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Analytical EAM alloy models for FCC metals.

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Abstract

An analytic electron density function ρ(r) and pair potential function φ(r) have been developed for FCC metals from their experimental binary alloy data. Values of the electron densities, derived from exact dilute limit heat of solution, were used to determine the pair potentials via the equation of state of* Rose et al [3]. *The parameters in the fitting functions have been calculated and tabulated in this study.

Keywords*:* Analytic Electron Density, Embedded Atom Method, Semi-Empirical Methods.

1.0 Introduction

One advantage of the original EAM model as given by [1] is that the embedding energy and core-core potentials can be obtained by fitting experimental data. The method, though simple, can handle structures and energies of complex metal systems such as defects and even alloys. In their work, the embedding function, F(ρ), and pair potential φ(r) were tabulated as spline functions. In that form, the results are not analytical. Besides, the empirical fits determined the embedding energy and its first and second derivatives at equilibrium [2]. These difficulties inspired Johnson to propose an analytical EAM model that can give good fit at distances other than the equilibrium. His simple exponential functions for atomic electronic densities and pair potentials could not sufficiently predict dilute-limit heat of solution for FCC metal alloys of Cu, Ag, Au, Ni, Pd and Pt. The disagreement in calculated and published values for Pd in Ni was unacceptable. One other problem is that the model is quite sensitive to input variables namely; atomic volume, cohesive energy, unrelaxed vacancy formation energy, bulk modulus and the Voigt-average shear modulus.

Cai and Ye [2] proposed an analytical model that included a long-range force in order to try to resolve the above problems. They assumed an exponential form for atomic electronic density, f(r). The pair potential took the form for Rose *et al* function [3] and the embedding function followed that of Barnerjea and Smith [4]. The parameters involved were obtained from fitting basic properties of pure metals. Their model ensures that the embedding energy has a positive curvature. A further advantage is that the model can be extended to accommodate the angular force because it is analytic. However, it could not sufficiently resolve the heat of solution of Pd in Ni.

Because F(ρ),φ(r) and f(r) can take on different functional forms in the EAM framework many other workers have proposed various forms to address specific problems [5,6]. Johnson [7] has rightly observed that the details of interactions between physical parameters of an impurity atom of type-b in a host lattice of type-a atom and the dilute-limit heat of solution is complex. Two important considerations must be kept in mind in the search for a new analytic function. The new function must satisfy the equation of state and it must give a good fit for interatomic potentials at distances away from the equilibrium point.

Rather than propose analytic expressions for calculation of dilute-limit heat of solution, the approach in this work is the converse. Here, we obtain expressions for f(r) from the experimental values of heat of solution. The electron density derived therefrom is flexible enough to give an appropriate pair-potential through the equation of state, and also to exactly fit the published values of heats of solution. The derived analytic functions and the results are presented in what follows for Ni and Cu. A brief review of an analytic nearest neighbour FCC model for alloying, based on the EAM, is given in section 2. Further details than contained here can be found in [7]. Results obtained are discussed in section 3 and concluding remarks are made in section 4.

2.0 Theory

In the EAM framework for an alloy with a host lattice of type-a atoms containing impurity atoms of type-b atoms, two kinds of embedding functions $F^a(\rho)$, and $F^b(\rho)$ exist. Similarly, one could specify two kinds of atomic electron density functions $f^a(r_a)$ and $f^b(r_a)$. But for the pair-potential, there are three kinds, often referred to in literature as φ^{aa}, φ^{bb}, and φ^{ab}. φ^{aa} and φ^{bb} are the same as that of their respective monoatomic models but φ^{ab} is assumed to be a density weighted average of the monoatomic pair potentials given as [7].

$$\varphi^{ab} = \tfrac{1}{2}\left[\frac{f^b(r_a)}{f^a(r_a)}\varphi^{aa} + \frac{f^a(r_a)}{f^b(r_a)}\varphi^{bb}\right] \tag{2.1}$$

The EAM model is quite useful in the treatment of alloys and the basic equations for the total energy, E_{tot} is [Rose et al]

$$E_{tot} = F(\rho) + \Phi(r) \tag{2.2a}$$

where

$$\rho = \sum_i f(r_i) \tag{2.2b}$$

and

$$\Phi(r) = \tfrac{1}{2}\sum_{i\neq j} \varphi(r_{ij}) \tag{2.2c}$$

Thus, one could write for FCC alloys, within a nearest neighbour model, the expressions

$$\rho(r) = 12\, f(r) \tag{2.3}$$

and

$$\Phi(r) = 6\varphi(r) \tag{2.4}$$

An adequate analytical function for ρ(r) and φ(r) with sufficient flexibility is needed to calculate E_{tot}. Idiodi and Obodi [8] have proposed the following functional form for the atomic electron density

$$\rho(r) = \rho_0\left[1 + P_2 x^2 + P_3 x^3 + P_4 x^4 + P_5 x^5 + P_6 x^6 + P_7 x^7\right] \tag{2.5a}$$

where

$$x = \left(\frac{r}{r_0} - 1\right) \tag{2.5b}$$

and

$$\theta = \left(\frac{-3V_{11}}{\rho_0}\right) \tag{2.5c}$$

and $Pi_{(i=2,\ldots,5)}$ are constants to be determined. P_2 is not a free parameter and it is determined self consistently form

$$P_2 = \frac{1}{2}\left[r_0^2 \rho'' \frac{(r_0)}{\rho_0} - \theta^2 \right] \qquad (2.5d)$$

Equation (2.5a) involves several unknowns. The first is ρ_0, for which we assume the form $\rho_0 = \frac{1}{\Omega}$ instead of $\rho_0 = \frac{E_c}{\Omega}$ prescribed by Johnson [7]. It is sensible that electron density is inversely proportional to atomic volume. There are also the other constants P_i which must be determined from the exact dilute-limit heats of solution of a given impurity in several hosts. For example, consider Cu as an impurity in Ag, Au, Ni, Pt and Pd as hosts. The respective heats of solution are sufficient to determine the parameters P_2 - P_7 for the electron density function of Cu (ρ_{Cu}). Thus, one could in turn obtain ρ_{Ag}, ρ_{Ni}, ρ_{Pd}, ρ_{Au}, and ρ_{Pt}. Having determined the various electron densities, the embedding function F(ρ) is calculated. In this study, we have usedfor F(ρ) the following function

$$F(\rho) = AE_c\left(\frac{\rho}{\rho_0}\right)\ln\left(\frac{\rho}{\rho_0}\right) \qquad (2.6)$$

A is taken as unity, E_c is the cohesive energy of the atom, host or impurity. E_{tot} is calculated from the formula [3]

$$E_{tot} = -E_c\left[1+\alpha x\right]e^{-\alpha x} \qquad (2.7)$$

where $\alpha = 3\left(\frac{\Omega B}{E_c}\right)^{1/2}$, Ω is the atomic volume and B is the bulk modulus. From equation (2.2) and (2.4), φ(x) can then be determined using $\varphi(x) = \frac{1}{6}\left(E_{tot} - F(\rho)\right)$ (2.8).

3.0 Results

The properties of six FCC metals used in this work are presented in Table 1

Table 1: Properties of pure FCC metals. Lattice constants (in Å), Bulk modulus (in 10^{12}ergs/cm^3), and cohesive energies (in eV) are from Ref. [3] and Ref. [9], elastic constants (in 10^{12}ergs/cm^3) are from Ref. [10]

	Ni	***Cu***	***Pd***	***Pt***	***Au***	***Ag***
B [10^{12}ergs/cm^3]	1.876	1.420	1.955	2.884	1.803	1.087
C_{11} [10^{12}ergs/cm^3]	2.612	1.762	2.341	3.580	2.016	1.314
C_{12}[10^{12}ergs/cm^3]	1.508	1.249	1.761	2.536	1.697	0.973
C_{44} [10^{12}ergs/cm^3]	1.317	0.818	0.712	0.774	0.454	0.511
a (Å)	3.5100	3.6150	3.8900	3.9200	4.0700	4.0800
Ω(Å^3)	10.8109	11.8104	14.7160	15.0591	16.8548	16.9793
r_0(Å)	2.4819	2.5562	2.7506	2.7719	2.8779	2.8850
$\rho_0 = \rho(r_0)$[Å^{-3}]	0.0925	0.0847	0.0680	0.0664	0.0593	0.0589
$\rho'(r_0)$[ρ_0/Å]	-0.6512	-1.1182	-1.7055	-1.8226	-1.9388	-1.3374
$\rho''(r)$[ρ_0/Å^2]	-1.3770	-2.7966	-4.4663	-4.4863	-5.3582	-3.2096
E_c[eV]	4.4400	3.5000	3.9400	5.8400	3.7800	2.9600
A	1	1	1	1	1	1
F(ρ_0) [eV]	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
F'(ρ_0) [eV/ρ_0]	4.4400	3.5000	3.9400	5.8400	3.7800	2.9600
F"(ρ_0) [eV/ρ_0^2]	4.4400	3.5000	3.9400	5.8400	3.7800	2.9600
ϕ(eV)	-0.7400	-0.5833	-0.6567	-0.9733	-0.6300	-0.4933

	Ni	*Cu*	*Pd*	*Pt*	*Au*	*Ag*
ϕ'[eV/ Å]	0.4819	0.6523	1.1200	1.7740	1.2215	0.6598
ϕ'' [eV/ Å^2)	3.7876	3.3050	4.5827	6.4255	4.4426	2.7771
V_{11} [ρ_0]	-0.5388	0.9528	-1.5638	-1.6840	-1.8599	-1.2861
W_{11}[ρ_0]	-1.8450	-3.8431	-6.5702	-6.3696	-8.5129	-5.4015
W_{12}[ρ_0]	0.0475	-0.1713	-0.7855	-0.8761	-1.2787	-0.4673
α	5.0635	5.1145	6.4039	6.4632	6.7201	5.9180
θ	1.6163	2.8583	4.6914	5.0520	5.5798	3.8583

As a preliminary report, the values for Ni and Cu only are presented in Table 2. ρ_0 is essentially the equilibrium electron density. $\rho(x)$ is plotted in Figure 1 for Cu and Ni to show the variation around the equilibrium point (r_0).

Table 2: Calculated coefficients P_i for fitting electron density.

	Ni	*Cu*
P_2	-4.72E+01	-1.12E+02
P_3	-4.00E+03	0.00E+00
P_4	1.59E+05	8.50E+04
P_5	-2.17E+06	-2.07E+06
P_6	1.22E+07	2.00E+07
P_7	-2.43E+07	-6.72E+07

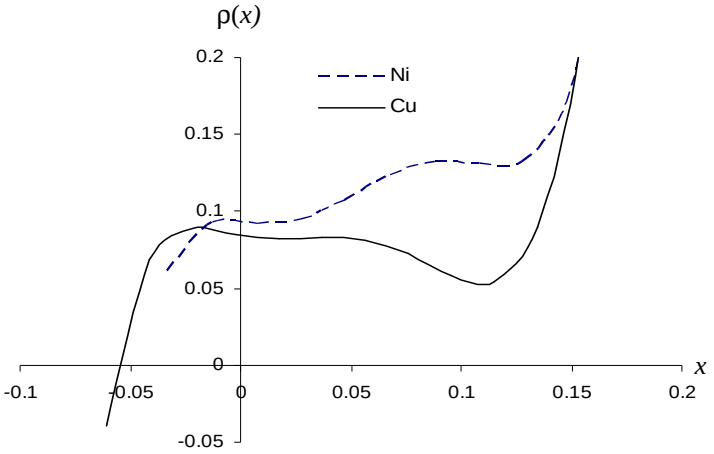


Figure 1: Electron density function, $\rho(x)$, plot for Ni and Cu

A seventh degree polynomial is used to exactly fit $\varphi(x)$ obtained from equation (2.8). The polynomial is

$$\varphi(x) = \varphi_0 + \gamma_1 x + \gamma_2 x^2 + \gamma_3 x^3 + \gamma_4 x^4 + \gamma_5 x^5 + \gamma_6 x^6 + \gamma_7^7 \quad (3.1)$$

The fitting parameters for the derived pair potentials, keeping φ_0 , γ_1 and γ_2 fixed at their equilibrium values, is as presented in Table3. γ_1 and γ_2 correspond to the first and second derivatives of the pair potential at equilibrium.

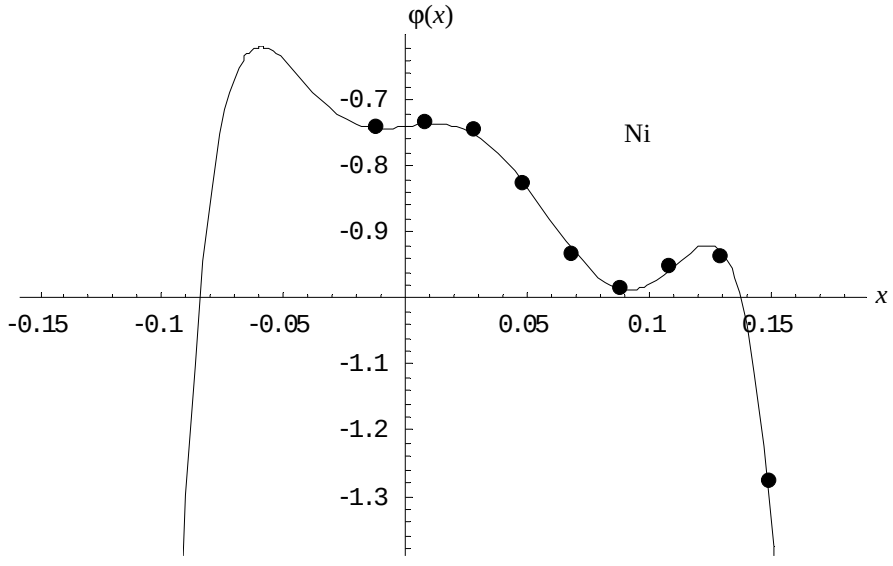
Table 3 Fitting parameters for the derived pair potentials.

	Ni	*Cu*
φ	-0.740	-0.583
γ_1	1.19E+00	1.66E+00
γ_2	1.16E+01	1.08E+01
γ_3	1.85E+03	5.96E+03
γ_4	-1.17E+04	-8.89E+03
γ_5	-9.28E+04	8.65E+03
γ_6	--1.54E+05	5.48E+04
γ_7	5.54E+06	8.25E+05

The exact fit is shown in Figure 2 for Ni and Cu only, while Table 3 provides the fitting parameters for the derived pair potentials. Note that the coefficients, γ_i, are not arbitrarily chosen but calculated to reproduce the exact heat of solution. Efforts are still being directed towards fashioning adequate relationship between the fitting parameters and material properties and the findings will be reported in the future for all the FCC metals.

4.0 Conclusions

The problem of finding the parameters of a suitably chosen electron density function and also the parameters of a pair potential function that will reproduce the experimental dilute limit heat of solution for six FCC binary alloys, within the EAM, has been studied in this work. The electron density derived from exact values of experimental heat of solution, was used to calculate an appropriate pair potential via the Rose *et al*'s equation. The functions obtained cannot be fitted by a single exponential function, as assumed by Johnson and others [2,8]. This may therefore account for the discrepancy between theory and experiment in their work.



(a)

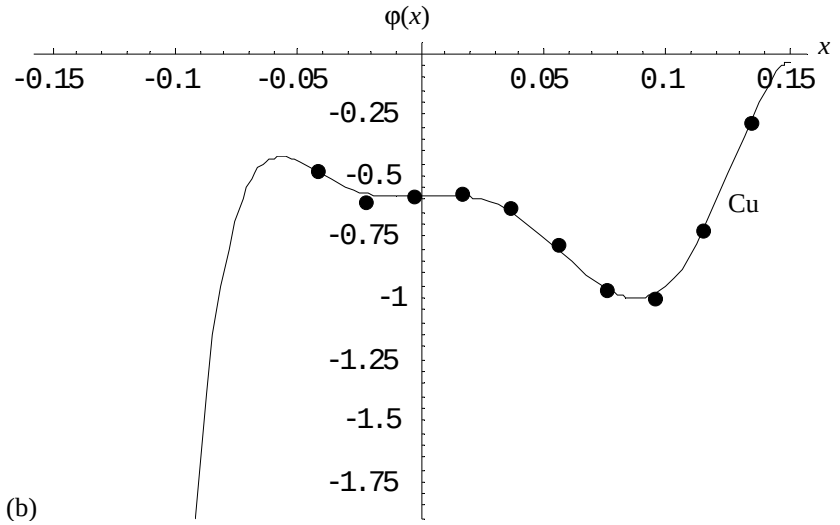


Figure 2. Exact fits for Pair Potential function for (*a*) Ni and (*b*) Cu metals. Shaded circles represents values of pair potential that exactly reproduce the experimental dilute-limit heat of solution while the line .represents the fit using equation (3.1)

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