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Temperature dependence of the activity of Al in dilute Ni(Al) solid solutions

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Activities of dilute Al solid solutions in Ni are determined from a first-principles approach. Both thermal lattice vibration and electronic contributions to free energies are considered and compared. Vibrational contributions tend to dominate the temperature dependencies of the free energies, though electron thermal effects are significant. Calculations show opposing temperature trends for the formation enthalpies and entropies, leading to a partial cancellation of their role in the overall energetics. Nevertheless, their remaining temperature effects are strong. Over the temperature range, $400\ \mathrm{K} < T < 1700\ \mathrm{K}$, the Al activity coefficient varies by 15 orders of magnitude, due to the relative strength of Al-Ni and Al-Al bonds. The Ni activity coefficient only varies less than 4% over the same range. Calculational results compare well with available experimental data. The thermodynamic principles elucidated from the calculations are used to provide a fundamental interpretation.

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I. INTRODUCTION

The thermodynamics of alloy solid solutions is directly linked to the activities, a_i, of the species in solution.[1] The salient issues are exemplified by the investigation[2] of the $\mathrm{Ni(Al)/Al_2O_3}$ system, which is important for aircraft engines, hot-section components of automotive catalytic converter supports, and electrical power generation.[3] In particular, the interfacial structures in this system at elevated temperature, as well as the adhesion energies, are crucially linked to performance and durability. In turn, these quantities depend sensitively on the temperature (T) dependence of the Al activity, $a_{\mathrm{Al}}(T)$. The intent of this article is to establish a method for determining accurate values of the temperature dependences of the enthalpy and entropy contributions to the Al activity.

Activities are related to chemical potentials, μ_i: specifically, for Al in a Ni solution,

$$\ln a_{\mathrm{Al}}(T,x) = [\mu_{\mathrm{Al}}(T,x) - \mu^0_{\mathrm{Al}}(T)]/kT. \tag{1}$$

Here, μ^0_{Al} is the Al chemical potential in pure, crystalline Al, while μ_{Al} is that in the solution $\mathrm{Ni}_{1-x}\mathrm{Al}_x$, where x is the atomic fraction of Al. They are also related to vapor pressures by

$$a_{\mathrm{Al}}(T,x) = p(T,x)/p^0(T), \tag{2}$$

where $p(T,x)$ is the ambient partial pressure of Al in solution and $p^0(T)$ the vapor pressure for crystalline Al. The latter provides a means of experimentally measuring the activity.[4,5] However, for Ni(Al) the activity is very small at the temperatures of interest and, therefore, is difficult to measure. Consequently, experimental results tend to be measurement sensitive[6] and a computational method capable of providing accurate results becomes a desirable complement.

Computations of activities in dilute solutions are significantly more challenging than calculations of the temperature dependences of the enthalpy and entropy of intermetallic alloys, such as NiAl and $\mathrm{Ni_3Al}$.[7–9] The dilute solution supercell, containing a single Al atom, is an order of magnitude larger than that for (say) NiAl. Consequently, the relevant entropy and enthalpy terms must be extracted as small differences between much larger energies. To the authors' knowledge, there has been only one previous attempt at computing activities in a dilute solid solution.[10] Even then, the calculations did not include either entropy effects or the temperature dependence of the enthalpy.

It is convenient to express the results of the following computations in terms of the Al activity coefficient γ_{Al} defined as

$$\gamma_{\mathrm{Al}}(T,x) = a_{\mathrm{Al}}(T,x)/x. \tag{3}$$

In dilute solutions, this coefficient is nearly independent of x (Henry's law)[1] because the Al-Al interactions are negligible. Similarly, as $x \to 0$, $a_{\mathrm{Ni}}(T,x) \to 1$ and $\gamma_{\mathrm{Ni}}(T,x) \to 1$ (Raoult's law). Note that once $\gamma_{\mathrm{Al}}(T)$ has been determined from first principles, the Ni activities can be approached through the Gibbs-Duhem relation,[1]

$$x d \ln a_{\mathrm{Al}} + (1-x) d \ln a_{\mathrm{Ni}} = 0, \tag{4}$$

which applies to variations at constant T and P.

The ensuing article is organized in the following manner. First the basic thermodynamic relationships are summarized and the approaches used for the computations are described. Thereafter, the accuracy of the methods for the Ni system is assessed by computing lattice constants, thermal expansion coefficients, and bulk modulus, and comparing with experimental results. Then, the energetics of the Ni(Al) dilute solution are computed, followed by a determination of the activities. Comparisons with measurements are included when available.

II. BASIC RELATIONSHIPS

The Al chemical potential difference [Eq. (1)] at temperature T is obtained as

$$\mu_{\mathrm{Al}}(T,x) - \mu^0_{\mathrm{Al}}(T) = \Delta H(T) - T\Delta S(T), \tag{5}$$

where $\Delta H(T)$ and $\Delta S(T)$ are, respectively, the differences in enthalpy and entropy for an isolated Al atom in the Ni solution and in the pure Al crystal. Then, $\mu_{\mathrm{Al}}(T,x)-\mu^0_{\mathrm{Al}}(T)$ is the free energy of solution of Al in Ni per Al atom. The Al configurational entropy difference is given by

$$\Delta S_{\mathrm{conf}} = -k \ln x. \tag{6}$$

Combining Eqs. (1), (3), (5), and (6) gives the activity coefficient

$$\gamma_{\mathrm{Al}} = \exp\{[\Delta H(T) - T\Delta S_{nc}(T)]/kT\}. \tag{7a}$$

The enthalpy of solution per Al atom is

$$\Delta H(T) = H_{\mathrm{Ni(Al)}}(T) - N_{\mathrm{Ni}}H^0_{\mathrm{Ni}}(T) - H^0_{\mathrm{Al}}(T), \tag{7b}$$

and the nonconfigurational entropy of solution per Al atom is

$$\Delta S_{nc}(T) = S_{\mathrm{Ni(Al)}}(T) - N_{\mathrm{Ni}}S^0_{\mathrm{Ni}}(T) - S^0_{\mathrm{Al}}(T), \tag{7c}$$

where Ni(Al) refers to a supercell of the dilute alloy containing one Al atom, and N_{Ni} is the number of Ni atoms in that supercell. For example, for a $2\times2\times2$ Ni(Al) substitutional solution, $N_{\mathrm{Ni}}=31$ and $x\cong 0.03$. The superscript 0 designates a component in its pure, crystalline state. Correspondingly, the chemical potentials of the components are

$$\mu^0_{\mathrm{Al}}(T) = H^0_{\mathrm{Al}}(T) - TS^0_{\mathrm{Al}}(T) \tag{8}$$

and

$$\mu^0_{\mathrm{Ni}}(T) = H^0_{\mathrm{Ni}}(T) - TS^0_{\mathrm{Ni}}(T). \tag{9}$$

All energies in Eq. (7) are calculated using the first-principles method within the quasiharmonic approximation,[11] which assumes that phonons can be treated as harmonic oscillators with frequencies dependent on lattice volumes through thermal expansion. To be specific, the static lattice energies at 0 K ($H^{0\ \mathrm{K}}$) are first calculated (as described in Sec. III) for a series of volumes. For each volume, phonon frequencies are calculated using the direct/supercell method[12] or the linear-response theory (LRT) method.[13] The vibrational Helmholtz free energy $F_{vib}(T)$ is given by

$$F_{vib}(T) = \frac{1}{2}\sum_{q,\alpha} h\upsilon_{q,\alpha} + k_T\sum_{q,\alpha} \ln(1 - e^{-h\upsilon_{q,\alpha}/k_T}), \tag{10a}$$

where $\upsilon_{q,\alpha}$ represents the frequency of the αth normal vibrational mode at wave vector $\mathbf{q}$. Assuming free thermal expansion, the Helmholtz free energy becomes equal to the Gibbs free energy. The vibrational entropy and enthalpy are then obtained from

$$S_{vib}(T) = \left. -\frac{\partial F_{vib}(T)}{\partial T}\right|_V, \tag{10b}$$

and

$$H_{vib}(T) \approx F_{vib}(T) + TS_{vib}(T). \tag{10c}$$

The approximation used for the thermally excited electronic Helmholtz free energy $F_{el}(T,V)$ is described elsewhere.[8,9] It is usually small but may not be negligible in Ni-based alloys.[8,9] The total Helmholtz free energies are obtained by

$$F(T,V) = H^{0\ \mathrm{K}}(V) + F_{vib}(T,V) + F_{conf}(T,V) + F_{el}(T,V), \tag{11}$$

which are then minimized with respect to the volume at each temperature to derive the equilibrium volume, $V^*(T)$. Once $V^*(T)$ is obtained, the calculations are repeated to obtain the quasiharmonic corrections for all energies. For simplicity, the electron-phonon interactions and magnetic contributions can be neglected. Such a treatment [Eqs. (10) and (11) with corresponding approximations as noted], has been successfully used to predict the bulk thermal properties of various metals and alloys, including Al,[8,9,14] Li,[14] Na,[14] Cu,[7] Ag,[15] Ni,[7–9] NiAl,[7–9] and $\mathrm{Ni_3Al}$.[8,9]

Once the Al activity coefficient γ_{Al} is computed, it can be related to the Ni activity coefficient γ_{Ni} via the Gibbs-Duhem relation, Eq. (4). To integrate Eq. (4) for γ_{Ni}, we follow Gaskell,[1] who assumes a regular solution to obtain

$$\ln \gamma_{\mathrm{Ni}} \approx [x/(1-x)]^2 \ln \gamma_{\mathrm{Al}}. \tag{12}$$

III. COMPUTATIONAL DETAILS

The dilute Ni(Al) solution throughout this manuscript is modeled as a single Al atom in a $2\times2\times2$ (fcc) $\gamma_{\text{-Ni}}$ superlattice, corresponding to a dilute concentration, $x\cong 0.03$ (i.e., $\mathrm{Ni_{.97}Al_{.03}}$). The Al atoms are fifth neighbors (over 7 Å) apart. This supercell is sufficiently large that Al atoms can be treated as noninteracting, and the concentration sufficiently dilute that $\gamma_{\mathrm{Al}}(T,x)\rightarrow\gamma_{\mathrm{Al}}(T)$. The enthalpy and entropy of solution involve an exchange of a single Al atom per cell from pure bulk Al into the Ni(Al) solution. To ensure maximum cancellation of numerical errors, the Ni and Ni(Al) calculations must be conducted with identical supercells, a $2\times2\times2$ (fcc) $\gamma_{\text{-Ni}}$ superlattice, which is employed throughout this manuscript. For electron eigenvalues and Brillouin zone integrations, a $6\times6\times6$ Monkhorst-Pack k mesh (generating 10 irreducible k points) is employed. For the vibrational computations, the supercell/direct method[13] and the same Monkhorst-Pack k mesh are employed. The ground-state structure of the alloy lattices was optimized until the total force on each ion converged within 0.02 eV/Å. All 0 K total energy and relaxation calculations are performed using the density functional theory (DFT) code VASP (Ref. 16) within the generalized gradient approximation (GGA) (Ref. 17) for the exchange correlation, and ultrasoft (US) pseudopotentials[18] with a plane-wave cutoff of 400 eV. For simplicity, all calculations are nonmagnetic unless otherwise noted: we ignore the ferromagnetic-paramagnetic transition, and approximate the paramagnetic Ni and Ni(Al) as nonmagnetic.[19] The vibrational computations also employ US-GGA pseudopotentials.

IV. LATTICE CONSTANTS AND ENERGETICS

To test the computational formulation, the vibrational frequencies of Ni are calculated for high-symmetry wave vectors ($\mathbf{q}=X$, L, and W), using the *ab initio* linear-response code PHONON (Ref. 20) with US-GGA pseudopotentials and cutoff energy, 30 Ry (~400 eV). The linear response code is

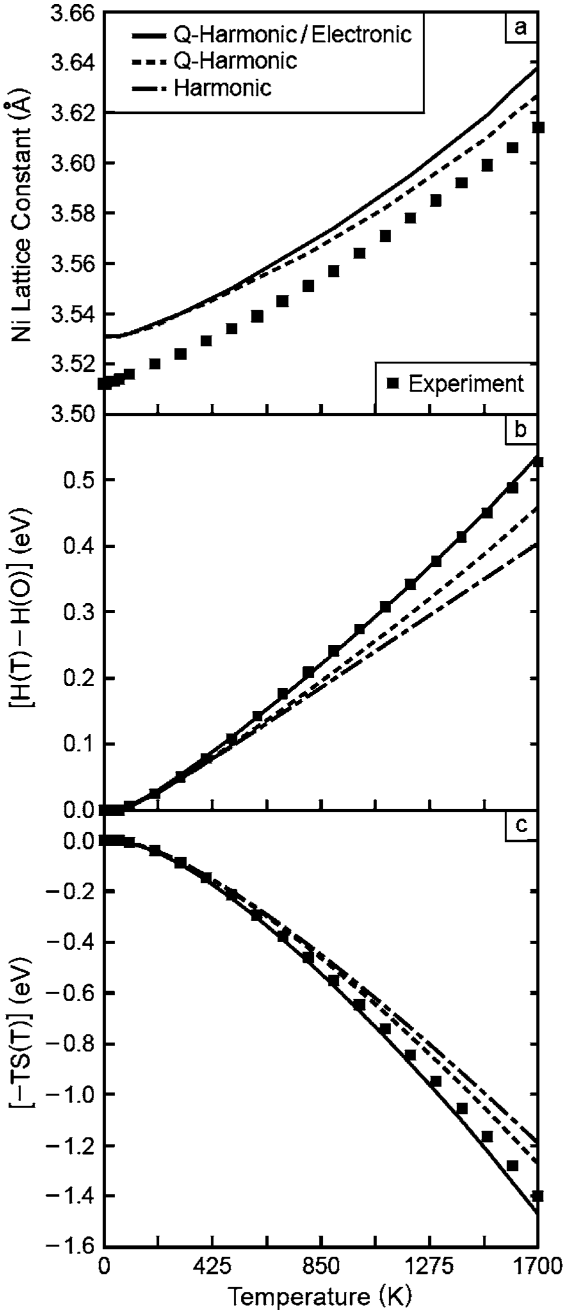

FIG. 1. (a) Calculated equilibrium lattice constants, (b) enthalphies, and (c) entropies of Ni using the harmonic approximation as well as the quasiharmonic approximation without and with thermal electronic excitations, all in comparison with experiment. Units of $H(T)$ and $-TS(T)$ are eV per Ni atom. The experimental lattice constants are obtained using the room-temperature data (Refs. 21 and 22) and the thermal expansion data recommended by Ref. 24. The experimental energy data are taken from the JANAF tables (Ref. 25). As the absolute enthalpy value has no real meaning, its zero enthalpy reference is assigned at 0 K.

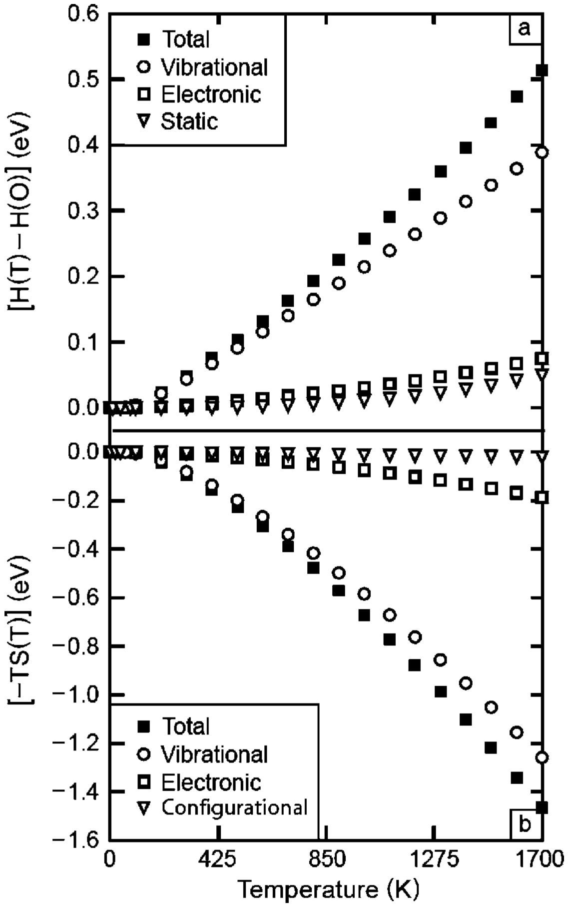

FIG. 2. Calculated (a) enthalpies, $H(T)-H(0)$, and (b) entropies, $-TS(T)$, of the $\mathrm{Ni}_{.97}\mathrm{Al}_{.03}$ solid solution at each temperature. Units are in eV per $\mathrm{Ni}_{.97}\mathrm{Al}_{.03}$ atom.

chosen because vibrational modes can be accurately and efficiently computed using a primitive cell (it will be shown below that this linear response code for Ni produces results that agree with the direct method). For each temperature, the lattice static and vibrational energies and the electron thermal excitation energies are computed for a set of lattice constants. The resulting total free energies are then fitted to the Murnaghan equation of state, whereupon the minimum Helmholtz energy of the equation of state yields the equilibrium lattice constant at that temperature. Computed equilibrium lattice constants are compared with measurements[21,22] on Fig. 1(a). The calculated values are larger, by about 0.02 Å, as expected with the GGA. But, because the difference is systematic, the calculated thermal expansion coefficient (the slope) is extremely accurate. Moreover, the bulk modulus calculated at 300 K ($B=186$ GPa) is identical to the measured value.[23]

The computed temperature dependences of the Ni enthalpy and entropy are compared with measurements on Figs. 1(b) and 1(c), respectively. The harmonic and quasiharmonic methods yield values that differ from the measurements at the higher temperatures. However, inclusion of the electronic thermal excitations yields almost exact correspondence with the measurements. This is important because the relatively high Ni electronic density of states across the Fermi level causes this contribution to become significant at high temperature.

V. SUBSTITUTIONAL ENERGETICS

To add Al atoms to the Ni host in dilute concentration, we consider first the 0 K energetics. We relax the Ni host

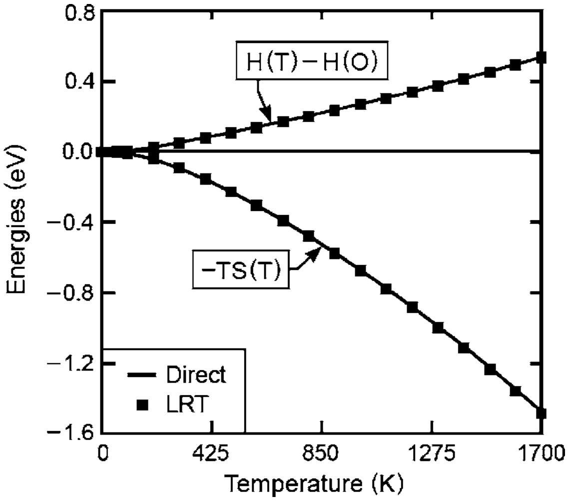

FIG. 3. Computed temperature dependences of enthalpy and entropy for Ni. The results labeled LRT are the linear-response theory results on the primitive cell, as taken from Figs. 1(b) and 1(c). The results labeled Direct are computed by the direct method on the $2\times2\times2$ cell.

structure around the Al atoms placed at selected sites. The isolated Al substitutional site in Ni is much more energy favorable than the interstitial site, by 4.46 eV at 0 K (4.38 eV if spin polarized). Interstitial solution (octahedral site) is endothermic, accompanied with significant lattice distortion. The substitutional $\mathrm{Ni}_{.97}\mathrm{Al}_{.03}$ solution is hereafter assumed for all temperatures considered.

The $\mathrm{Ni}_{.97}\mathrm{Al}_{.03}$ supercell is assumed to have the same thermal expansion as pure Ni, because of the weak dependence of thermal expansion on Al concentration.[22] Since our linear-response PHONON code is not efficient for the large $2\times2\times2$ $\mathrm{Ni}_{.97}\mathrm{Al}_{.03}$ supercells, vibrational frequency calculations are performed using the direct method[12] and, as discussed below, US-GGA pseudopotentials implemented in VASP at the wave vector $\mathbf{q}=0$ (Γ point). Temperature effects on the static lattice, thermal vibrations, and electron thermal excitations on the enthalpy are obtained separately and compared with each other in Fig. 2(a). Evidently, lattice thermal vibrations contribute the majority of the positive temperature dependence of the enthalpy. Also note that the contributions from the temperature dependence of the electron thermal excitations are larger than those from the static lattice enthalpies. Entropy increases resulting from lattice vibrations, configuration interaction, and electron-thermal excitations are compared on Fig. 2(b). Vibrational entropy is the dominant contribution at all temperatures, but the electron-thermal entropy contributions become significant at high temperatures. The configurational entropies are relatively negligible.

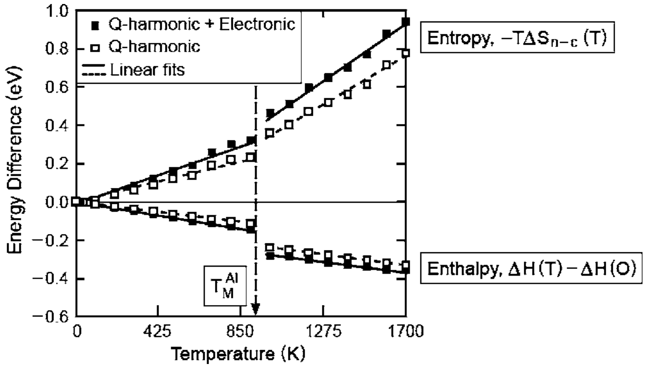

FIG. 4. Values for the enthalpy of solution, $\Delta H(T)$, and the nonconfigurational entropy of solution term, $-T\Delta S_{nc}=-T\Delta S_{vib}-T\Delta S_{el}$, calculated using the quasiharmonic approximation, with and without thermal electronic excitations. All enthalpy terms have their $T=0$ K values subtracted to more clearly show their temperature dependence. The discontinuities at 933 K indicate that the reference state of Al is changed at its melting point from fcc to liquid.

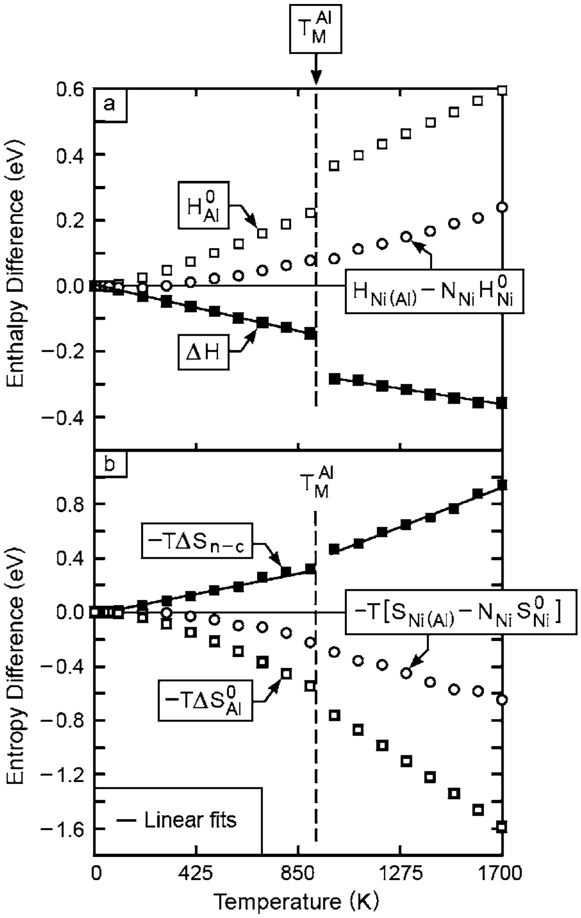

FIG. 5. Terms for (a) the enthalpy of solution, $\Delta H(T)$, and (b) the nonconfigurational entropy of solution term $-T\Delta S_{nc}$, calculated with the quasiharmonic approximation including thermal electronic excitations. All enthalpy terms have their $T=0$ K values subtracted to more clearly show their temperature dependence. The experimental data (energetics of pure Al) are taken from the JANAF tables (Ref. 25). Lines are best fits to computed points. The discontinuities at 933 K indicate that the reference state of Al is changed at its melting point from fcc to liquid.

Given the criticality for computational accuracy that both the Ni and $\mathrm{Ni}_{.97}\mathrm{Al}_{.03}$ calculations be treated on the same footing, we repeat the vibrational computations for Ni on the same $2\times2\times2$ supercell with the same methods. The results obtained on the $2\times2\times2$ supercell with the direct method are compared in Fig. 3 with the LRT results are taken from

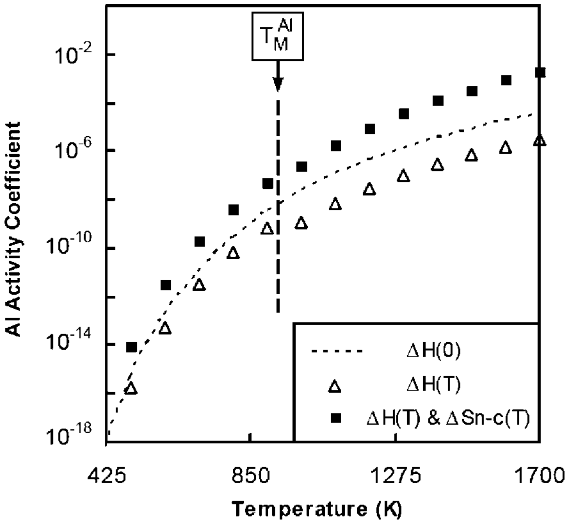

FIG. 6. Calculated Al activity coefficient in $Ni_{.97}Al_{.03}$ using various approaches to Eq. (7a). Here $\Delta H(T)$ and $\Delta S_{nc}(T)$ are calculated within the quasiharmonic approximation and including thermal electronic excitations.

Fig. 1. Since the results agree closely, we confidently proceed with the direct method.

Before proceeding, we note that Al has a relatively low melting temperature (T_m=933 K). Due to the difficulty of simulating a molten phase using first-principles DFT, we have chosen to use the enthalpy and entropy data for molten Al from the JANAF tables.[25] The JANAF data for enthalpy are given as differences from the room temperature value. To convert these data to absolute values, we supply a VASP computed Al bulk enthalpy at 300 K. The enthalpy and entropy of solution [see Eqs. (5) and (7)], including quasiharmonic vibrational energies and electron thermal contributions, are plotted in Fig. 4. Note that the temperature dependence of the enthalpy of solution, $\Delta H(T)$, is opposite in sign to that of the entropy of solution, $-T\Delta S_{nc}(T)$. The vibrational contributions tend to dominate the temperature dependences of both $\Delta H(T)$ and $-T\Delta S_{nc}(T)$, consistent with Figs. 1 and 3 for bulk Ni and $Ni_{.97}Al_{.03}$, respectively. The enthalpy of solution decreases by ~0.36 eV per Al atom over $0\ K \leq T \leq 1700$ K, while the entropy of solution terms increase by ~0.93 eV. For the lower temperatures ($0\ K \leq T \leq 933$ K), the slope of $-T\Delta S_{nc}(T)$ is about twice that of $\Delta H(T)$. Namely, the positive temperature effects on the nonconfigurational entropy term $-T\Delta S_{nc}(T)$ are about half compensated by a simultaneous decrease of the enthalpy of solution $\Delta H(T)$, consistent with the theoretical derivation proposed by Ozoliņš *et al.*[26] For higher temperatures ($T > 933$ K), the slope of $-T\Delta S_{nc}(T)$ is about 5–6 times larger than that of $\Delta H(T)$, mainly due to the more rapidly increasing entropy of liquid Al than its enthalpy. The discontinuity at T=933 K corresponds to the experimentally determined latent energy of melting for Al.

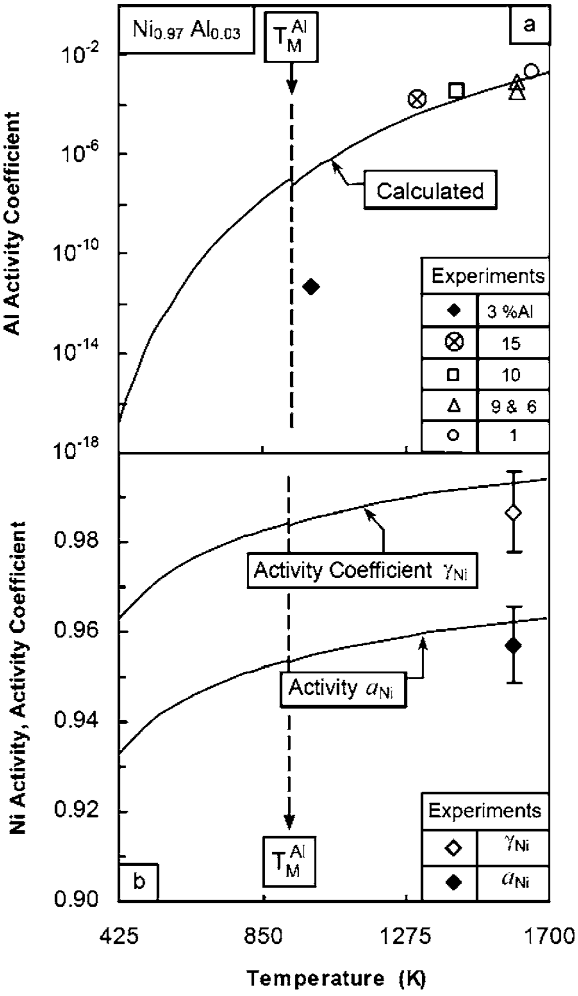

FIG. 7. (a) Calculated activity coefficient of Al in $Ni_{.97}Al_{.03}$ in comparison with the available experimental measurements: ◆ 30, × 28, □ 27, △ 6, and ○ 29. (b) Calculated values of the activity and activity coefficient for Ni in $Ni_{.97}Al_{.03}$ in comparison with the experimental results [the latter by interpolating using experimental 5% Al at 1600 K (Ref. 6)].

VI. ACTIVITIES

The $\Delta H(T)$ and $-T\Delta S_{nc}(T)$ in Figs. 4 and 5 can be used to predict the temperature dependence of the Al activity coefficient [Eq. (7)]. Results are shown in Fig. 6. Due to the relatively large and negative enthalpy of solution of Al in Ni, γ_{Al} is extremely low at low temperatures. It is order of 10^{-18} at 400 K. This arises because the Al-Ni bonds are much stronger than the Al-Al bonds (as expected from the higher cohesive energy and melting temperature of Ni). The dashed curve of Fig. 6 is the Al activity coefficient obtained by ignoring the temperature dependence of the free energy of solution, namely, by taking $\Delta H(T)-T\Delta S_{nc}(T)$ to be $\Delta H(0)$. The other curves in Fig. 6 show the effects of including the temperature dependences of $\Delta H(T)$ and/or $-T\Delta S_{nc}(T)$. The following implications can be drawn: (i) These temperature dependencies can change the activity coefficient by orders of magnitude. (ii) The temperature dependence of the enthalpy tends to reduce the activity coefficient,while that of the entropy tends to increase it. (iii) For temperatures $T < 1000$ K, since $d\Delta H(T)/dT$ is about half $-T\Delta S_{nc}(T)$ (Fig. 4), the fully temperature-dependent Al activity coefficient (Fig. 6) differs from the γ_{Al} computed from $\Delta H(0)$ by less than one order of magnitude. The difference gradually increases with increase in temperature, because the slope of the entropy term is substantially higher than that of the enthalpy above the Al melting temperature. Evidently, temperature-dependent enthalpies and entropies are essential for reasonable accuracy.

The computed activity coefficients are compared with experimental data in Fig. 7(a). The comparison is examined over three temperature arranges. (i) Above 1300 K, a few experimental data are available.[6,27–29] The agreement with measurements is remarkable. Even though some of the Al concentrations are well above the 3% assumed in our computations, the agreement suggests that these data may be in the region where Henry's law is still valid. (ii) No experiments have been reported below 980 K, possibly due to the extremely low values, so no comparisons can be made. (iii) At the intermediate temperature, 1000 K, γ_{Al} is still only 2.4×10^{-7}. The only experimentally ascertained activity coefficient near this temperature ($\sim10^{-12}$ at 980 K),[30] is about five orders of magnitude lower than the calculated value. We surmise that because there is such good agreement at the higher temperatures, the measurement is erroneous, consistent with a conclusion reached in Ref. 6.

The activity of the host Ni, a_{Ni}, is quite different from a_{Al}, because the Ni neighbors are predominantly Ni atoms, similar to the case for pure Ni. Thus one would expect $\gamma_{\mathrm{Ni}}\to1$ and $a_{\mathrm{Ni}}\to x_{\mathrm{Ni}}$ (Raoult's law), as noted earlier. Figure 7(b) shows the calculated Ni activity a_{Ni} and activity coefficients γ_{Ni} are close to 1 as expected. In fact, they only vary by less than 4% over the range $400<T<1700$. Note that the computed values agree fairly well with experiment.[6]

VII. CONCLUSION

We have presented a direct method for calculating the temperature dependence of activities in binary solid solution from first principles. The method has been illustrated for dilute Ni(Al) solid solutions.

The computations have revealed that lattice vibrations dominate the temperature dependences of both the enthalpy and the entropy of solution. Moreover, electron thermal excitations are significant.

Due to the relatively large enthalpy of solution of Al in Ni, arising from the Al-Ni bonds being significantly stronger than Al-Al bonds, the Al activity coefficient γ_{Al} is found to be quite small at low temperatures, of the order of 10^{-18} at 400 K. Again due to the large enthalpy of solution, the Al activity coefficient varies by 15 orders of magnitude, over $400\text{ K}<T<1700\text{ K}$. At the same time, that for Ni varies less than 4%. The latter arises because Ni is the dominant atomic species.

The Al enthalpies of solution $\Delta H(T)$ in Ni become increasingly negative with increasing T while entropies of solution $-T\Delta S_{nc}(T)$ become increasingly positive. Their effects on activities have been identified: the former tends to reduce the Al activity and the latter to increase it. While the temperature dependencies of the enthalpy and entropy partially cancel in the total free energy of solution, nevertheless their net effect is significant. Below the Al melting point (933 K), these temperature dependencies contribute an order of magnitude to the Al activity coefficient γ_{Al}. At higher temperatures, the temperature derivative of the $-T\Delta S_{nc}(T)$ term is five to six times that of the $\Delta H(T)$ term. Consequently, these temperature dependencies make an even larger contribution to γ_{Al}.

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