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ELECTRON DENSITIES DERIVED FROM EMBEDDED ATOM (EAM)

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Abstract
Electron densities of impurity atoms have been obtained using three embedding functions based on the three models proposed by Johnson (1989), Idiodi and Obodi (1993) and Oh and Johnson (1988). The calculations were for the following fcc metals: Ni, Cu, Pd, Pt, Au and Ag. Experimental values of dilute limit heat of solution of the binary alloys of these metals were used as input parameters. The purpose was to investigate whether consistent values of the electron density could be obtained from these functional forms using Johnson's alloy .model. From the results for each impurity electron density (p) as a function of atomic distance (r), the three derived models showed similar trend except for pd impurity. However, from the calculated results, the impurity electron densities did give consistent values.

Keywords: Embedding Function, Heat of Solution, Electron Density, Impurity

Introduction

The non-uniformity in the energies and structure of metals and alloys have been the concern of physicists. The study of these problems requires techniques that can handle a large number of atoms, which in turn requires a model that is both accurate and computationally simple (Foiles *et al* 1986). Although some of these problems have been addressed with various pair potential models, there are still some significant problems associated with the application of pair potentials. For instance, the pair potential of metals do not have environmental dependence and does not account for the directional nature of the bonding. In other words, the pair potential do not give adequate description of properties of metals (Vitek, 1996). All these problems led to the evolution of embedded atom method (EAM).

The EAM is a semi-empirical approach which tackles the many - body problem by determining a functional form for the cohesive energy (Hergert *et al,* 2004). This model gives a more realistic picture of crystal properties than can be obtained by the pair potential model. In the original EAM, the total energy of the system can be given as

$$E_{tot} = F(\rho_i) + \phi(r) \quad (1)$$

and

$$F(\rho_i) = E_{tot} - \phi(r) \quad (2)$$

Where E_{tot} is the total energy, $F(p_i)$ is the embedding function, $\Phi(r)$ is the pair potential and p_i is the electron density. One of the advantages of the original EAM model is that the embedding energy can be obtained by fitting experimental data (Daw and Baskes, 1984).

Embedded Atom Method (EAM)

The embedded atom method (EAM) is a semi-empirical scheme based on the local electron density theory that has been shown to accurately describe a large number of properties of materials. Stott and Zaremba (1980) presented a model to estimate the energy of an impurity in a host electronic system and stated that the energy was a function of the host electron density in which it was immersed. Also, Norskov and Lang (1980) proposed that the embedding energy could be considered as a function of the electron density. Based on these works, Daw and Baskes (1984) developed the EAM. The basic principle of the EAM is that each atom is viewed as an impurity embedded in a host of other atoms.

Accordingly, the basic equations of the EAM as given by Daw and Baskes (1984) are

$$E_{tot} = \sum_i E_i \quad 3$$

$$E_i = F_i(\rho_i) + \frac{1}{2}\sum_{j \neq i} \phi_{ij}(r_{ij}) \quad 4.$$

$$\rho_i = \sum_{i \neq i} \psi_i(r_{ij}) \quad 5$$

E_i is the internal energy associated with atom *i*, p_i is the electron density at atom *i*, $F_i(p_i)$ is the embedding function and $\Phi_{ij}(r_{ij})$ is the pair-potential between atoms *i* and *j* separated by the distance r_{ij}. The embedding function, $F_i(p_i)$ is universal in that it does not depend on the source of the background electron density. Thus, the same embedding function is used to calculate the energy of an atom in an alloy as well as in pure metals. This universality makes the EAM particularly appealing for the studies of alloys (Foiles *et al,* 1986; Lee and Baskes, 2000).

In the EAM, the energy of each atom is computed from the energy needed to embed the atom in the local electron density as provided by the other atoms of the metal. The EAM can also be used to perform large - scale computer simulation of a wide variety of phenomena. Despite the numerous advantages of EAM over pair-potential, the EAM have shown some weaknesses such as the atomic density not being analytically obtained. Instead it was fitted from atomic electron densities as calculated by Clementi and Roetti (1974). Also in the EAM, there are too many parameters to be determined. EAM has been successfully applied to several problems in condensed matter physics such as bulk properties of pure metals, alloys, surfaces, grain boundaries, mechanical properties, vacancy formation energy and di-vacancy binding energy and covalent materials (Jelinek *et al*, 2012; Zhou *et al,* 2021).

Purpose of Study

Electron density derived from different embedding functions are not expected to differ since they are essentially a material property. The purpose of this work is therefore to find out if this agreement in electron density values of impurity atoms derived from Johnson's model (1989), Idiodi and Obodi's model (1993) and Oh and Johnson's model (I9S8) would hold. The derived electron densities from these models were also compared with calculated values.

Method

The electron density of the impurity atom was calculated from the experimental values of dilute - limit heat of solution based on Johnson's alloy model. This was calculated for six face-centred cubic (fcc) metals - Cu, Ni, Au, Ag, Pd and Pt. Johnson (1989) proposed the assumption that for fcc metals, only the nearest neighbors contribute to the pair - interaction and electron density. The embedding function $F(p_i)$ is universal, in that it does not depend on the source of the background electron density. Thus, the same embedding function used to calculate the energy of an atom in an alloy is used in the pure material.

For an alloy with a host lattice of type - *h* atoms containing impurity of type - *i* atoms, two kinds of embedding function $F^h(p)$ and $F^i(p)$ exist. Similarly, one could specify two kinds of atomic electron density function, $F^h(r_e^h)$ and $F^i(r_e^h)$. For the pair - potential, there are three kinds often referred to as ϕ^{hh}, ϕ^{ii} and ϕ^{hi}. ϕ^{hh} and ϕ^{ii} are the same as that of their respective monoatomic models while ϕ^{hi} is referred to as cross-potential (Li *et al* (2008)).
The relevant equation for the dilute - limit heat of solution , ΔQ, of an impurity atom in a host metal as given by Johnson (1989) is

$$\Delta Q = -F^h(\rho) - 12\phi^{hh}(r) + F^i(\rho) + 12\phi^{hi}(r) - 12F^h(\rho) + 12F^h(\Delta\rho) - E_h + E_i \qquad 6$$

From equation (6), $F^h(\rho)$ is the embedding function of the host atom, $F^i(\rho)$ is the embedding function of the impurity atom, ϕ^{hh} (r) is the pair functional of the host atom, ϕ^{hi}(r) is the pair functional of the alloy (host + impurity), r is the distance between the atoms, $\Delta\rho$ is the change in electron density. E_h is the energy of the host atom and E_i is the energy of the impurity atom. Equation (6) will be calculated in four steps following Johnson's binary alloy model.

Step I - Remove host:- $F^h(\rho)$ - 12 ϕ^{hh} (r)

Step II - Add impurity: $F^i(\rho)$ + 12 ϕ^{hh} hi (r)
Step III - Adjust neighbours: -12 $F^h(\rho)$ + 12 $F^h(\Delta\rho)$
Step IV - Adjust cohesive energy:- - e_h + E_i
Where

$$\Delta\rho = \frac{-\rho^{hh} + \rho^{ii}}{12} \quad 6a$$

$$\phi^{hh}(r_e^h) = \frac{1}{6}\left[E_h - F^h(\rho_e^h)\right] \quad 6b$$

$$\phi^{ii}(r_e^i) = \frac{1}{6}\left[E_i - F^i(\rho_e^h)\right] \quad 6c$$

$$\phi^{ii}(r_e^h) = \frac{1}{6}\left[-E_i\left(1+\alpha\left(\frac{r_e^h}{r_e^i}-1\right)\right)e^{-\alpha\left(\frac{r_e^h}{r_e^i}-1\right)} - F^i(\rho_e^i)\right] \quad 6d$$

and

$$\phi^{hi}(r_e^h) = \frac{1}{2}\left[\frac{\rho_e^i}{\rho_e^h}\phi^{hh}(r_e^h) - \frac{\rho_e^h}{\rho_e^i}\phi^{ii}(r_e^h)\right] \quad 6e$$

If equations (6a) to (6e) are substituted back into equation (6), the only unknown in the full expression is the electron density of the impurity atom (p_{ie} (r_e^h). This quantity is obtained by iterating the expression using Microsoft Excel (2007) in order to calculate the electron density for each combination of impurity/host atom.

Calculation of Electron Density using different embedding functions

Three embedding functions were employed in this work to determine impurity electron. density within the framework of Johnson's binary alloy model. The embedding functions are due to Johnson (1989), Idiodi and Obodi (1993) and Oh and Johnson (1988).

Johnson's Model

Using Johnson's model, some of the constants used were

$$a_h = \sqrt[3]{4\Omega_h}\ ,\ a_i = \sqrt[3]{4\Omega_i}\ ,\ r_h = \frac{a_h}{\sqrt{2}}\ ,\ r_i = \frac{a_i}{\sqrt{2}}\ ,$$

$$f_h = f_h e^{-\alpha h\left(\frac{r_h}{r_h}-1\right)},\quad f_i = f_i e^{-\alpha i\left(\frac{r_i}{r_h}-1\right)},\quad \rho_{ix} = 12 f_{ix},$$

$$\rho_h = 12 f_h,\quad \rho_i = 12 f_i,\ \text{and}\ \Delta\rho = -f_h + f_i$$

The embedding function for determining impurity electron density was given as follows (Johnson, 1989)

$$F(\rho_h) = AE_h \frac{\rho^h}{\rho^h}\log\left(\frac{\rho^h}{\rho^h}\right) \quad 7a$$

$$F(\rho_i) = AE_i \frac{\rho^h}{\rho^i}\log\left(\frac{\rho^h}{\rho^i}\right) \quad 7b$$

$$F(\Delta\rho) = AE\,\frac{\rho^h + \Delta\rho}{\rho^h}\log\left[\frac{\rho^h + \Delta\rho}{\rho^h}\right] \qquad 7c$$

$$\phi^{hh}(r) = \frac{1}{6}[E_h - F(\rho_h)] \qquad 7d$$

$$\phi^{ii}(r) = \frac{1}{6}\left[-E_i\left(1+\alpha_i\left(\frac{r^h}{r^i}-1\right)e^{-\alpha_i\left(\frac{r^h}{r^i}-1\right)} - AE_i\,\frac{\rho_{ix}}{\rho_i}\log\left(\frac{\rho_{ix}}{\rho_i}\right)\right)\right] \qquad 7e$$

$$\phi^{hi}(r) = \frac{1}{2}\left[\left(\frac{\rho_{ix}}{\rho_h}\right)\phi^{hh} + \left(\frac{\rho_h}{\rho_{ix}}\right)\phi^{ii}\right] \qquad 7f$$

Equations 7a to 7f were substituted into the equation of dilute-limit heat of solution (eq 6)

3.2 – Idiodi and Obodi's Model

Under this model, the constants are the same as those used in Johnson's model. The embedding function for binary alloys with h as host and i as impurity was taken as (Idiodi and Obodi, 1993)

$$F(\rho_h) = F_{oh}\left(\frac{\rho^h}{\rho^h}\right)^{\lambda Gh} e^{-\alpha Gh}\left(\frac{\rho^h}{\rho^h} - i\right) \qquad 8a$$

$$F(\rho_i) = F_{oi}\left(\frac{\rho^h}{\rho^i}\right)^{\lambda Gi} e^{\alpha Gi}\left(\frac{\rho^h}{\rho^i} - 1\right) \qquad 8b$$

$$F(\Delta\rho) = F_{oh}\left(\frac{\rho^h + \Delta\rho}{\rho^h}\right)^{\lambda Gh} e^{-\alpha Gh}\left(\frac{\rho^h + \Delta\rho}{\rho^h}\right) \qquad 8c$$

$$\phi^{hh}(r) = \frac{1}{6}\left[E_h - F(\rho^h)\right] \qquad 8d$$

$$\phi^{ii}(r) = \frac{1}{6}\left[-E_i\left(1+\alpha_i\left(\frac{r_h}{r^i}-1\right)e^{-\alpha_i\left(\frac{r^h}{r^i}-1\right)} - F_{oi}\left(\frac{\rho_{ix}}{\rho_i}\right)^{\lambda Gi} e^{-\alpha Gi}\left(\frac{\rho_{ix}}{\rho_i} - 1\right)\right)\right] \qquad 8e$$

$$\phi^{hi}(r) = \frac{1}{2}\left[\left(\frac{\rho_{ix}}{\rho_h}\right)\phi^{hh} + \left(\frac{\rho_h}{\rho_{ix}}\right)\phi^{ii}\right] \qquad 8f$$

All these (eq 8a to 8f) were substituted into the equation of the dilute – limit heat of solution (equation 6).

Oh and Johnson's Model

Under Oh and Johnson's model, the constants are also the same as those used in Johnson and Idiodi and Obodi''s models. The embedding function for the binary alloys were taken as follows (Oh and Johnson, 1988)

$$F(\rho_h) = AE_h\left[1 - n\log\left(\left(\frac{\rho^h}{\rho^h}\right)\right)\right]\left(\frac{\rho^h}{\rho^h}\right)^n \qquad 9a$$

$$F(\rho_i) = AE_i\left[1 - n\log\left(\left(\frac{\rho^h}{\rho^i}\right)\right)\right]\left(\frac{\rho^h}{\rho^i}\right)^n \qquad 9b$$

$$F(\Delta\rho) = AE_h\left(1 - n\log\left(\frac{\rho^h + \Delta\rho}{\rho^h}\right)\right)\left[\frac{\rho^h + \Delta\rho}{\rho^h}\right]^n \qquad 9c$$

$$\phi^{hh}(r) = \frac{1}{6}[E_h - F(\rho_h)] \qquad 9d$$

$$\phi^{ii}(r) = \frac{1}{6}\left[-E_i\left(1 + \alpha_i\left(\frac{r^h}{r^i} - 1\right)e^{-\alpha_i\left(\frac{r^h}{r^i} - 1\right)} - AE_i\left[1 - n\log\left(\frac{\rho_{ix}}{\rho_i}\right)\right]\right)\right]\left(\frac{\rho_{ix}}{\rho_i}\right)^n \qquad 9e$$

$$\phi^{hi}(r) = \frac{1}{2}\left[\left(\frac{\rho_{ix}}{\rho_i}\right)\phi^{hh}(r) + \left(\frac{\rho_h}{\rho_{ix}}\right)\phi^{ii}(r)\right] \qquad 9f$$

All these equations (9a to 9f) were substituted into equation 6,

Results

The derived impurity electron density for each metal in different hosts is presented in this section. It is noted that iteration of various non-linear equations yielded more than one root, implying that the electron densities are multi-valued. Each root depended on the initial value of iteration. Sometimes the roots are the same for any two of the starting numbers. Also, Cu impurity in Ni was observed to be unstable in Oh and Johnson's model. Apart from these, all other iterations gave solutions.

(a) Nickel Impurity

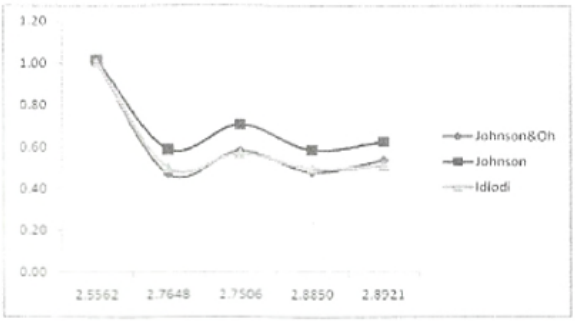

Figure 1: Plot of electron density , ρ for Ni impurity as a function of atomic distance r (Å)

(b) – Copper Impurity

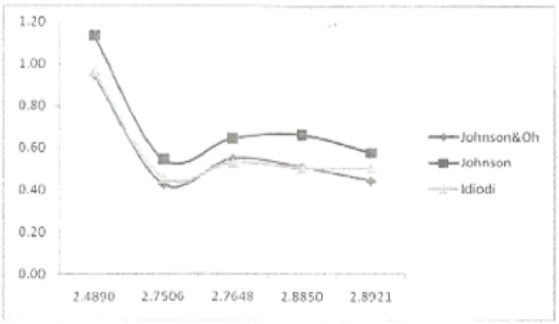

Figure 2: Plot of electron density , ρ for Cu impurity as a function of atomic distance r (Å)

(c) – Palladium Impurity

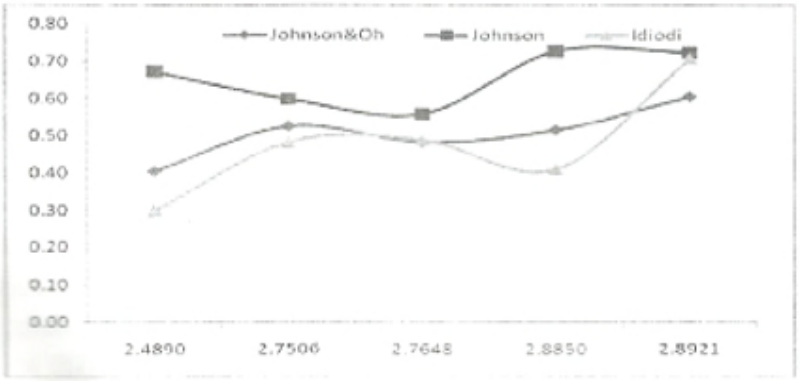

Figure 3: Plot of electron density, ρ, for Pd impurity as a function of atomic distance r (Å)

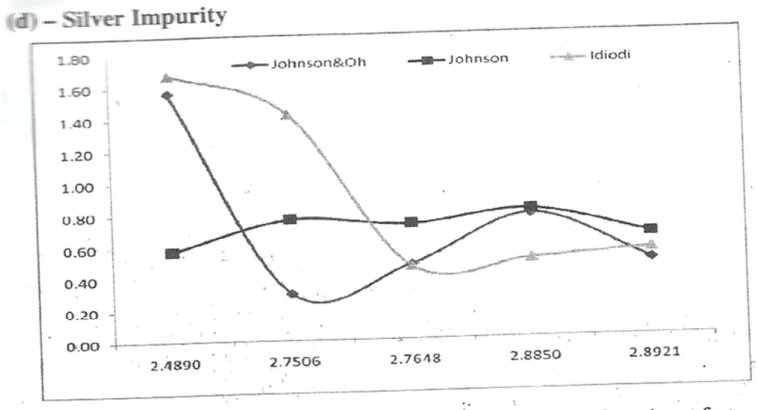

Figure 4: Plot of electron density , ρ, for Ag impurity as a function of atomic distance r (Å)

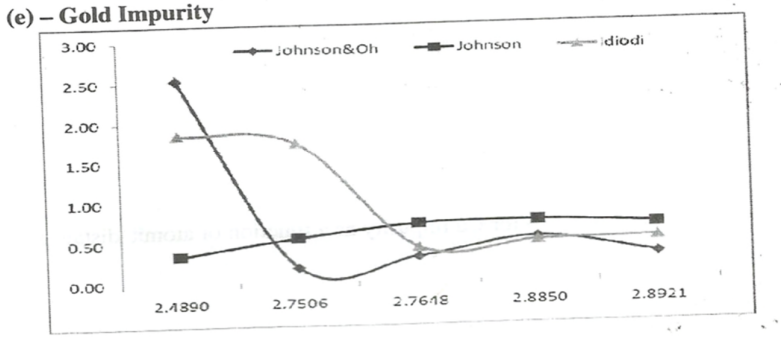

Figure 5: Plot of electron density , ρ, for Au impurity as a function of atomic distance (Å)

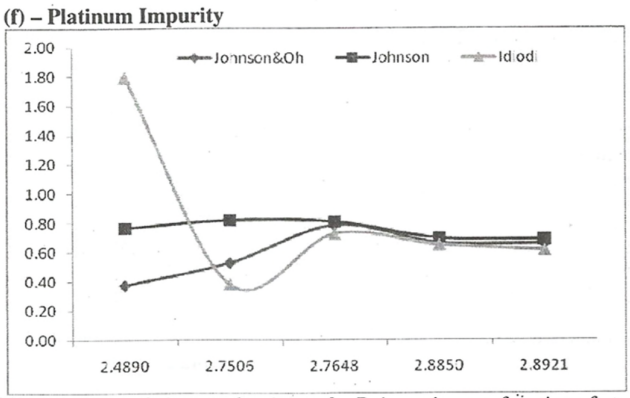

Figure 6: Plot of electron density, ρ, for Pt impurity as a function of atomic distance r (Å)

Discussion

The electron density values from Ni and Cu impurities showed a similar trend for the derived models -Johnson, Oh and Johnson and Idiodi and Obodi's embedding functions. All the models have positive curvature for Ni impurity. For Ag, Au and Pt, the impurity electron density values were inconsistent at atomic distances lower than $2{,}7648^0$A but followed a similar trend at atomic distances higher than 2.7648^0A. Pd gave dissimilar trend of electron density values except for Pt host where the values for Oh and Johnson, Idiodi and Obodi were very close. For all the three models the values of the derived electron density from Johnson's embedding function are consistently higher and almost at constant values. The consistency in the trend of the embedding functions is likely due to the fact that they were derived from the same atomic cluster arrangement (Johnson, 1989).

All the models are in good agreement with experimental values of the dilute-limit heat of solution. The heats of solution for alloys of Ni, Cu, Ag, Au and Pt derived with Johnson, Oh and Johnson and Idiodi and Obodi's embedding functions were consistent with available experimental data. The heats of solution involving Pd impurity gave the largest discrepancies and the values were not consistent. This could be as a result of the alloys being immiscible up to the melting point. Some of the heats of solution calculated were mere predictions as the detailed thermodynamic data were not available. So they have remarkable disagreement with experimental data (Zhang and Wen, 2007).

It is therefore possible to derive suitable electron densities from dilute limit heats of solution for fee metals using different embedding functions to satisfy the universal equation of state. An important application of this approach is that it enables one to compare electron densities derived from various forms of embedding function in RAM literature.

Conclusion

Electron densities for six fee metals have been derived that exactly reproduced their respective dilute limit heat of solution. They were derived using three different embedding functions from Johnson's model, Idiodi and Obodi's model and Oh and Johnson's model. For Ni and Cu impurities, Oh and Johnson and Idiodi and Obodi's models agree but have lower values than Johnson's model. However, computation using Oh and Johnson's model for Ni impurity in Cu and Cu impurity in Ni were unstable.

The three derived models tend to converge at atomic distance of 2.7648°A for Au, Ag and Pt, but showed dissimilar trends at lower distances (fig. 4, 5 and 6).

This work shows that it is possible to derive consistent electron densities regardless of the form of embedding function for a consistent set of prescribed material properties.

The observed differences between them may be the reason for non-uniqueness of the electron density derived from them.

Recommendation

i. Electron density in this derived form could be tested for embeddingfunctions using some other models

ii. Use the derived electron densities to calculate basic material properties in the EAM framework.

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