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Surface energy calculation for Rhodium (Rh) treated as *fcc* metal with both positive and negative Cauchy's discrepancy by using the GEAM

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ABSTRACT

The fcc metal Rhodium is treated as having both positive and negative Cauchy's discrepancy and the three low-index surfaces of the metal calculated using the generalized embedded-atom method (GEAM), a model developed by [1]. The low-index surface energies investigated are $\{\Gamma_{(111)}, \Gamma_{(100)}$ *and* $\Gamma_{(110)}\}$*. The predicted values are in good agreement with the experimental values. The result shows* $\Gamma_{(111)}$ *having the lowest and* $\Gamma_{(110)}$ *having the highest energy value.*

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 [2,3] had been applied to calculate surface energy of different metals such as: face-centered cubic (fcc), body-centered cubic (bcc), and diamond structures [3,4-9]. 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, $C_{12} < C_{44}$) and the prediction of surface energy that is about 50% lower than the polycrystalline experimental value for single crystal surface energy [5].

The need to improve on the original EAM of [2,3] resulted in several modifications such as; the modified embedded-atom method (MEAM) [5, 6, 10], the analytical embedded atom method (AEAM) by Johnson et al. [9,10,11], and the modified analytical embedded atom method (MAEAM) [13,14].

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This study focuses on the fcc metals Rhodium. One of the three most valuable metals which exists within the platinum group of metals. Available records seems not to be exact on the values its elastic constants C_{12} and C_{44}. Some researchers had presented Rh as a metal with positive Cauchy discrepancy $(C_{12} > C_{44})$[13] and some as metal with negative Cauchy's discrepancy$(C_{12} < C_{44})$[15]. We have decided to use the generalized embedded atom method (GEAM) parameters' iterated values to calculate the low-index surface energy of both cases.

MATERIALS AND METHODS

Like every other models of the EAM, the total energy of a system in the GEAM, E_c is approximated to be, the sum total of the embedding and the pair potential function.

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

where $F(\varrho)$ denotes the energy required to immerse an atom in the background electron density $\varrho(R)$ at site *i*, and $\phi_{i,j}(R)$ denotes the screened pair potential between atoms *i* and *j*.
While the other models of the EAM tends to focus more in modifying the density function of the original EAM, the generalized embedding method (GEAM) designed by [1], decided to consider the embedding function and had modified the work of [16] to design a four parameter generalized embedding function $F(\varrho)$.

$$F(\varrho) = AE_0(\varrho/\varrho_0)^{\lambda}[\ln(\varrho/\varrho_0)^{\alpha} - k] \quad (2)$$

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 $\boldsymbol{F_i(\varrho_{h,i})}$ 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 $\boldsymbol{\varrho_{h,i}}$ as the electron density function at position *R*, then within a nearest neighbour model, it can be shown that for a monoatomic *fcc* solid [3,17,18].

$$6\phi_1(r_0) + F(\varrho_0) = U_0 \quad (3)$$

$$\phi_1'(r_0) + 3F'(\varrho_0)\, V_{11}/r_0 = 0 \quad (4)$$

$$\phi_1''(r_0) + \frac{a}{4\Omega_0}\{F'(\varrho_0)[2W_{11} - 8W_{12} - 5V_{11}]\} - \frac{a}{4\Omega_0}\{2F''(\varrho_0)V_{11}^2\} = \frac{3aB_0}{4} \quad (5)$$

$$G_{11} + \frac{a}{4\Omega_0}F'(\varrho_0)W_{11} + \frac{a}{4\Omega_0}F''(\varrho_0)V_{11}^2 = \frac{a}{4}C_{11} \quad (6)$$

$$G_{12} + \frac{a}{4\Omega_0}F'(\varrho_0)W_{12} + \frac{a}{4\Omega_0}F''(\varrho_0)V_{11}^2 = \frac{a}{4}C_{12} \quad (7)$$

$$G_{12} + \frac{a}{4\Omega_0}F'(\varrho_0)W_{12} = \frac{a}{4}C_{44} \quad (8)$$

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: $\boldsymbol{F(\varrho)}$, $\boldsymbol{\varrho(r)}$ and $\boldsymbol{\phi(r)}$.
The mono-vacancy formation energy E_{iv}^f is of the form;

$$E_{iv}^{f} = 12F\left(\frac{11}{12}\varrho_0\right) - 11F\ (\varrho_0) - U_0 \quad (11)$$

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

Solving equations (7) and (8) gives,

$$\boldsymbol{V_{11}} = \pm\sqrt{\frac{\boldsymbol{\Omega_0(C_{12}-C_{44})}}{\boldsymbol{F''(\varrho_0)}}} \quad (12)$$

In equation (12), we demand that $\boldsymbol{F''(\varrho_0)}$ be positive definite for metals with $\boldsymbol{C_{12} > C_{44}}$, while for metal with $\boldsymbol{C_{12} < C_{44}}$, $\boldsymbol{F''(\varrho_0)}$ must be negative definite .[1]

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

$$F(\varrho_0) = -AE_0k \quad (13)$$

$$F'(\varrho_0) = \frac{-F(\varrho_0)}{\varrho_0}\left[\lambda - \frac{\alpha}{k}\right] \quad (14)$$

$$F''(\varrho_0) = \frac{F(\varrho_0)}{{\varrho_0}^2}\left[\lambda^2 - \frac{2\lambda\alpha}{k} + \frac{\alpha}{k} - \lambda\right] \quad (15)$$

To obtain the GEAM parameters, $\boldsymbol{A, \lambda, \alpha}$ 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;

$$\lambda = \frac{\ln\left\{\frac{\frac{1}{12}[E_{iv}^{f} + 11F\ (\varrho_0) + U_0]}{AE_0[\ln(\frac{11}{12})^{\alpha} - k]}\right\}}{\ln(11/12)} \quad (16)$$

Knowing $\boldsymbol{A}$, $\boldsymbol{\lambda}$, $\boldsymbol{\alpha}$ and **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 DISCUSSIONS

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 [19]. Different sets of iterated values of $\boldsymbol{\alpha}$ and **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 Rh are in Table 1. Rh with $C_{12} > C_{44}$ is denoted with Rh(+) while that with $C_{12} > C_{44}$ is denoted as Rh(-).

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Table 1: Input Parameters for fcc metals Rh(+)[13] and Rh(-)[15].

	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}	
Rh(+)	3.8034	1.7100	5.7500	4.1300	1.9400	1.8400	2.7000
Rh(-)	3.8034	1.7100	5.7500	4.1300	1.9200	1.9400	2.7000

Table 2: Calculated model's parameters for *Rh(+)* 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
α	1.8000	1.6500	1.6000	1.5000	0.4400
K	0.9000	0.7000	0.6500	0.5500	-0.1500
λ	2.0558	2.1405	2.1531	2.1845	3.9897
$F(\varrho_0)$ [eV]	-5.1750	-4.0250	-3.7375	-3.1625	0.8625
$F'(\varrho_0)$[eV/ϱ_0]	-0.2890	0.8719	1.1526	1.7166	5.9711
$F''(\varrho_0)$[eV/$\varrho_0 2$]	20.9729	21.3027	21.1381	20.8745	27.9453
$V_{11}[\varrho_0]$ (-)	-0.2023	-0.2007	-0.2015	-0.2028	-0.1753
$W_{11}[\varrho_0]$	-9.0190	2.4541	1.7570	1.0448	0.0664
$W_{12}[\varrho_0]$	0.9920	-0.1950	-0.1230	-0.0486	0.0445

Table 3: Calculated model's parameters for *Rh(-)* 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
α	0.4400	1.6800	1.6800	1.6800	1.6400
K	-0.2500	0.1800	0.1400	0.1600	0.1600
λ	-3.5253	12.8693	16.2189	14.3144	14.1830
$F(\varrho_0)$ [eV]	-1.4375	1.0350	0.8050	0.9200	0.9200
$F'(\varrho_0)$[eV/ϱ_0]	-2.5642	-80.8789	-104.9876	-91.5535	-86.0450
$F''(\varrho_0)$[eV/$\varrho_0 2$]	-2.5642	-80.8789	-104.9876	-91.5535	-86.0450
$V_{11}[\varrho_0]$ (-)	-0.2588	-0.0461	-0.0404	-0.0433	-0.0447
$W_{11}[\varrho_0]$	0.5989	0.6820	0.7533	0.7207	0.6936
$W_{12}[\varrho_0]$	0.2310	0.0934	0.0961	0.0950	0.0935

Table 4: Predicted values of three low-index surface energy for Rh*(+)* in Ergs/cm ^{2} and the experimental average value for Rhodium [20].

Model	Present work				EXPERIMENTAL AVERAGE
	Γ_{111}	Γ_{100}	Γ_{110}	AVERAGE	
I	2061.733	2868.121	3142.659	**2690.838**	2700
II	2065.301	2868.995	3137.984	**2690.760**	
III	2057.274	2855.641	3123.043	**2678.653**	
IV	2043.332	2832.027	3096.165	**2657.174**	
V	2131.584	2900.206	3096.420	**2709.403**	

Table 5: Predicted values of three low-index surface energy for Rh*(-)* in Ergs/cm ^{2} and the experimental average value for Rhodium [20].

Model	Present work				EXPERIMENTAL AVERAGE
	Γ_{111}	Γ_{100}	Γ_{110}	AVERAGE	
I	1429.970	2560.307	4515.975	**2835.418**	2700
II	1931.999	2776.658	3039.707	**2582.788**	
III	2218.850	3071.456	3241.862	**2844.056**	
IV	2065.971	2919.366	3139.562	**2708.300**	
V	2069.043	2920.477	3139.783	**2709.768**	

Table 4 and Table 5 show the three low-index surfaces for Rh either as Rh(+) or Rh(-). In all, the surface energies of the $\mathbf{\Gamma}_{100}$ surface are lower than that of the $\mathbf{\Gamma}_{110}$ surface while the $\mathbf{\Gamma}_{111}$ (the close-packed) surface has the lowest surface energy of the three. These findings are in agreement with the works of [8,13].

CONCLUSION

The low-index surface energies of Rh irrespective of the nature of C_{12} and C_{44} have been calculated using the generalized embedded atom method (GEAM) iterated parameter values, and the findings show a trend of $\Gamma_{111} < \Gamma_{100} < \Gamma_{110}$ for all the values. And their average being within the range of $0.3\% - 1.6\%$ for Rh(+) and $4.4\% - 5.3\%$ for Rh(-). This result is in no doubt in good agreement with experimental average and a good improvement over the EAM predictions in [8,9,13]. Thus the GEAM will be a useful instrument for calculating relative values of surface energy and other metal properties.

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