LETTER TO THE EDITOR

A first-principles phase stability study on the Au–Ni system

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Abstract. We present a first-principles statistical mechanics theory that incorporates the calculation of electronic total energies in the local density approximation, configurational entropies, vibrational modes and relaxation effects in disordered systems. Applications of the theory to the binary Au–Ni system are given using the linear muffin-tin orbital method for the total energy calculations, the cluster variation method for the description of the configurational entropy and the Debye–Grüneisen approximation for the vibrational modes. The solubilities of both ends of the phase diagram, calculated with no adjustable parameters, are compared with experiment.

A binary substitutional system can exist in 2^N configurations that can be formed by occupation of any of the N sites of a lattice by either an A or a B atom. In theoretical studies of the energetics of substitutional systems, it is often necessary to find the ground-state configuration for a given lattice type, or to calculate finite-temperature thermodynamic averages. These applications require, in principle, sampling of the possible 2^N configurations. Even limiting N to ~50 sites, this is a formidable task for first-principles electronic structure methods as it involves a huge number of calculations.

A general approach to the energetics of substitutional systems is the cluster expansion (CE) [1, 2], in which the configurational energy is expressed in terms of effective multisite interactions and correlation functions. When the CE converges rapidly, the energies of the 2^N configurations are approximately linearly dependent. In this case, knowing a few of the energies allows us to determine the rest. Thus the advantage of the CE is that it extracts information from a small set of structures to make predictions for the energies of all other structures. Connolly and Williams [3] proposed to use *ab initio* total energy calculations of ordered compounds together with the *a priori* knowledge of the multisite correlation functions in these compounds in order to obtain the set of effective pairs and multisite chemical interactions that could be used to describe the energy of disordered alloys. The attractiveness of this inversion method is that it can use all the power of *ab initio* total energy methods. In particularly, self-consistency, exchange and correlation effect, use of full potentials, converged total energy expressions and relativistic effects are included. Moreover, the results of the electronic structure calculations can be extended to include the volume and elastic relaxation effects as well as the lattice vibration effects. In particular, these last contributions are known to play an important role for systems where there is a significant difference in the molar volumes of the constituent elements. In this letter, we present preliminary results for the solid-state portion of the Au–Ni phase

diagram, emphasizing the different roles played by chemical, vibrational and relaxation-type contributions. We make contact with microscopic electronic theory via the linear muffin-tin orbital (LMTO) method [4], which is used to calculate the total energies of selected compounds in the Au–Ni system. The contributions to the free energy due to relaxations will be discussed in terms of volume-relaxation and cell-external-relaxation contributions [5, 6]. The lattice vibration effects will be incorporated, using a Debye–Grüneisen model as proposed by Sanchez *et al* [7]. Thus, all quantities needed to determine the total free energies in the framework of the cluster variation method (CVM) [8] are obtained from first principles with no adjustable parameters. In the next section, the calculation procedure and the theoretical background are briefly reviewed. The final section is devoted to results and discussion.

The central energetic quantities used in the theoretical discussion of phase stability are the formation energy $\Delta E_F(\sigma_x)$ of the ordered compound A/B in the structure σ and the mixing energy $\Delta E_{mix}(x)$ of a random alloy $A_{1-x}B_x$ of composition x. These are defined as the excess energies taken with respect to the equivalent amounts of the solid constituents A and B at their equilibrium volumes V_A and V_B on the given lattice:

$$\Delta E_F(\sigma_x) = E_\sigma(\text{ord}) - \left[(1-x)E_A + xE_B\right] \tag{1}$$

$$\Delta E_{mix}(x) = E_\sigma(\text{rand}) - \left[(1-x)E_A + xE_B\right]. \tag{2}$$

The ordering energy is defined as the difference:

$$\delta E_{ord}(\sigma_x) = \Delta E_F(\sigma_x) - \Delta E_{mix}(x). \tag{3}$$

If $\delta E_{ord} < 0$, the random alloy could develop short-range order of the type underlying the structure σ. When $\Delta E_F(\sigma) < 0$, the long-range-ordered configuration σ could become a stable 'ground-state structure' whereas $\Delta E_F(\sigma) > 0$ means that the ordered structure σ is unstable with respect to phase separation into A and B. To calculate the mixing energy $\Delta E_{mix}(x)$ of the random alloy, we use the Ising-like cluster expansion, in which the energy of any of the 2^N configurations can be mapped into an Ising Hamiltonian [2]

$$E_{\text{Ising}}(\sigma) = V_0 + \sum_i V_i \hat{S}_i(\sigma) + \sum_{j<i} V_{ij} \hat{S}_i(\sigma)\hat{S}_j(\sigma) + \sum_{k<j<i} V_{ijk}\hat{S}_i(\sigma)\hat{S}_j(\sigma)\hat{S}_k(\sigma) + \dots \tag{4}$$

where the V are effective interaction energies for sites, pairs, three bodies etc. In this case, the alloy is treated as a lattice problem whereby configuration σ is defined by specifying the occupation of each of the N lattice sites i by an A atom (where the spin variable is $\hat{S}_i = +1$) or a B atom ($\hat{S}_i = -1$).

The interaction energies are found by mapping (4) onto a set of directly calculated formation energies $\Delta E_F(\sigma)$ for N_σ structures [5]:

$$\sum_\sigma^{N_\sigma} \omega_\sigma \left[\Delta E_F(\sigma) - E_{\text{Ising}}(\sigma)\right]^2 = \min. \tag{5}$$

We include in (4) N_F trial 'figures' or clusters F (pairs, three-body, four-body, ...) and $N\sigma$ structures. Solving (5) we find a set of interactions $\{V_F\}$. Their transferability is then examined by using them to predict via (4) the energy of a new set of structures σ' not included in the inversion scheme of (5). Convergence is tested by comparing these predictions with the directly calculated $\Delta E_F(\sigma')$ values of (1). The energy of the perfectly random alloy is then found by taking the configurational average of (4), i.e. $\Delta E_{mix}(x) = \langle \Delta E_{\text{Ising}}(\sigma) \rangle$.

We have carried out the formalism described here using in (5) the $N\sigma = 11$ structures: FCC (A and B), L1$_2$ and DO$_{22}$ (A$_3$B), MoPt$_2$ (A$_2$B), L1$_0$, L1$_1$ and phase 40 (AB). The N_F

clusters used in (4) are (i) V_0 and V_1 ('empty' and single site), (ii) V_2, the pair interaction between first-nearest neighbours and (iii) V_3 and V_4, the three- and four-body terms. The choice of both structures and figures will be discussed in a forthcoming paper [9]. Total energies are calculated using the local density scalar-relativistic theory, as implemented by the LMTO method [4], including the combined correction terms [10] in the atomic-sphere approximation (ASA). This means that the unit cell is divided into overlapping spheres and, inside these spheres, the potential is assumed to be spherically symmetric. We include basis sets up to $l = 2$ (i.e. d orbitals) and treat the valence electrons scalar relativistically. The total energies are calculated for varying volumes in order to locate the equilibrium volume. The calculations are considered to converge when the deviation between the input and output potential is less than 0.01 mRyd. To evaluate integrals over the Brillouin zone, we use a uniform mesh of sampling points, which ensure that the total energy converges to within 0.05 mRyd per atom. However, some comments have to be made on the sensitivity of ΔE values with respect to the choice of the sphere radii. Indeed, it is known that there may be problems with the ASA concerning the comparison between different structures, which is the purpose of our study. In the ASA, the non-spherical parts of the potential, the higher partial waves and the interstitial region are neglected. The ASA is a reasonable approximation provided that there are very few electrons in the interstitial region, or rather that the touching muffin-tin spheres can be substituted by overlapping Wigner–Seitz (WS) spheres that fill the electron-containing parts of space but do not overlap more than about 30% into any one sphere, i.e. $S_{R'} + S_R - |R' - R| < 0.3 S_R$ for all R. However, even with these constraints, there is still some degree of freedom in the choice of the WS spheres. Equal WS radii lead to unphysically important charge transfer between the alloy constituents when atomic volumes of the two species are very different. A guiding principle for choosing the relative sphere sizes for an ASA calculation is that the radii should be chosen to be as close as possible to the atomic radii of the corresponding elemental solids [10]. This means that the net charge inside any sphere will be rather small, typically a few tenths of the charge of an electron. Experience shows that this charge neutrality is valid for most cases, such as the transition-metal–transition- or noble-metal alloys [10]. A comparison with the results provided by the full-potential method [11] indicates the validity of such a choice.

Introduction of the thermal vibration effects can be done using the vibrational free energies of the ordered compounds calculated in the Debye–Grüneisen approximation [3]. In this case, the electronic binding energy $E_\sigma(\text{ord})$ is replaced by the following vibrational free energy:

$$F_\sigma^{\text{vib}}(\text{ord}) = E_\sigma(\text{ord}) + E_\sigma^{\text{vib}} - T S_\sigma^{\text{vib}} \qquad (6)$$

where E_σ^{vib} and S_σ^{vib} are the thermal vibration energy and the vibration entropy respectively. In the Debye–Grüneisen model [12], the vibration energy is given by

$$E_\sigma^{\text{vib}} = E_0 + 3k_B T D(\theta_D / T) \qquad (7)$$

where k_B is the Boltzmann constant, θ_D is the Debye temperature, E_0 is the zero-point energy given as $E_0 = 9/8 k_B \theta_D$, and $D(\theta_D / T)$ is the Debye function [12]. The vibrational entropy is given by

$$S_\sigma^{\text{vib}} = 3k_B \{4/3 D(\theta_D / T) - \ln[1 - \exp(-\theta_D / T)]\}. \qquad (8)$$

It should be noted that, by following the original prescription of Morruzi *et al* [12], the Debye temperature θ_D is given as $41.63(rB/M)^{1/2}$, where M is the average mass, the numerical constant is a scaling factor which gives approximate agreement with empirical data, and the bulk modulus B is derived from the calculated binding curve. Anharmonic

effects in the vibrating lattice are usually described in terms of the Grüneisen constant, γ, which can be defined as $\gamma = -\partial \ln \theta_D / \partial \ln \Omega$, and which gives the volume dependence of θ_D. The CE method of (1)–(5) can now be applied using the vibrational free energy F_σ^{vib} of each phase instead of the electronic contribution, E_σ. Note that, in this case, the set of effective interaction energies is not only volume dependent but also temperature dependent.

Once the effective interaction energies have been derived, the total free-energy functional of a phase is given by

$$F_\sigma^{tot} = \sum_F V_F \xi_F(\sigma) - T S^{conf}\big[\{\xi_F(\sigma)\}\big] \tag{9}$$

where the phase σ is specified by a set of correlation functions $\{\xi_F(\sigma)\}$ defined from the spin products in (4) and where $S^{conf}[\{\xi_F(\sigma)\}]$ represents the configurational entropy contribution.

The rest of the procedure is to minimize the free-energy functional F^{tot} with respect to both the volume Ω and the set $\{\xi_F\}$ of correlation functions at a given temperature T. It is noted that the tetrahedron approximation of the CVM is employed to evaluate the configurational entropy term in (9). We used the Newton–Raphson method to find the solution of the non-linear equations.

The molar volumes and atomic positions in disordered alloys and ordered intermetallic compounds generally deviate from what simple rules might suggest (e.g. the Vegard rule, or ideal FCC positions for atomic coordinates); we refer collectively to these deviations as 'relaxation'. Relaxation exists if there is a size mismatch as in the Au–Ni system. We will distinguish 'volume relaxation' from 'sublattice relaxations'.

Volume relaxation can be obtained in a sequential process as follows. (i) The first term is the 'volume deformation' energy, i.e., the energy required to change the volumes of A and B from their equilibrium volumes V_A and V_B to the volume V_σ of the final compound σ with the composition x. It vanishes if the constituents are size matched and is positive otherwise. Since this contribution depends primarily on x and not on the individual configuration, it affects neither the ordering temperature nor relative energies of configurations at a fixed composition. It could, however, determine whether or not an homogeneous ordered phase will decompose into its constituents. (ii) The second term is the energy to form the compound $\sigma(V_\sigma)$ in its ideal structure, A and B both being prepared at the final volume. This contribution is often called the 'spin-flip' energy.

We can distinguish two levels of approximation for 'volume relaxation', in the context of the CE method. (i) The 'global' volume relaxation is based on the assumption that the effective local volumes occupied by tetrahedron clusters in the disordered alloy are independent of their configuration. (ii) The 'local' volume relaxation assumes that the local volume of each tetrahedron cluster in the alloy is allowed to relax fully to the value found in the ordered state.

The effective cluster interactions as a function of Au composition for a random alloy *without the contribution of vibrational modes* are shown in figure 1, where the calculations are carried out with global volume relaxations $V_F(g)$ or with local volume relaxations $V_F(l)$. They show (i) that the absolute value of the nearest-neighbour pair interaction, i.e. V_2, is over an order of magnitude greater than the other interactions; furthermore, the overall behaviour and magnitude of the three- and four-body interactions is similar in both cases; (ii) the most significant difference seen in figure 1 is related to the sign of V_2. In the local volume relaxation, $V_2(l)$ remains essentially constant with composition and is negative, indicating phase separation. On the other hand, $V_2(g)$ varies strongly with composition and is positive, indicating a short-range ordering tendency in the alloy. For the following, we will keep the 'local' volume relaxation, which seems to be the most plausible scheme for systems with strong size mismatch [7,9].
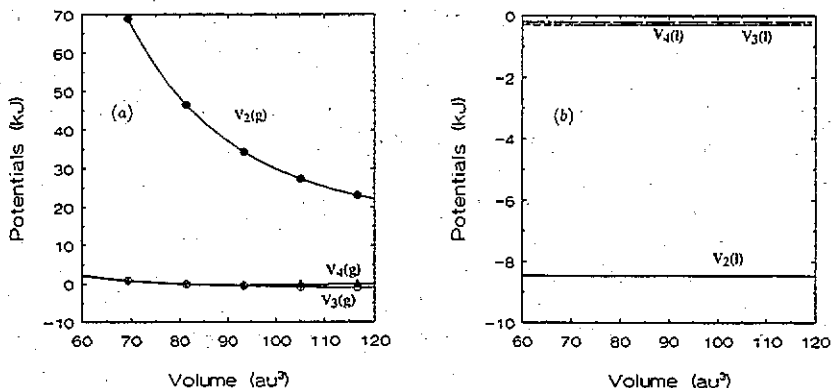
Figure 1. Calculated effective interactions for the nearest-neighbour (2), triangle (3), and tetrahedron (4) clusters using (a) global volume relaxation $V_n(g)$ and (b) local volume relaxation $V_n(l)$.
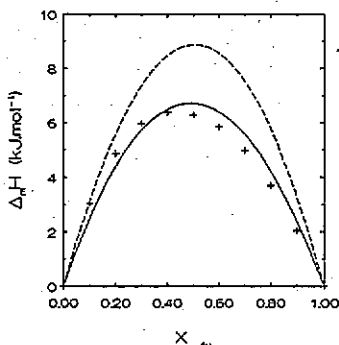

Figure 2. The energy of formation of a random alloy without vibrational modes calculated using local volume relaxations (dashed line), and local volume relaxations with cell-external relaxations (solid line); crosses extrapolate to 0 K the experimental results of Hultgren and co-workers [13].
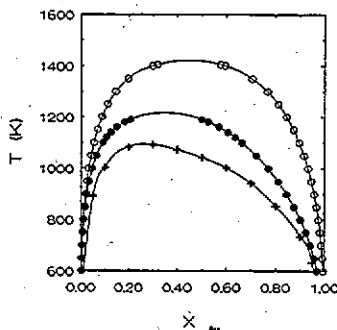
Figure 3. The calculated miscibility gap using the relaxation scheme with (●) and without (○) vibrational modes. The experimental [14] phase diagram (+) is shown for reference.

The cell-external-relaxation energy is the energy gained when the unit-cell vectors are allowed to relax, e.g., the tetragonal c/a ratio for $L1_0$, phase 40 or DO_{22} structure and the orthorhombic c/a and b/a ratios in $MoPt_2$ structure. This term vanishes by symmetry for $L1_2$ structure. Like the volume deformation, this contribution tends to vanish for size-matched systems, but in this case, it depends on the atomic configuration σ and energy lowering. In figure 2, we plot the energy of formation of the random alloys including local volume relaxation with or without cell-external-relaxation effects. We also compare our calculated curves with the estimated experimental curve at 0 K deduced from the measurements of Hultgren and co-workers [13] at 1150 K. This extrapolation to 0 K is done with the Kirchoff relation and the C_p measurements:

$$\Delta H_T = \Delta H_{T_0} + \int_{T_0}^{T} \Delta C_p \, dT. \tag{10}$$

We see that our theoretical scheme predicts, in agreement with experiment, a positive energy of mixing. Therefore, the random alloys are unstable with respect to phase separation into Ni- and Au-rich phases. Furthermore, the agreement between calculated and experimental curves is better for the scheme that includes both types of relaxation. The remaining discrepancy is mainly due to the neglect of 'cell-internal' relaxation, which can be treated using the full-potential approach coupled with the choice of special structures in the CE method. This effect will be discussed in a separate paper [9].

The phase diagram calculated using the relaxation scheme, including short-range order effects in the tetrahedron approximation of the CVM, with and without the contribution of the vibrational modes, is shown in figure 3. Also shown in figure 3 is the experimental Au–Ni phase diagram. As seen in the figure, the contribution due to the vibrational modes lowers the miscibility gap at its maximum temperature by approximately 200 K. In particular, the theory yields good overall agreement with the solubility limits observed experimentally in the solid portion of the Au–Ni phase diagram. The critical temperature is still overestimated by approximately 150 K. However, in view of the fact that the only input to the calculations is the atomic numbers of the constituent elements, and, furthermore, that the model used for the vibrational modes is rather simple, we consider the agreement between theory and experiment to be very satisfactory.

In conclusion, we have used a first-principles theory of alloy phase equilibrium based on the cluster expansion of the vibrational free energies of configurationally ordered compounds, the CVM and the implementation of the volume- and cell-external-relaxation scheme. The theory applied to the Au–Ni system yields results in good agreement with experiment. The contributions of relaxation dominate the behaviour of the configurational energy whereas the contribution of the vibrational modes was also shown to play an important role. This is particularly true in the Au–Ni system where there is an appreciable difference in the volume of the constituent elements. A more satisfactory result may be obtained by incorporating the thermal vibration effects into a lattice that is allowed to distort locally. Such an approach will be discussed in a forthcoming paper.

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