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Towards a self consistent embedding function for Lithium

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Abstract

Two different embedding functions $F_A(\rho)$ and $F_B(\rho)$ obtained by two different research groups working with the embedded atom method (EAM) equations for bcc metallic Lithium are here shown to belong to the same class of functions recently characterised by Oni-Ojo et al [see the preceding paper]. The consequences of this harmonization are discussed.

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1.0 Introduction

Yuan et al [1] recently reported the following embedding function, designated as $F_A(\rho)$, for bcc metallic Lithium:

$$F_A(\rho) = AE_0\left(\rho/\rho_0\right)\left[\ln\left(\rho/\rho_0\right) - K\right] \tag{1.1}$$

At the equilibrium value of the election density, i.e. $\rho = \rho_0$, we get from (1.1) the results

MODEL A:
$$\left.\begin{aligned} F_A(\rho_0) &= 2.0001\ eV \\ F_A'(\rho_0) &= 3.4356\ eV/\rho_0 \\ F_A''(\rho_0) &= 1.4355\ eV/\rho_0^2 \end{aligned}\right\} \tag{1.2}$$

with $A = 0.87$, $K = -1.3933$, and $E_0 = 1.65$eV and where a prime denotes differentiation with respect to ρ.

On the other hand, one of us [2] has also previously reported a completely different embedding function for bcc metallic Lithium, herein designated as $F_B(\rho)$, in the form

$$F_B(\rho) = \mu\left[f_1\left\{e^{\alpha f} - e^{-\alpha f\left(\rho/\rho_0 - 1\right)}\right\}\right]^{\lambda f} \tag{1.3}$$

and which yields the following equilibrium values:

MODEL B:
$$\left.\begin{aligned} F_B(\rho_0) &= -7.5056\ ev \\ F_B'(\rho_0) &= -6.2187\ eV/\rho_0 \\ F_B''(\rho_0) &= 2.0709\ eV/\rho_0^2 \end{aligned}\right\} \tag{1.4}$$

with $\mu = -1$, $f_1 = 22.1970$, $\alpha_f = 0.3074$, $\lambda_f = 0.97$.

Since we are unable to immediately see the connection between (1.1) and (1.3) or between (1.2) and (1.4), we seek in this paper to place both embedding functions in the same class of admissible embedding functions recently obtained for Lithium [see the preceding paper, Ref. 3]. How this is done is then the purpose of this communication. A theory for the exact analytical form of the embedding function does not currently exist in the literature.

The organization of this paper is as follows.

In the next Section we collect together the basic equations of the embedded atom method (EAM) for a bcc metal and then briefly indicate how one arrives at the results (1.3) and (1.4). In Section 3 we first generalize the embedding function (1.1) and then place both functions (F_A and F_B) in the same class. Some preliminary deductions are made from the generalized embedding function and concluding remarks are given in Section 4

2.0. The Basic equations of the EAM for a bcc metal

We refer the interested reader to the several published papers [4-10] on the embedded atom method (EAM) for details, and confine ourselves here strictly to the aspects required for this study. If $F(\rho)$ denotes the embedding function and $\phi_1(r)$ denotes the nearest neighbour pair potential, and $\rho(r)$ is the electron density at position r, then within a nearest neighbour model it can be shown that for a monoatomic bcc solid

$$U_0 = 4\phi_1(r_0) + F(\rho_0) \tag{2.1}$$

$$0 = 4\phi_1'(r_0) + F'(\rho_0)V_{11}/a \tag{2.2}$$

$$B = (9C_{44} - 4C_{11})/5 - \frac{2}{\Omega_0}F'(\rho_0)W_{12} - \frac{1}{2\Omega_0}F''(\rho_0)V_{11}^2 \tag{2.3}$$

$$C_{11} = G + \frac{1}{\Omega_0}F'(\rho_0)W_{11} + \frac{1}{\Omega_0}F''(\rho_0)V_{11}^2 \tag{2.4}$$

$$C_{12} = G + \frac{1}{\Omega_0}F'(\rho_0)W_{12} + \frac{1}{\Omega_0}F''(\rho_0)V_{11}^2 \tag{2.5}$$

$$C_{44} = G + \frac{1}{\Omega_0}F'(\rho_0)W_{12} \tag{2.6}$$

where

$$G = -\frac{4}{3\sqrt{3}a^2}\phi_1'(r_0) + \frac{2}{3a}\phi_1''(r_0) \tag{2.7}$$

and U_0 is the energy per atom, i.e., the negative of the cohesive energy. B and C_{ij} are, respectively, the Bulk modulus and the elastic constants written in the Voigt notation. $r_0\left(=\sqrt{3}\,a/2\right)$ is the equilibrium nearest neighbour distance; a is the lattice constant; $\Omega_0\left(=a^3/2\right)$ is the volume per atom; while V_{11}, W_{11}, and W_{12} are three basic parameters of the EAM. In this work we shall treat them as three parameters to be consistently determined so that equations. (2.1 – 2.7) are satisfied.

The six equations (2.1 – 2.6) contain nine unknown parameters ϕ_1, ϕ_1', ϕ_1'', F, F', F'', V_{11}, W_{11}, W_{12}; and the standard physical inputs required to determine these unknowns are the lattice constant a, the cohesive energy E_0 (= - U_0), the bulk modulus B, and the three

elastic constants C_{11} , C_{12} , and C_{44}. An expression for the monovacancy formation energy E_{1v}^f in the form

$$E_{1v}^f = 8F(\rho_v) - 7F(\rho_0) - U_0 \qquad (2.8)$$

is often considered as an additional equation that would aid in the determination of the unknown quantities.

In equation (2.8), ρ_v is the background electron density at site *i*, which is a nearest neighbour to the monovavancy. We document in the Appendix the details of the method used by us to arrive at the solutions (1.3) and (1.4). In Table 1 we collect together the input parameters used for the calculations, and in Table 2 we provide the nine EAM parameters determined by solving equations (2.1-2.7) for the two different models.

In most applications of the EAM ,
$$\rho_v = \frac{7}{8}\rho_0 \qquad (2.9)$$

but in the modified embedded atom method (MEAM) employed by Yuan et al [1], ρ_v has a different value from that given by (2.9). Within the MEAM this value of ρ_v will give a vacancy formation energy of 0.495eV for Li. If we, however, stick to the formulas (2.8) and (2.9) then it is easily verified that the embedding functions (1.1) and (1.3) predict different vacancy formation energies for Lithium.

Model A:
$$E_{1v}^f = 0.308eV \qquad (2.10)$$

Model B:
$$E_{1v}^f = 0.495eV \qquad (2.11)$$

The resolution of this problem within the EAM is taken up in the next section.

3.0 **Generalized Embedding Function for Lithium**

To be able to handle the two embedding functions on the same footing, we follow Oni-Ojo et al [3] and consider a generalized version of (1) in the form

$$F(\rho) = \frac{F(\rho_0)}{(-K)}\left(\rho/\rho_0\right)^{\lambda}\left[\ln\left(\rho/\rho_0\right)^{\alpha} - K\right] \qquad (3.1)$$

showing clearly that F(ρ) is a four-parameter model. For Lithium, K takes the value – 1.3933 [1].
Taking into account formulae (2.8) and (2.9), the embedding function (3.1) will yield the equilibrium value $F(\rho_0)$ and the desired experimental value of $E_{1v}^f = 0.495eV$, provided

$$\lambda = \ln\frac{\left\{\dfrac{\frac{1}{8}\left[E_{1v}^f + 7F(\rho_0) + U_0\right]}{\left[\dfrac{F(\rho_0)}{K}\right]\left[\ln\left(\dfrac{7}{8}\right)^{\alpha} - K\right]}\right\}}{\ln\left(\dfrac{7}{8}\right)} \qquad (3.2)$$

The parameter-fitting of the two models reveal that, while the values

$$\left.\begin{aligned}\alpha &= 0.76\\ \lambda &= 1.0784\\ F(\rho_0) &= F_A(\rho_0)\end{aligned}\right\} \qquad (3.3)$$

will reproduce the solution set (12) , the values

$$\left.\begin{aligned} &\alpha = 0.5 \\ &\lambda = 0.4619 \\ &F(\rho_0) = F_B(\rho_0) \end{aligned}\right\} \qquad (3.4)$$

reproduces the solution set (1.4).

The successful harmonization of the two different models through the generalized form (3.11) is one of the major achievements of this study. Differentiation of equation (3.1) with respect to ρ yields immediately

$$F'(\rho_0) = \frac{F(\rho_0)}{\rho_0}\left[\lambda - \frac{\alpha}{K}\right] \qquad (3.5a)$$

and

$$F''(\rho_0) = \frac{F(\rho_0)}{\rho_0^2}\left[\lambda^2 - \frac{2\lambda\alpha}{K} + \frac{\alpha}{K} - \lambda\right] \qquad (3.5b)$$

It is clear from (3.5a) and (3.5b) that the generalized form (3.1) is quite rich in structure unlike (1.1) which gives

$$F_A'(\rho_0) = \frac{F(\rho_0)}{\rho_0}\left[1 - \frac{1}{K}\right] \qquad (3.6a)$$

$$F_A''(\rho_0) = \frac{F(\rho_0)}{\rho_0^2}\left[-\frac{1}{K}\right] \qquad (3.6b)$$

Thus, whereas $F_A''(\rho_0)$ is always positive definite, $F''(\rho_0)$ may be positive or negative depending on the values of α and λ [3].

At exactly the equilibrium electron density ρ_0, it is clear that the solution (1.2) satisfies a second order linear differential equation of the form

$$\frac{d^2F}{d\rho^2} - \frac{1}{\rho}\frac{dF}{d\rho} + \frac{F}{\rho^2} = 0 \qquad (3.7)$$

Infact, for all values of ρ , (1.1) is a solution of (3.7). Following Oni-Ojo et al [3], we immediately generalize (3.7) to the form

$$\frac{d^2F}{d\rho^2} - \frac{\gamma_1}{\rho}\frac{dF}{d\rho} + \frac{\gamma_0}{\rho^2}F = 0 \qquad (3.8)$$

where γ_1 and γ_0 are parameters to be determined later. Correspondingly we generalize the solution (1.1) to a function of the form (3.1), and search for the condition for (3.1) to solve (3.8). This can be got by putting (3.1) into (3.8). A much weaker condition, however, which holds only at the equilibrium value $\rho = \rho_0$ is clearly

$$\lambda^2 - 2\alpha\frac{\lambda}{K} + \left(\frac{\alpha}{K} - \lambda\right)(1 + \gamma_1) + \gamma_0 = 0 \qquad (3.9)$$

The full implications of equation (3.9) are currently being studied and will be reported in the future. For now, within the EAM, the (110) unrelaxed surface energy of bcc Lithium can be got from the simple formula

$$\Gamma_{110} = \frac{\sqrt{2}}{a^2}\left[F\left(\frac{6}{8}\rho_0\right) + \frac{6}{8}\{U_0 - F(\rho_0)\} - U_0\right] \qquad (3.10)$$

Using equation. (3.10), Model A and B yield, respectively, the values 274 Ergs/cm^2 and 298 Ergs/cm^2. A simple average of these two values give an unrelaxed surface energy of 286 Ergs/cm^2 , in excellent agreement with the relaxed value of 287.2 Ergs/cm^2 obtained by Yuan et al [1]. A simple minded conclusion is that the material described by Model B is slightly harder than that described by model A.

It is usual in the literature [6] to consider a simple exponential fit for the electron density ρ(r) and the pair potential $\phi_1(r)$. It is clear from Table 2 that the values of $\phi_1(r_0)$, $\phi'_1(r_0)$ and $\phi''_1(r_0)$ do not support such a fit.

A function of the form (1.3) was shown by Idiodi and Obodi [8] to be a solution of the nonlinear differential equation

$$\alpha_{2f} FF'' + \alpha_{1f} FF' + \alpha_{0f} (F')^2 = 0 \qquad (3.11)$$

where α_{2f} , α_{1f} and α_{0f} are parameters, defined for fcc metals and bcc metals in [8] and [2] respectively. It can be verified that the function (1.1), and consequently, Model A is not a solution of (3.11). We have, however, shown that both (1.1) and (1.3), in some neighbourhood of the equilibrium density ρ_0 , can be fitted by the generalized form (3.1) or (3.8). This has been made possible by the fact that the EAM equations specify only the equilibrium values of F, F′, and F″.

Table 1: Physical quantities for bcc Li used to determine the EAM parameters

The quantities listed are the lattice constant a(Å) , the unrelaxed vacancy formation energy $E_{1v}^{f}(eV)$, the cohesive energy E_0 (eV), the bulk modulus B(10^{12} ergs/cm^3) , and the three elastic constants (C_{11} , C_{12} , C_{44}) in units of 10^{12} ergs/cm^3. The values have been lifted from Yuan et al [1].

Physical Quantity	A	E_{1v}^{F}	E_0	B_0	C_{11}	C_{12}	C_{44}
Value	3.51	0.495	1.65	0.120	0.134	0.113	0.0958

Table 2: Calculated EAM Parameters for bcc Lithium

Parameter	**Unit**	**Model A**	**Model B**
$F(\rho_0)$	*eV*	2.0001	-7.5056
$F'(\rho_0)$	eV/ρ_0	3.4356	-6.2187
$F''(\rho_0)$	eV/ρ_0^2	1.4355	2.0709
$\phi_1(r_0)$	***EV***	-0.9125	1.4638
$\phi'_1(r_0)$	EV/Å	0.0984	-0.1483
$\phi''_1(r_0)$	*EV*/Å^2	0.4513	0.3701
V_{11}	ρ_0	-0.4021	-0.3348
W_{11}	ρ_0	-0.0419	0.0232
W_{12}	ρ_0	-0.1244	0.0687

4.0 Conclusion

This study has successfully harmonized into one class, two different solutions to the same set of EAM equations. This class is characterized by the generalized form (3.1) or (3.8). Clearly the embedding function (3.1) is much richer in structure than the embedding function described by equation (1.1). It is this flexibility or richness in structure that made the harmonization possible.

The path pursued here can be viewed as an alternative approach to the one adopted by Yuan et al [1]. Yuan et al employed the MEAM which by design entails working with a simple embedding F(ρ) and a more complex density function ρ(r) that contains a lot of parameters. We have in this study, however, employed the EAM and shifted focus from ρ(r) to the embedding function itself.

APPENDIX

Calculation Algorithm for Solving the EAM Equations

The steps leading to the embedding function

$$F(\rho) = \mu\left[f_1\left\{ e^{\alpha_f} - e^{-\alpha_f\left(\rho/\rho_0 - 1\right)} \right\} \right]^{\lambda_f} \tag{A1}$$

can be found in Ref. 8 and will not be repeated here. From (A1), expressions for $F(\rho_0)$, $F'(\rho_0)$, and $F''(\rho_0)$ can be easily derived. The calculation procedure is then as follows:

1st Step: Initialize all input parameters like

a, C_{11} , C_{12} , C_{44} , B_0 , U_0 (= - E_0) , E_{1v}^F , and Ω_0 for bcc metals, $\Omega_0 = a^3/2$ and $\lambda_f = 0.97$.

2nd Step: Guess a value for $\alpha_f \left(0 < \alpha_f < 4\right)$ and then calculate the following:

$$X = \left(\frac{e^{\alpha_f} - 1}{e^{\alpha_f} - e^{\alpha_f/8}} \right)^{\lambda_f} \tag{A2}$$

$$F(\rho_0) = X \frac{\left(U_0 + E_{1v}^F\right)}{(8 - 7X)} \tag{A3}$$

$$F'(\rho_0) = F(\rho_0).\lambda_f \cdot \alpha_f \Big/ \left(e^{\alpha_f} - 1 \right) \tag{A4}$$

$$F''(\rho_0) = \left(1 - e^{\alpha_f}/\lambda_f\right) \cdot [F'(\rho_0)]^2 / F(\rho_0) \tag{A5}$$

$$b_1 = -12\ F'(\rho_0)/\sqrt{3} \tag{A6}$$

$$V_{11} = -\sqrt{\Omega_0 (C_{12} - C_{44})/F''(\rho_0)} \tag{A7}$$

3rd Step: Verify self-consistency condition on α_f by calculating α_f from the formula

$$\alpha_f = \ln\left[\lambda_f \left\{ 1 + \frac{\Omega_0 (C_{12} - C_{44})}{(b_1 V_{11} + C_1)} \right\} \right] \tag{A8}$$

where

$$C_1 = \frac{3a^3}{5}\left[22\ C_{11} + 5C_{12} - 27\,C_{44}\right] \tag{A9}$$

If Guessed $\alpha_f \neq$ calculated α_f, then repeat steps 2 to 3 until this self-consistency condition on α_f is satisfied. Once α_f has been determined and hence $F(\rho_0)$, $F'(\rho_0)$, $F''(\rho_0)$, and V_{11} are known, then the remaining EAM parameters can be easily determined from equations (2.1 – 2.6).

The above calculation algorithm is efficient and it has been used in [2] to obtain EAM parameters for several bcc metals.

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