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Alloy models with the embedded-atom method

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A simple analytic nearest-neighbor embedded-atom-method model developed for monatomic fcc metals has been extended to study alloying. The two-body potential between different species of atoms is taken as a function of the two-body potentials for the pure metals with a unique form which yields alloy models with the same invariance to electron density transformations as monatomic models. With several approximations, all model parameters are given by experimentally measured physical quantities. The dilute-limit heats of solution for all binary alloys of Cu, Ag, Au, Ni, Pd, and Pt have been calculated, with generally good agreement with available experimental values except for Pd, for which the calculated values are uniformly too high. The qualitative relationships between the physical parameters of the solute and solvent and the heat of solution have been determined.

I. INTRODUCTION

Foiles *et al.*[1] have developed fcc alloy models based on the embedded-atom method (EAM) of atomistic computer modeling.[2] Numerical fitting is used to tabulate the necessary EAM functions in a manner similar to that used for their monatomic models.[2,3] The nature of EAM models for fcc monatomic metals has also been studied with an analytic nearest-neighbor model for fcc metals.[4] Although overly simplified for detailed defect calculations, this approach contains the basic physical character of the EAM and, for example, provides a useful mechanism for studying the functional dependence of the model on physical input parameters.[5] In the present report, the general requirements of EAM alloying models are discussed, a new form of alloy potential is derived, and the results of applying a slightly modified version of the simple analytic model to alloying are presented.

II. THEORY

The basic equations of the EAM,[2,3] in the notation used by Johnson,[4] are

$$E_t=\sum_i F(\rho_i)+\tfrac{1}{2}\sum_{i,j}{}' \phi(r_{ij}) , \qquad (1)$$

$$\rho_i=\sum_j{}' f(r_{ij}) , \qquad (2)$$

where E_t is the total internal energy, ρ_i is the electron density at atom i due to all other atoms, $f(r_{ij})$ is the electron density at atom i due to atom j as a function of the distance between them, r_{ij} is the separation distance between atoms i and j, $F(\rho_i)$ is the energy to embed atom i in an electron density ρ_i, and $\phi(r_{ij})$ is a two-body potential between atoms i and j. Although the physical interpretation is different, these equations are identical in form to those developed by Finnis and Sinclair[6] (FS). The EAM is based on density-functional theory using concepts given by Stott and Zaremba (quasiatom approach[7]) and Nørskov and Lang (effective-medium approach[8]), while the FS equations are based on the tight-binding method. Jacobsen *et al.* have recently derived general equations for crystalline energy as a function of the positions of the ions using effective-medium theory.[9] When approximations are applied to this formulation for the purpose of evaluation, the same underlying equations are obtained, while again the physical interpretation remains distinct.

For an alloy model, an embedding function $F(\rho)$ and an atomic electron-density function $f(r)$ must be specified for each atomic species, and a two-body potential $\phi(r)$ specified for each possible combination of atomic species. Since the electron density at any location is taken as a linear superposition of atomic electron densities, and since the embedding energy is assumed to be independent of the source of the electron density, these two functions can be taken directly from monatomic models. As discussed below, the electron-density functions are only determined to within a scaling factor from fitting to monatomic properties, so the relative scaling factor between elements must be specified for an alloy model.

For a binary alloy with a- and b-type atoms, ϕ^{aa} and ϕ^{bb} are given by the monatomic models, and ϕ^{ab} and ϕ^{ba} are assumed to be equal. The alloy potential could be determined independent of the monatomic potentials if sufficient data were available, but the assumption is commonly made that it is a function of the monatomic potentials. For example, Foiles *et al.*[1] tested both geometric and arithmetic averages, and used geometric averages in their reported calculations.

A monatomic EAM model is invariant to a transformation in which a term linear in the electron density is added to or subtracted from the embedding function and an appropriate adjustment is made to the two-body potential[2-6,10] (see Appendix). Thus, the reported forms for monatomic EAM-model functions involve an arbitrary choice and, with transformation, models which appear to be very different are, in fact, found to be similar. A problem with using a geometric or arithmetic average is that the arbitrary choices in the monatomic models have a significant effect on the alloy potentials. Indeed, the geometric average is imaginary if one of the monatomic two-body potentials is negative and the other positive. This problem did not occur with the Sandia alloy calculations because their two-body potentials were always taken as positive.[1]

It has been suggested that all models with the EAM format be transformed to a normalized form in which the slope of the embedding function is zero at the equilibrium electron density.[11] In this case, the two-body potential becomes the effective two-body potential[2-6,10,11] that controls the energy change for any atomic configuration in which the electron density at atom sites is not significantly altered. The effective two-body potentials are negative in some range of distances, and so a geometric average cannot be used.

As shown in the Appendix, if the form

$$\phi^{ab}(r)=\frac{1}{2}\left[\frac{f^b(r)}{f^a(r)}\phi^{aa}(r)+\frac{f^a(r)}{f^b(r)}\phi^{bb}(r)\right] \tag{3}$$

is used for all alloy potentials, then alloy models are also invariant to transformations in the monatomic models from which they are derived, and this invariance holds for any number of different elements in an alloy. There is no physical requirement for this invariance, but it yields better results in the calculations reported below and has been successfully applied in some Si-Ge alloy calculations.[12] To avoid singularities, the cutoff distance for the electron-density function for a specific element must be equal to or greater than the cutoff distance for the two-body potential.

As pointed out by Ackland,[13] the Finnis-Sinclair model,[6] although mathematically equivalent to the EAM for monatomic calculations, is different for alloys. Unlike the atomic electron densities in the EAM, the hopping integrals in the FS model depend on the type of atom at each end of the interaction. Thus only the two functions f^a and f^b are required for EAM alloy calculations, while f^{aa}, f^{bb}, f^{ab}, and f^{ba} are necessary for FS alloy calculations.

III. HEATS OF SOLUTION

In the analytic model,[4] both the electron density and two-body potential were taken as decreasing exponential functions requiring two parameters each:

$$f(r)=f_e\exp[-\beta(r/r_e-1)] \ , \tag{4}$$

$$\phi(r)=\phi_e\exp[-\gamma(r/r_e-1)] \ . \tag{5}$$

The embedding function is determined by fitting the model to a universal equation of state[14] in the form of a Rydberg function, resulting in

$$F(\rho)=-E_c(1-\ln x)x-6\phi_e y \ , \tag{6}$$

where $x=(\rho/\rho_e)^{\alpha/\beta}$, $y=(\rho/\rho_e)^{\gamma/\beta}$, and $\alpha=3(\Omega B/E_c)^{1/2}$. The model parameters are determined from the lattice constant a or atomic volume Ω, the cohesive energy E_c, the unrelaxed vacancy-formation energy E_{UF}, the bulk modulus B, the Voigt-average shear modulus G, and the atomic electron density evaluated at the nearest-neighbor distance from quantum calculations. This last input is used to specify β, but uncertainty about the ionization state to use to approximate the solid electron density makes the result questionable. For a number of cases, β is near the value 6, so this was taken as a starting point for each element for fitting. Finally, the value of f_e is unspecified in a monatomic model: it cancels from all calculations. However, relative values of f_e for the different elements are required for alloy models, and so these ratios were also used for fitting.

Of the 30 possible heats of solution for binary alloys of the six fcc metals Cu, Ag, Au, Ni, Pd, and Pt, data for 22 are available experimentally,[15] which are the same data as those used by Foiles *et al.*[1] The dilute limit of the unrelaxed heat of solution for atom type b as an impurity or solute and atom type a as the host or solvent, for example, was calculated as follows.

(a) Remove host: $-F^a(\rho_e^a)-12\phi^{aa}(r_e^a)$.

(b) Add impurity: $+F^b(\rho_e^a)+12\phi^{ab}(r_e^a)$.

(c) Adjust neighbors: $-12F^a(\rho_e^a)+12F^a(\rho_e^a+\Delta\rho)$, $\Delta\rho=-f^a(r_e^a)+f^b(r_e^a)$.

(d) Adjust cohesive energy: $-E_c^a+E_c^b$.

Here, ρ_e^a is the equilibrium electron density at an atom site in a perfect crystal of a-type atoms and r_e^a is the equilibrium nearest-neighbor distance in this perfect crystal.

Numerical fitting techniques were used to match the 22 heats of solution by varying the β's and f_e's, and the overall fit to the data was reasonably good using the form in Eq. (3), while quite poor using arithmetic averaging. However, the results were not acceptable because the model parameters were not robust with respect to minor variations in the input data: including or eliminating certain heats of solution could cause large changes in the β's and f_e's.

From the analysis of numerous variations in input, a pattern did emerge which leads to a useful model. The two adjustable parameters for each metal are determined by the relationships $f_e=SE_c/\Omega$ and $\phi_e=E_c/6$, where S is an arbitrary scaling constant taken as 1 for convenience, and the second relation determines the β's. It is physically realistic for the electron density to be proportional to the cohesive energy and inversely proportional to the atomic volume, and the β's determined with this scheme are all near 6, as found from the atomic wave functions. The input physical quantities Ω, E_c, E_{UF}, ΩB, and ΩG and the model parameters f_e, ϕ_e, α, β, and γ are listed in Table I for all six metals.

The unrelaxed heats of solution for all combinations of the six fcc elements Cu, Ag, Au, Ni, Pd, and Pt are given in Table II, together with the available experimental data. The general agreement excluding the values involving Pd is illustrated in Fig. 1 and the data with Pd are shown in Fig. 2. The Pd results are seen to follow the same trend in agreement, but are uniformly too high.

TABLE I. The input parameters Ω, E_c, E_{UF}, ΩB, and ΩG, and the model parameters f_e, ϕ_e, α, β, and γ. Ω is in Å^3 and the other inputs are in eV. The dimensions of f_e cancel (i.e., it acts as a scaling factor), ϕ_e is in eV, and α, β, and γ are dimensionless. The input data are the same as that used by Foiles *et al.* (Ref. 1), except for E_{UF}. They list E_f, and the values they give for Ni, Pd, and Pt have been increased.

	Inputs					Model parameters				
Atom	Ω	E_c	E_{UF}	ΩB	ΩG	f_e	ϕ_e	α	β	γ
Cu	11.81	3.54	1.30	10.17	4.05	0.30	0.59	5.09	5.85	8.00
Ag	17.10	2.85	1.10	11.10	3.61	0.17	0.48	5.92	5.96	8.26
Au	16.98	3.93	0.90	17.70	3.29	0.23	0.65	6.37	6.67	8.20
Ni	10.90	4.45	1.70	12.28	6.45	0.41	0.74	4.98	6.41	8.86
Pd	14.72	3.91	1.54	17.92	4.99	0.27	0.65	6.42	5.91	8.23
Pt	15.06	5.77	1.60	26.60	6.12	0.38	0.95	6.44	6.69	8.57

The heats of solution calculated with the present analytic model are unrelaxed values, and relaxtion of the solvent atoms near the solute will give a decrease in energy. From the details of the relaxed alloy calculations of Foiles *et al.*,[1] it is found that the decrease in energy due to relaxation E_r is predominantly dependent on the size mismatch and can be approximated by the relation $E_r=[1.167(\Omega_i/\Omega_h-1)]^2$, with subscripts i and h indicating impurity and host, respectively. The fitting values are shown in Fig. 3, and the resultant heats of solution with this approximation for relaxation are shown in Fig. 4. Comparison to Fig. 1 indicates an overall improvement for binary alloys of the five metals included in these figures. Since all heats of solution involving Pd are too high, relaxation changes are in a direction to improve the agreement. The corrections are relatively small, however, because Pd is intermediate in size and therefore the improvement relative to Fig. 2 is minor and a replot is not warranted.

IV. DISCUSSION

Even with the simplicity of the present EAM model—nearest-neighbor interactions only and no adjustable parameters—the agreement shown in Fig. 1 indicates that it accounts for the basic physical character of alloying energies. To investigate the parameter dependence of the heats of solution, a "standard state" is defined by averaging each one of the five physical inputs over all six metals. These were used as the solvent inputs, and 243 (3^5) unrelaxed heats of solution were calculated by independently varying each parameter for the solute to be smaller, equal, and greater than that of the solvent. The process was repeated by varying the solvent instead, but this essentially gave no additional insight. The lattice constant was varied by ±5%, the cohesive and unrelaxed vacancy formation energies by ±25%, and the bulk and shear moduli by ±40%.

The details associated with the relationship between

TABLE II. Heats of solution for binary alloys of the six elements Cu, Ag, Au, Ni, Pd, and Pt. The results of the unrelaxed calculations are listed first, the values with the approximation for relaxation second, and the experimental values (Ref. 15), where available, are listed last. All energies are in eV.

	Host					
Impurity	Cu	Ag	Au	Ni	Pd	Pt
Cu		0.41	0.03	0.10	0.11	−0.21
		0.28	−0.10	0.09	0.06	−0.27
		0.25	−0.13	0.11	−0.39	−0.30
Ag	0.85		−0.07	1.95	0.32	0.64
	0.58		−0.07	1.51	0.28	0.62
	0.39		−0.16		−0.11	
Au	−0.03	−0.04		0.78	−0.06	0.59
	−0.29	−0.04		0.36	−0.09	0.57
	−0.19	−0.19			−0.20	
Ni	0.08	0.77	0.34		0.32	−0.11
	0.07	0.59	0.17		0.23	−0.21
	0.03		0.22		−0.09	−0.33
Pd	0.16	0.31	−0.01	0.72		−0.01
	0.08	0.28	−0.03	0.55		−0.01
	−0.44	−0.29	−0.36	0.06		
Pt	−0.32	0.67	0.47	−0.27	−0.04	
	−0.42	0.65	0.45	−0.47	−0.04	
	−0.53			−0.28		

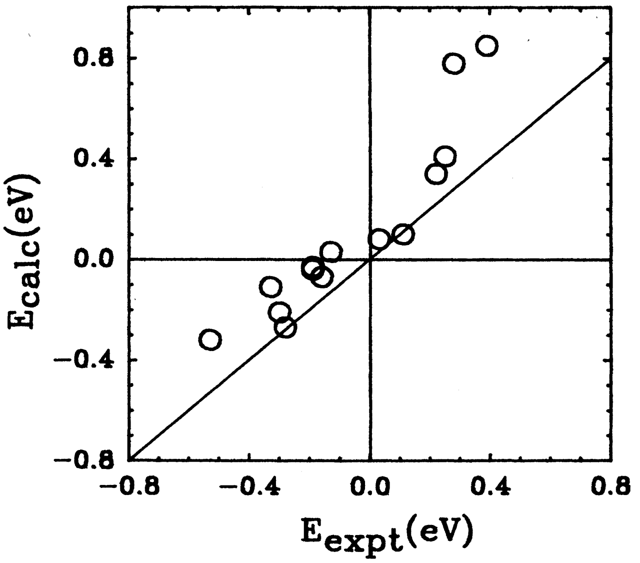

FIG. 1. The heats of solution with the unrelaxed calculation vs the available experimental values for the binary alloys of Cu, Ag, Au, Ni, and Pt, in eV. The diagonal line indicates perfect agreement.

the physical parameters of the solute and solvent and the heat of solution are complex. However, some general qualitative features of the pattern were found.

The lattice constant and the cohesive energy are the most significant parameters. If they are equal for the solute and solvent, the heat of solution $E_s = 0$, independent of the other parameters. If the size of the solute is

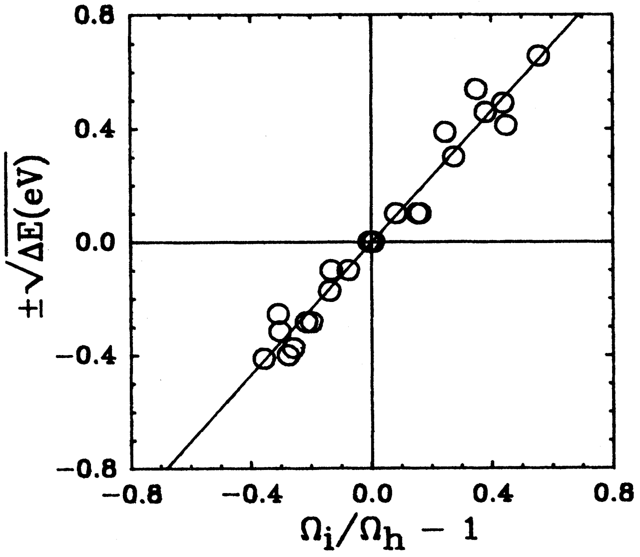

FIG. 3. The square root of the decrease in the heat of solution with relaxation for the binary alloys listed in Figs. 1 and 2 from the calculations of Foiles *et al.* (Ref. 1) as a function of $\Omega_i/\Omega_h - 1$, with subscripts *i* and *j* indicating impurity and host, respectively. The sign of the ordinate values is taken the same as the abscissa values to yield a straight line rather than a V-shaped line. The diagonal line is a least-squares fit to the data and was not constrained to pass through the origin.

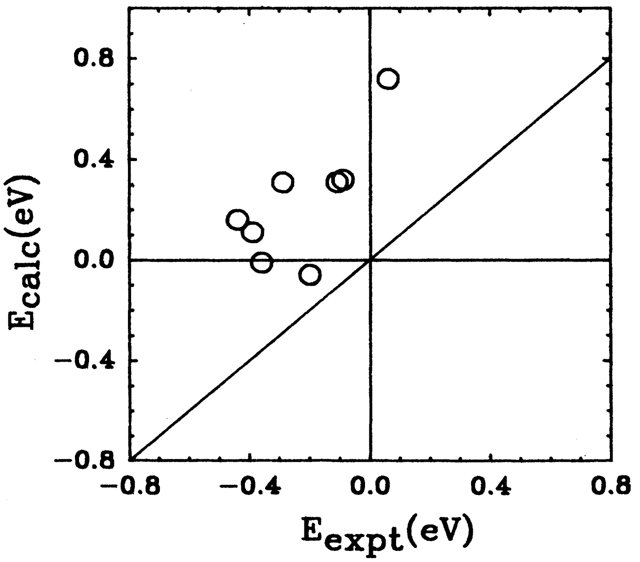

FIG. 2. The heats of solution with the unrelaxed calculation vs the available experimental values for binary alloys of Cu, Ag, Au, and Ni with Pd, in eV. The diagonal line indicates perfect agreement.

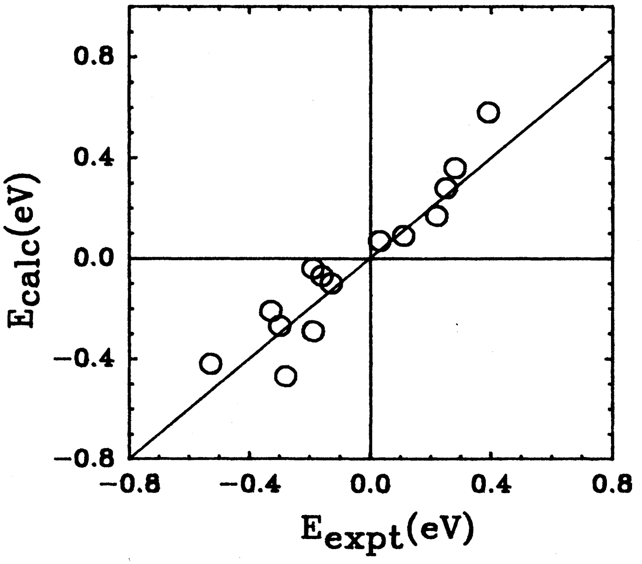

FIG. 4. The calculated results shown in Fig. 1 adjusted for relaxation with the approximation obtained by a linear least-squares fit to the data in Fig. 3. The diagonal line indicates perfect agreement.

larger while the cohesive energy is less than the corresponding quantities in the solvent, or vice versa, the heats of solution are positive, independent of the other parameters. However, if the size of the solute and its cohesive energy are both greater or both less than the corresponding solvent quantities, the heats of solution are negative or, in several cases, positive but small. The effect of the vacancy-formation energy of the solute is not very regular, but it contributes to a more negative heat of solution when the heat of solution is initially negative if it varies in the opposite sense as the cohesive energy. Increasing the bulk modulus of either the solute or the solvent increases the heat of solution, while increasing the shear modulus of either generally decreases the heat of solution.

For the sequence $\Omega:E_c:E_{\mathrm{UF}}:B:G$, and with $+$ or $-$ indicating that the solute values are greater or less than those of the solvent, respectively, and $*$ indicating either greater or less, the sequence $++--+$ gave the most negative E_s, with $++-**$ all being strongly negative. The next most negative series was $--+**$ with $--+-+$ being most negative. For large heats of solution, the series $+-*+-$ was greatest with $+-++-$ most positive, followed by the series $-+*+-$ with $-+++-$ most positive.

V. SUMMARY

An analytic nearest-neighbor EAM model with no adjustable parameters has been developed for fcc metals which uses the following physical input:

(a) equilibrium lattice constant,
(b) cohesive energy,
(c) unrelaxed vacancy-formation energy,
(d) bulk modulus, and
(e) Voigt-average shear modulus.

The electron-density functions [Eq. (4)] and the two-body potentials [Eq. (5)] are taken as exponentially decreasing functions, and a universal equation of state[14] is used to determine the embedding functions [Eq. (6)]. An analytic form for two-body alloy potentials as a function of the monatomic two-body potentials is given [Eq. (3)], which yields an alloy model which is independent of arbitrary electron-density transformations in the monatomic models.

The heats of solution for alloys of Cu, Ag, Au, Ni, and Pt calculated with this model are consistent with available experimental data, while calculated heats of solution involving Pd are too high. The most negative heats of solution occur when the lattice constant and the cohesive energy of the solvent vary from those of the solute with the same sign, and the most positive heats of solution occur when they vary with opposite signs. The effect of varying the vacancy-formation energy of the solute is irregular, but there is a tendency towards a decreasing heat of solution if it varies in the opposite sense as the cohesive energy. Increasing the bulk modulus of the solute or the solvent increases the heat of solution, while increasing either sheer modulus generally decreases the heat of solution.

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APPENDIX

As has been shown,[2-6,10] a monatomic EAM model is invariant to the transformation to the embedding function,

$$G(\rho)=F(\rho)+k\rho\ , \tag{A1}$$

and the concurrent transformation to the two-body potential,

$$\psi(r)=\phi(r)-2kf(r)\ , \tag{A2}$$

with k an arbitrary constant. This can be demonstrated as follows. Substituting these two equations in Eq. (1) gives

$$E_t=\sum_i G(\rho_i)-k\sum_i \rho_i+\tfrac{1}{2}\sum_{i,j}{}'\,\psi(r_{ij})+k\sum_{ij}{}'\,f(r_{ij})\ . \tag{A3}$$

The second and fourth terms on the right-hand side of Eq. (A3) cancel by use of Eq. (2), giving Eq. (1) in terms of the transformed functions. The constraint on alloy two-body potentials such that an alloy model is invariant to the above transformation to either or both of its constituents is developed in this appendix.

In a binary alloy of type-a and type-b atoms, Eq. (1) becomes

$$\begin{aligned}E_t=&\sum_{i^a}F^a(\rho_i)+\tfrac{1}{2}\sum_{i^a,j^a}\phi^{aa}(r_{ij})+\tfrac{1}{2}\sum_{i^a,j^b}\phi^{ab}(r_{ij})+\sum_{i^b}F^b(\rho_i)\\&+\tfrac{1}{2}\sum_{i^b,j^b}\phi^{bb}(r_{ij})+\tfrac{1}{2}\sum_{i^b,j^a}\phi^{ba}(r_{ij})\ ,\end{aligned} \tag{A4}$$

with i^a and i^b indicating summation over type-a and type-b atoms, respectively, and the transformed embedding functions and two-body potentials are given by

$$G^a(\rho)=F^a(\rho)+k^a\rho\ , \tag{A5a}$$

$$G^b(\rho)=F^b(\rho)+k^b\rho\ , \tag{A5b}$$

$$\psi^{aa}(r)=\phi^{aa}(r)-2k^af^a(r)\ , \tag{A6a}$$

$$\psi^{bb}(r)=\phi^{bb}(r)-2k^bf^b(r)\ . \tag{A6b}$$

Substituting Eqs. (A5) and (A6) into Eq. (A4) yields

$$\begin{aligned}E_t=&\sum_{i^a}G^a(\rho_i)-k^a\sum_{i^a}\rho_i+\sum_{i^b}G^b(\rho_i)-k^b\sum_{i^b}\rho_i\\&+\tfrac{1}{2}\sum_{i^a,j^a}\psi^{aa}(r_{ij})+k^a\sum_{i^a,j^a}{}'\,f^a(r_{ij})\\&+\tfrac{1}{2}\sum_{i^a,j^b}\phi^{ab}(r_{ij})+\tfrac{1}{2}\sum_{i^b,j^b}\psi^{bb}(r_{ij})\\&+k^b\sum_{i^b,j^b}{}'\,f^b(r_{ij})+\tfrac{1}{2}\sum_{i^b,j^a}\phi^{ba}(r_{ij})\ .\end{aligned} \tag{A7}$$

The condition for this to equal Eq. (A4) in terms of the transformed functions is

$$\psi^{ab}(r)=\phi^{ab}(r)-k^{a}f^{b}(r)-k^{b}f^{a}(r) , \tag{A8}$$

where the relations $\phi^{ab}(r)=\phi^{ba}(r)$, $\psi^{ab}(r)=\psi^{ba}(r)$, and

$$\sum_{i^a,j^b} f(r_{ij})=\sum_{i^b,j^a} f(r_{ij})$$

have been used. Indeed, Eq. (A8) applies as well if $a=b$.

If the alloy potentials are taken as linear functions of the monatomic potentials, i.e.,

$$\phi^{ab}(r)=M^{a}(r)\phi^{aa}(r)+M^{b}(r)\phi^{bb}(r) , \tag{A9a}$$

$$\psi^{ab}(r)=M^{a}(r)\psi^{aa}(r)+M^{b}(r)\psi^{bb}(r) , \tag{A9b}$$

then the transformation property, Eq. (A8), holds if

$$2k^{a}f^{a}(r)M^{a}(r)+2k^{b}f^{b}(r)M^{b}(r)-=k^{a}f^{a}(r)+k^{b}f^{b}(r) . \tag{A10}$$

For independent k^a and k^b, the *M*'s must be

$$M^{a}(r)=\frac{1}{2}\frac{f^{b}(r)}{f^{a}(r)} , \tag{A11a}$$

$$M^{b}(r)=\frac{1}{2}\frac{f^{a}(r)}{f^{b}(r)} , \tag{A11b}$$

which gives Eq. (3) in the main text. No functional relationship other than this linear form was found which could satisfy the condition for invariance and, by continuing the above development, Eq. (3) is found to maintain the invariance property for alloys with any number of constituents.

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