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Surface Energy Calculation for FCC Metals with Negative Cauchy's Discrepancy using the GEAM

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ABSTRACT

The three low-index surfaces of fcc metals with negative Cauchy's discrepancy, strontium (Sr) and Iridium (Ir) are here investigated using the generalized embedded-atom method (GEAM), a model developed by Oni-Ojo et al. (2007) and the corresponding surface energies calculated. The low-index surface energies studied are: $\Gamma_{(111)}$, $\Gamma_{(100)}$ and $\Gamma_{(110)}$, with $\Gamma_{(111)}$ having the lowest and $\Gamma_{(110)}$ having the highest energy value. The predicted values are in good agreement with the experimental values.

INTRODUCTION

The surface energy is a very important physical quantity for understanding various surface phenomena such as absorption, corrosion, crystal formation, and so on.

The embedded - atom method (EAM) first introduced by Daw and Baskes (1983 and 1984 had been applied to calculate surface energy of different metals such as: face-centered cubic (fcc), body-centered cubic (bcc), and diamond structures (Adams and Foiles, 1999, Baskes. 1992, Baskes and Nelson. 1989, Smith and Banerjia, 1987, Foiles et al, 1986, Johnson, 1988 and Daw and Baskes, 1984). The original EAM was however faced with the challenges of not being able to predict surface energy of fcc metals with negative Cauchy's discrepancy (ie, $\boldsymbol{C_{12} < C_{44}}$) and the prediction of surface energy that is about 50% lower than the polycrystalline experimental value for single crystal surface energy (Baskes, 1992).

The need to improve on the in the original EAM of Daws and Baskes resulted in several modifications such as; the modified embedded-atom method (MEAM) (Baskes, 1987 and 1992 and Baskes and Nelson, 1989), the analytical embedded atom method (AEAM) by Johnson et al. (1988, 1989 and 1990), and the modified analytical embedded atom method (MAEAM) by Zhang et al. (2008).

This study focusses on the two fcc metals with negative Cauchy's discrepancy visa vice strontium (Sr) and iridium (Ir) using the generalized embedded atom method (GEAM) iterated values to calculate the low-index surface energy.

MATERIALS AND METHODS

Within the EAM, total energy of a system E_{tot} is approximated to be, the sum total of the embedding and the pair potential function.

$$E_{tot} = \sum_{j\neq i} F_i(\rho_{h,i}) + \frac{1}{2}\sum \phi_{i,j}(R_{i,j}) \quad (1)$$

where $F(\rho)$ denotes the energy required to immerse an atom in the background electron density $\rho(R)$ at site *i*, and $\phi_{i,j}(R)$ denotes the screened pair potential between atoms *i* and *j*.

Unlike the other models of the EAM that focused on modifying the density function of the original EAM, Oni-Ojo et al (2007) in constructing the GEAM had modified the work of Yuan et al. (2003) to design a generalized embedding function $F(\rho)$.

$$F(\rho) = AE_0\left(\rho/\rho_0\right)^{\lambda}\left[\ln\left(\rho/\rho_0\right)^{\alpha} - k\right] \quad (2)$$

Where, $\boldsymbol{A}$, $\boldsymbol{\lambda}$, $\boldsymbol{\alpha}$ and $\boldsymbol{K}$ are the GEAM parameters that provide flexibility to the model.

In practice, functional forms are chosen for $\boldsymbol{F_i(\rho_{h,i})}$ and $\phi_{i,j}$ in equation (1) and the parameters in each of these functions are determined by fitting to a limited set of bulk properties. With U_0 as the total energy per atom (negative of the cohesive energy E_0) and $\boldsymbol{\rho_{h,i}}$ as the electron density function at position *R*, then within a nearest neighbour model, it can be shown that for a monoatomic *fcc* solid (Daw and Baskes, 1984, Idiodi and Aghemenloh, 1998 and 1999 and Oni-Ojo et al. 2007).

$$U_0 = 6\phi_1(r_0) + F(\rho_0) \quad (3)$$

$$0 = \phi_1'(r_0) + 3F'(\rho_0)\,V_{11}/r_0 \quad (4)$$

$$\frac{3aB_0}{4} = \phi_1''(r_0) + \frac{a}{4\Omega_0}\{F'(\rho_0)[2W_{11} - 8W_{12} - 5V_{11}]\} - \frac{a}{4\Omega_0}\{2F''(\rho_0)V_{11}^2\} \quad (5)$$

$$\frac{a}{4}C_{11} = G_{11} + \frac{a}{4\Omega_0}F'(\rho_0)W_{11} + \frac{a}{4\Omega_0}F''(\rho_0)V_{11}^2 \quad (6)$$

$$\frac{a}{4}C_{12} = G_{12} + \frac{a}{4\Omega_0}F'(\rho_0)W_{12} + \frac{a}{4\Omega_0}F''(\rho_0)V_{11}^2 \quad (7)$$

$$\frac{a}{4}C_{44} = G_{12} + \frac{a}{4\Omega_0}F'(\rho_0)W_{12} \quad (8)$$

where $G_{11} = \frac{\phi_1'(r_0)}{2r_0} + \frac{\phi_1''(r_0)}{2}$ (9)

and $G_{12} = \frac{-5\phi_1'(r_0)}{4(r_0)} + \frac{\phi_1''(r_0)}{4}$ (10)

The equations (3) – (6) are the basic equations of the EAM and they depend on three fundamental functions: $\boldsymbol{F(\rho)}$, $\boldsymbol{\rho(r)}$ and $\boldsymbol{\phi(r)}$.

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

$$E_{iv}^f = 12F\left(\frac{11}{12}\rho_0\right) - 11F(\rho_0) - U_0 \quad (11)$$

With E_{iv}^{f} treated as a known physical input parameter in this work.

Solving equations (7) and (8) gives,

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

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

At equilibrium, the equation (2) yields equations (13)-(15), where the prime denotes first and second differentiation with respect to the electron density, $\boldsymbol{\rho}$.

$$F(\rho_0) = -AE_0k \quad (13)$$

$$F'(\rho_0) = \frac{-F(\rho_0)}{\rho_0}\left[\lambda - \frac{\alpha}{k}\right] \quad (14)$$

$$F''(\rho_0) = \frac{F(\rho_0)}{{\rho_0}^2}\left[\lambda^2 - \frac{2\lambda\alpha}{k} + \frac{\alpha}{k} - \lambda\right] \quad (15)$$

To obtain the GEAM parameters, $\boldsymbol{A}$, $\boldsymbol{\lambda}$, $\boldsymbol{\alpha}$ and $\boldsymbol{K}$, we demand that the embedding function in equation (2) reproduced and satisfy the mono-vacancy formation energy equation (11) and the result gives;

$$\lambda = \frac{\ln\left\{\frac{\left[\frac{1}{12}\left[E_{iv}^{f}+11F(\rho_0)+U_0\right]\right]}{AE_0\left[\ln\left(\frac{11}{12}\right)^{\alpha}-k\right]}\right\}}{\ln\left(\frac{11}{12}\right)} \quad (16)$$

Knowing $\boldsymbol{A}$, $\boldsymbol{\lambda}$, $\boldsymbol{\alpha}$ and $\mathbf{K}$, the EAM functions and parameters are calculated and the results are there after used to calculate the surface energy. It is proper to state here that the flexibility of the model are provided by the robust parameters.

RESULTS AND DISCUSSION

The GEAM parameters are determined by fixing the parameter$A = \pm 1$, the parameter $\boldsymbol{\lambda}$ is obtained from equation (16) using iterated values of α and K (Oni-Ojo, 2011). Different sets of iterated values of $\boldsymbol{\alpha}$ and $\mathbf{K}$ that produced good results were selected from the lot and the corresponding values EAM parameters and surface energies obtained are presented in Table 2 to Table 5, while the physical input parameters for Sr and Ir are in Table 1.

Table 1: Input Parameters for fcc metals Sr and Ir

	Lattice Constant a (Å)	Mono-vacancy Formation energy E_{iv}^{f} (eV)	Cohesion energy E_0 (eV)	Elastic constant (Gpa)			Bulk Modulus B (GPa)
				C_{11}	C_{12}	C_{44}	
Sr	6.0860	1.0800	1.7200	0.1532	0.0600	0.1002	0.1150
Ir	3.8400	1.9700	6.9300	5.9000	2.4900	2.6200	3.5500

Table 2: Calculated model's parameters for *Sr* corresponding to the iterated values of α and K

EAM Parameter	Model				
	I	II	III	IV	V
A	-1.0000	-1.0000	-1.0000	-1.0000	-1.0000
$\boldsymbol{\alpha}$	0.9000	0.9200	1.0000	1.0500	0.9200
K	0.1500	0.2000	0.1000	0.1000	0.1500
$\boldsymbol{\lambda}$	8.7648	6.9985	12.9397	13.2040	8.8520
$F(\rho_0)$ [eV]	0.2580	0.3440	0.1720	0.1720	0.2580
$F'(\rho_0)$[eV/ρ_0]	0.7133	0.8251	0.5056	0.4651	0.7014
$F''(\rho_0)$[eV/$\rho_0$2]	-8.0292	-6.1252	-16.2192	-18.1705	-8.4999
V_{11} [ρ_0] (-)	-0.4197	-0.4805	-0.2953	-0.2790	-0.4079
W_{11} [ρ_0]	0.3220	0.0430	1.0477	1.2231	0.3652
W_{12} [ρ_0]	0.9630	0.8910	1.2100	1.2900	0.9700

Table 3: Calculated model parameters for *Ir* corresponding to the iterated values of α and K

EAM Parameter	Model					
	I	II	III	IV	V	VI
A	-1.0000	-1.0000	-1.0000	-1.0000	-1.0000	-1.0000
$\boldsymbol{\alpha}$	0.4800	0.5000	0.8800	0.9200	0.9400	0.9800
K	-0.3000	-0.3000	0.2000	0.2000	0.2000	0.1500
$\boldsymbol{\lambda}$	-2.9789	-3.0566	9.2481	9.3918	9.4630	12.7096
$F(\rho_0)$ [eV]	-2.0790	-2.0790	1.3860	1.3860	1.3860	1.0395
$F'(\rho_0)$[eV/ρ_0]	2.8668	2.8897	6.7195	6.6415	6.6016	6.4202
$F''(\rho_0)$[eV/$\rho_0$2]	-1.4975	-1.1313	-0.9756	-4.1442	-5.7748	-11.1378
V_{11} [ρ_0] (-)	-0.8758	-1.0076	-1.0851	-0.5265	-0.4460	-0.3211
W_{11} [ρ_0]	1.9699	1.6767	-0.5824	0.5534	0.7241	1.0195
W_{12} [ρ_0]	1.0800	1.1400	0.8170	0.5410	0.5020	0.4480

Table 4: Predicted values of three low-index surface energy for Sr in Ergs/cm^2 and the experimental average value for Strontium (Aghemenloh and Idiodi, 1998)

Model	Present work				EXPERIMENTAL
	Γ_{111}	Γ_{100}	Γ_{110}	AVERAGE	AVERAGE
I	292.7033	369.1301	407.3345	356.3893	
II	278.4410	347.5393	387.5549	337.8451	
III	316.7900	400.7654	432.7196	383.4250	410
IV	316.1647	400.5057	432.6591	383.1098	
V	292.0784	368.7011	407.1579	355.9791	

Table 5: Predicted values of three low-index surface energy for *Ir* in Ergs/cm^2 and the experimental average value for Iridium (Wen and Zhang, 2007)

Model	Present work				EXPERIMENTAL
	Γ_{111}	Γ_{100}	Γ_{110}	AVERAGE	AVERAGE
I	1626.4022	2721.5012	4363.1610	2903.6881	
II	1717.4875	2973.2520	4865.7365	3185.4920	
III	2289.8574	3209.1756	3496.0241	2998.3524	3000
IV	2280.9658	3203.4295	3493.8156	2992.7370	
V	2276.5527	3200.6135	3492.7487	2989.9716	
VI	2585.0289	3561.5649	3765.1332	3303.9090	

From the Table 4 and Table 5, the three low-index surfaces of both Sr and Ir are presented as predicted in this present work, the surface energies of the Γ_{100} surface as can be seen are all lower than that of the Γ_{110} surface while the Γ_{111} (the close-packed) surface has the lowest surface energy of the three. This order is in agreement with the work previously reported by other researchers like Foiles et al. (1986) and Wen and Zhang, (2007).

CONCLUSION

The three low-index surface energies of Sr and Ir have been calculated using the generalized embedded atom method (GEAM) iterated parameter values, and the findings show a general order of $\Gamma_{111} < \Gamma_{100} < \Gamma_{110}$ for all the values. And their average deviation are within the range of 17.6% to 6.5% for Sr and 3.2% to 0.1% for Ir. This result is in no doubt in good agreement with experimental average and a good improvement over the other EAM. As a result, the GEAM will be a useful instrument for calculating relative values of surface energy and other metal properties.

A method for characterizing and fitting the GEAM parameters, $\boldsymbol{\alpha}$ and K, using appropriate formula is being investigated and will be reported when completed.

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