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An Approach Towards a Self-Consistent EAM Model for *bcc* Metals Lithium and Vanadium

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ABSTRACT
Recently, a four-parameter embedding function that is sufficiently rich to handle both positive and negative Cauchy discrepancy ($\mathbf{C_{12} - C_{44}}$) has been produced by modifying the embedding function of Yuan et al. (2003)[1], a modification to MEAM92, which failed to produce a reasonable surface energy when applied to bcc Vanadium V. We compute the three low-index surface energies of Li and V using the novel model Generalized Embedding Atom method (GEAM) (Oni-Ojo et al, 2007) parameters (iterated values), and the results fall within the experimental average.

INTRODUCTION

Semi-empirical atomistic simulations have shown to be an invaluable asset in the investigation of metallic properties and structure. The selection of an acceptable interatomic potential, or the way the constituent atoms interact, is fundamental to any such investigation. More fundamental techniques are usually too complicated to perform the necessary computations efficiently, while simple potentials are usually too rigid to represent real metals effectively.

Daw and Baskes (1983 and 1984) devised the embedded atom technique (EAM) for creating a mathematical model of a metal. In this method, the energy needed to insert an impurity atom in a lattice is exclusively determined by the electron density at that specific location. In this strategy, each atomic species is assumed to have a distinct energy function that is determined only by electron density. The EAM predictions have been positive in that the model's results are comparable with experimental values that are available.

Three functions need to be found in order to use the EAM practically: the pair potential $\phi(R)$ between any two atoms, the density function $\rho(R)$, and the embedding function $F(\rho)$. But for single crystal surface energy, the EAM estimate is almost 50% less than the polycrystalline experimental value (Baskes, 1992).

Attempts to improve the EAM resulted in the development of the modified embedded atom method (MEAM) by Baskes et al. (1989). For numerous materials, the MEAM parameters are provided in (Baskes, 1992). Although various MEAM variants have been developed (Lee et al, 2001, Baskes, 1997, Baskes, 1999), the theory and characteristics of the MEAM92 described in (Baskes, 1992) are the most often employed.

The primary distinction between EAM and MEAM is in the development of the density function $\rho(R)$. The electron density at site i, ρ_i, in the EAM is given by a linear superposition of spherically averaged atomic electron densities from nearby atoms to the site i, but in the MEAM ρ_i is enhanced by angular dependent components.

Yuan et al. (2003)[1] added a parameter K to the embedding function $F(\rho)$ in MEAM92, hence introducing yet another modification to the EAM. With hopes that, if the relaxation of surface atom locations were to be taken into account, this would allow them get over the difficulties they ran into while calculating the surface energy of bcc lithium. Despite this alteration, the model predicted a mono-vacancy formation energy that was 50% higher than the experimental value when it was applied to bcc Vanadium (2003)[2].

Oni-Ojo et al (2005, 2007) have adopted a different strategy in response to the issues faced by Yuan and Coworkers by concentrating their investigation on the embedding function's structure, which has not seen as much development as the density function $\rho(R)$. In terms of the embedding function $F(\rho)$, Yuan et al.'s work (2003)[1,2] was successfully generalized using a simplified form for the atomic electron density $\rho(R)$, as is found in various simplified versions of the EAM. Additionally, a more flexible embedding function $F(\rho)$ was developed, which is characterized by a second order

linear differential equation. The outcomes of this work demonstrate the rich structure of the Generalized Embedding Atom Method (GEAM), our generalized model.

The curvature of F(ρ) at the equilibrium electron density ρ(R) determines the Cauchy discrepancy ($\boldsymbol{C_{12} - C_{44}}$) in the typical EAM (Daw and Baskes, 1984). The GEAM embedding function F(ρ), is adaptable enough to accommodate both positive and negative curvature. As a result, the model is free of the problems associated with the use of restrictive variants of F(ρ).

MATERIALS AND METHODS

The EAM is founded on density functional theory, which posits that the energy of a material can be represented as a distinct functional of electron density (Hohenberg and Kohn, 1964, Kohn and Sham, 1965). The most important aspect of the electron density in the EAM is regarded to be the local electron density at each atomic site, as provided by the surrounding atoms. The total energy is split into two parts: electrostatic interaction and the energy needed to embed an atom in a homogeneous electron gas. As a result, the total energy is given by

$$\boldsymbol{E_{tot}} = \sum_{j\neq i} \boldsymbol{F_i}\left(\boldsymbol{\rho_{h,i}}\right) + \frac{1}{2}\sum_{i,j} \phi_{i,j}(\boldsymbol{R_{i,j}}) \qquad (1)$$

Where F(ρ) is atom i's embedding energy, $\rho_{h,i}$ is the host electron density at atom *i* due to the surrounding atoms, $\phi_{i,j}$(R) is a short-ranged electrostatic interaction between atoms *i* and *j*, $R_{i,j}$ is the distance between atoms *i* and *j*, and all summations are over all atoms. The superposition of atomic electron densities is commonly used to approximate the host electron density.

By obtaining the EAM energy form using density functional theory, Daw (1989) was able to show the physical source of the variables in equation (1). Daw's derivation is based on the assumption that the electron density may be represented by a superposition of atomic electron densities, which overlooks band-structure effects. For fcc metals, both of these hypotheses are more accurate than for bcc metals. Jacobsen et al. (Jacobsen et al., 1987) also used ab initio techniques to generate EAM-type functions, and their results suggest that fcc metals may be a better fit for the EAM-type approach than bcc metals.

In spite of the remarks made earlier, the EAM has been applied to a variety of solids, and one of the most unexpected and compelling arguments in favor of the method is its capacity to accurately predict a broad range of material properties (Adams and Foiles, 1990). The F(ρ), $\phi(R)$ and ρ(R) are the three main components of the EAM, as shown in equation (1).. To identify the three functions, the EAM, as originally devised by Daw and Baskes (1983), involves some painstaking numerical fitting to various physical parameters. Several efforts (Adams and Foiles, 1990, Johnson, 1988, Idiodi et al, 1991, Idiodi and Obodi, 1993) have been made inside the EAM in recent years to avoid the tedious numerical fitting required to find EAM functions. As a result, Idiodi and Obodi (1993) developed an embedding function with three parameters,

$$F(\rho) = \mu\left[f_0\left\{e^{\alpha_f} - e^{-\alpha_f\left(\frac{\rho}{\rho_0}-1\right)}\right\}\right]^{\lambda_f} \qquad (2)$$

or

$$F(\rho) = f_0\left(\frac{\rho}{\rho_0}\right)^{\lambda_f} e^{-\alpha_f\left(\frac{\rho}{\rho_0}-1\right)} \qquad (3)$$

Where $\mu = \pm 1$, and f_0, α_f and λ_f, are to be determined. Within the MEAM, Baskes (1992) utilized a simple embedding function (2.4) to study several solids.

$$F(\rho) = AE_0\left(\rho/\rho_0\right).ln\left(\rho/\rho_0\right) \qquad (4)$$

The sublimation energy is denoted by E_0 in (4), and A is the only parameter that needs to be found. Even with its simplicity (4), the ρ(R) used in the MEAM still needs to be fitted quite laboriously.

The work of Yuan et al., (2003)[1] applied MEAM92 to bcc Lithium but modified (4) the form in (5).

$$F(\rho) = AE_0\left(ln\left(\rho/\rho_0\right) - K\right) \qquad (5)$$

The only parameters to be determined are A and K. Though (5) assisted in resolving the issues they experienced in Li, they failed with bcc Vanadium (Yuan *et al.*, 2003)[2].

As a result of the aforementioned issues, the shortcomings in the MEAM already mentioned by (Baskes et al., 1989) and the inability of the Standard EAM to work in materials for which the Cauchy discrepancy is negative, Oni-Ojo et al.(2005, 2007) adopted an entirely different strategy and looked within the EAM, adopting a simplified form of the atomic electron density that is found in various EAM versions (Adams and Foiles, 1990, Johnson, 1988). They also generalized the work of Yuan et al. (2003)[1,2] in terms of the embedding function F(ρ) and created a more flexible embedding function.

In practice, functional forms for $\boldsymbol{F_i}\left(\boldsymbol{\rho_{h,i}}\right)$ and $\phi_{i,j}$ are chosen, and the parameters in these functions are established by fitting to a small number of bulk properties. If U_0 signifies total energy per atom (negative of cohesive energy E0) and $\boldsymbol{\rho_{h,i}}$ in the electron density function at location *R*, then we have for a monoatomic bcc solid (Daw and Baskes, 1984, Yuan et al, 20031, Johnson, 1988, Johnson and Oh, 1989, van Midden and Sasse, 1992) within a closest neighbour model.

$$U_0 = 4\phi_1(r_0) + F(\rho_0) \qquad (6)$$

$$0 = 4\phi_1'(r_0) + F'(\rho_0)\,V_{11}/a \qquad (7)$$

$$B = \frac{(9C_{44}-4C_{11})}{5} - \frac{2}{\Omega_0}F'(\rho_0)W_{12} - \frac{1}{2\Omega_0}F''(\rho_0)V_{11}^2 \qquad (8)$$

$C_{11} = G + \frac{1}{\Omega_0}F'(\rho_0)W_{11} + \frac{1}{\Omega_0}F''(\rho_0)V_{11}^2$ (9)

$C_{12} = G + \frac{1}{\Omega_0}F'(\rho_0)W_{12} + \frac{1}{\Omega_0}F''(\rho_0)V_{11}^2$ (10)

$\frac{a}{4}C_{44} = G + \frac{1}{\Omega_0}F'(\rho_0)W_{12}$ (11)

where $G = \frac{4\phi_1'(r_0)}{3\sqrt{3}a^2} + \frac{2.\phi_1''(r_0)}{3a}$ (12)

and U_0 is the energy per atom, B is the bulk modulus and C_{ij} the elastic constants written in the Voigt notation. $r_0 = \frac{\sqrt{3}a}{2}$ is the equilibrium nearest neighbor distance; a is the lattice constant; $\Omega_0 = \frac{a^3}{2}$ is the volume per atom; while V_{11}, W_{11} and W_{12} are three basic EAM parameters.

The equations (6) – (11), are the fundamental equations of the EAM and they depend on the three fundamental functions $\boldsymbol{F(\rho)}$, $\boldsymbol{\rho(r)}$, $\boldsymbol{\phi(r)}$ and their first and second derivatives.

The mono-vacancy formation energy E_{iv}^f is of the form

$E_{iv}^f = 8F\left(\frac{7}{8}\rho_0\right) - 7F(\rho_0) - U_0$ (13)

In this work, E_{iv}^f is chosen to be a known physical input and from (11) and (10), gives;

$\boldsymbol{V_{11} = \pm\sqrt{\frac{\Omega_0(C_{12}-C_{44})}{F''(\rho_0)}}}$ (14)

For materials with $\boldsymbol{C_{12} > C_{44}}$, we demand that $\boldsymbol{F''(\rho_0)}$ be positive definite while for materials with $\boldsymbol{C_{12} < C_{44}}$, $\boldsymbol{F''(\rho_0)}$ must be negative definite, Oni-Ojo et al.(2007).

The embedding functions (2-5) have a limitation in terms of flexibility. In an earlier study, Oni-Ojo et al. (2007) developed a generalized embedded function $\boldsymbol{F(\rho)}$ by altering the work of Yuan et al (2003)[1] to a robust and flexible embedding function.

$F(\rho) = AE_0\left(\rho/\rho_0\right)^{\lambda}\left[\ln\left(\rho/\rho_0\right)^{\alpha} - k\right]$ (15)

Where, $\boldsymbol{\lambda}$, $\boldsymbol{\alpha}$ and K are the variables that provide flexibility to the new model.

$F(\rho_0) = -AE_0k$ (16)

$F'(\rho_0) = \frac{-F(\rho_0)}{\rho_0}\left[\lambda - \frac{\alpha}{k}\right]$ (17)

$F''(\rho_0) = \frac{F(\rho_0)}{{\rho_0}^2}\left[\lambda^2 - \frac{2\lambda\alpha}{k} + \frac{\alpha}{k} - \lambda\right]$ (18)

At equilibrium, equation (15) yields (16)-(18), where the prime signifies first and second differentiation with respect to the electron density, $\boldsymbol{\rho}$. We achieved results for $A = \pm 1$ in this study, and the parameters, $\boldsymbol{\lambda}$, $\boldsymbol{\alpha}$ and K are determined by demanding that the embedding function $\boldsymbol{F(\rho)}$ fulfill equation (13), and so,

$\lambda = \frac{\ln\left\{\frac{\frac{1}{12}\left[E_{iv}^f + 11F(\rho_0) + U_0\right]}{AE_0\left[\ln\left(\frac{11}{12}\right)^{\alpha} - k\right]}\right\}}{\ln\left(11/12\right)}$ (19)

Knowing $\boldsymbol{\lambda}$, $\boldsymbol{\alpha}$ and K, the EAM functions and parameters are calculated.

RESULTS AND DISCUSSION

The EAM parameters were derived using some of the iterated values for the GEAM parameters A, $\boldsymbol{\alpha}$, $\boldsymbol{\lambda}$, and **K** (Oni-Ojo, M.Phil, thesis, 2011) for Li and V. Tables 2 and 3 show the values. Table 1 shows the input parameters.

Table 1. Values nput Parameters for bcc Li and V. Lattice Constant a (Å), Bulk Modulus B_0 and Elastic Constant GPa, Cohesive E_0 and monovacancy formation energy, E_{iv}^f (eV).

	Cohesion energy *E0* (eV)	Mono-vacancy Formation energy E_{iv}^f (eV)	Lattice Constant *a* (Å)	Elastic constant (Gpa)			Bulk Modulus B (GPa)
				C_{11}	C_{12}	C_{44}	
Li	1.630	0.340	3.491	0.148	0.125	0.108	0.116
V	5.310	2.200	3.030	2.290	1.210	0.444	1.570

Table 2: Calculated EAM Model Parameters for *bcc Li* corresponding to the iterated GEAM values of α *and K.*

EAM Parameter	Model					
	I	II	III	IV	V	VI
A	1	1	-1	-1	1	1
α	0.3800	0.3400	0.3600	0.3600	1.0550	1.0440
K	-0.9800	-0.6000	0.5000	0.5400	0.0400	0.0313
λ	1.4079	1.7761	3.3586	3.1723	2.9184	2.9651
$F(\rho_0)$ [eV]	1.6170	0.9900	0.8250	0.8910	-0.0660	-0.0517
$F'(\rho_0)$[eV/ρ_0]	2.9035	2.3194	2.1768	2.2325	1.5481	1.5693
$F''(\rho_0)$[eV/$\rho_0$2]	2.0670	2.7965	3.1391	2.9654	8.0502	8.1915
V_{11} [ρ_0] (-)	-0.2881	-0.2881	-0.2719	-0.2798	-0.1698	-0.1683
W_{11} [ρ_0]	0.0225	0.0281	0.0300	0.0292	0.0421	0.0416
W_{12} [ρ_0]	-0.1772	-0.2219	-0.2364	-0.2305	-0.3324	-0.3279
$\phi_1(r_0)$ [eV]	-0.8168	-0.6600	-0.6188	-0.6353	-0.3960	-0.3996
$\phi_1'(r_0)$[eV/Å]	0.0693	0.0476	0.0422	0.0445	0.0187	0.0188

$\phi_1''(r_0)$[eV/Å^2]	0.0915	0.0844	0.0826	0.0833	0.0749	0.0749

Table.3: Calculated EAM Model Parameters for *bcc Li* corresponding to the iterated GEAM values of *α and K*

EAM Parameter	Model					
	I	**II**	**III**	**IV**	**V**	**VI**
A	-1	1	-1	-1	-1	-1
α	0.0690	0.3800	0.2200	0.2400	0.2600	0.3000
K	0.3297	-0.3800	1.3400	2.7000	1.2000	3.4000
λ	3.3986	1.7891	1.6452	1.3241	1.7548	1.2743
$F(\rho_0)$ [eV]	1.7507	2.0178	7.1154	14.3370	6.3720	18.0540
$F'(\rho_0)$[eV/ρ_0]	5.5836	5.6278	10.5384	17.7093	9.8013	21.4135
$F''(\rho_0)$[eV/$\rho_0$2]	12.1477	8.0508	4.8779	4.0523	4.9757	3.8441
V_{11} [ρ_0] (-)	-0.7399	-0.9088	-1.1676	-1.2810	-1.1561	-1.3153
W_{11} [ρ_0]	0.4909	0.4871	0.2601	0.1548	0.2797	0.1280
W_{12} [ρ_0]	-2.8449	-2.8225	-1.5073	-0.8970	-1.6207	-0.7418
$\phi_1(r_0)$ [eV]	-1.7652	-1.8320	-3.1064	-4.9118	-2.9205	-5.8410
$\phi_1'(r_0)$[eV/Å]	0.3409	0.4220	1.0152	1.8718	0.9349	2.3238
$\phi_1''(r_0)$[eV/Å^2]	-0.8572	-0.8262	-0.6001	-0.2737	-0.6308	-0.1014

Table 4: Predicted values of Γ_{100}, Γ_{110} and Γ_{111} for Lithium (Li) in Ergs/cm^2 and the experimental average value for Li (Wen and Zhang, 2008).

Model	Present work				EXPERIMENT
	Γ_{111}	Γ_{100}	Γ_{110}	AVERAGE	
I	393.4173	600.9522	290.4442	428.2713	520
II	426.0098	657.4041	307.3183	463.5774	
III	446.7022	693.2444	317.6405	485.8624	
IV	439.8954	681.4548	313.6928	478.3477	
V	564.2788	896.8931	399.4785	620.2168	
VI	565.5201	899.0431	401.0606	621.8746	

Table 5: Predicted values of Γ_{100}, Γ_{110} and Γ_{111} for Vanadium (V) in Ergs/cm^2 and the experimental average value for V (Wen and Zhang, 2008).

Model	Present work				EXPERIMENT
	Γ_{111}	Γ_{100}	Γ_{110}	AVERAGE	
I	2261.6915	3437.4527	1758.8847	2,486.01	2600
II	2116.1246	3185.3235	1661.4923	2,320.98	
III	1920.2954	2846.1373	1561.6336	2,109.36	
IV	1854.3474	2731.9120	1531.9344	2,039.40	
V	1930.0727	2863.0722	1565.6818	2,119.61	
VI	1837.1673	2702.1553	1524.3323	2,021.22	

CONCLUSION

The GEAM is used to determine the three low-index surface energies for Li and V, and the projected findings show that a trend of $\Gamma_{110} < \Gamma_{111} < \Gamma_{100}$ was maintained for both metals, and their average is within that of experimental results. Judging from the results of this study, the use of a flexible embedding function with enough robust parameters was able to predict results comparable to those achieved experimentally for studied bcc metals. As a result, the GEAM is viewed as a model with potentials to produce good results when applied to other metallic qualities. The model's application to other fcc and bcc metals is now being evaluated, and the results will be released as soon as they are available.

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