PHYSICAL REVIEW B VOLUME 45, NUMBER 1 1 JANUARY 1992-I

Rapid Communications

Rapid Communications are intended for the accelerated publication of important new results and are therefore given priority treatment both in the editorial office and in production. A Rapid Communication in **Physical Review B** *should be no longer than 4 printed pages and must be accompanied by an abstract. Page proofs are sent to authors.*

Method for calculating alloy energetics

Guillermo Bozzolo
Analex Corporation, 3001 Aerospace Parkway, Brook Park, Ohio 44142-1003

John Ferrante
National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio 44135

John R. Smith
Physics Department, General Motors Research Laboratories, Warren, Michigan 48090-9055

(Received 29 July 1991)

A semiempirical method for the computation of alloy energies is introduced. It is based on the equivalent-crystal theory of defect-formation energies in elemental solids. The method is both simple and accurate. Heats of formation as a function of composition are computed for some binary alloys of Cu, Ni, Al, Ag, Pd, Pt, and Au using the heats of solution in the dilute limit as experimental input. The separation of heats into strain and chemical components helps in understanding the energetics. In addition, lattice-parameter contractions seen in solid solutions of Ag and Au are accurately predicted. Good agreement with experiment is obtained in all cases.

Recently, there has been substantial success in predicting the heats of formation of binary alloys both with first-principles and semiempirical methods.[1-7] There is still a good deal of progress to be made, however, in that experimental trends in the cohesive energy and heats of formation as a function of composition are often not accurately reproduced.

In this work, we propose a method for calculating heats of formation, cohesive energies, and lattice parameters as a function of concentration for binary alloys. We make use of equivalent-crystal theory (ECT),[8-10] a semiempirical approach to calculating the energetics of solids with defects that has successfully reproduced surface energies and surface relaxation in metals and semiconductors.

We seek to develop an approach that requires only information about pure metal properties and certain experimentally determined alloys properties. We build on the formulation of ECT by dividing the total binding energy of the alloy into a chemical energy and a strain or structural energy (see, e.g., Refs. 1 and 3). The strain energy associated with a given atom is computed as if all of its neighbors were of the same atomic species. It arises from neighbor locations being different from in the elemental single-crystal environment. The remainder of the total energy is defined to be the chemical energy, which is due to some of an atom's neighbors being of a different atomic species.

We now proceed to outline the procedure for calculation of the heats of formation versus concentration for fcc binary alloys. We first apply the method to ordered alloy structures and then use the Connolly and Williams[11] procedure for relating the ordered compounds to the disordered ones.

The contribution to the heat of formation of an A atom in the alloy A-B, is written[2] as a sum of a distortion or strain energy ε_s, and a chemical energy ε_c:

$$\varepsilon_A = \varepsilon_s^{(A)} + \varepsilon_c^{(A)} . \tag{1}$$

We approximate the strain energy associated with atom A by replacing all of its B neighbors by A atoms at the same sites. This "strain" may involve defect-formation energies such as surface energies, vacancy-formation energies, etc. It is obtained from a standard defect energy calculation of ECT as applied to elemental solids.[10] The strain energy becomes

$$\varepsilon_s = \Delta E F^* [a_s^* (i)] , \tag{2}$$

where $F^*[a_s^*] = 1 - [1 + a_s^*] e^{-a_s^*}$ and $a_s^* = (a_s - a_e)/l$. a_e is the equilibrium lattice parameter, ΔE is the cohesive energy, and l is a scaling length[10] for the pure species A or B. Finally, a_s is the lattice parameter of the equivalent crystal. For this simple case of crystalline alloys, a_s is the actual alloy lattice parameter. There is an Eq. (2) for each atom. The remaining part of ε_A we call the chemical energy $\varepsilon_c^{(A)}$. This is the energy change due to some neighbors of A atoms being B atoms rather than A atoms, or vice versa.

We have found that the chemical energy ε_c can be accurately computed as follows:

$$\varepsilon_c = \gamma \Delta E e^{-a_s^*} F^*[a_c^*] \,, \tag{3}$$

where $\gamma = 1$ for $a_c^* \geq 0$, $\gamma = -1$ for $a_c^* < 0$, and a_s^* is the argument of the strain energy term, Eq. (2). The argument a_c^* for an A atom is determined from the solution R_1 of the following equation:

$$N_1 R_1^{p_A} e^{-\alpha_A R_1} - \sum_i R_A^{p_A} e^{-\alpha_i R_A} = 0 \,, \tag{4}$$

where $\alpha_i = \alpha_A$ if the neighbor is an A atom and $\alpha_i = \alpha_A + \Delta_{BA}$ if the neighbor is a B atom, R_A is the ground-state nearest-neighbor distance for the elemental A crystal, $p_A = 2n_A - 2$, and n_A is the principal quantum number for atom A. Equations exactly analogous to Eqs. (1)–(4) apply to the computation of ε_B. Equation (3) is referenced to the case where all atoms are identical. Equations (3)–(4) determine the excitation energy of an elemental solid due to atomic substitutions with no distortion or strain. They are therefore complementary to the strain energy Eq. (2). As in ECT, we choose to vary the lattice constant of the crystal being perturbed, and denote the equivalent crystal as that crystal whose nearest-neighbor distance R_1 is such that the perturbation energy terms [Eq. (4)] are equal to zero. Note that the strain and chemical energies are coupled nonlinearly. The coupling function $e^{-a_s^*}$ guarantees that the chemical energy will go to zero exponentially with increase in interatomic spacings, as it should. Finally, the constants Δ_{AB} and Δ_{BA} are determined so the corresponding predicted heats of solution agree with the experimental values.[12,13]

Strictly speaking, the ECT (Refs. 8–10) only applies to defect energies in elemental solids, while here we attempt to compute a chemical energy associated with the change from an elemental solid to an alloy. Nevertheless, in formulating Eqs. (3) and (4), we followed the perturbative spirit of the ECT by assuming that a significant term in the chemical energy, given by the left-hand side of Eq. (4), is of the same form as the principal perturbation term of ECT. We introduce the interaction between different species in the right-hand side of Eq. (4) by means of the parameters Δ_{AB} and Δ_{BA} which are fixed by alloy properties. The form of Eq. (3) was chosen to satisfy a few simple conditions. From Eq. (4), the lattice constant a_c^* is zero when all neighbors of an atom are atoms of its same species, i.e., when there is no chemical change. Thus $\varepsilon_c(0) = 0$. Second, there must be a provision for $\varepsilon_c(a_c^*)$ to range to values greater than and less than zero, since ΔH, the heat of formation, covers that range (see Fig. 1). Finally, $\varepsilon_c(a_c^*)$ is a function which is everywhere continuous and has continuous first derivatives. The function in Eq. (3) satisfies all these conditions and has some similarity to Eq. (2) through the common use of the universal form $F^*[a^*]$.

We have now outlined a procedure constructed entirely in terms of pure metal components plus two additional parameters, Δ_{AB} and Δ_{BA}, which must be fixed from alloy properties. We now proceed to show how these two parameters can be specified by use of the Connolly-Williams approach and experimental values of the heat of solution. We first compute the heat of formation of the ordered compounds $A_m B_{4-m}$ within the tetrahedron approximation.[11] Following the method of Ref. 11, the heat of formation of the disordered phase as a function of composition is computed. The excess internal energy per atom for the ordered alloy is given by

$$\Delta E_m(r) = E_m(r) - \tfrac{1}{4} m E_4(R_A) - (1 - \tfrac{1}{4} m) E_0(R_B) \,, \tag{5}$$

where E_4 and E_0 are the cohesive energies of the pure materials, and $E_m(r) \equiv (m/4)\varepsilon_A(r) + (1 - m/4)\varepsilon_B(r)$ is the binding-energy curve for the alloy. Following Connolly-Williams,[11] the excess energy for the disordered compound $A_x B_{1-x}$ is given by

$$\Delta E_D(r,x) = \sum_m c_m(x) \Delta E_m(r) \,, \tag{6}$$

where $c_m(x) = \binom{4}{m} x^m (1-x)^{4-m}$. ΔH is given by the minimum value of $\Delta E_D(r,x)$ for each value of x. The heats of solution $E_{BA} = \{\partial \Delta H / \partial x\}_0$ and $E_{AB} = -\{\partial \Delta H / \partial x\}_1$ are then $E_{BA} = \Delta E_{m=3}(R_A)$ and $E_{AB} = \Delta E_{m=1}(R_B)$. We then solve this system of equations, subject to the minimization constraint of $\Delta E_D(r,x)$, for the values of Δ_{BA} and Δ_{AB} which reproduce the experimental heats of solution.[13]

Note that the amount of effort to apply Eqs. (1)–(6) is trivial. In fact, once Δ_{AB} and Δ_{BA} are determined, one can actually solve for alloy heats of formation with a hand calculator if desired. Figure 1 shows the results of this procedure for predicting the heats of formation versus concentration curves for some of the compounds of Cu, Ni, Al, Ag, Pd, Pt, and Au. Note that in all cases there is both qualitative and quantitative agreement with experiment. We further note that the ΔH are computed from differences of numbers which are typically 1 or 2 orders of magnitude larger than ΔH and thus the degree of agreement between experiment and theory is perhaps surprising.

In general, these curves result from a competition between chemical and strain energies. For all of the alloys exhibited except for Cu-Ni and Ag-Al the chemical-energy contributions to ΔH of the ordered alloys were negative. That is, the chemical energy was attractive, promoting mixing of the elements. This was even true for Cu_3Ni and Ag_3Al. On the other hand, the strain energies were positive for all the alloys, as defined. So strain effects promote segregation and chemical effects typically promote mixing. For Ag-Cu, the strain energy dominates presumably due to the significant difference in lattice constants. For the noble metals Ag-Au the two lattice constants are close and the chemical energies dominate. Ni-Pd and Ag-Al exhibit similar behavior, but for different reasons. For both of these alloys, ΔH is small and actually changes sign with x. Lattice constants for Al and Ag are close, leading to quite small strain energies. Chemical energies are also relatively small, however, and are negative for Ag_3Al but positive for AgAl and $AgAl_3$. This change in sign of the chemical energies is presumably the source of the change in sign of ΔH for Ag-Al. The lattice constants of Ni and Pd are not as close, so there is a significant strain energy. Chemical energies are also relatively strong for Ni-Pd, and, in fact, tend to cancel the strain energy in NiPd. Although lattice constants of Ni

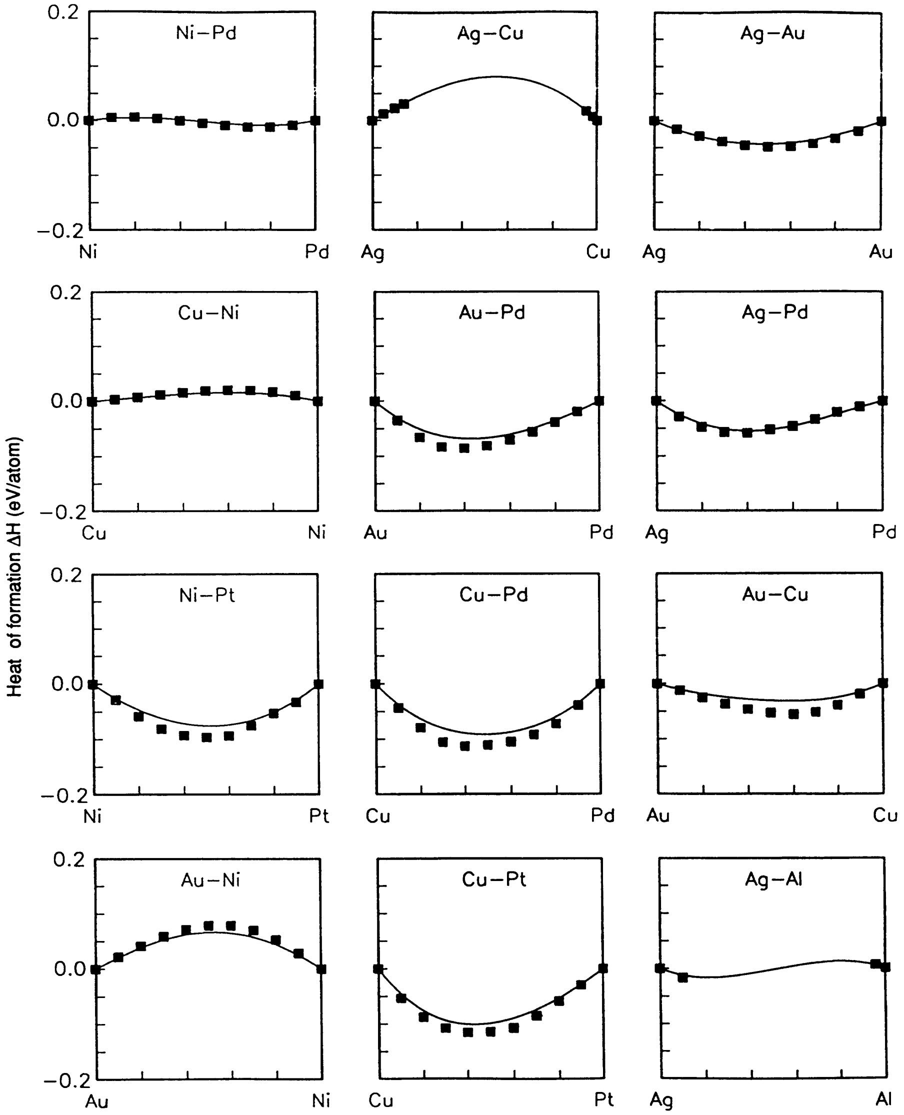

FIG. 1. Comparison between the heat of formation as a function of concentration for different alloys: the solid curve indicates the results obtained in this work and the symbols indicate the experimental values.

and Cu are relatively close, leading to relatively weak strain energies, chemical energies are also weak and, in fact, are positive (repulsive) for CuNi and $CuNi_3$. The result is a weakly positive ΔH for Ni-Cu, suggesting segregation. For the rest of the alloys, the chemical energy tends to dominate the strain energy, suggesting mixing. The only other alloy exhibited where the strain energy is not significant is Al-Au. That, coupled with the relatively large chemical energies, explains why ΔH can be relatively large for Al-Au.

As suggested in the introduction, it is difficult to accurately predict the dependence of the heat of formation on concentration as we have. This difficulty is perhaps emphasized in the case of Ni-Pd, where different calculations,[5] including the embedded-atom method[5,14] and the method of Miedema and de Chatel[7] disagree on the sign of the heat of formation as well as the behavior in the dilute limit. While the method of Miedema and de Chatel[7] provides reasonably accurate results, the EAM (Ref. 5)

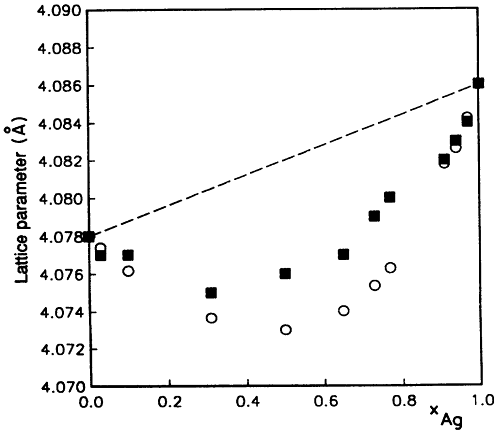

FIG. 2. Comparison between the results obtained in this work (circles) and experimental values (solid squares) for the lattice parameters of Ag-Au alloys as a function of composition. Vegard's law results are also shown (dashed line).

results are rather inaccurate. There are other versions of EAM for alloys. Johnson[4] employed an EAM method to compute heats of formation, and he also found that Pd alloy predictions appeared to be rather inaccurate.

The predictive power of our formalism is further emphasized in our estimates of the lattice parameters of binary alloys, for which there is no experimental input in this method. Figure 2 shows the lattice parameters of the solid solutions of Ag and Au, which show a peculiar behavior given by an experimentally seen contraction with respect to the pure metals.[15] The contraction is due to an attractive chemical energy dominating a weak strain energy. The strain energy is weak because of small lattice mismatch. The agreement with experiment again demonstrates the sensitivity of this approach.

In conclusion, we have developed a semiempirical procedure for the concentration dependence of the heats of formation and lattice parameters of binary alloys. This method accurately predicts the experimental behavior qualitatively and quantitatively.

---

[1] S.-H. Wei, A. A. Mbaye, L. G. Ferreira, and Alex Zunger, Phys. Rev. B **36**, 4163 (1987).

[2] K. Terakura, T. Oguchi, T. Mohri, and K. Watanabe, Phys. Rev. B **35**, 2169 (1987).

[3] S. Takizawa, K. Terakura, and T. Mohri, Phys. Rev. B **39**, 5792 (1989).

[4] R. A. Johnson, Phys. Rev. B **39**, 12554 (1989).

[5] P. R. Maarleveld, P. B. Kaars, A. W. Weeber, and H. Bakker, Physica B **142**, 328 (1986), and references therein.

[6] G. J. Ackland and V. Vitek, Phys. Rev. B **41**, 10324 (1990).

[7] A. R. Miedema and P. F. de Chatel, *Theory of Alloy Phase Formation* (AIME, New York, 1980), p. 344.

[8] John R. Smith and Amitava Banerjea, Phys. Rev. Lett. **59**, 2451 (1987). See also J. R. Smith, T. A. Perry, and A. Banerjea, in *Atomistic Simulation of Materials Beyond Pair Potentials,* edited by V. Vitek and D. J. Srolovitz (Plenum, New York, 1989), p. 279.

[9] John R. Smith, Guillermo Bozzolo, Amitava Banerjea, and John Ferrante, Phys. Rev. Lett. **63**, 1269 (1989). See also John R. Smith and Amitava Banerjea, Phys. Rev. B **37**, 10411 (1988).

[10] John R. Smith, Tom Perry, Amitava Banerjea, John Ferrante, and Guillermo Bozzolo, Phys. Rev. B **44**, 6444 (1991).

[11] J. W. D. Connolly and A. R. Williams, Phys. Rev. B **27**, 5169 (1983).

[12] As Ackland and Vitek point out (Ref. 6), there are problems due to limited experimental data in the input for the semiempirical calculations in that high-temperature data is used as input for zero-temperature calculations, and heats of solution (the slope of the heats of formation curve at zero concentration of solute) are estimated from high concentrations of solute (~0.1) where the approximation of a single dilute atom breaks down.

[13] R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, *Selected Values of the Thermodynamic Properties of Binary Alloys* (Wiley, New York, 1963).

[14] S. M. Foiles, M. I. Baskes, and M. S. Daw, Phys. Rev. B **33**, 7983 (1986).

[15] W. B. Pearson, *Handbook of Lattice Spacings and Structures of Metals* (Pergamon, New York, 1967).