

## Effect of chemical and elastic interactions on the phase diagrams of isostructural solids

L. G. Ferreira,\* A. A. Mbaye,† and Alex Zunger  
*Solar Energy Research Institute, Golden, Colorado 80401*  
 (Received 28 January 1987)

It is shown how the introduction of volume-dependent elastic interactions into lattice models of order-disorder transformations, in addition to the familiar constant-volume interactions (analogous to Ising "spin energies"), leads to qualitatively new features in a binary  $A_xB_{1-x}$  phase diagram.

The formation of an ordered compound  $A_mB_{M-m}$  ( $M = \text{const}$ ) from its isostructural constituent elemental solids  $A$  and  $B$  can be conceptualized to consist of an "elastic" step, where the separate end-point solids  $A_mA_{M-m}$  and  $B_mB_{M-m}$  are compressed and dilated, respectively, to the cell dimensions of  $A_mB_{M-m}$  through an investment of an elastic energy  $\Delta F$ , followed by a "flip" of the necessary number of  $A$  and  $B$  atoms on these prepared lattices, involving a "chemical" (or, "substitutional") energy  $\epsilon^{(m)}$ , to create  $A_mB_{M-m}$ . Many classical models,<sup>1-3</sup> constituting the working paradigms of metallurgy and structural chemistry,<sup>4</sup> have rationalized the stability ( $\Delta F + \epsilon^{(m)} < 0$ ) or instability ( $\Delta F + \epsilon^{(m)} > 0$ ) of ordered phases by representing the balance between elastic ( $\Delta F$ ) and chemical ( $\epsilon$ ) energies through phenomenological constructs, such as the mismatch between the atomic radii<sup>1</sup> of  $A$  and  $B$  (for the elastic energy), and various scales of electronegativity mismatch<sup>2,3</sup> (for the chemical energy). However, while the temperature-composition phase diagrams of even binary isostructural solids<sup>5</sup> manifest far more diverse phenomena than merely the existence or nonexistence of ordered phases (disordering, miscibility gaps, spinodals, etc.), the complexity associated with the *configurational* degrees of freedom underlying such phenomena has generally limited their modeling to the description of order-disorder events on a *fixed lattice*, common to  $A$ ,  $B$ , and  $A_mB_{M-m}$ , i.e., including only substitution energies<sup>6,7</sup>  $\{\epsilon^{(m)}\}$ . Inspired by the analogous spin- $\frac{1}{2}$  three-dimensional Ising problem,<sup>6</sup> such efforts have generally focused on the determination of a set of fixed "chemical energies"  $\epsilon^{(m)}$  (analogous<sup>6,7</sup> to the Ising many-spin interaction parameters) which best describe actual phase phenomena through approximate solutions of the configurational Hamiltonian, neglecting, however,  $\Delta F$ .

Whereas the introduction of an ever increasing set of ("multiatom") interaction parameters<sup>7-9</sup>  $\{\epsilon^{(m)}\}$ , extension of the range of interaction to second, and even further neighbors,<sup>10,11</sup> introduction of *ad hoc* composition-dependent interaction energies  $\epsilon^{(m)}(x)$ , and improvements in the methods of solution (Monte Carlo simulations,<sup>10,11</sup> high-temperature expansion<sup>6,7</sup>) have generally resulted in a greater degree of realism,<sup>8-11</sup> such models often produce but a "caricature of real alloys,"<sup>10</sup> even for the simplest and best-studied isostructural face-centered-cubic (fcc) systems. This state of affairs is manifested, among others, by the inability of constant interaction energy (i.e.,  $\Delta F = 0$ ) lattice models to predict from the same Hamil-

tonian<sup>9</sup> both order-disorder critical temperatures (decided solely by  $\epsilon^{(m)}$ ) and excess thermodynamic energies (e.g., mixing enthalpies, decided primarily by<sup>12,13</sup>  $\Delta F$ ), the occurrence for fcc lattices of a triple point at abnormally low temperatures,<sup>11</sup> and the systematic failure to obtain realistically *narrow* single-phase regions at low temperatures for ("antiferromagnetically") ordered structures<sup>8,9</sup> or to predict the coexistence of miscibility gaps with ordering. We will show that these shortcomings reflect primarily the omission of elastic effects ( $\Delta F$ )—the single most important mechanism of atomic packing in phenomenological models of structural chemistry<sup>1</sup> and in semiconductor alloy phase diagrams.<sup>12,13</sup>

We start by outlining the way in which the phase diagram of  $A_xB_{1-x}$  can be constructed from the interaction energies in this system.<sup>6,7,14</sup> To do so, we define *clusters* of lattice points within which interactions are to be retained. The largest cluster size  $M$  will decide the maximum order of multisite interactions (in this work, including one, two, three, and four body) within the interaction range one is prepared to consider (e.g., nearest neighbors). Each of the  $M$  sites of a cluster is occupied either by an atom  $A$  or  $B$ . By periodically repeating each cluster, one obtains a set of *ordered structures* whose sublattices are generated by the repetition of the cluster sites. For each ordered structure  $n$  we define the volume-dependent ( $V$ ) excess energy relative to the constituent solids  $A$  and  $B$  as

$$\Delta E(n, V) = E(n, V) - X_n E_B(V_B) - (1 - X_n) E_A(V_A), \quad (1)$$

where  $n$  specifies the set of occupations (by  $A$ 's or  $B$ 's) of the  $M$  cluster sites (or of the  $M$  sublattices),  $E_A$  and  $E_B$  are the energies of pure elemental solids  $A$  and  $B$  at their equilibrium volumes  $V_A$  and  $V_B$ , respectively, and  $X_n$  is the concentration of the  $B$  atoms in either the cluster or the corresponding ordered solid. At equilibrium [where  $V_n$  satisfies  $d\Delta E(n, V)/dV = 0$ ] the excess energy simply gives the formation enthalpy  $\Delta H^{(n)}$  of this ordered crystal from its constituent elemental solids.

For a *disordered* alloy we define the *state of order*  $\sigma$  as one of the  $2^N$  possible arrangements of atoms  $A$  and  $B$  in the lattice with  $N$  sites. For such nonperiodic disordered arrangements of atoms, one counts the number of clusters with a given set  $n$  of its  $M$  site occupations. One thus defines the frequency  $\xi_n(\sigma)$  of occurrence of the cluster occupation  $n$  as the number of such clusters divided by the total number of clusters with  $M$  sites. (For example, in an fcc alloy, we take the basic cluster as a tetrahedron of

nearest neighbors, i.e.,  $M=4$ .) In the alloy of  $N$  sites there are  $2N$  tetrahedra whose vertices are distinguished by the sublattice to which they belong, and therefore there are  $2^M=16$  different cluster occupations  $n$ , or distinct ordered structures. The excess energy of the alloy in the state of order  $\sigma$  is then written in terms of the excess energies of the ordered structures  $\Delta E(n, V)$  and the frequencies  $\xi_n(\sigma)$  as

$$\Delta E(\sigma, V) = \sum_n \xi_n(\sigma) \Delta E(n, V) . \quad (2)$$

Letting  $P_n(x, T) = \langle \xi_n(\sigma) \rangle$  be the canonical ensemble probability of finding the cluster occupation  $n$  at the temperature  $T$  and concentration  $x = \sum_n P_n(x, T) X_n$ , the equilibrium free energies are  $F(x, T) = \Delta H(x, T) - TS(x, T)$ , where the mixing enthalpy of the alloy is

$$\Delta H(x, T) = \sum_n P_n(x, T) \Delta E(n, V_{\text{eq}}) , \quad (3)$$

$S(x, T)$  is the entropy, and  $V_{\text{eq}}(x)$  is the alloy's equilibrium molar volume [which minimizes  $F(x, T)$ ]. The knowledge of  $\{\Delta E(n, V)\}$ —replaced in many previous models,<sup>7-11</sup> by a set of constants  $\{\varepsilon^{(n)}\}$ —can then be used through standard methods<sup>6,7</sup> to construct  $F(x, T)$  and hence the whole phase diagram.

Rather than use constants for  $\Delta E(n, V)$ , we will now show that the effective energies to be used in phase diagram calculations [Eq. (2)] can be separated into a volume- and composition-independent ("chemical") part  $\varepsilon^{(n)}$  and a volume-dependent but  $n$ -independent ("elastic") part  $g(x, V)$ :

$$\Delta E(\sigma, V) = \sum_n \xi_n(\sigma) \varepsilon^{(n)} + g(x, V) , \quad (4)$$

if the equilibrium molar volume  $V_{\text{eq}}(x)$  does not depend on the state of order<sup>15</sup>  $\sigma$ . Conventional Ising alloy models<sup>7-11</sup> retain only the first term in Eq. (4). Whereas the second term clearly does not affect constant-composition order-disorder phenomena (since  $g$  is  $n$  independent), we will show that  $g(x)$  has a dramatic effect on those aspects of the phase diagram that represent multiple-phase coexistence, and that it cures many of the shortcomings of conventional Ising models of alloys even if only nearest-neighbor chemical interactions are included.

To verify that the assumption of state-of-order independence of volumes leads to Eq. (4), one first considers two ordered structures  $n$  and  $m$  with the same concentration ( $X_n = X_m$ ). Mix these ordered structures with a third one  $l$ , to form an alloy with excess energy

$$\Delta E(\sigma, V) = a\Delta E(n, V) + b\Delta E(l, V)$$

(and an analogous expression for mixing  $l$  with  $m$ ). If the equilibrium volume is to be the same for both alloys (because they have the same concentration  $aX_n + bX_l = aX_m + bX_l$ ), then  $\Delta E(n, V)$  and  $\Delta E(m, V)$  can differ only by a volume-independent constant. This shows that the difference  $\Delta E(n, V) - \Delta H^{(n)}$  depends on  $n$  only through its concentration  $X_n$ , or that it can be expanded in a power series  $\sum_k Y_k(V) X_n^k$ . Inserting this expansion into Eq. (2), and using the concentration  $x = \sum_n \xi_n(\sigma) X_n$  of the  $B$  atoms in the alloy and the normalization condition

$\sum_n \xi_n(\sigma) = 1$ , one verifies that up through the linear ( $k=1$ ) term  $\Delta E(\sigma, V)$  depends on  $x$  but not on  $\sigma$ . On the other hand, the higher powers of  $X_n$  lead to terms in Eq. (2) which depend on the state of order  $\sigma$ . However, if the equilibrium volume is to depend only on  $x$ , the functions  $Y_k(V)$  for  $k \geq 2$  must be volume independent. Thus, we get the form of Eq. (4) and further show that  $g(x, V)$  is linear in  $x$ , or that

$$g(x, V) = (1-x)F_A(V) + xF_B(V) . \quad (5)$$

This shows rigorously that when the volume is state-of-order independent, the excess alloy energy  $\Delta E(\sigma, V)$  is just a concentration-weighted average of the corresponding energies of the end-point compounds.

Since in practice there may be some state-of-order dependence of  $V_{\text{eq}}(x)$ , one could derive more accurate expressions for  $F_A(V)$  and  $F_B(V)$  from information at all  $x$ 's (not just  $x=0$  and  $x=1$ ). Under our assumption of state-of-order independence of  $V_{\text{eq}}(x)$ , the bulk modulus  $B(x) = V d^2 \Delta E(\sigma, V) / dV^2$  also depends only on  $x$ . Furthermore, at the special compositions  $X_n$ , one has  $V_{\text{eq}}(X_n) = V_n$  and  $B(X_n) = B_n$ . Equation (5) can then be expressed in terms of these quantities by taking  $dg(x, V) / dV = 0$  at  $V_{\text{eq}}$  and

$$d^2 g(x, V) / dV^2 = B(x) / V_{\text{eq}}(x) ,$$

from which one obtains upon integration

$$F_A(V) = \int_0^{X(V)} x Z(x) dx$$

and

$$F_B(V) = \int_{X(V)}^1 (1-x) Z(x) dx , \quad (6)$$

where  $x = X(V)$  is the inverse function of  $V = V_{\text{eq}}(x)$  and

$$Z(x) = \left[ \frac{dV_{\text{eq}}}{dx} \right]^2 B(x) / V_{\text{eq}}(x) .$$

At equilibrium, when  $dg(x, V) / dV = 0$ , the volume disappears from the equation as  $x = X(V_{\text{eq}})$  and the excess alloy energy is

$$\Delta E(\sigma) = \sum_n \xi_n(\sigma) \varepsilon^{(n)} + G(x) , \quad (7)$$

where

$$G(x) = g(x, V_{\text{eq}}) = (1-x)F_A(V_{\text{eq}}) + xF_B(V_{\text{eq}}) .$$

Equation (7) is the central result of this paper.<sup>15</sup> Its first term ("chemical energy") is the well-known<sup>7-11</sup> constant-volume configuration-dependent (many-site) interaction energy. It represents the energy of an alloy that has the same equilibrium volume as its constituents  $V_A = V_B = V_{\text{eq}}(x)$ , i.e., when the lattice mismatch is zero. The new second term represents the configuration-independent ("elastic energy") of the medium and vanishes by Eq. (6) in the (unusual) case when the constituents have the same equilibrium volume as the alloys, i.e., when  $dV_{\text{eq}}/dx = 0$ . In analogy with the "generalized perturbation method,"<sup>16</sup> Eq. (7) reflects the fact that ordering energies  $\varepsilon^{(n)}$  represent fluctuations about an energy  $G(x)$  for the "effective medium," common to both the ordered and the disordered phases.

To demonstrate the consequences of the interplay between “chemical” and “elastic” energies, we compare the calculated phase diagram and thermodynamic functions of the Cu-Au system<sup>5</sup> in two ways: (i) retaining in Eq. (7) both chemical and elastic terms (the “ $\epsilon$ - $G$  approach”) or (ii) retaining just the chemical term (the “ $\epsilon$ -only” approach).  $G(x)$  and  $\epsilon^{(n)}$  can be simply extracted from the experimental data<sup>17</sup> on Cu-Au, i.e., from (i)  $\{V_n, B_n, \Delta H^{(n)}\}$  and (ii) the three critical temperatures<sup>5</sup>  $T_1=663$  K,  $T_2=683$  K, and  $T_3 \cong 500$  K for order-disorder transition of  $\text{Cu}_3\text{Au}$ ,  $\text{CuAu}$ , and  $\text{CuAu}_3$ , respectively. Since these temperatures depend solely on  $\epsilon = \Delta H^{(n)} - G(X_n)$  [by Eq. (7)], given  $\Delta H^{(n)}$ , it suffices to fix  $G(X_n)$  at the stoichiometric compositions  $X_n = \frac{1}{4}$ ,  $\frac{1}{2}$ , and  $\frac{3}{4}$ . This is done by adjusting  $dV/dX$  in  $G(X)$  of Eq. (6) at these three compositions. The full  $G(x)$  curve is obtained by (i) interpolating  $V_n$  (with the adjusted derivatives) to obtain  $V(x)$ , (ii) interpolating  $B_n$  to find  $B(x)$ , and (iii) integrating Eq. (6). The resulting  $G(x)$  is represented in Fig. 1 by the solid curve. For purposes of illustration it suffices to represent this  $G(x)$  by the simple form  $\Omega x(1-x)$  (solid dots in Fig. 1), where  $\Omega = 13.408$  kcal/mol, with virtually no loss in precision. We find  $\epsilon^{(1)} = -4.024$ ,  $\epsilon^{(2)} = -5.264$ , and  $\epsilon^{(3)} = -3.628$  kcal/mol. The four values ( $\epsilon$  and  $\Omega$ ) completely specify the Hamiltonian used. Note that the elastic energy is substantial on the scale of the chemical energies, and that the common assumption of Vegard’s rule ( $dV_{\text{eq}}/dx = \text{const}$ ) substantially overestimates  $G$  (dashed line in Fig. 1). We have calculated the phase diagrams [Figs. 2(a) and 2(b)], and the enthalpy [Eq. (3)] at  $T=800$  K (Fig. 3) using the cluster variation method (CVM),<sup>14</sup> retaining up to four-body (“tetrahedron”) interactions within the first nearest neighbors.

As stated before, both the  $\epsilon$ - $G$  and the  $\epsilon$ -only approaches yield the same critical temperatures [compare Figs. 2(a) and 2(b), where we obtain the critical temperatures 681.6, 676.1, and 497.4 K at the critical compositions 0.265, 0.497, and 0.727, for  $n=1, 2$ , and 3, respec-

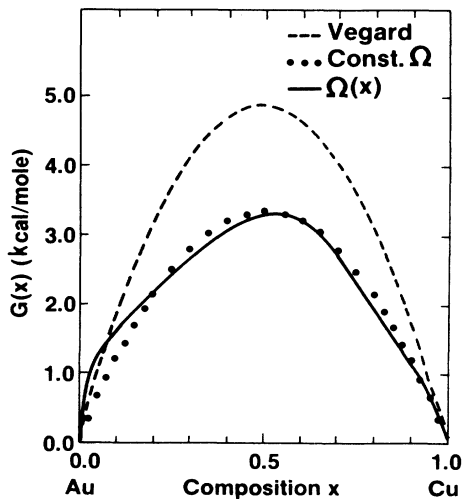


FIG. 1. Effective elastic energy  $G(x)$  for the Cu-Au system.

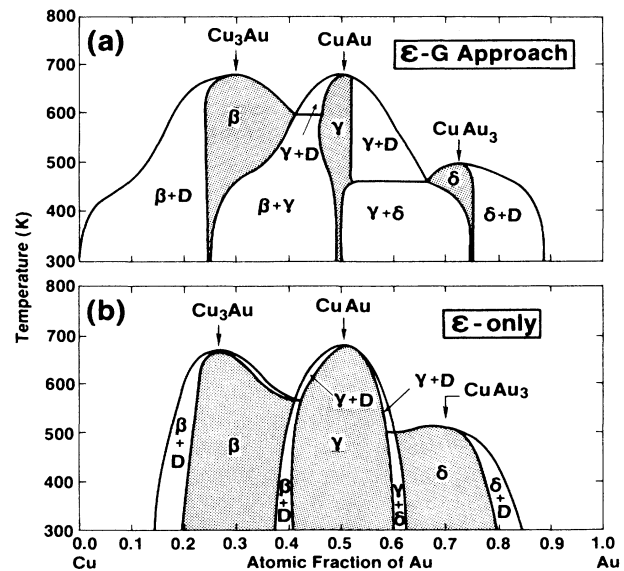


FIG. 2. CVM-calculated phase diagrams for the Cu-Au system using Eq. (7) with  $\epsilon^{(1)} = -4.024$ ,  $\epsilon^{(2)} = -5.264$ ,  $\epsilon^{(3)} = -3.628$  kcal/mol, and  $G(x) = 13.408x(1-x)$  kcal/mol. (a) Both  $\epsilon$  and  $G(x)$  retained in Eq. (7); (b) only  $\epsilon$  retained. Shaded areas denote single-phase regions.  $\beta = \text{Cu}_3\text{Au}$ ,  $\gamma = \text{CuAu}$ ,  $\delta = \text{CuAu}_3$ , and  $D$  denotes the disordered phase.

tively]. In contrast, the  $\epsilon$ - $G$  approach cures the systematic problems of the normal Ising ( $\epsilon$ -only) approach in describing multiple-phase phenomena even though only nearest-neighbor interactions are retained. This is evidenced by the following observations: (i) Whereas the observed mixing enthalpy  $\Delta H(x, T)$  of the disordered alloy [Eq. (3)] can be accurately reproduced in the  $\epsilon$ - $G$  approach solely by fitting critical order-disorder temperatures [solid line in Fig. 3(a)], if elastic energies are ignored [dashed curve in Fig. 3(a)], the calculated enthalpy<sup>9</sup> is far too small (here, too negative by a factor of  $\sim 4-5$ ). This simply reflects the fact that  $\Delta H^{(n)}$  is given by  $\epsilon^{(n)} + G(X_n)$ , but that only

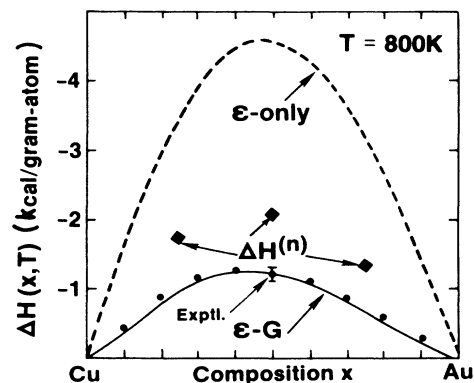


FIG. 3. Calculated enthalpy of mixing [Eq. (3)] at  $T=800$  K. Solid dots give the experimental (Ref. 5) results with their typical error bars.  $\blacklozenge$  denotes the  $\Delta H^{(n)}$  values of the ordered phases.

a piece of it ( $\varepsilon^{(n)}$ ) decides the critical temperatures. This further clarifies why fitting of  $\Delta H^{(n)}$  in the  $\varepsilon$ -only approach leads to erroneous critical temperatures, whereas fitting of critical temperatures leads to erroneous enthalpies.<sup>9</sup> (ii) *Elastic energies act to stabilize ordered phase.* This is evidenced by a far narrower single-phase region (shaded areas in Fig. 2) and far wider two-phase region (clear areas in between) in the  $\varepsilon$ - $G$  calculation [Fig. 2(a)] relative to the  $\varepsilon$ -only calculation [Fig. 2(b)]; the latter approach further fails to describe the rapid narrowing of the ordered phase domains at low temperatures. (iii) It has been recently demonstrated through accurate (Monte Carlo<sup>10,11</sup>) calculations that retention of only the constant-energy terms in the Ising Hamiltonian [ $\varepsilon$ 's in Eq. (7)] leads in the antiferromagnetic fcc model to the unphysical occurrence of a triple point  $T_t$  (equilibrium between a disordered phase of composition  $x$  and ordered phases of compositions  $X_1$  and  $X_2$ ) at very low temperatures, whereas more approximate solutions (i.e., using the cluster variation method) to the same Hamiltonian place  $T_t$  at higher temperatures [e.g., see Fig. 2(b), where  $D$ ,  $\gamma$ , and  $\beta$  coexist at  $T_t$ ], in better, but fortuitous agreement with experiment. We show that inclusion of elastic effects in the Hamiltonian must push  $T_t$  to finite temperatures even in the exact solution. At any composition  $x$ , where

$X_1 < x < X_2$ , let  $f_1$  and  $f_2$  be the fractions of the alloy disproportionating into  $X_1$  and  $X_2$  (where  $f_1X_1 + f_2X_2 = x$  and  $f_1 + f_2 = 1$ ). If one were to retain only the first term in Eq. (7), it must be greater or equal to  $f_1\varepsilon^{(1)} + f_2\varepsilon^{(2)}$ . When equal, all three phases could be at equilibrium at  $T=0$ , hence  $T_t=0$ . However, since the second term of Eq. (7) has a *negative* curvature, i.e.,

$$d^2G/dx^2 = - [B(x)/V_{eq}(x)](dV_{eq}/dx)^2 < 0,$$

one always has  $G(x) > f_1G(X_1) + f_2G(X_2)$ , a condition which forbids the three-phase equilibrium at  $T_t=0$ . Finally, we note that incorporation of elastic effects was recently shown<sup>13</sup> to produce a coexistence of miscibility gaps *and* ordering in the same phase diagram, as well as predict (metastably) ordered structures even if  $\Delta H^{(n)} > 0$ .

The ease of incorporating the elastic term  $G(x)$  into Ising-type Hamiltonians [Eq. (7)] and its simple evaluation from structural and elastic data promise to produce far more realistic descriptions of alloy phase diagrams<sup>13</sup> than hitherto possible with purely configurational Hamiltonians.

This work was supported in part by the Office of Energy Research, Materials Science Division, through Grant No. DE-AC02-77-CH00178.

\*Permanent address: University of São Paulo, São Paulo, Brazil.

†Permanent address: Laboratoire de Physique du Solide et Energie Solaire, Centre National de la Recherche Scientifique, 06560 Valbonne, France.

<sup>1</sup>W. B. Pearson, *The Crystal Chemistry and Physics of Metal Alloys* (Wiley, New York, 1972).

<sup>2</sup>L. S. Darken and R. W. Gurry, *Physical Chemistry of Metals* (McGraw-Hill, New York, 1953).

<sup>3</sup>A. R. Miedema, R. Boom, and F. R. deBoer, *J. Less-Common Met.* **40**, 283 (1975).

<sup>4</sup>A. F. Wells, *Structural Inorganic Chemistry* (Clarendon Univ. Press, Oxford, 1975).

<sup>5</sup>R. Hultgren, R. D. Desai, D. T. Hawkins, H. G. Gleiser, and K. K. Kelley, *Selected Values of the Thermodynamic Properties of Binary Alloys* (American Society for Metals, Cleveland, 1973).

<sup>6</sup>C. Domb, in *Phase Transition and Critical Phenomena*, edited by C. Domb and H. S. Green (Academic, London, 1974), Vol. 3, p. 357.

<sup>7</sup>D. De Fontain, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1979), Vol. 37, p. 73.

<sup>8</sup>C. M. van Baal, *Physica* **64**, 571 (1973).

<sup>9</sup>R. Kikuchi, J. M. Sanchez, D. De Fontain, and H. Yamauchi, *Acta Metall.* **28**, 651 (1980).

<sup>10</sup>D. F. Styer, M. K. Phani, and J. Lebowitz, *Phys. Rev. B* **34**,

3361 (1986).

<sup>11</sup>K. Binder, *Phys. Rev. Lett.* **45**, 811 (1980).

<sup>12</sup>G. P. Srivastava, J. L. Martins, and A. Zunger, *Phys. Rev. B* **31**, 2561 (1985).

<sup>13</sup>A. A. Mbaye, L. G. Ferreira, and A. Zunger, *Phys. Rev. Lett.* **58**, 49 (1987).

<sup>14</sup>R. Kikuchi, *J. Chem. Phys.* **60**, 1071 (1974).

<sup>15</sup>While it might be possible to fit a phase diagram using *ad hoc* composition-dependent chemical energies  $\varepsilon^{(n)}(x)$ , we find this to be artificial. The rigorous form of Eq. (7) is better motivated on general grounds.

<sup>16</sup>F. Ducastelle and F. Gautier, *J. Phys. F* **6**, 2039 (1976).

<sup>17</sup>We use  $V_n$  of 7.111, 8.294, 8.767, 9.506, and 10.213 cm<sup>3</sup>/mol and (Ref. 5)  $\Delta H^{(n)}$  of 0.0, -1.71, -2.10, -1.37, and 0.0 kcal/mol for  $n=0$  (Cu), 1, 2, 3, and 4 (Au), respectively. [Landolt-Börnstein, *New Series*, edited by K.-H. Hellwege (Springer-Verlag, Berlin, 1971), Vol. 6, p. 323; *ibid.* (1979), Vol. 11, pp. 9 and 13]. For  $B_n$  we use the observed values  $B_0=138$  GPa and  $B_4=171$  GPa, and fit the remaining  $B_n$ 's to the form  $\alpha V^\beta$  with  $\alpha=43.250789$  and  $\beta=0.5914625$ . This agrees to within 5% with the measured values for  $n=1$  and 2. To obtain critical temperatures comparable to those of the more precise Monte Carlo method (Ref. 10), we reduced all energies ( $\Delta H^{(n)}$  and  $G$ ) by the factor  $0.967/1.026=0.943$ , representing the ratio of Monte Carlo to CVM critical temperatures for the simple Ising model.