First-principles calculation of the Ag-Cu phase diagram

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Total-energy band calculations based on the augmented-spherical-wave method are used to determine the binding curves of the elements and of selected compounds in the Ag-Cu system. The calculated total energies, together with vibrational free energies determined by a Debye-Grüneisen analysis of the binding curves and configurational entropies determined by the cluster variation method, are used to calculate the solid-state portion of the Ag-Cu phase diagram. The solubilities at both ends of the phase diagram, calculated with no adjustable parameters, are in excellent agreement with experiment. For the Ag-Cu system, it is shown that local volume relaxation effects are very important and that significant improvement in the calculated phase diagram is obtained by including vibrational free energies.

I. INTRODUCTION

The development of local-density-functional theory[1] has led to total-energy band calculations as a function of volume, which, using only atomic numbers, correctly reproduce 0-K ground-state properties of the elements[2] and of ordered compounds. More recently, a Debye-Grüneisen analysis[3] of calculated binding energies has yielded theoretical bulk moduli Debye temperatures, and Grüneisen constants that lead to free energies and to theoretical thermal properties that, for simple elemental systems, are in reasonable agreement with experiment. Furthermore, in the past several years, there has been considerable interest in combining these total-energy calculations with configurational statistical mechanics in order to obtain temperature-composition phase diagrams of alloys. Such computations require, of course, a tractable representation for both the configurational energy and entropy.

The cluster variation method (CVM) proposed by Kikuchi[4] provides an elegant and relatively simple solution to the computation of configurational entropy. This method has been successfully used, for example, to investigate alloy phase equilibrium for complex Hamiltonians, which include pair and many-body interactions.[5-8] The CVM, which was originally proposed in the context of the variational principle of statistical mechanics, can also be shown to follow from a truncated cluster expansion of the configurational entropy.[9,10] Implementation of the CVM requires the description of atomic configurations of clusters of lattice sites, which can be conveniently accomplished using multisite correlation functions.[10,11] More generally, it has been shown by Sanchez, Ducastelle, and Gratias[10] that any function of configuration can be formulated in terms of multisite characteristic functions which form an orthonormal basis in configuration space. Although this cluster expansion can be applied to any function that depends upon the configuration of the system, of which the energy is only a particular case, its usefulness rests heavily on the rate of convergence in terms of the size and complexity of the clusters.

The cluster expansion of the expectation value of the configurational energy results in the commonly used bilinear expression in terms of effective multisite interactions and correlation functions, the latter being expectation values of the orthogonal characteristic functions.[10,11] Connolly and Williams[12] 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 a set of effective pair and multisite chemical interactions that could be used to describe the energy of disordered alloys. The attractiveness of the proposal of Connolly and Williams rests on the fact that the treatment of the configurational thermodynamics of partially ordered alloys, i.e., alloys displaying both short- and/or long-range order, becomes essentially isomorphic to a generalized Ising model where the chemical interactions are of relatively short range. Although these interactions will in general include many-body terms, as well as temperature and volume dependence, they can be easily treated using the CVM to calculate configurational free energies and, from

them, the solid-state portion of phase diagrams.

Among the first applications of the Connolly-Williams method were studies of temperature-composition phase diagrams of noble-metal alloys[13] and semiconductor alloys.[14] Subsequently, numerous other cases have been investigated with relatively good results.[15−21] In general, these calculations show that the cluster expansion of the configurational energy converges relatively fast. Thus, the Connolly-Williams approach is seen to offer a practical method for the determination of the chemical interactions in a *disordered* alloy system from total-energy band calculations of a relatively small set of *ordered* compounds.

The most serious shortcomings of the first-principles phase-diagram calculations carried out to date[13−20] are the inadequate treatment of local volume and elastic relaxation and the neglect of vibrational entropies. The treatment of local relaxations presents such a formidable task that no attempts have been made to include this effect in the application of the Connolly-Williams method. The contributions due to *local* volume relaxations as distinguished from *global* volume relaxations which are routinely and easily incorporated,[13−21] and of vibrational entropies are expected to be more tractable. In particular, local volume relaxations should play an important role for systems where there is a significant difference in the molar volumes of the constituents elements, such as the Ag-Cu alloys considered here. This point is well illustrated, for example, by the large difference between the calculated Ag-Cu phase diagram of Mohri *et al.*,[16] and that of Wei *et al.*[22] The former uses a global volume relaxation scheme and shows large discrepancies, while the latter uses a total volume relaxation scheme and gets much better agreement with experiment.

Although local volume relaxations and vibrational contributions to the free energy are generally acknowledged to be important, most theoretical determinations of phase diagrams have either neglected them,[13−18] or have included them by using empirical methods and parameters determined experimentally.[19,20] Recently, a local volume relaxation scheme that uses only calculated total energies has been proposed and applied to the Ru-Nb system.[21]

In the present work, we carry out a first-principles calculation of the solid-state portion of the Ag-Cu phase diagram, which includes vibrational free energies in the Debye-Grüneisen approximation, and which allows for the relaxation of local volumes. Thus, all quantities needed to determine the total free energy are obtained from first principles with no adjustable parameters. The proposed first-principles theory of alloy phase equilibrium yields a Ag-Cu phase diagram that exhibits solubility limits in good agreement with experiment. In particular, we point to the significant discrepancies between our results and previous first-principles theories that neglect both local volume relaxations and vibrational free energies.

II. CLUSTER EXPANSION

Here we briefly summarize the main aspects of the cluster expansion of configurational properties in binary alloys. A more general treatment of the theory, applic-

able to multicomponent systems, is given in Ref. 10. As mentioned, the cluster expansion provides the basis for the description of disordered alloys from the knowledge of the energy (binding curves) of ordered compounds.

In a binary crystal with N sites, there are 2^N different atomic configurations that may be formally described by assigning a spin operator σ_i, taking values $+1$ and -1 for each of the atomic species, at each crystal site i. A configuration in the crystal is then fully specified by the N-dimensional vector $\sigma = \{\sigma_1, \sigma_2, \ldots, \sigma_N\}$.

Consider a single site i. The set of two polynomials in the discrete variable σ_i, namely the polynomial of order 0, $\phi_0(\sigma_i) = 1$, and the polynomial of order 1, $\phi_1(\sigma_i) = \sigma_i$, form a complete and orthonormal set, with the inner product between two functions of configuration $f(\sigma_i)$ and $g(\sigma_i)$ in the one-dimensional discrete space spanned by σ_i defined as

$$\langle f(\sigma_i) \cdot g(\sigma_i) \rangle = \frac{1}{2} \sum_{\sigma = \pm 1} f(\sigma_i) g(\sigma_i) . \tag{1}$$

The set of orthonormal characteristic functions in the N-dimensional discrete space spanned by the vector σ is obtained from the direct product of the $\phi_0(\sigma_i), \phi_1(\sigma_i)$, where i spans all crystal sites $(i = 1, 2, \ldots, N)$. For a binary system, the resulting characteristic functions $\Phi_\alpha(\sigma)$ are given by products of the spin operator σ_i over the sites of all possible clusters $\alpha = \{i_1, i_2, \ldots, i_n\}$ in the crystal by[10]

$$\Phi_\alpha(\sigma) = \prod_{i \in \alpha} \sigma_i = \sigma_{i1}\sigma_{i2} \cdots \sigma_{iN} , \tag{2}$$

where n labels the set of inequivalent clusters in the crystal. Accordingly, there is a one-to-one correspondence between the set of orthogonal functions $\Phi_\alpha(\sigma)$ and the set of all clusters α in the crystal, including the empty cluster for which $\Phi_0(\sigma) = 1$.

Since the characteristic functions $\Phi_\alpha(\sigma)$ form a complete and orthonormal set,[10]

$$\frac{1}{2^N} \sum_\sigma \Phi_\alpha(\sigma) \Phi_\beta(\sigma) = \delta_{\alpha,\beta} , \tag{3}$$

any function of configuration, $F(\sigma)$, may be written as

$$F(\sigma) = \sum_\alpha F_\alpha \Phi_\alpha(\sigma) , \tag{4}$$

where the sum extends over all clusters in the crystal, including the empty cluster, and where F_α is given by

$$F_\alpha = \langle F(\sigma) \cdot \Phi_\alpha(\sigma) \rangle = \frac{1}{2^N} \sum_\sigma F(\sigma) \Phi_\alpha(\sigma) . \tag{5}$$

Thus, the terms F_α are the projections of $F(\sigma)$ on the orthogonal cluster basis.

It should be noted that the space-group symmetry of the crystal requires that the cluster projections F_α of the function $F(\sigma)$ be the same for all clusters α which are related by a symmetry operation (translation or point group). Accordingly, the cluster expansion in Eq. (4) becomes

$$F(\sigma) = \sum_{n=0}^{N} F_n \Theta_n(\sigma) . \tag{6}$$

In the case of a disordered lattice, these clusters are only distinguished by their number of points and their geometry. In Eq. (6), the $\Theta_n(\sigma)$ are given by

$$\Theta_n(\sigma) = \sum_{\alpha \in n} \Phi_\alpha(\sigma) \ . \tag{7}$$

In view of the orthogonality of the $\Phi_\alpha(\sigma)$, we also have

$$\frac{1}{2^N} \sum_\sigma \Theta_n(\sigma)\Theta_m(\sigma) = z_n N \delta_{n,m} \ , \tag{8}$$

where $z_n N$ is the total number of n-type clusters in the crystal.

The most common applications of Eq. (6) are for the cluster expansion of expectation values of functions of configurations, such as the average of the configurational energy in the Connolly-Williams method. With the notation $\xi_n = \langle \Phi_\alpha(\sigma) \rangle$ for the expectation value of the characteristic functions, where α is any cluster belonging to the equivalent set n, we obtain

$$\bar{F} = \langle F(\sigma) \rangle = N \sum_{n=0}^N z_n F_n \xi_n \ . \tag{9}$$

As mentioned, the usefulness of this cluster expansion rests on the fast convergence of the projections F_n. In Sec. IV, the cluster expansion given by Eq. (9) is used to obtain the renormalized contributions to the configurational energy arising from chemical interactions, local volume relaxations, and vibrational modes.

III. BAND CALCULATIONS

The experimental Ag-Cu phase diagram displays a wide miscibility gap separating Ag- and Cu-rich fcc solid solutions with, respectively, maximum solubilities of approximately 14% Cu and 5% Ag occurring at a eutectic temperature of 1052 K.[23] Therefore, only fcc structures and fcc-based compounds need to be considered in our calculations. In particular, the band-structure calculations are carried out for the fcc end members and for the set of ordered compounds, which include AgCu in the $L1_0$ structure and Ag_3Cu and $AgCu_3$ in the $L1_2$ structure. These five systems are sufficient to determine the chemical interaction parameters for all clusters up to the regular nearest-neighbor tetrahedron cluster in the fcc lattice.

Our electronic-structure calculations utilize the augmented-spherical-wave (ASW) method,[24] with exchange and correlation treated in the local-density approximation. Total-energy calculations for the pure elements and for each compound are performed for approxi-

mately 30 values of the volume per atom, Ω, centered around the equilibrium volume, Ω_0, using 570 k points in the irreducible wedge of the Brillouin zone. Energy minimization is used to find both Ω_0 and the ratio of atomic radii r_{Ag}/r_{Cu}.

As outlined by Moruzzi, Janak, and Schwarz,[3] the resulting total-energy curves are fit to a Morse function of the form

$$E(r) = A - 2Ce^{-\lambda(r-r_0)} + Ce^{-2\lambda(r-r_0)} \ , \tag{10}$$

where $E(r)$ is the calculated electronic total energy of the rigid lattice, and A, C, λ, and r_0 are fitting parameters. Here, the independent parameter r is the Wigner-Seitz atomic radius related to the volume per atom by the relation $\Omega = (4\pi/3)r^3$. For the compounds, we use an *effective* Wigner-Seitz radius, which is a weighted average of the constituent atomic radii. It is easily verified that r_0 is the Wigner-Seitz radius corresponding to Ω_0 and that C is the cohesive energy for the rigid lattice.

Table I shows the result of a least-squares fit to the Morse function of Eq. (10) for the systems considered. Also listed for each system are the theoretical bulk modulus B, Debye temperature Θ_{D0}, and Grüneisen constant γ, determined within the Debye-Grüneisen approximation following the method of Ref. 3. With increasing Cu concentration, we note a relatively smooth decrease in r_0, λ, and γ, and an increase in C, B, and Θ_{D0}.

The calculated binding curves for the rigid lattice, together with the Debye temperatures and the Grüneisen constants listed in Table I, permit the determination of the vibrational free energy as a function of the Wigner-Seitz radius (or the volume per atom) and temperature for chemically ordered compounds. In the Debye-Grüneisen approximation, the free energy $F(r,T)$ is given by[25]

$$F(r,T) = \tfrac{9}{8}k_B\Theta_D + E(r)$$

$$- k_B T[D(\Theta_D/T) - 3\ln(1 - e^{-\Theta_D/T})] \ , \tag{11}$$

where the k_B is Boltzmann's constant and D is the Debye function. In the Grüneisen approximation, the volume dependence of the Debye temperature is given by

$$\Theta_D = \Theta_{D0} \left[\frac{r_0}{r} \right]^{3\gamma} \ , \tag{12}$$

where Θ_{D0} is the Debye temperature corresponding to Ω_0.

For the ordered compounds, the free-energy given by Eq. (11) represents the volume and temperature-

TABLE I. Morse parameters for Ag (fcc), Ag_3Cu ($L1_2$), AgCu ($L1_0$), $AgCu_3$ ($L1_2$), and Cu (fcc) structures.

System	r_0 (a.u.)	λ (a.u.$^{-1}$)	C (Ry)	A (Ry)	B (kbar)	Θ_D (K)	γ
Ag (fcc)	3.0550	1.5470	0.1772	$-10\,389.795$	1083.3	203.6	2.363
Ag_3Cu	2.9702	1.5490	0.1880	$-8\,611.226$	1185.2	251.1	2.300
AgCu	2.8769	1.5671	0.1963	$-6\,832.662$	1307.6	275.8	2.254
$AgCu_3$	2.7764	1.5137	0.2260	$-5\,054.081$	1455.4	306.3	2.101
Cu (fcc)	2.6658	1.5099	0.2481	$-3\,275.512$	1655.7	347.0	2.023

dependent binding energy in the absence of configurational disorder.

IV. THE EFFECTIVE INTERACTIONS

As pointed out by Connolly and Williams, the cluster expansion of Eq. (9), applied to the energy of a set of ordered compounds for which the correlation functions are known, can be used to obtain effective chemical interactions. Here we propose to apply the same procedure using the vibrational free energies of the ordered compounds calculated in the Debye-Grüneisen approximation. The resulting temperature and volume-dependent effective interactions are then used in a CVM treatment of the configurational entropy in order to include contributions due to configurational disorder into the total free energy.

In practice, the Connolly-Williams method depends upon the convergence of the cluster expansion for relatively small clusters and the availability of a set of total energies for which the required inversion of Eq. (9) is defined. At present, selection criteria for clusters giving a converged cluster expansion are not available.[26] Thus the maximum interaction range is assumed a priori, much as is done with the correlation range in the CVM. In some instances, attempts to ascertain the accuracy of the approximation have been made by comparing the total energy of compounds not included in the inversion procedure with the values obtained using the assumed cluster expansion.[19]

For the fcc or bcc lattices in the tetrahedron approximation, the inversion of Eq. (9) is straightforward, requiring the calculation of total energies for only five high-symmetry structures. For larger cluster approximations, this inversion is not immediately apparent and ad hoc approaches, such as least-squares fitting of the calculated total energies, have been proposed.[19] It can be shown, however, that within a given maximum cluster approximation, there is always a natural set of relevant structures, given by the vertices of a convex configurational polyhedron, for which the inversion of Eq. (9) is unique.[27]

Here, we restrict our calculations to the case of an fcc lattice in which the maximum range of interaction is defined by the nearest-neighbor tetrahedron cluster. The correlation functions $\xi_{k,n}$, where k labels the five relevant structures and n labels the subclusters of the tetrahedron, i.e., the empty ($n=0$), point ($n=1$), pair ($n=2$), triangle ($n=3$), and tetrahedron ($n=4$) clusters, are listed in Table II. The cluster expansion of the vibrational free energy (per atom) for these five ordered structures, $F_k(r,T)$, gives

$$F_k(r,T) = \sum_{n=0}^{4} z_n V_n(r,T)\xi_{k,n} , \qquad (13)$$

where $V_n(r,T)$ are the volume- and temperature-dependent effective interactions.

In the tetrahedron approximation, Eq. (13) can be inverted using general orthogonality properties of the $\xi_{k,n}$. At a fixed Wigner-Seitz radius and temperature, we have

TABLE II. Configurational parameters for Ag (fcc), Ag_3Cu ($L1_2$), AgCu ($L1_0$), $AgCu_3$ ($L1_2$), and Cu (fcc) structures.

System	ω_k	$\xi_{k,0}$	$\xi_{k,1}$	$\xi_{k,2}$	$\xi_{k,3}$	$\xi_{k,4}$
Ag (fcc)	1	1	1	1	1	1
Ag_3Cu	4	1	$\frac{1}{2}$	0	$-\frac{1}{2}$	-1
AgCu	6	1	0	$-\frac{1}{3}$	0	1
$AgCu_3$	4	1	$-\frac{1}{2}$	0	$\frac{1}{2}$	-1
Cu (fcc)	1	1	-1	1	-1	1
N_n		1	1	6	4	1

$$V_n(r,T) = \frac{N_n}{2^4 z_n} \sum_{k=0}^{4} \omega_k \xi_{k,n} F_k(r,T) , \qquad (14)$$

where N_n is the number of n-type clusters in a tetrahedron and ω_k is the number of equivalent configurations for the tetrahedron cluster associated with structure k (see Table II).

Implementation of the CVM with Eqs. (13) and (14), in which the interactions are obtained using the same volume for all five compounds, yields a total free-energy functional that depends on the configurational variables ξ_n and volume (or r). Volume relaxation is then incorporated globally by minimizing this functional with respect to r, in addition to the usual minimization with respect to the correlation functions ξ_n. This 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. Although this assumption has been applied to most of the first-principles calculations done to date,[13-20] it would appear physically implausible in cases where there is a significant difference between the atomic volumes of the constituents elements.

In order to account for the effect of local volume relaxations, Becker, Sanchez, and Tien[21] proposed to obtain the cluster interactions from the total energies $F_k(r_k,T)$ of each compound calculated at different Wigner-Seitz radii r_k. The Wigner-Seitz radius r_k corresponds to the equivalent volume per atom occupied by the tetrahedron cluster characteristic of each compound k in the disordered alloy. Equation (14) becomes

$$V_n(r,T) = \frac{N_n}{2^4 z_n} \sum_{k=0}^{4} \omega_k \xi_{k,n} F_k(r_k,T) , \qquad (15)$$

where r stands for the set of Wigner-Seitz radii.

The set r may be chosen, for example, by minimization of the total free energy with respect to each of the r_k, which may be easily shown to be equivalent to the minimization of the vibrational free energy for each of the five compounds independently. Thus, in this scheme, the local volume of each tetrahedron cluster in the alloy is allowed to relax fully to the value found in the ordered state. An alternative approach intermediate to global volume relaxation and total relaxation of local volumes, both of which appear physically implausible, is to define atomic volumes Ω_{Ag} and Ω_{Cu} for each component in the alloy. Adopting a microscopic version of Vegard's law, the Wigner-Seitz radius r_k for each ordered structure k,

or equivalently the volume per atom Ω_k, is given by

$$\Omega_k = (1-c_k)\Omega_{Ag} + c_k\Omega_{Cu} \; , \tag{16}$$

where c_k is the concentration of Cu in the ordered compound k. The local atomic volumes are then obtained variationally by minimization of the total free energy with respect to both Ω_{Ag} and Ω_{Cu}. This approach, which results in partial relaxation of the local volumes in the alloy, has been shown to accurately reproduce the order-disorder phase diagram in the Ru-Nb system.[21]

V. CONFIGURATIONAL ENTROPY

The CVM may be formulated in terms of a cluster expansion of the configuration entropy.[9,10] For a given probability distribution $X(\sigma)$, the configurational entropy is given exactly by

$$S = -k_B \sum_\sigma X(\sigma)\ln X(\sigma) \; , \tag{17}$$

where the sum is carried over all 2^N configurations in the crystal.

Consider an infinite series of clusters with entropies defined by

$$S_\alpha = -k_B \sum_{\sigma_\alpha} X_\alpha(\sigma_\alpha)\ln X_\alpha(\sigma_\alpha) \; , \tag{18}$$

where the cluster probability distribution $X_\alpha(\sigma_\alpha)$ is given by the sum of the $X(\sigma)$ over all configurational variables σ_i outside cluster α. This series of cluster entropies trivially converges to the exact configurational entropy as the size of the cluster α increases to include all points in the crystal. Using an exact Möbius transformation, we may also write the cluster entropies S_α in terms of a set of *irreducible* cluster contributions, $\hat{S}_\alpha$, as[10]

$$S_\alpha = \sum_{\beta \subseteq \alpha} \hat{S}_\beta \; , \tag{19}$$

where the sum runs over all the subclusters of α, including α, and excludes the empty cluster.

The key approximation made in the CVM consists of neglecting the irreducible entropy contributions $\hat{S}_\alpha$ for clusters larger than a given maximum cluster. This closure condition allows us to express the total configurational entropy S in terms of a *finite* sum of irreducible contributions. Using the space-group symmetry of the crystal, Eq. (19) for $\alpha \rightarrow N$ becomes[10]

$$S = N \sum_{n=1}^m z_n \hat{S}_n \tag{20}$$

or, in terms of the cluster entropies

$$S = N \sum_{n=1}^m z_n a_n S_n$$

$$= -N k_B \sum_{n=1}^m z_n a_n \sum_{\sigma_n} X_n(\sigma_n)\ln X_n(\sigma_n) \; , \tag{21}$$

where, as in Sec. II, n labels inequivalent clusters and m labels the maximum cluster. The coefficients a_n, obtained by inverting Eq. (19), are given by[10]

$$\sideset{}{'}\sum_{\beta \subseteq \alpha} a_\beta = 1 \; , \tag{22}$$

where the equation is valid for each subcluster α of the maximum cluster, and where the sum runs over all subclusters β of the maximum clusters that contain or equal α. In the tetrahedron approximation of the fcc lattice, the coefficients a_n are equal to 5, -1, 0, and 1 for the point, pair, triangle, and tetrahedron clusters, respectively.

The total free-energy functional (per atom) of the disordered alloy, including local volume relaxations and vibrational modes, is given by

$$F_{tot} = \sum_{n=0}^m z_n V(\mathbf{r},T)\xi_n$$

$$+ k_B T \sum_{n=1}^m z_n a_n \sum_{\sigma_n} X_n(\sigma_n)\ln X_n(\sigma_n) \; . \tag{23}$$

Here the effective interactions $V(\mathbf{r},T)$ are given by Eq. (15). Using the cluster expansion described in Sec. II, the cluster probability distributions can be written in terms of the multisite correlation functions:[10]

$$X_n(\sigma_n) = \frac{1}{2^n}\left[1 + \sum_{n=1}^4 \Theta_n(\sigma_n)\xi_n\right] \; , \tag{24}$$

where $\Theta_n(\sigma_n)$ are the characteristic functions defined as sums of products of the configurational variables σ_i for lattice sites i belonging to cluster n [see Eqs. (2) and (7)]. Thus the free-energy functional given by Eq. (23) is a function only of the set of Wigner-Seitz radii $\mathbf{r}$ and of the correlation functions ξ_n.

At a given temperature and concentration, the latter being given by the point correlation ξ_1, the equilibrium free energy is obtained by minimizing the free-energy functional with respect to the remaining correlation functions, ξ_n (with n equal to 2, 3, and 4), and the set of Wigner-Seitz radii $\mathbf{r}$. As mentioned in Sec. IV, the minimization with respect to $\mathbf{r}$ may be carried out using three different schemes: (i) constraining r_k to be all equal, which results in global volume relaxation without allowing relaxation of local volumes; (ii) varying the r_k independently, which results in total relaxation of local volumes: and (iii) subjection of the r_k to the external constraints, such as that of Eq. (16), which gives partial relaxation of the local volumes.

VI. RESULTS AND DISCUSSION

The effective cluster interactions as a function of Cu concentration for a random alloy without the contribution of vibrational modes are shown in Fig. 1, where the calculations are carried out with $V_n(l)$ and without $V_n(g)$ local volume relaxations. The latter is referred to as global volume relaxation and, for the local volume relaxations, we use the partial relaxation scheme outlined in Sec. IV [Eq. (16)]. We point out that there are no appreciable differences between total and partial volume relaxations due to the fact that in the present calculations for the Ag-Cu system Vegard's law is closely obeyed. Although, as we shall see, the contributions due to short-
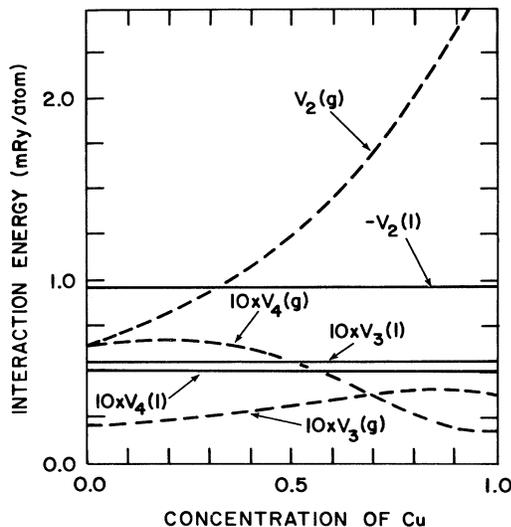
FIG. 1. Calculated effective interactions for the nearest-neighbor (2), triangle (3), and tetrahedron (4) cluster using global volume relaxation $V_n(g)$ and local volume relaxation $V_n(1)$.
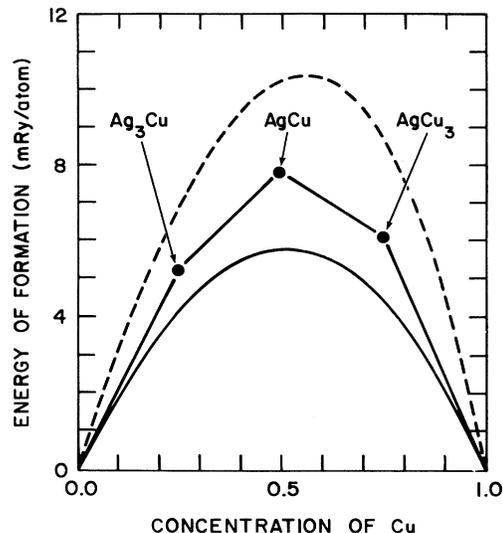

FIG. 2. Energy of formation of a random alloy without vibrational modes calculated using global (dashed line) and local (solid line) volume relaxations, compared to the energy of formation of the ordered compounds Ag_3Cu, $AgCu$, and $AgCu_3$ at 0 K.

range order and to the vibrational modes are important in the determination of the phase diagram, these contributions are small on the scale of the binding energies. Thus, Fig. 1 is representative of the behavior of the cluster interactions at all temperatures of interest.

An important feature seen in Fig. 1 for both global and local volume relaxations is that the absolute value of the triangle and tetrahedron interactions are over an order of magnitude smaller than the nearest-neighbor pair interactions, which underscores the fast convergence of the cluster expansion, Eqs. (4) or (9), with cluster size. Furthermore, the overall behavior and magnitude of the three- and four-body interactions is similar in both cases, although the variations with concentration are more pronounced in the case of global volume relaxation.

The most significant difference seen in Fig. 1 is with regard to the nearest-neighbor pair interactions $V_2(g)$ and $V_2(1)$. Aside from the fact that $V_2(g)$ varies appreciably with concentration whereas $V_2(1)$ remains essentially constant, both interactions have opposite sign. For the global relaxation scheme, $V_2(g)$ is positive indicating a short-range ordering tendency in the alloy. On the other hand, $V_2(1)$ is negative, which is indicative of the segregation behavior actually observed in Ag-Cu alloys.

The profound differences between global and local relaxations are also seen in Fig. 2, where we plot the energy of formation of the random alloys together with the energy of formation of the ordered compounds, the latter connected by straight lines. We see that both relaxation schemes predict, in general agreement with experiment, a positive energy of mixing. Therefore, the random alloys are unstable with respect to phase separation into Ag- and Cu-rich phases. In fact, despite the short-range ordering tendency of the globally relaxed system, the positive energy of mixing is approximately twice that of the locally relaxed alloys. More importantly, Fig. 2 also shows that, for global volume relaxations, the random alloy is unstable with

respect to ordering while, as one would expect in the Ag-Cu system, the opposite is true for the local relaxation scheme. Thus, although the general *macroscopic* thermodynamic behavior, i.e., phase separation, predicted by both relaxation schemes is the same, the *microscopic* pictures are entirely different. In the locally relaxed system there is a local tendency for clustering, whereas the globally relaxed system shows a local ordering tendency. Although at present there is no experimental evidence known to the authors to rule out either behavior, the picture presented by the global relaxation scheme would seem unusual, if not implausible. In particular, this scheme would predict the appearance of metastable ordered structures in supersaturated Ag-Cu solid solutions obtained, for example, by rapidly quenching from the liquid phase.

The phase diagram calculated using global volume relaxations, including short-range-order effects in the tetrahedron approximation of the CVM, with and without the contribution of the vibrational modes, is shown in Fig. 3. Also shown in Fig. 3 is the experimental Ag-Cu phase diagram[23] displaying a eutectic temperature at 1052 K. The high-temperature miscibility gap calculated without the contribution of the vibrational modes extends to approximately 3400 K, well into the liquid phase of the Ag-Cu system. These results are in agreement with previous calculations by Mohri *et al.*[16] Although the results are improved by including vibrational modes in the total free energy, which lowers the miscibility gap at its maximum temperature by approximately 800 K, there is still a pronounced disagreement with the experimental phase diagram. We consider the discrepancy between experiment and theory shown in Fig. 3 as further evidence that the commonly used global relaxation scheme[13−20] is essentially flawed. We point out that the
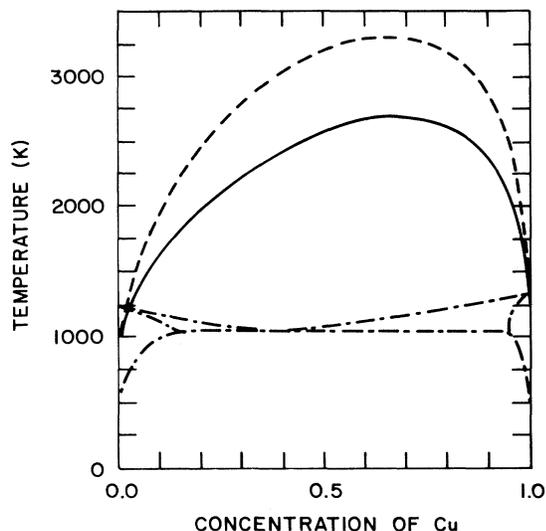
FIG. 3. Calculated miscibility gap using global volume relaxation with (solid line) and without (dashed line) vibrational modes. The experimental (Ref. 23) phase diagram (dash-dotted lines) is shown for reference.
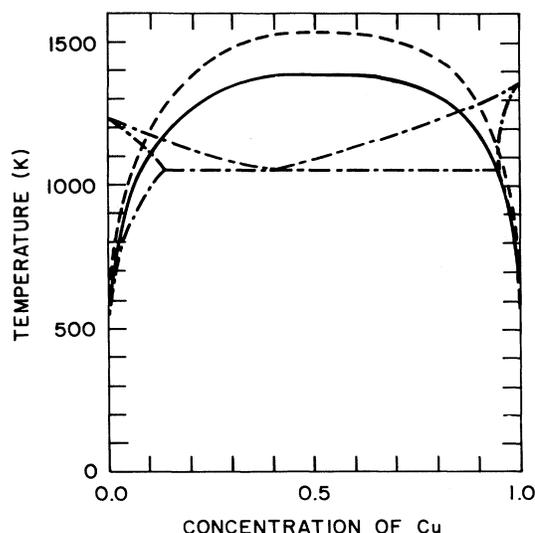

FIG. 4. Comparison between the experimental (dash-dotted lines) phase diagram and the miscibility gap calculated using local volume relaxations with (solid line) and without (dashed line) vibrational modes.

same conclusions are reached for order-disorder systems, as shown in a recent calculation of the Ru-Nb phase diagram that includes both local volume relaxations and vibrational modes.[21]

The miscibility gaps calculated in the tetrahedron approximation of the CVM with and without vibrational modes using the partial relaxation of local volumes described in Sec. IV is shown in Fig. 4. 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-state portion of the Ag-Cu phase diagram. The agreement is excellent for the Cu-rich side of the phase diagram and not as good on the Ag-rich end. However, in view of the fact that the only input to the calculations are the atomic numbers of the constituent elements and, furthermore, that the model used for the vibrational modes is somewhat crude, we consider the agreement between theory and experiment to be very satisfactory.

In conclusion, we have outlined 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 a local volume relaxation scheme. The theory applied to the Ag-Cu system yields results in good agreement with experiment. The contribution of the vibrational modes was shown to play an important role, although, in general, local volume relaxations tend to dominate the behavior of the configurational energy. This is particularly true in the Ag-Cu system where there is an appreciable difference in the volume of the constituent elements. The neglect of local volume relaxations was shown to result in an unlikely microscopic picture for Ag-Cu alloys where the system shows a much stronger tendency to phase separate than experimentally observed, yet, on a local scale, it shows a tendency for ordering. We have pointed out that this apparent flaw of the local relaxation scheme, which manifests itself in significant discrepancies between calculated and experimental phase diagrams, is not intrinsic to segregating systems such as the Ag-Cu alloys studied here, but it is also apparent in Ru-Nb alloys, which show order-disorder transitions.[21]

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