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Abstract

We introduce a new, approximate sum rule for determining bulk properties of multicomponent systems, in terms of the pure components properties. We apply this expression for the study of lattice parameters, cohesive energies and bulk moduli of binary alloys. The correct experimental trends (i.e., departure from average values) are predicted in all cases.

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In this paper we introduce a new expression for the direct calculation of equilibrium properties of alloys in terms of the pure components. From this new rule, which can be obtained as a particular case from the method for alloys energetics introduced recently by Bozzolo, Ferrante and Smith[1], we can simultaneously derive three separate expressions for obtaining the lattice parameter, cohesive energy and bulk modulus of alloys.

Consider an alloy of N different elements $A_{x_A} B_{x_B} ...$ where x_i denotes the concentration of the atomic species i. Let $E_C(x)$, $a(x)$ and $B(x)$ be the cohesive energy, lattice parameter and bulk modulus, respectively, of the alloy characterized by the concentrations $x : (x_A, x_B, ...)$. Then, our approximate expression for the binding energy as a function of concentration x and lattice parameter r, $E(x,r)$, in terms of the corresponding expressions for the pure elements is given by

$$E(x,r) = \sum_i x_i E_i(r) \tag{1}$$

As mentioned above, this expression, as well as its range of applicability, has a theoretical foundation in the recently proposed BFS[1] method. There is no formal derivation of this rule, but, in the framework of BFS, we can find an explanation for its origin and some idea about its validity and shortcomings. This will discussed at length elsewhere. Here, our goal is to provide three new approximate rules that would enable one to describe equilibrium alloy properties in terms of pure materials in a simple way. Although it is approximate, recent first-principles calculations closely follow the general behavior predicted by Eq. (1). Terakura et al[2] analyzed the phase stability of several binary alloys systems composed of Ni, Pd or Pt as one element and Cu, Ag and Au as the other. From their LDA band calculations they found that their predictions for the excess energy $\Delta E_m(r)$ for the ordered

alloy structures $A_m B_{4-m} (m = 0, ..., 4)$ admit a simple parametrization of the form

$$\Delta E_m(r) = \left(\frac{p_m}{r}\right)^{2n} - \left(\frac{q_m}{r}\right)^n + r_m \tag{2}$$

where the parameters p_m, q_m and r_m are listed in Ref. 2, with $n = 3.5$ and $m = 0, 4$

represent the pure elements.. The excess energy for the disordered alloy can be represented

by a similar functional form[3],

$$\Delta E_D(r, x) = \left(\frac{P_x}{r}\right)^{2n} - \left(\frac{Q_x}{r}\right)^n + R_x \tag{3}$$

with $P_x^{2n} = \sum_{m=0}^{4} c_m(x) p_m^{2n}$, $Q_x^n = \sum_{m=0}^{4} c_m(x) q_m^n$ and $R_x = \sum_{m=0}^{4} c_m(x) r_m$, where

$c_m(x) = \binom{4}{m} x^m (1 - x)^{4-m}$. If these results behaved according to Eq. (1), then a di-

rect consequence of this rule,

$$\Delta E_D(r, x = \frac{m}{4}) = \Delta E_m(r) \; ; \; m = 0, ..., 4 \tag{4}$$

would also have to be satisfied. In terms of the coefficients used in Ref. 2, this condition

can be written as set of simultaneous requirements on these coefficients:

$$P_{m/4}^{2n} = p_m^n \; , \; Q_{m/4}^n = q_m^n \; , \; R_{m/4} = r_m \; ; \; m = 1, 2, 3. \tag{5}$$

We show the results of this comparison in Table 1 for the Cu-Ag, Cu-Au and Ag-Au alloys,

where agreement in the two sides of Eq. (5) is a test of the sum rule. Although the

comparison is not exact (it's not supposed to be), the agreement is surprisingly good,

making the use of Eq. (1) a viable alternative to expressions[4] for obtaining alloy cohesive

energies, bulk moduli and lattice parameters, such as Vegard's law[5] for lattice parameters.

The application of Eq. (1) is greatly simplified by the fact that the binding energy

curve of a pure element i, $E_i(r)$, can be represented by a Rydberg function[6]

$$E_i(r) = -E_{C,i}(1 + a^*) e^{-a^*} \tag{6}$$

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with $a^* = q_i(r - a_i)/l_i$, where a_i is the equilibrium lattice parameter of species i and the scaling length l_i is related to the cohesive energy of the pure element $E_{C,i}$ and its bulk modulus B_i as $l_i^2 = E_{C,i}/12\pi q_i B_i$. q_i is the ratio between the equilibrium Wigner-Seitz radius and equilibrium lattice parameter of species i.

Although it is a well-known fact that the binding energy curve (including alloys) is of a universal nature[6,7], the functional form chosen to represent it is just one of many choices. If we used this functional form in Eq. (1), a representation of the alloys binding energy curve could only be achieved by a numerical fit to a Rydberg function. To avoid this complication, and in order to provide simple analytical expressions for approximate values of the static properties of the alloys, we expand the Rydberg function to second order on both sides of Eq. (1) thus obtaining a simple system of equations for $E_C(x)$, $B(x)$ and $a(x)$. The ensuing expressions for these quantities are

$$a(x) = \frac{< Qa^2B >}{< QaB >}, \tag{7}$$

$$B(x) = \frac{1}{Q_x} \frac{< QaB >^2}{< Qa^2B >}, \tag{8}$$

and

$$E(x) = < E > - < Qa^3B > + \frac{< Qa^2B >}{< QaB >} \tag{9}$$

where

$$< O > = \sum_i x_i O_i \tag{10}$$

and $Q_i = 12\pi q_i^3$.

If, for example, we focus our attention on binary alloys of elements with the same structure as the pure crystals, the $Q's$ cancel in Eqs.(7)-(9). Moreover, it is a simple exercise to examine these expressions for their departure from the corresponding average

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values $\Delta O(x) = <O_x> - <O>$ (for $O = a, B$ and E_C). The derivative at the origin of ΔO for each one of these quantities are

$$\left(\frac{d\Delta a(x)}{dx}\right)_{x_A=0} = (a_A - a_B)\frac{(a_A B_A - a_B B_B)}{a_B B_B}, \qquad (11)$$

$$\left(\frac{d\Delta B(x)}{dx}\right)_{x_A=0} = -\frac{B_A}{a_B^2}(a_A - a_B)^2 \qquad (12)$$

and

$$\left(\frac{d\Delta E_C(x)}{dx}\right)_{x_A=0} = -a_A B_A(a_A - a_B)^2. \qquad (13)$$

Similar expressions can be obtained for the limit $x_A = 1$. Eq.(11) allows for deviations above and below the average values, whereas Eqs. (12) and (13) predict cohesive energies and bulk moduli below the average values for all concentrations. For this simple case, the maximum deviation of the lattice parameter from the average value $<a>$ is given by

$$\Delta a_{max} = \frac{\delta \gamma \lambda}{(1 + \gamma)(e_A \gamma + e_B)} \qquad (14)$$

where $\delta = a_A - a_B$, $\lambda = a_A e_A - a_B e_B$, $e_i = a_i B_i$ and $\gamma^2 = e_B/e_A$. This maximum deviation occurs at $x_A = \frac{\gamma}{1+\gamma}$. Finally, it is straightforward to show that Vegard's law can be recovered as a particular case when $\gamma = 1$.

The predictions of the trends predicted by Eq. (11) were successfully tested against 34 binary alloys of fcc (Ag, Al, Au, Cu, γ-Fe, Ir, Ni, Pd, Pt), bcc (Cr, Cs, α-Fe, K, Li, Mo, Na, Nb, Rb, Ta, V, W) elements, as well as Si and Ge in their diamond and fcc phases for which complete experimental data of the solid solutions is available[8]. Similar results are found if other representations of the binding energy curves are used in our proposed rule (Eq. (1)).

The trends in Eq. (11) depend on a coupling between the lattice parameter and compressibility as might be expected intuitively. This result is a consequence of the fact that

in our expression (Eq. (1)) the binding energy of the pure materials determine the behavior of the alloys. However, the specific functional form depends on the choice adopted for representing the binding energy curve (in this case, a simple quadratic expansion of the Rydberg function). The simple example studied in this work predicts the correct trends in the slopes (Eq. (11)) of the deviation from the average values as well as the trends in the relative deviations for different alloys.

We have presented a new method for estimating the cohesive energy, lattice parameter and bulk modulus for alloys from pure element properties. The method has been successfully tested by comparisons with ab-initio calculations and trends in experimental data.

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System	m	$P_{m/4}$	p_m	$Q_{m/4}$	q_m	$R_{m/4}$	r_m
AgAu$_3$	1	8.46	8.45	11.37	11.35	1.98	1.96
AgAu	2	8.33	8.33	11.07	11.07	1.82	1.82
Ag$_3$Au	3	8.21	8.21	10.77	10.77	1.66	1.66
CuAg$_3$	1	7.84	7.82	10.11	10.08	1.51	1.50
CuAg	2	7.60	7.59	9.77	9.79	1.50	1.52
Cu$_3$Ag	3	7.34	7.32	9.42	9.41	1.46	1.47
CuAu$_3$	1	8.26	8.22	11.07	11.01	1.95	1.93
CuAu	2	7.91	7.88	10.45	10.45	1.77	1.79
Cu$_3$Au	3	7.52	7.47	9.78	9.75	1.59	1.59

Table 1: Comparison of the parameters (P,Q,R) and (p,q,r) as defined by Eqs. (2) and (3)

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