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Formation energy of disordered alloys from the energetics of ordered compounds

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The cluster expansion technique is used in combination with first-principles calculations of the total energy of ordered compounds to study the energetics of the disordered phase for a number of alloy systems. The effect of short-range order, as seen in the energy differences between an alloy with the configuration corresponding to finite temperature and the perfectly random one is studied. The role of relaxation due to large size mismatch is discussed in terms of an effective cluster volume approximation. Very good agreement with measured energies of formation is obtained when short-range order and relaxation effects are taken into account.

Perfectly ordered crystalline solids can be studied to a very precise level by exploiting their underlying periodicity. Several different methods, mainly those based on density functional theory,[1] are fast and accurate enough to study different important properties of ordered solids; furthermore, their availability has allowed extensive testing and applications. On the other hand, when a system departs from perfect order the situation becomes more complex. In particular, for substitutionally disordered alloys, traditional band-structure calculations cannot be used and one has to resort to different techniques to approximate the lost periodicity. Among these methods, the coherent phase approximation[2] has been the most successful. It has been able to account for a large number of the observed properties of these materials.[3] However, its application is rather difficult and has remained a task for specialists.

Recently, a different approach, one based on a combination of band-structure calculations for ordered compounds with the *cluster expansion* technique[4] has enjoyed widespread attention.[5–7] In this approach, which is based on a mapping of an Ising model of the alloy, the energy of any configuration of atoms on a fixed parent lattice is written in terms of effective interaction parameters (EIP) for clusters of atoms: empty, point, pair, triplet, and so on. These EIP are the same for all the (substitutionally) different configurations of the given alloy on a parent lattice, this means, for example, that they are the same for all the configurations an fcc binary alloy of species A and B can have (long-range ordered, short-range ordered, or disordered). The structural differences between the different configurations of an alloy are represented in this formalism by spin products. In an Ising model for the binary alloy one assigns the pseudospin $+1$ for one kind of atoms and -1 for the other kind. For a given configuration and a given cluster of atoms one averages the product of these pseudospins to obtain the spin products; these will depend on the configuration and on the size (and shape) of the cluster being considered. In this way, the energy (as a function of volume) can be written as

$$E^{\sigma}(V)=\sum_{n,k}^{2^N} J_{n,k}(V)\prod\nolimits_{n,k}^{\sigma} , \tag{1}$$

where $J_{n,k}(V)$ is the volume dependent EIP for the kth cluster of n atoms (allowing differentiation between, say, the linear cluster of four atoms and the tetrahedron) and $\prod_{n,k}^{\sigma}$ is the spin product for that particular cluster in configuration σ, for a lattice of N sites, 2^N is the number of different clusters. This expansion is exact provided one includes the 2^N terms; of course, in practice this expansion will be truncated. The question of convergence for such truncated approximations is then of foremost importance. Although we do not have any means of assuring convergence in general, we can show convergence in some particular cases. Recently, we studied the Ni-Pt alloy,[8] which forms three ordered compounds based on the fcc lattice, and a substitutionally disordered phase also based on the fcc lattice. We calculated the formation energies of several different ordered compounds of Ni-Pt using the linear-muffin-tin-orbital (LMTO) method[9] in the full potential (FP) implementation,[10] and compared those with the results obtained using Eq. (1) truncated to include all the clusters contained in a regular tetrahedron of nearest neighbors. The structures calculated include some with negative formation energies (which are not necessarily ground-state structures) and some with positive formation energies (unstable towards segregation in the pure elements); in any case these energies are very small (of the order of mRy/atom), posing a strong test for accuracy. The structures considered, within the tetrahedron approximation, give results within one mRy/atom of the explicitly (LMTO) calculated values. We will take this as an estimation of the error associated with Eq. (1) when applied to the calculation of the formation energy of the *disordered* phase.

The other important question regarding Eq. (1) is of

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course how to obtain the EIP. While it is possible to calculate them directly,[7] the usual approach is to obtain them through an inversion of Eq. (1).[5] The procedure is to calculate the formation energies for a number of ordered compounds explicitly (in our case through the LMTO method), and by inverting Eq. (1) obtain as many EIP as ordered structures were used as input. For the tetrahedron approximation one needs five ordered structures to obtain five EIP.

In the following we will use the above-described approach to calculate the formation energies of the disordered phase for a number of binary alloys. First, we calculate the formation energies of five ordered compounds (based on the fcc lattice) for each alloy employing the LMTO method in the atomic sphere approximation (ASA).[11] These compounds are the two pure elements (A and B), the two $L1_2$ structures (A_3B and AB_3), and the equimolar $L1_0$ structure. We obtain five EIP with these energies, which are then used to calculate the free energy of the disordered alloy as a function of temperature and composition by combining this energy with the configurational entropy as given by the *cluster variation method;*[12] minimization of the free energy gives the equilibrium configuration for the disordered alloy and thus the formation energy of this phase.

Within this framework, the purpose of this paper is to address two main issues concerning the calculation of formation energies in disordered alloys. One is the effect of the partial order present in the disordered alloy at finite temperatures and the other is the effect of the size mismatch (and the volumetric relaxation this causes) in some of these alloys.

To illustrate our first point, we consider Cu-Au and Ni-Pt alloys. Experimentally, both show perfect miscibility at high temperatures, forming disordered alloys in the whole concentration range, indicating that the formation energy of the disordered alloy is always negative. Figure 1 shows this quantity for these two systems. Squares (joined by a continuous line to guide the eye) refer to the experimentally determined values,[13] the other two sets of points are the calculated disorder formation energies. The points labeled "random" (triangles) correspond to a calculation where the completely random distribution (i.e., infinite temperature) was assumed. For both Ni-Pt and Cu-Au, the formation energy of this configuration is positive in the whole concentration range. At finite temperature (circles) (the value was chosen to be the same as the experiment) the existing short-range order allows a considerable stabilization of the disordered phase, particularly striking in the Ni-Pt case as it changes the sign of the formation energy in the whole interval. Allowing short-range order can stabilize the disordered phase by a sizable amount, of the order of the formation energy itself. In addition, these two alloy systems have a considerable size mismatch between their constituent elements; given by the relative difference of the equilibrium lattice constant of the pure elements, $x_{AB}=2(a_A-a_B)/(a_A+a_B)$, we have $x_{\mathrm{NiPt}}=0.13$ and $x_{\mathrm{CuAu}}=0.14$. This big size mismatch forces considerable relaxation, i.e., different bond lengths for the different pairs of atoms (AA, AB, or BB) depending on the environment around the particular bond. We will consider this later.

In Fig. 2 we present the formation energy of the disordered phase for the Ag-Au system. Silver and gold are perfectly miscible even at low temperatures (there are no known ordered compounds). The formation energy, as in the previous case, is negative; but the size mismatch of the two elements is very small. We do not find an important energetic effect coming from the calculation of the energy at finite temperature. The formation energy changes only slightly from the calculated value for the perfectly random alloy. This indicates that there is very little short-range order, partly as a consequence of the similarity of these two species. The agreement with the measured values is extremely good.

Next we turn our attention to alloys with a positive formation energy for the disordered phase. Having a positive formation energy the alloy can be stabilized only by entropy effects. In the case of Ni-Au there is a miscibility gap at low temperatures, although at 1150 K there is a solid solution for all concentrations. With no energy

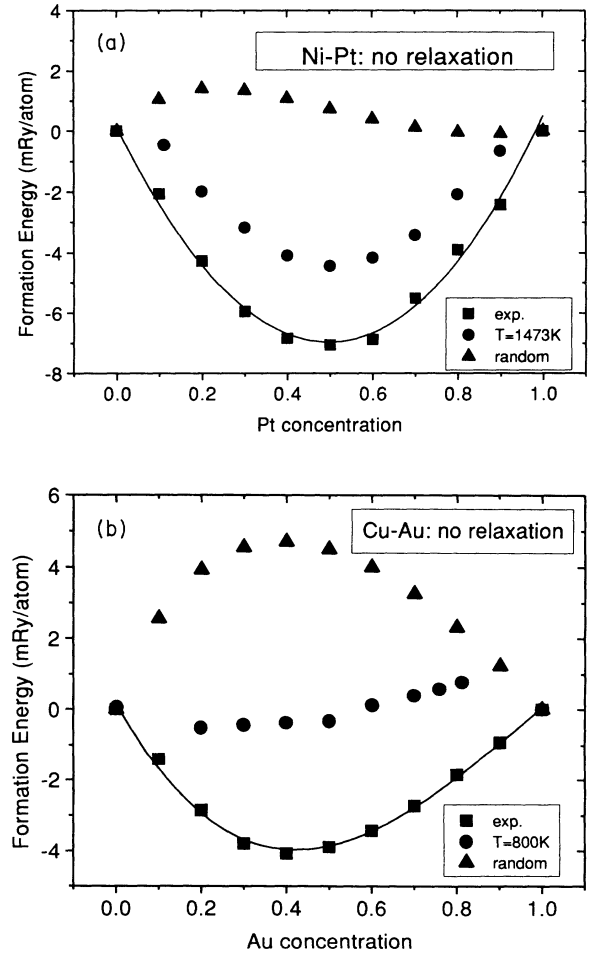

FIG. 1. Formation energy for the disordered phase in (a) NiPt and (b) CuAu alloys. Squares (labeled exp.) refer to measured values (Ref. 13). Circles correspond to the present calculation at the finite temperature indicated. Triangles refer to the present calculation for the perfectly disordered alloy. These results correspond to the unrelaxed model.

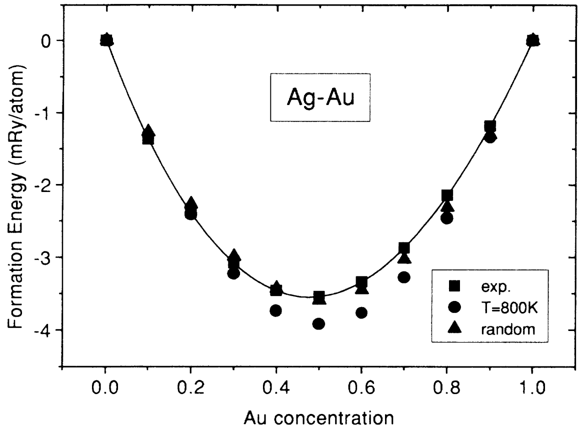

FIG. 2. Same as in Fig. 1 but for the Ag-Au alloy. Measured values are taken from Ref. 13.

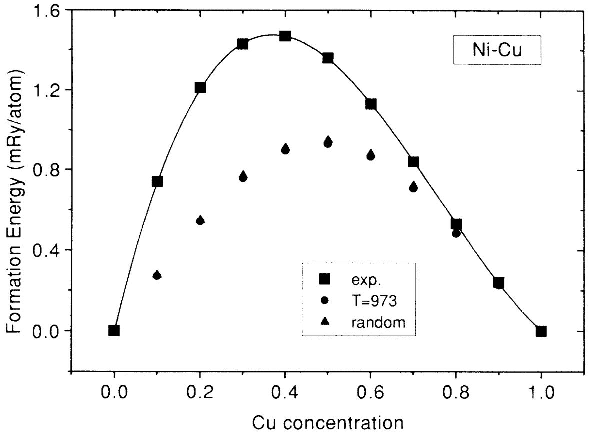

FIG. 4. Same as in Fig. 1 but for the Ni-Cu alloy. Measured values are taken from Ref. 13.

gain for the interaction of Ni-Au, the short-range order is almost null. This is seen (Fig. 3) in the similarity between the calculated formation energies for the perfectly random alloy and for the one at $T=4000$ K. The big size mismatch present in this system ($x_{\mathrm{NiAu}}=0.15$) causes the calculated energies of formation to be bigger than the measured ones (relaxation will stabilize the alloy, as we will see below). One important effect of this overestimation of the energy is that the disordered alloy is not stable at all in our calculation at the experimentally studied temperature of 1150 K, and is only stable near the dilute limits at 4000 K.[14]

In Fig. 4 we show our results for the Ni-Cu system. These two elements have very similar sizes ($x_{\mathrm{NiCu}}=0.03$), and the formation energy is positive and very small. Again, having no attractive interaction for the formation of clusters of unlike atoms, short-range order is practically absent and the formation energy for the alloy at 973 K is very similar to the formation energy of the perfectly random alloy. Interestingly, in this case in which no relaxation effects are expected, the calculated formation energy is slightly underestimated. (Note the much smaller formation energy for this system as compared with previous cases. This quantity is now very close to the limits in the precision of the LMTO method used here.)

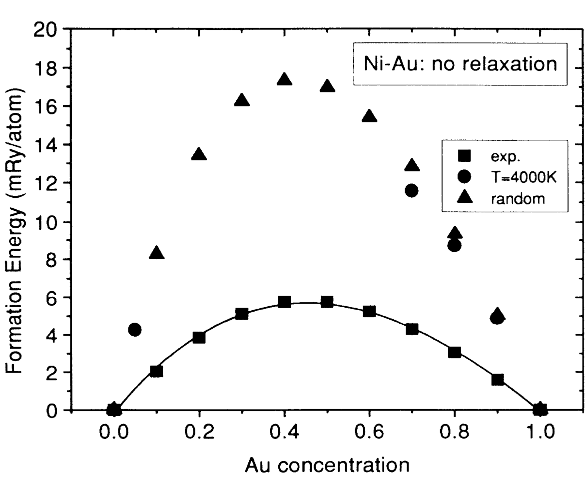

FIG. 3. Same as in Fig. 1 but for the Ni-Au alloy. Measured values are taken from Ref. 13.

So far we have shown that the method used here is a sensible one and results in calculated values which are close to the measured ones. This is particularly so in the case of small size mismatches in which no relaxations of the atomic positions are expected. When the system has a negative formation energy for the solid solution (favoring the formation of clusters of unlike atoms) the short-range order is very important, and the difference between a finite-temperature configuration and that of a perfectly random alloy results in sizable energy differences. This is not the case for alloy systems in which the dominant interaction tends towards segregation of the two species: no short-range order is present.

As a final point in the present paper we will apply a model recently proposed for approximately treating the relaxation.[8] Our model is based on the observed dependence of the nearest-neighbor distances for the different kinds of nearest neighbors for a disordered alloy. Using extended x-ray absorption fine structure, Renaud *et al.*[15] were able to measure nearest-neighbor distances for the three different pairs of atoms in $\mathrm{Ni}_{1-x}\mathrm{Au}_x$ as a function of x, d_{AA}, d_{AB}, and d_{BB}. Their measurements showed an almost linear dependence of these distances. These relaxations of the nearest-neighbor distances can be modeled in a simple way. Considering an harmonic nearest-neighbor pair force model with force constants $K_{i,j}$ we can estimate the relaxation of AB bonds around an A atom and of an AA bond, with both bonds embedded in B in the dilute limit. Fixing the next-nearest-neighbor shell and assuming that $d^0_{AB}=(d^0_{AA}-d^0_{BB})/2$, one obtains

$$\begin{aligned} d_{AB}-d^0_{BB}&=(d^0_{AB}-d^0_{BB})/[1+3(K_{BB}/K_{AB})]\;, \\ d_{AA}-d^0_{BB}&=(d^0_{AA}-d^0_{BB})\frac{2-(K_{AB}/2K_{AA})}{2+3(K_{AB}/K_{AA})}\;, \end{aligned} \tag{2}$$

where d^0_{ii} corresponds to the pure element. This simple model predicts nearest-neighbor distances in reasonable agreement with the experimental results of Ref. 15 and

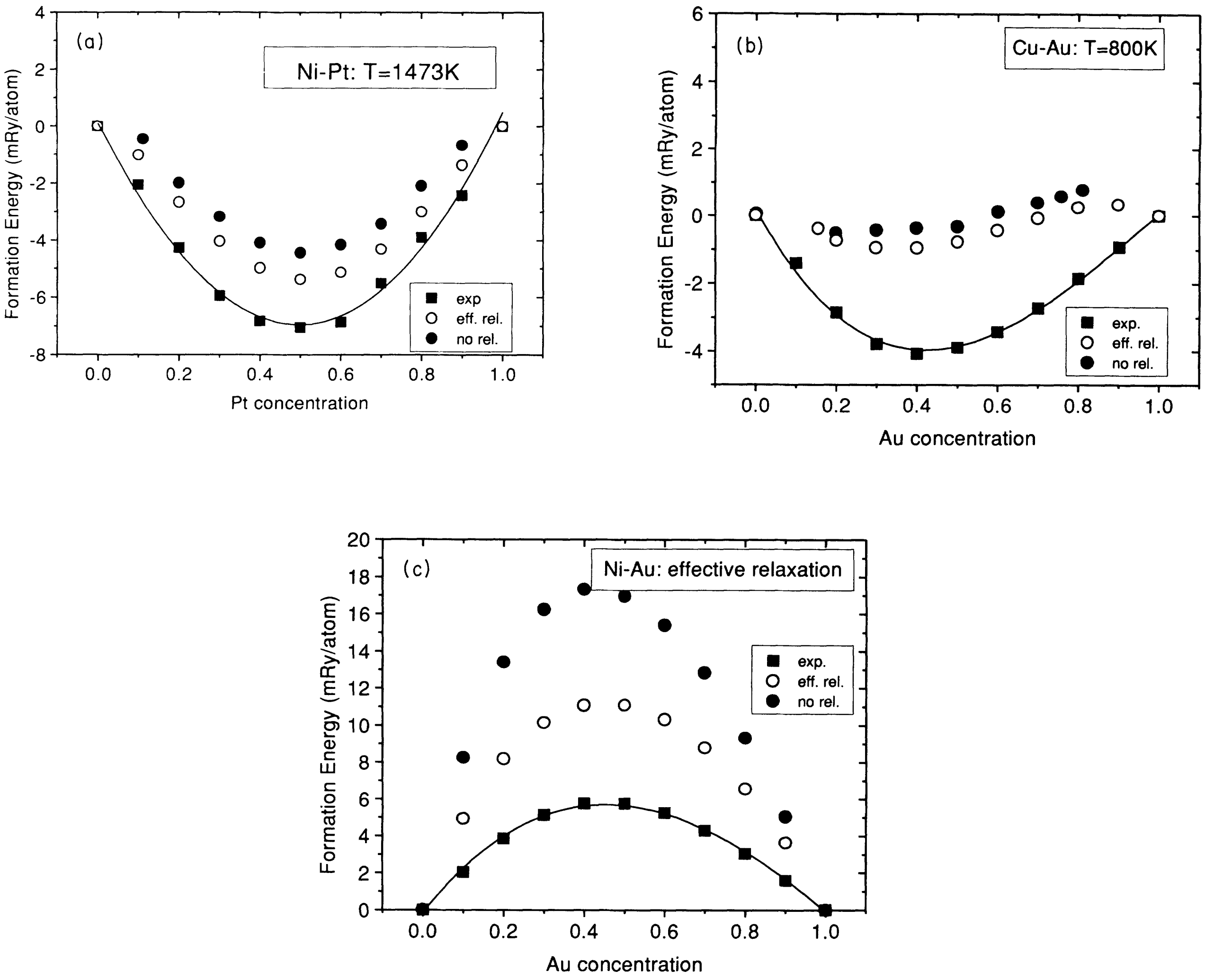

FIG. 5. Formation energy for the disordered phase in (a) Ni-Pt, (b) Cu-Au, and (c) Ni-Au alloys. Squares (labeled exp.) refer to measured values (Ref. 13). Open circles correspond to the present calculation with the use of the effective volume relaxation model. Solid disks correspond to the present calculation, for the same temperature, without relaxation. Temperatures are as indicated except for Ni-Au which correspond to the perfectly random alloy.

also with results of more involved calculations as those of Mousseau and Thorpe.[16]

We have used this model to estimate the nearest-neighbor distances for the alloys considered. The nearest-neighbor distances are used to calculate the volume of the different clusters considered in the cluster expansion [Eq. (1)]. This model has been shown to reproduce the observed phase diagrams in much better agreement with the measured one than the phase diagrams obtained without consideration of relaxation.[8] In Fig. 5 we present results obtained using this model for the formation energy of the disordered alloy (at a finite temperature, equal to the one used in the measurements) for Ni-Pt, Cu-Au, and Ni-Au. We compare these results with those obtained without relaxation at the same temperature [Figs. 1(a), 1(b), and 3, respectively]. The agreement with the measured formation energies is improved substantially.

In the present paper we have shown the important effects of the use of the finite-temperature configuration (i.e., considering the short-range order) in the calculation of the formation energy of the disordered phase. We have also applied a model for the consideration of the elastic relaxation and shown its importance for alloys in which the constituting elements have a big size mismatch. We have achieved this by using simple approximations that describe the essence of the physical effect. A better agreement between the measured and calculated values is possible and will require more detailed models, particularly for the volume effects caused by relaxation. Nevertheless, our simple treatment of these effects allow the present technique of combining zero temperature all electron quantum-mechanical calculations of ordered compounds with the cluster expansion method to describe quantitatively the energetics of the disordered alloy.

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