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Density-functional theory applied to phase transformations in transition-metal alloys

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A new theory of cluster expansions has been derived, which allows one, for the first time, to estimate the energy of a disordered system from first principles. The cluster variables are derived from a series of density-functional calculations on ordered compounds. The disordering temperatures calculated with this theory show the correct trends for binary alloys of $4d$ transition metals, and are in excellent agreement with the experimental phase diagrams in most cases.

It is by now now well accepted that the density-functional theory[1–3] provides an accurate description of the electronic structure of both small[4,5] and extended[6,7] systems. In particular, the application of this theory to metallic alloys[8] has shown that it is capable of predicting their formation energies with errors on the order of 0.01 eV/atom. However, most of the successful descriptions of bonding in extended systems have been for periodic crystals with a small number of atoms per unit cell. Despite the success of the coherent-potential approximation and related methods[9] in describing electronic densities of states of nonperiodic solids, its application to the formation energies of alloys is quite difficult.[10] The lack of order in nonperiodic solids, as in solid solutions (chemical disorder), or in amorphous solids (structural disorder), makes it difficult to solve the density-functional equations in a systematic way, even though one has a strong degree of confidence in its applicability to such systems.

The point of this paper is to provide an interface between the first-principles theory for ordered compounds and a description of more general systems. This is accomplished through the use of the cluster expansion of Sanchez and de Fontaine.[11] This expansion allows not only the possibility of describing disordered solids, but also the introduction of temperature (through the methods of statistical mechanics) and the subsequent description of phase transformations. The feasibility of this approach is due to the computational efficiency of the augmented spherical wave method,[12] as well as its accuracy in the description of chemical trends in metallic alloys.

For a binary alloy consisting of atoms A and B on a lattice of fixed symmetry, the total energy can be expressed as[11]

$$E(r)=\sum_n v_n(r)\xi_n \ , \tag{1}$$

where $v_n(r)$ are many-body interaction potentials, the ξ_n are multisite correlation functions defined on an nth order cluster, r is a lattice parameter, and the sum is over all cluster types on a fixed (i.e., coherent) lattice. The correlation functions can be written as

$$\xi_n=\frac{1}{N_n}\sum_{\{p_1\}}\sigma_{p_1}\sigma_{p_2}\cdots\sigma_{p_n} \ , \tag{2}$$

where σ_p is a spinlike variable which takes the values $+1$ or -1 depending on whether the lattice point p is occupied by an A or a B atom. The sum is over all nth-order clusters of a given type in the lattice. N_n is the total number of such clusters.

As an example, we consider the case of a face-centered cubic lattice. If we assume that only clusters consisting entirely of nearest neighbors are important, then the cluster sum of Eq. (1) truncates at the fourth order. Therefore, there are five interaction potentials, v_n, $n=0,4$, to be determined from the density-functional calculations. We choose the five ordered structures of Table I for this determination.

By use of the correlation functions of Table I, the total-energy curves for the ordered compounds can be inverted, as follows, to give the interaction poten-

TABLE I. Cluster correlation functions for five structures on an fcc lattice. ξ_0 represents the structure-independent term, $\xi_1=x_A-x_B$ is the "point" correlation function, and ξ_2, ξ_3, and ξ_4 correspond to NN pairs, NN triangles, and NN tetrahedra, respectively, where NN means nearest neighbor.

		Correlation functions				
Formula	Structure	ξ_0	ξ_1	ξ_2	ξ_3	ξ_4
A	fcc	1	1	1	1	1
A_3B	$L1_2$	1	$\frac{1}{2}$	0	$-\frac{1}{2}$	-1
AB	$L1_0$	1	0	$-\frac{1}{3}$	0	1
AB_3	$L1_2$	1	$-\frac{1}{2}$	0	$\frac{1}{2}$	-1
B	fcc	1	-1	1	-1	1

tials

$$v_n(r) = \sum_{m=0}^{4} \xi_{n,m}^{-1} E_m(r) \quad , \tag{3}$$

where the index m denumerates the structures of Table I, and E_m are the total energies determined from density-functional theory. In the cases we have considered, it appears that the cluster expansion is rapidly convergent, i.e., $|v_4| \lesssim |v_3| \lesssim |v_2|$.

A significant difference between the interaction potentials given by Eq. (3), and those normally used[11] is that ours are functions of the lattice parameter. This implies an effective concentration dependence, whereas v_n are usually assumed to be concentration independent. This is an important distinction, since if the v_n are constant, there is a simple relation between them and the compound heats of formation. For example, this quantity for the $L1_0$ structure would be just $\Delta H(L1_0) = -4v_2/3$, as can be seen from Eq. (1) and Table I, whereas there is a more complicated relationship involving all of the v_n when they are r dependent. Therefore a constant v_2 is always positive when an ordered compound forms, i.e., $\Delta H < 0$, whereas there is no such connection in the general case. Also, the significance of constant v_n is that they describe an nth-order dependence of E on concentration, i.e., v_2 alone would give a parabolic dependence, v_3 introduces a third-order asymmetry, and v_4 is a fourth-order term. This concentration dependence remains in the present formulation, but there are additional terms dependent on derivatives of v_n.

There is a connection which can be made between these interaction potentials and a many-body expansion. For example, for the truncated series considered here, v_4 can be considered to be dependent on a combination of four-body potentials:

$$v_4 \propto (\phi_{AAAA} - 4\phi_{AAAB} + 6\phi_{AABB} - 4\phi_{ABBB} + \phi_{BBBB}) \quad ,$$

where ϕ_{AAAA} is a four-body interaction of four A atoms at the corners of a regular nearest-neighbor tetrahedron, etc. Similarly, v_3 is a combination of three- and four-body interactions, and so on. (See Ref. 11 for details.)

For a random distribution of A and B atoms, the correlation functions reduce to

$$\xi_{n,D} = (x_A - x_B)^n \quad , \tag{4}$$

where x_i, $i = A,B$, are the relative concentrations of A and B atoms. Using the interaction potentials and the random correlations of Eq. (4), we can now calculate the total energies of the disordered state of a binary alloy,[13] $E_D(r) = \sum_{n=0}^{4} v_n(r)\xi_{n,D}$. In order to estimate T_D, the disordering temperature, we assume a mean-field value for the entropy of the disordered state[14]:

$$S_D = -k(x_A \ln x_A + x_B \ln x_B) \quad , \tag{5}$$

where k is Boltzmann's constant. This expression, of course, represents the entropy of a *random* distribution of A and B atoms. If partial order is present, a more accurate equation must be used. A useful and accurate representation is provided by the Kikuchi approximation[15–17] which expresses S_D in terms of the cluster probabilities. It should be noted that Eq. (5) represents only the *entropy of mixing*. We neglect the vibrational, electronic, and magnetic contributions to the entropy.

At a particular concentration $x_A = 1 - x_B$, let ΔH_O be the heat of formation of the ordered state and ΔH_D that of the disordered state. ΔH_i, $i = O,D$ represent the total energies of the respective states relative to the segregated limit. We distinguish three basic types of phase diagrams, dependent on the relative sign of ΔH_O and ΔH_D, and three subtypes, dependent on their relative magnitude. These are shown schematically in Fig. 1.

We now estimate the disordering temperature by

$$T_D \sim \frac{\Delta H_D}{S_D} \quad , \quad \text{type I} \; ; \tag{6a}$$

$$T_D \sim \frac{(\Delta H_D - \Delta H_O)}{S_D} \quad , \quad \text{type II} \; ; \tag{6b}$$

$$T_D = 0 \quad , \quad \text{type III} \; . \tag{6c}$$

These estimates for T_D are, of course, quite approximate. Exact calculations are not available, even for the simplest case, i.e., $v_3 = v_4 = 0$, which is equivalent to a three-dimensional Ising model in a nonzero field. The interaction is ferromagnetic $(v_2 < 0)$ for type I,

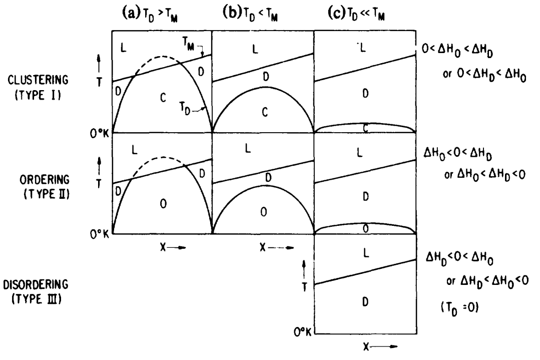

FIG. 1. Schematic phase diagrams for the three basic types. x is the concentration $(= x_B)$, T is the absolute temperature, T_D is the disordering temperature, and T_M is the experimental melting point. L denotes the liquid phase, C means clustering (phase segregation), D is for disordering (solid solutions), and O is a region where ordered compounds occur. In order to compare with the experimental phase diagrams, we distinguish among three subtypes: (a) where $T_D > T_M$ for most concentrations; (b) where $T_D \lesssim T_M$; and (c) where $T_D \ll T_M$. We note that types I(c), II(c), and III will in most cases be experimentally indistinguishable.

and antiferromagnetic ($v_2 > 0$) for type II. The special case of a type I compound with $x_A = x_B = \frac{1}{2}$ is known quite well from high-temperature expansions[18] and Monte Carlo calculations.[19] The antiferromagnetic case is known approximately from Monte Carlo calculations.[20]

By comparison with the more accurate calculations, it turns out (see Ref. 21) that the linear approximation using Eqs. (5) and (6) results in disordering temperatures which are too low for type I, and too high for type II (at least, for the nearest-neighbor pair interaction model). The approximation is slightly more accurate than mean-field theory, and gives qualitatively correct trends. For example, it gives approximately the same dependence of T_D on the ratio v_4/v_2 as found in the Monte Carlo calculations of Ref. 19. The results could probably be improved by the use of the cluster variation method.

Calculations have been performed for all binary combinations of the 4d transition metals, i.e., from Y ($Z = 39$) to Pd ($Z = 46$). The resulting phase diagram types, both theoretical and experimental, are shown in Fig. 2. We find that the interaction potentials, v_n, $n = 2, 4$, are quite small when there is a small mismatch between *d*-band centers, e.g., RuRh, and is large when the *d* bands are far apart, e.g., YPd. If the *d* bands are filled, for example, for CuAg (not shown in Fig. 2), one finds that v_3 and v_4 are very small, so that a pair-potential model would be quite appropriate. However, this is *not* the case for most transition-metal alloys, for which the *d* bands are partially occupied, and directional bonding becomes important.

As can be seen from Fig. 2, there is a general tendency toward ordering in the center of the series, and clustering at the extremes. Disordering occurs at the bottom boundary between them, with a greater tendency toward disorder at the left (small Δz). With a few exceptions, the theory presented here reproduces these trends. In particular, the theoretical type is the same as the experimental for 16 of the 28 cases, and shows partial disagreement for the other 12. In 5 of the disagreements, there is considerable doubt as to accuracy of the experimental data.

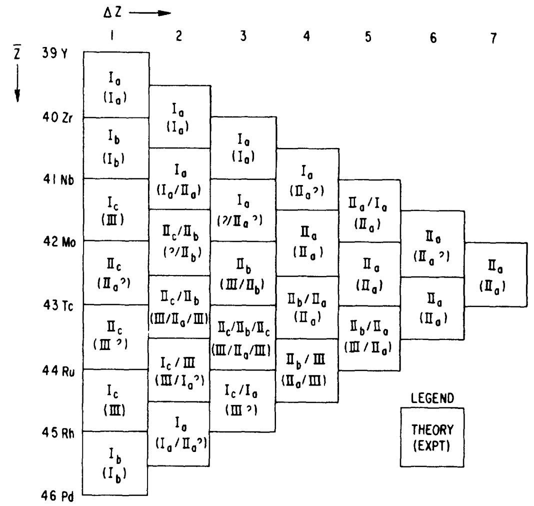

FIG. 2. Plot of phase diagram types for the 4*d* transition series, according to the classification of Fig. 1. The horizontal coordinate is Δz, the difference between the atomic numbers of the constituents, and the vertical coordinate $\bar{z}$ is their average. The upper type is that corresponding to the present calculations. The lower (in parentheses) is the experimental type as published in Ref. 22. The notation I/II means that the alloy is type I at the left of the phase diagram (smaller *Z*) and type II to the right, etc. (?) indicates incomplete (or questionable) experimental data. Note that types I_c, II_c, and III are experimentally indistinguishable.

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