthalpy of the stable element reference (SER) at 298.15 K and 1 bar, and T is the absolute temperature. The thermodynamic properties of Cu and Nd are taken from the Scientific Group Thermodata Europe (SGTE) compilation by Dinsdale [25].

All the compounds (Cu_6Nd, Cu_5Nd, Cu_4Nd, Cu_7Nd_2, Cu_2Nd and CuNd) were modeled as stoichiometric phases, and the Gibbs energies of these compounds with formula Cu_xNd_{1-x} were expressed with the following expression:

$$G_{Cu_xNd_{1-x}} - H^{SER} = x\,{}^0G_{Cu}^{Fcc\_A1} + (1-x)\,{}^0G_{Nd}^{DHCP} + \Delta G_f^{Cu_xNd_{1-x}} \quad (4)$$

in which H^{SER} is the abbreviation of $xH_{Cu}^{SER} + (1-x)H_{Nd}^{SER}$, x is the mole fraction of Cu, and $\Delta G_f^{Cu_xNd_{1-x}} = A + BT$ represents the Gibbs energy of formation of the compound Cu_xNd_{1-x}. The parameters A and B are to be optimized.

The Gibbs energy of the liquid phase is described by the R–K polynomial as Eq. (2) above.

The thermodynamics parameters obtained in the present work are listed in Table 3. The presently calculated Cu–Nd phase diagram is shown in Fig. 4 without experimental data and in Fig. 5 with experimental data for comparison. As shown in Fig. 5, the calculation can reproduce the experimental data well. The solid line in Fig. 3 is the molar Gibbs energies of mixing at 1800 K resulting from present work. The inverse miscibility gap existing in the previous thermodynamic descriptions [3] has been eliminated. The calculated enthalpies of formation of Cu_6Nd, Cu_5Nd, Cu_2Nd and αCuNd at 298.15 K by CALPHAD are listed in Table 2, together with the experimental data and the calculated results at 0 K by DFT. The calculated enthalpies of formation using CALPHAD fitted well with the first-principles calculated results and experimental determined data. Fig. 6 is the calculated enthalpy of mixing of the liquid at 1523 K compared with the experimental data [14]. Fig. 7 shows the calculated enthalpy increments compared with the experimental data [13]. It should be mentioned that the phase boundaries derived from the experimental data [13] are not consistent with the well accepted Cu–Nd phase diagram. As a result, the calculated enthalpy increments show some deviations from the experimental data.

5. Conclusion

The enthalpies of formation of the compounds Cu_6Nd, Cu_5Nd, Cu_2Nd and αCuNd were calculated using DFT. The thermodynamic constraints to eliminate the artificial phase relations were imposed during the thermodynamic optimization procedure. Taking into account all the experimental data and the first-principles calculated enthalpies of formation of the compounds, the thermodynamic evaluation of the Cu–Nd system was performed under the thermodynamic constraints. The thermodynamic calculation can account for the experimental data in the literature and the first-principles calculated enthalpies of formation of the compounds. Furthermore, all the artificial phase relations, which are found with the previously published thermodynamic parameters, were eliminated. It has been demonstrated that the thermodynamic constraints are critical to obtain a set of reliable thermodynamic parameters for the binary Cu–Nd system.

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