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Using Nb-Ni μ phase first principles results to calculate finite temperature thermodynamic properties in the Bragg-Williams approximation

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Results of first-principles (FP) total energy calculations for 32 different configurations of the μ phase in the binary system Nb–Ni are used in the compound energy formalism (CEF) to model finite temperature thermodynamic properties. A comparison with Cluster Expansion Hamiltonian-Cluster Variation Method (CEH-CVM) calculations indicates that the CEF describes temperature dependent site occupancies as well as the CEH-CVM within the temperature range of interest for applications. This suggests that the Bragg-Williams-Gorski Approximation (BWGA) used in the CEF is sufficient to describe site occupancies and thermodynamics of the μ phase. A phase diagram is calculated using the μ phase description derived in the present work together with a previous Calphad description for the other phases of this system. The FP-CEF approach significantly improves the description of the thermodynamic properties as a function of composition compared to the Calphad procedure generally used up to now.

Keywords: thermodynamics; phase equilibria; intermetallic phases; crystallography; ab initio; Calphad; Gibbs energy modelling; TCP phases; Frank-Kasper phases

1 Introduction

First-principles (FP) total energy calculations are becoming abundant, but only a few are used to construct Cluster Expansion Hamiltonians (CEH) for Cluster Variation Method (CVM) or MonteCarlo (MC) calculations of FP phase diagrams

¹Current adress.

(FP-PD) (FP-CEH-CVM-PD [1] or FP-CEH-MC-PD [2]). Most FP-PD calculations deal with a single parent Bravais lattice (e.g. BCC) in binary systems. The resulting "coherent" phase diagrams display the equilibria between ordered (superlattices, e.g. B2, D0₃, etc) and disordered phases (e.g. A2) over the whole range of composition and temperature and in particular metastable equilibria which are difficult to study by other approaches. A few studies consider several parent Bravais lattices, BCC and FCC for instance, or even treat ternary cases [3].

FP-PD usually achieve qualitative agreement with experiment, providing correct phase diagram topologies but even when non-configurational contributions are included, the experimental phase boundaries are poorly reproduced by the theoretical approach. Thus, FP-PD generally lack the accuracy required for technical applications.

Another shortcoming of FP-PD is that the liquid phase is usually not considered, although some CVM calculations including this phase are in progress [4]. Description of the solid-liquid transformation is possible with Molecular Dynamics but, so far, it has only been applied to stoichiometric phases.

Beside the theoretical procedures described above, the more empirical approach called Calphad [5] is widely used to calculate phase diagrams and thermodynamic properties. The Gibbs energy of each phase is described as a function of composition, temperature, etc, by means of parametric models. These models are usually defined within the compound energy formalism (CEF) [6,7,8] which can describe, in multicomponent systems, substitutional and interstitial solutions, intermetallic phases with wide homogeneity range, order/disorder transformations, etc. Parameters are determined through a minimisation procedure comparing all the phase diagram and thermodynamic information (e.g. phase boundaries, invariant equilibrium temperatures, enthalpies, chemical potentials).

Calphad models and their parameters are stored in databases used in calculations of multicomponent phase equilibria in any range of composition, temperature, etc. Interpolations and extrapolations into unstudied regions and even not reachable experimentally are thus possible. In particular, metastable equilibria can be calculated but empirical parameters not physically based can lead to unreasonable results. Such weakness can become problematic when used in, for example, the simulation of a diffusion controlled process where the second derivatives of the Gibbs energy are required. Calphad databases are much in demand for processing and development of materials which may contain as many as 15 elements. Such technical alloys usually have a main element so that dedicated databases have been constructed for, e.g. Al-light alloys, steels, Ni-superalloys.

For these materials, many topologically closed packed (TCP) phases, e.g. the μ ($D8_5$), σ ($D8_a$) and the Laves phases ($C14$, $C15$, $C36$), may appear. They are brittle and deplete the alloying elements from the matrix. Consequently their formation should be avoided or their growth controlled. Trends indicating their stability ranges were extensively studied by W. Hume-Rothery, who, trying to stimulate theoretical physicists, stated almost 40 years ago [9]: "The stability of metallic phases is a fa-

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cinating and exciting problem. Experiment and empirical generalisations are ahead of qualitative theory,...” Nowadays, the Gibbs energy of these phases is still poorly modelled even using the pragmatic Calphad approach. This is mainly due to lack of experimental information on these phases, particularly site occupancy data as function of composition and temperature. Experimental site occupancy determination is difficult because most of these phases have multiple sublattices (5 in the case of the μ and σ phases). Furthermore, experiments are limited to stable composition ranges. The versatile CEF allows thermodynamic descriptions considering as many distinct sublattices as there are crystallographic sites. Many parameters are then needed (32 in the case of a binary μ phase) but only a few of them can be assessed from experimental information because the other ones would require data far outside the stable range. As a result many parameters are poorly constrained and this makes extrapolations into multicomponent systems unreliable. The Calphad models decreasing the number of parameters overcome this issue but often do not describe important features of these phases.

As suggested by Burton *et al.* [10], the combination of FP-CEH-(CVM or MC) and Calphad should be profitable and it is now under development [11]. One way to link the first-principles energetics to Calphad formalisms was recently proposed by Fries and Sundman, and named First-Principles CEF (FP-CEF) [12]. The objective is to incorporate the maximum amount of the theoretical predictions into the descriptions while still maintaining some simplicity in order to allow the application to multicomponent systems. Calculated FP energies of the 32 possible ordered configurations on the 5 sublattices of the $D8_a$ σ phase in Re-W binary system [13] were directly imported into the CEF. A composition dependent Gibbs energy for the σ phase was obtained over the whole binary composition range. The temperature dependence was provided by the BWGA of the CEF. Comparison of the FP-CEF and FP-CEH-CVM using the same set of energies [13] showed the potential of the procedure because almost all features of the CVM results are reproduced by the CEF.

Furthermore, calculated compositional variations of the site occupancies allowed identification of sublattices that behave in a similar way indicating which may be grouped to simplify the CEF model. Grouping sublattices to reduce the number of parameters is a compulsory approximation in the Calphad assessments. When there is insufficient data for the site occupancy, the decisions are made based on simple arguments (site coordination, atom radius, homogeneity range). Even when experimental site occupations are available, only the limited composition range where the phase is stable is accessible experimentally. The experimentally derived sublattice groupings are thus often rather speculative. Fortunately, FP results over the whole composition range permit this grouping to be derived theoretically.

Fries and Sundman [12] also tested their FP-CEF description of the Re-W σ phase by calculating a phase diagram that included all the phases of this system. In an existing Calphad assessment, they replaced the previous σ phase Gibbs energy description with their FP-CEF one. A satisfactory phase diagram was obtained but no comparison of calculated and experimental thermodynamic properties was possible because none had yet been measured in this system. Therefore, any Calphad

In the present work, a similar approach was applied to the Ni-Nb binary system which is better characterised experimentally than the Re-W system. Many experimental data are available including some thermodynamical properties [14] and crystallographic information on the site occupations of the 5 different sites of the μ phase [15] on which the present work is focused. Also a previous Calphad assessment [16] and extensive FP calculations for the μ phase [17] are available.

2 The CEF

The CEF is a generalized Bragg-Williams-Gorsky approximation (BWGA), which implies random distributions of species (atoms, ions, vacancies) in each crystallographic site; i.e. short range order is ignored. In the CEF [6,7,8], the general molar Gibbs energy expression is

$$G = G^{srf} - TS^{conf} + G^{xs} \quad (1)$$

The reference term for the model, G^{srf} , is the sum of Gibbs energies of all configurations with a single species, i , on each sublattice, s , weighted by the product of site fractions, $y_i^{(s)}$. The μ phase has five sublattices with different numbers of sites with different coordination numbers and can be described as $(\text{Nb,Ni})_3 (\text{Nb,Ni})_6 (\text{Nb,Ni})_6 (\text{Nb,Ni})_6 (\text{Nb,Ni})_{18}$. This model defines $2^5=32$ ordered configurations. Thus, the Gibbs energy surface of reference is expressed by

$$G^{srf} = \sum_{ijklm} y_i^{(1)} y_j^{(2)} y_k^{(3)} y_l^{(4)} y_m^{(5)} {}^oG_{ijklm} \quad (2)$$

In the present treatment, these compound Gibbs energies, ${}^oG_{ijklm}$, are assumed to be exactly the first-principles (FP) total energies calculated at 0 K by Sluiter et al. [17]. The only additional term necessary to calculate the Gibbs energy at any temperature is the entropy of mixing, expressed as:

$$S^{conf} = -R \sum_s a^{(s)} \sum_{i=\text{Nb,Ni}} y_i^{(s)} \ln(y_i^{(s)}) \quad (3)$$

where $a^{(s)}$ is the number of sites on sublattice s . The excess term G^{xs} is set to zero which means that the properties of the μ phase are directly calculated from the FP results in the CEF.

3 Results and Comparison

Site occupancies and thermodynamic properties calculated with the CEF as functions of composition and temperature are shown in figures 1, 2, 3 and 4. They are compared with the site occupations obtained by Joubert and Feutelais [15] by Rietveld refinement and also to the CEH[18,19]-CVM [20] results after Sluiter et al. [17].

1 Most features of the CEH-CVM results are reproduced by the BWGA, in par-
2 ticular in the range of stability (x -T) of the μ phase. Calculations are in agreement
3 with the results of Joubert and Feutelais [15] for the sites of coordination 12 ($3a$
4 and $18h$), but only qualitative for the other sites. In the Nb-rich range, the retrograde
5 behaviour of the $6c1$ and especially the $6c2$ sites calculated in the CEH-CVM is
6 incorrect and could be easily rectified by properly truncating the cluster expansion
7 as shown and explained by Sluiter et al. [21]. This problem is overcome by the
8 completeness of the expansion guaranteed by CEF. Curves from CEH-CVM model,
9 Figs. 1-4, still exhibit this retrograde behaviour but these differences are not rele-
10 vant because they occur in a range of composition where the μ phase is not stable.
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14 Figure 3 (a) and (b) show that the variations of the Gibbs energy and enthalpy
15 with temperature are small compared to variations with composition. This is also
16 shown in figure 4 on the reduced scale where the phase is stable. Figure 3 (c) shows
17 the variation of the entropy with composition for three temperatures. The low min-
18 ima indicate a high degree of order close to the stoichiometries of the most stable
19 configurations. As discussed previously by different authors [22,23,24], these minima
20 imply sharp peaks on the C_p curves versus composition (Fig. 3 (d)) .
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24 To calculate the phase relationship between the μ phase and the other stable
25 phases in the system, structural energy differences (lattice stabilities) must be con-
26 sidered. FP total energies of the pure elements in several crystal structures are
27 listed in Table 1. They were used to calculate the thermodynamic properties of the
28 μ phase with respect to the Nb bcc and Ni fcc shown in figure 5.
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30 [Insert table 1 about here]
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32 [Insert figure 5 about here]
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35 Agreement between calculated and experimental enthalpies of formation, as mea-
36 sured by Argent and Pearcey [14], is very good. Dashed lines in figure 5 are the
37 thermodynamic properties of the μ phase calculated from Bolcavage and Kattner [16]
38 description which are also in very good agreement with the experimental value be-
39 cause these were used in the optimisation procedure carried out by Bolcavage and
40 Kattner [16]. FP-CEF and Bolcavage and Kattner Gibbs energy and enthalpy be-
41 have similarly in a wide range of composition. But in the composition range of the
42 μ phase it retains the same slope while the FP-CEF predicts an almost constant
43 value. The shape of the Gibbs energy and of the enthalpy is actually very different
44 in the Nb rich side where it seems unreasonably constrained by the value chosen for
45 pure Nb in the μ phase.
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49 Only one phase is analysed in the present paper; a FP-PD calculation showing
50 the equilibrium among all the phases in this binary system is thus not possible.
51 Therefore, in order to calculate a phase diagram with the new μ phase model, de-
52 scriptions of the other phases (liquid, fcc, bcc, Ni_3Nb) were taken from the Calphad
53 assessment by Bolcavage and Kattner [16]. The resulting phase diagram is presented
54 in figure 6 (solid lines) together with the phase diagram calculated with the original
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[Insert figure 6 about here]

The FP-CEF predicted stability field for the μ phase is in good agreement with the field calculated by the standard Calphad procedure but it is slightly narrower than experimentally determined. Some contributions not taken into account, in particular vibrational effects, could correct this point but it could also be due to an overestimation of the stability of the neighbouring phases from the original Calphad assessment by Bolcavage and Kattner [16]. Nevertheless, the overall agreement is very promising for the ability to actually predict the stability of TCP phases using FP values within the versatile Calphad approach.

4 Conclusions and Perspectives

Site occupancy diagrams are critical for describing the properties of complex non-stoichiometric phases such as the μ phase. The FP-CEF yields as good an approximation of the temperature and composition dependencies of μ phase site occupancies as the FP-CEH-CVM calculations; at least in the range of temperatures and compositions of practical interest. The short range order, which is ignored in CEF, might therefore not be essential for modelling TCP phases.

That FP-CEF thermodynamic description of phases based on FP total energies without any adjustable parameters, yield close agreement with experimental data is highly promising for a future combination of FP and Calphad techniques to predict phase equilibria involving phases of large homogeneity range in multicomponent systems.

Confirmation of these conclusions should come from phase diagram calculations using FP results also for the other phases of this system and in particular for the intermetallic phase Ni_3Nb . This phase is experimentally observed in its stable crystallographic structure $D0_a$ (Cu_3Ti) but also in the metastable one $D0_{22}$ (Al_3Ti). This latter phase, known as γ'' , contributes to the structural strengthening of Ni superalloys containing Nb. The FP study of these structures could clarify the competition between the μ , $D0_a$ and $D0_{22}$ phases in this particular system and in multicomponent alloys of technological interest.

It should now be possible to perform a new Calphad assessment, which has a better physical basis and therefore more predictive ability. This would be based on the definition of the Gibbs energy of the μ phase over the whole range of composition as shown here. It would also benefit from the consideration of recent measurement of mixing enthalpies in the liquid phase [25] that is still difficult to treat with FP.

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element	structure	energy (eV/atom)	energy (kJ/mol)
Ni	fcc	-5.420	-522.9
	μ	-5.276	-509.0
Nb	bcc	-9.974	-962.2
	μ	-9.796	-945.0

Table 1: FP total energies of Ni and Nb in the non-spin polarized fcc, bcc and μ phase structures.

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Figure 1: Comparison of the site occupancies at four different temperatures calculated with the CEF (full lines) and with the CEH-CVM (dotted lines). Results of Rietveld refinement by Joubert and Feutelais [15] (symbols) at 1273 K are also shown. The vertical gray lines at 1000 K show the compositions studied versus temperature in the figures 2 and 4.

Figure 2: Comparison of the site occupancies at three different compositions ($\text{Nb/Ni} = 7/6, 1, 6/7$) as function of temperature calculated with CEF (full lines) and with the CEH-CVM (dotted lines) by Sluiter et al. [16].

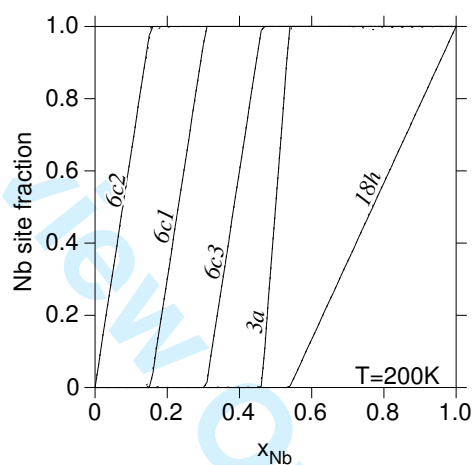
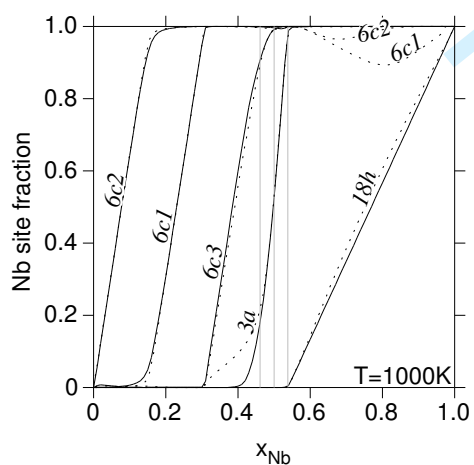
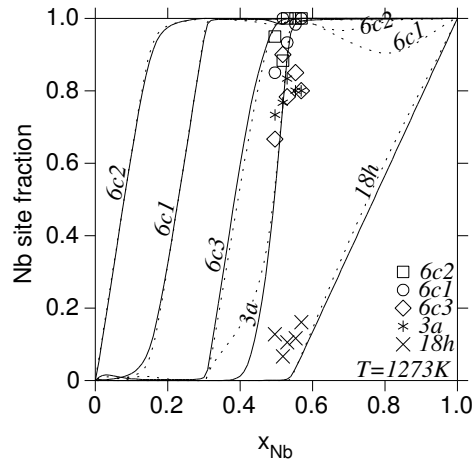
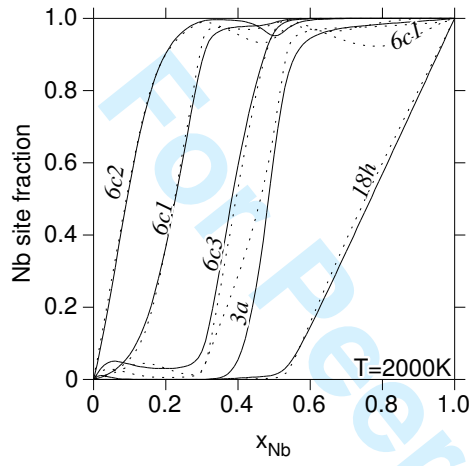
Figure 3: Comparison of the Gibbs energy, enthalpy, entropy and heat capacity of the μ phase at three temperatures (200K, 1000K and 2000K) relative to the elements in the μ state calculated with CEF (full lines) and with the CEH-CVM (dotted lines) derived in the present work based on [16]. The CEH-CVM C_p are calculated by finite difference and is not shown at 200K because they are not considered accurate enough.

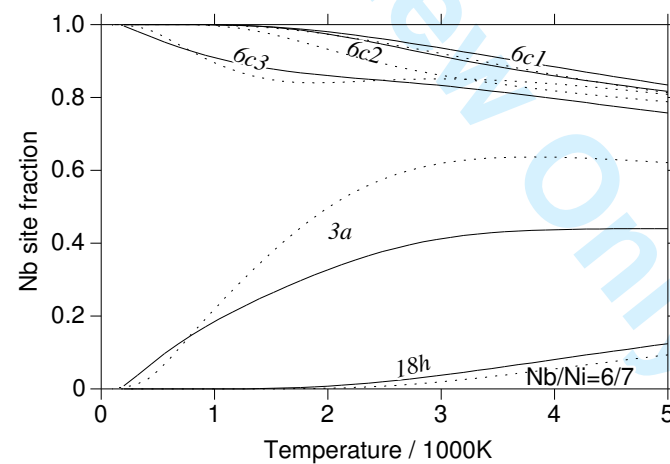
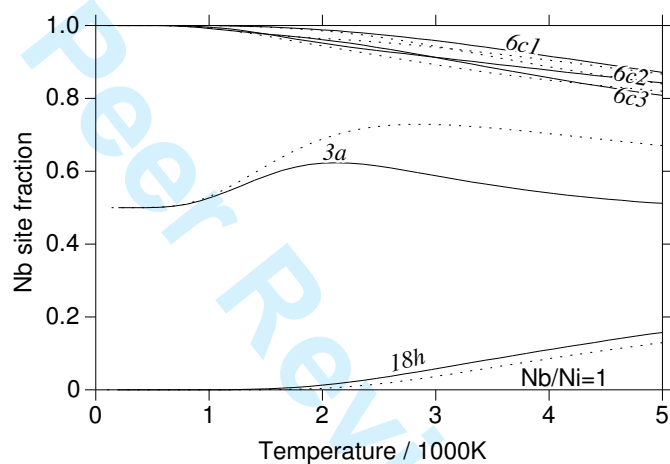
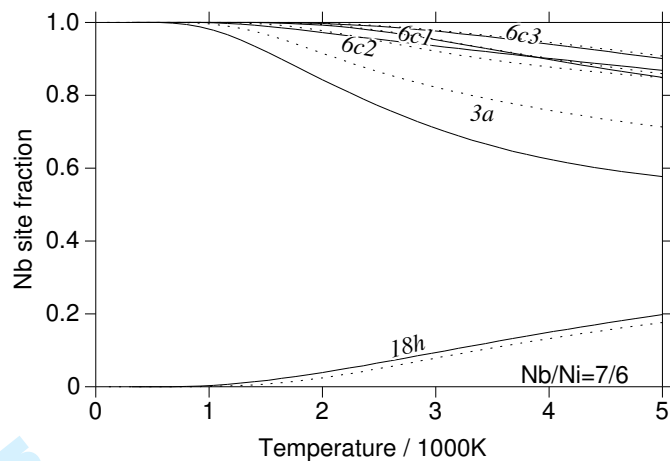
Figure 4: Comparison of the Gibbs energy, enthalpy, entropy and heat capacity of the μ phase at three compositions ($x_{\text{Nb}} = 0.538, 0.500, 0.462$) relative to the elements in the μ state calculated with CEF (full lines) and with the CEH-CVM (dotted lines) by Sluiter et al. [16].

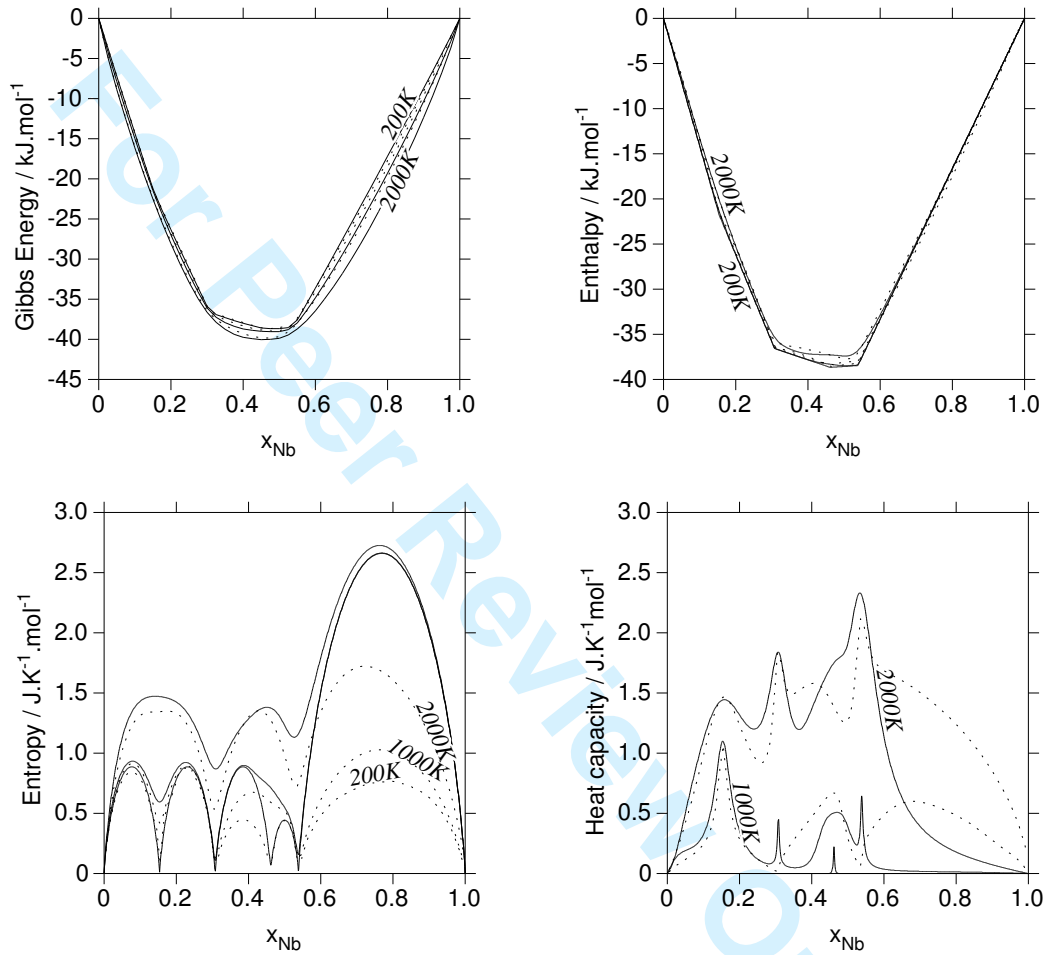
Figure 5: Calculated thermodynamic properties of the μ phase calculated at three temperatures (200K, 1000K, 2000K) relative to the elements Nb bcc and Ni fcc with the present FP-CEF and the previous description by Bolcavage and Kattner [15] (dashed line). The calculated enthalpies are compared to the experimental value by Argent and Pearcey [15] (\bullet).

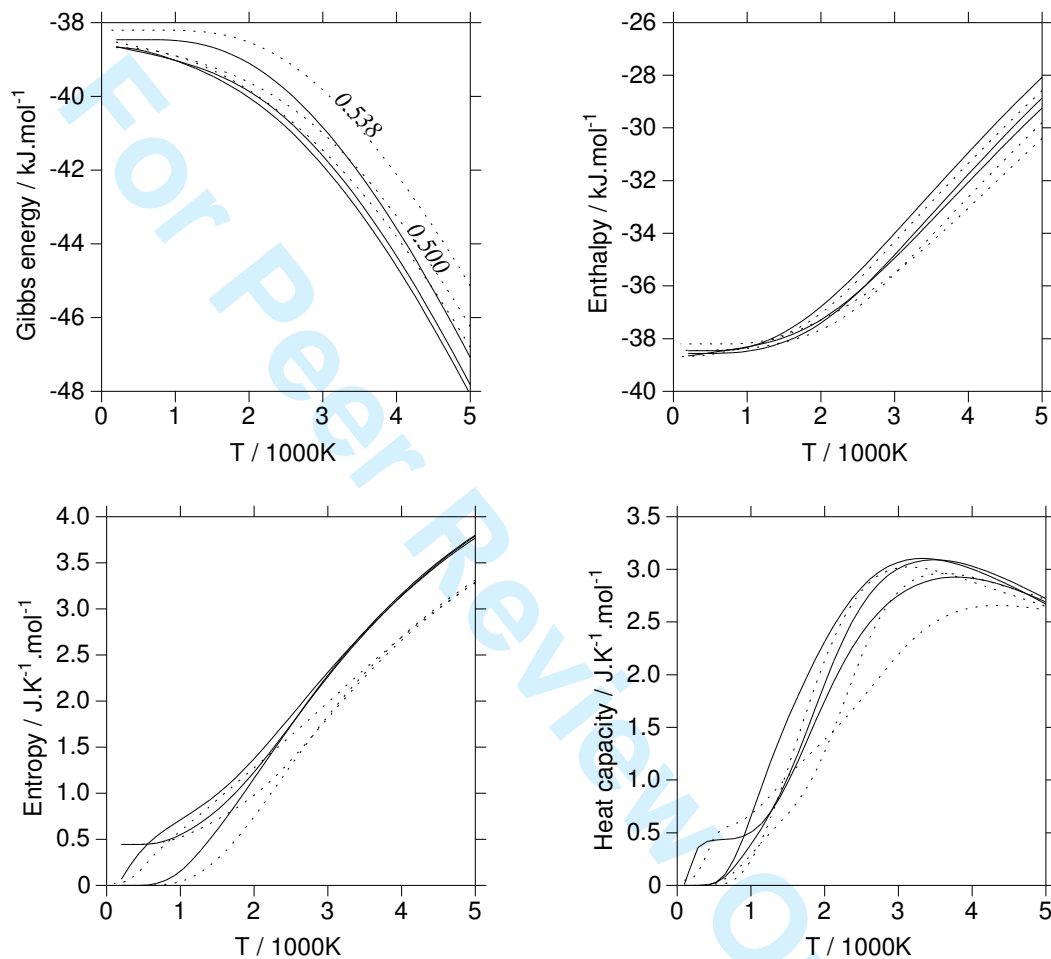
Figure 6: Calculated phase diagram compared with the one from Bolcavage and Kattner [15] (dashed lines) and the experiments used by them (\circ) and the more recent ones from Joubert and Feutelais [15] (\bullet).

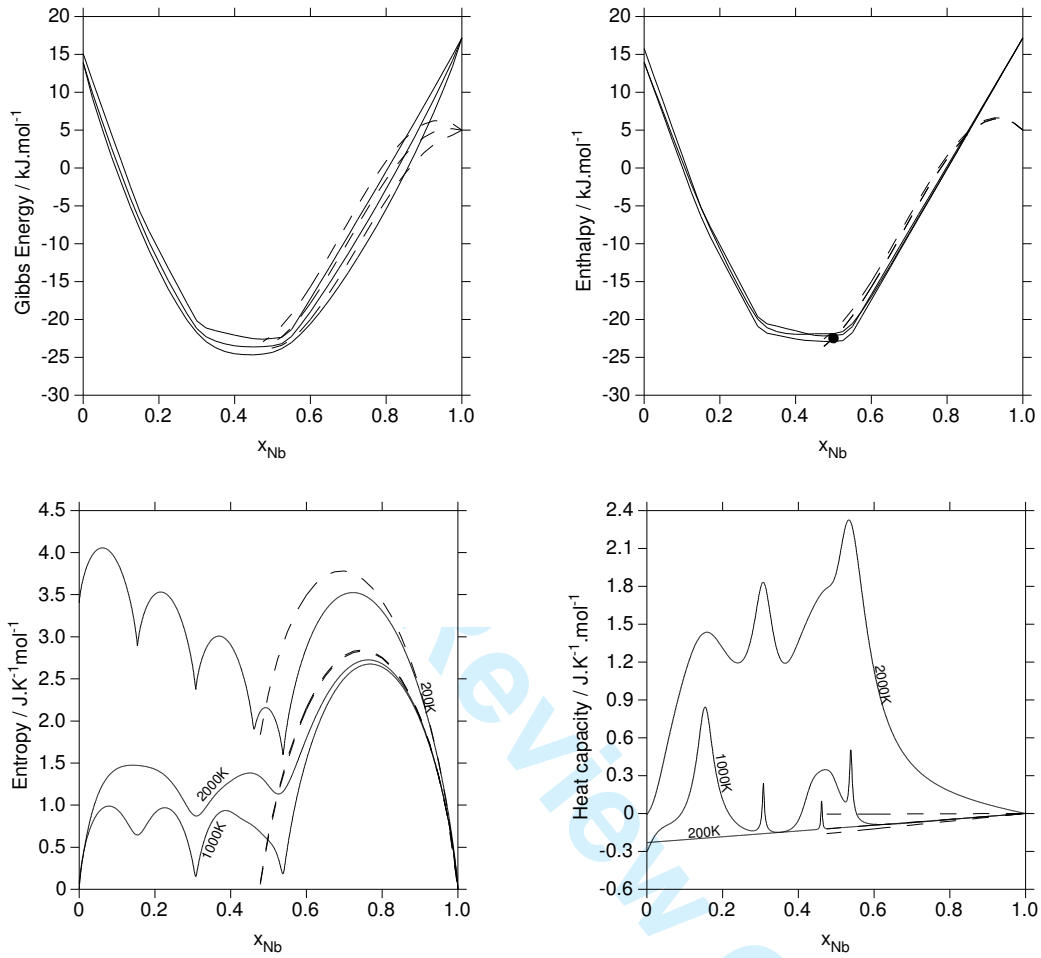
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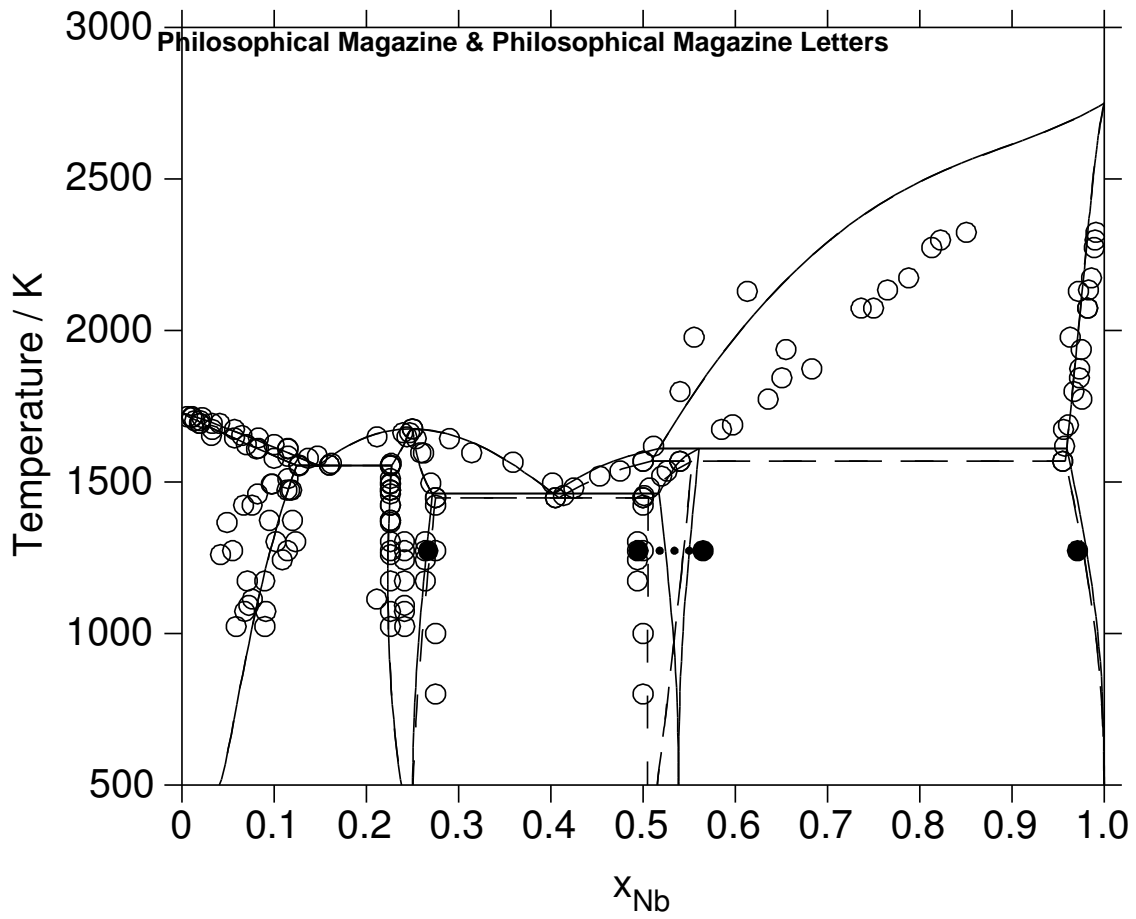












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