

## IMPLEMENTATION OF EQUIVALENT CRYSTAL THEORY WITHIN A GENERALIZED EMBEDDED –ATOM METHOD

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### ABSTRACT

This paper employs the concept of an equivalent crystal within a Generalized Embedded – Atom Method to calculate the (111) surface energies of four fcc metals – AL, Au, Pd, and Pt. The results obtained for all four metals are found to be comparable to first principles calculations and experimental data.

### I INTRODUCTION

The theoretical problem of calculating the surface energies of metals has continued till date to attract the attention of several workers [1-16]. In a previous paper, Idiodi and Aghemenloh [11] demonstrated for the first time how the concept of an equivalent crystal due to Smith et al [12], may be applied within the Embedded-Atom method (EAM) [6-7]. In that work, the (111) surface energies of four fcc metals (Al, Au, Pd, and Pt) were calculated. While the surface energy obtained for Al was in good agreement with experiment [16], the results for the other three fcc metals, though better than the results from previous studies [6-10], were found, surprisingly, to be still much lower than experimental data [16]. The failure of that theoretical effort for the three fcc metals (Au, Pd, and Pt) has prompted us to generalize the EAM. The generalization leads to excellent surface energy values for all four fcc metals. This paper, therefore, is essentially a repeat calculation of the study first performed by Idiodi and Aghemenloh [11], but this time, in the much richer context of a generalized embedded – atom method (GEAM).

In section II we give the basic equations of the GEAM, and in section III we discuss the method of calculating surface energies when one takes into account the concept of an equivalent crystal at the metal surface. Section IV is devoted to results, and concluding remarks are given in section V.

### II THEORY

Within the framework of density – functional theory [17] the total internal energy for an arbitrary arrangement of atoms (or, ions and electrons) which constitute a metallic solid can be written as a unique functional of the total electron density. In the embedded – atom method (EAM) this total internal energy  $E_{tot}$  takes the form [6,7].

$$E_{tot} = \sum_i F_i(\rho_{h,i}) + \frac{1}{2} \sum_{i,j(j \neq i)} \phi_{ij}(r_{ij}), \quad (2.1)$$

where  $\rho_{h,i}$  is the host electron density at atom  $i$  due to contributions from the remaining atoms of the system. In the embedded - atom method  $\rho_{h,i}$  is given by

$$\rho_{h,i} = \sum_{j(j \neq i)} \rho_j(r_{ij}) \quad (2.2)$$

$\rho_j(r_{ij})$  is the contribution to the density at atom  $i$  from an atom situated at position  $j$ .  $F(\rho)$  is the energy to embed atom  $i$  into the background electron density  $\rho$ . The embedding function  $F(\rho)$  contains all the many -body interactions which contribute to the total internal energy of the solid.  $\phi_{ij}(r_{ij})$  is the core-core pair potential between atoms  $i$  and  $j$  separated by the distance  $r_{ij}$ . The inversion of (2.2), if possible, provides immediately an expression for  $r$  as a function of the density  $\rho$ .

The ground state properties of the solid can be calculated from (2.1) and (2.2) in a straight - forward way [6,7]. Then for an fcc metal one obtains the usual EAM equations for the cohesive energy, the equilibrium condition, the elastic constants and the monovacancy formation energy. Following our previous theoretical effort [8,9] on the connection between the unified separable potential model [8] and the EAM [6], one can write a generalized version of the EAM equations, within a nearest neighbour model, in the form

$$U_o = E_{tot}/N \quad (2.3)$$

$$U_o = 6\phi_1 + F(\rho_e) \quad (2.4)$$

$$0 = 6\phi_1' + [3V_{11}/r_1] F'(\rho_e) \quad (2.5)$$

$$3aB_o/4 = \phi_1'' + \frac{a}{4\Omega_o} [F'(\rho_e)\{2W_{11} - 8W_{12} - 5V_{11}\}] + \frac{a}{4\Omega_o} [F''(\rho_e)V_{11}^2\{2t_1 - 4t_2 - 4t_3\}] \quad (2.6)$$

$$\frac{a}{4} C_{11} = \left[ \frac{\phi_1'}{2r_1} + \frac{\phi_1''}{2} \right] + \frac{a}{4\Omega_o} [F'(\rho_e)W_{11} + t_1 F''(\rho_e)V_{11}^2] \quad (2.7)$$

$$\frac{a}{4} C_{12} = \left[ -\frac{5\phi_1'}{4r_1} + \frac{\phi_1''}{4} \right] + \frac{a}{4\Omega_o} [F'(\rho_e)W_{12} + t_2 F''(\rho_e)V_{11}^2] \quad (2.8)$$

$$\frac{a}{4} C_{44} = \left[ -\frac{5\phi_1'}{4r_1} + \frac{\phi_1''}{4} \right] + \frac{a}{4\Omega_o} [F'(\rho_e)W_{13} + t_3 F''(\rho_e)V_{11}^2] \quad (2.9)$$

$$E_{iv}^F = 12F\left(\frac{11}{12}\rho_e\right) - 11F(\rho_e) - U_o \quad (2.10)$$



The above equations have been written in a form closely resembling the EAM equations.  $N$  is the number of atoms or ions in the crystal, while  $u_0$  is the energy per atom, i.e., the negative of the experimental cohesive energy.  $B_0$  and  $C_{ij}$  are, respectively, the bulk modulus and the elastic constants written in the Voigt notation.  $r_1 (= a/\sqrt{2})$  is the equilibrium nearest-neighbour distance, and  $a$  is the equilibrium lattice constant.  $\Omega_0 (= a^3/4)$  is the volume per atom in an fcc lattice that has one atom per lattice site.  $\phi_1$  is a nearest-neighbour repulsive pair potential whose first and second derivatives with respect to the radial distance  $r$  are respectively,  $\phi_1'$  and  $\phi_1''$  (all quantities being evaluated at the equilibrium pair separation  $r = r_1$ ).  $F'(\rho_e)$  and  $F''(\rho_e)$  are the first two derivatives of the embedding function  $F(\rho)$  with respect to the density  $\rho$ , evaluated at the equilibrium density  $\rho = \rho_e$ .  $E_{IV}^F$  is the monovacancy formation energy.

The generalization of the EAM is reflected in (2.4) to (2.10) through the appearance of the parameters  $t_1, t_2, t_3$  and  $W_{13}$ . If  $t_1 = t_2 = 1, t_3 = 0$  and  $W_{13} = W_{12}$ , we recover the usual EAM equations [6-9]. (2.4) to (2.10) constitute the basic equations of the generalized embedded atom method (GEAM) for a nearest-neighbour model of an fcc metal. It is important to point out here that the usual EAM equations [6-9] cannot be applied to a solid for which the elastic constant  $C_{12}$  is less than  $C_{44}$ , since  $F''(\rho_e)$  must be positive definite for metallic solids. So long as  $t_2$  is non-zero (even if  $W_{13}=W_{12}$  and  $t_3=0$ ) the GEAM does not suffer from such a defect, and this by itself is an important reason for the above generalization.

In the EAM equations, the parameters  $V_{11}, W_{11}, W_{12}$ , the embedding  $F$  function  $F$  with its first and second derivatives and the pair potential  $\phi$  with its first and second derivatives are all unknowns in the theory. The physical inputs required to determine these unknowns are the lattice constant  $a$ , the experimental cohesive energy ( $= -U_0$ ), the bulk modulus  $B_0$ , the monovacancy formation energy  $E_{IV}^F$  and the three elastic constants  $C_{11}, C_{12}$ , and  $C_{44}$ . In early EAM calculations [7], the embedding function  $F(\rho)$  was determined by a complicated numerical fitting procedure. We had earlier by-passed such a cumbersome procedure by exploiting fully the connection between the unified separable potential model [8] and the EAM [6]. The pursuit of such an approach [8,9] revealed that the EAM equations can be solved by an embedding function of the type

$$F(\rho) = -\left[ f_1 \left\{ e^{\alpha_f} - e^{\alpha_f(\rho/\rho_e - 1)} \right\} \right]^{\lambda_f} \quad (2.11)$$

where  $f_1, \alpha_f$  and  $\lambda_f$  are parameters to be determined. Once  $f_1, \alpha_f$  and  $\lambda_f$  are known, then  $F(\rho_e), F'(\rho_e)$  and  $F''(\rho_e)$  are immediately known from (2.11). In

addition to obtaining the embedding function (2.11), an efficient self consistent algorithm for determining the various unknown parameters in the EAM equations was found. This was practically applied to determine EAM parameters for some fcc metals in references 8 and 9. A generalized version of this algorithm, which emerges from an application of this same approach [8,9] to the GEAM equations, is given in Appendix 1 of this work. In conclusion, the GEAM equations can also be solved by an embedding function of type (2.11).

In the GEAM however, the parameters  $t_1$ ,  $t_2$ ,  $t_3$  and  $W_{13}$  are additional unknown parameters. Henceforth, for simplicity sake, it will be assumed that  $t_3 = 0$  and  $w_{13}=w_{12}$ , as in the usual EAM. Then there are only two additional unknowns,  $t_1$  and  $t_2$ , in the GEAM discussed in the subsequent analysis. Appendix 2 contains the details of an algorithm employed to determine the various unknowns in the GEAM, under conditions different from those covered in Appendix 1. Once the several unknowns in the theory have been determined, then various physical quantities of interest may now be calculated. One of such physical quantities is the surface energy.

### III: CALCULATION OF SURFACE ENERGIES

According to Daw and Baskes [6], the surface energy of a solid is computed by using the energy of each atom,

$$E_i = F(\rho_{h,i}) + \frac{1}{2} \sum_{j(j \neq i)} \phi(r_{ij}) \quad (3.1)$$

which is the contribution of the  $i^{\text{th}}$  atom to the total energy in (2.1). For atoms in the bulk, the sublimation energy is given by  $-E_i = -E_{bi} \equiv -U_0$ . But surface atoms, that have lost some neighbours, will have a higher energy  $E_{si}$ . The difference  $(E_{si} - E_{bi})$  summed over all atoms and divided by the surface area gives the total surface energy. Within a nearest - neighbor fcc model, a surface atom on the (111) surface has lost three atoms. It follows that the (111) surface energy, denoted  $\Gamma_{111}$ , is given by the formula [6]

$$\Gamma_{111} = \frac{4}{\sqrt{3}a^2} [E_{si} - E_{bi}] \quad (3.2)$$

This translates to

$$\Gamma_{111} = \frac{4}{\sqrt{3}a^2} \left[ F\left(\frac{9}{12}\rho_e\right) + \frac{9}{12} \cdot 6\phi_{1s} - U_0 \right] \quad (3.3)$$

If it is assumed that the repulsive pair potential is the same for bulk atoms as well as surface atoms, then

$$\phi_{1s} = \phi_{1b} = \phi \quad (3.4)$$

and taking into account (2.4), (3.3) becomes

$$\Gamma_{111} = \frac{4}{\sqrt{3}a^2} \left[ F_b\left(\frac{9}{12}\rho_e\right) + \frac{9}{12} \{U_0 - F_b(\rho_e)\} - U_0 \right] \quad (3.5)$$



where  $F_b$ , here and elsewhere, denotes the embedding function of the bulk crystal. Since we do not think that the assumption (3.4) is justifiable, it becomes imperative that we address the question of how  $\phi_{1s}$  is to be calculated. In order to treat this question, we have borrowed the idea of an equivalent crystal from the Equivalent Crystal Theory (ECT) method of Smith et al [12].

An atom on the (111) face of an fcc crystal that has lost 3 nearest neighbours, must be viewed to be an equivalent crystal; equivalent to the actual bulk crystal in every sense apart from the fact that the electron density in this equivalent crystal is lower than the electron density in the bulk crystal. Since the density is inversely proportional to the cube of the lattice constant, it follows that the lattice constant  $a_s$  of the equivalent crystal may be determined from the formula

$$\frac{\frac{9}{12} \rho_c}{\rho_c} = \frac{k/a_s^3}{k/a_b^3} \quad \text{i.e.} \quad \frac{9}{12} = \frac{a_b^3}{a_s^3} \quad (3.6)$$

where  $k$  is a proportionality constant, and  $a_b (= a)$  is the bulk crystal lattice constant. Note that, with the exception of the lattice constant, the equivalent crystal has the same parameters ( $t_1, t_2, t_3, U_0, B_0, C_{11}, C_{12}, C_{44}$ , and  $E_{IV}^F$ ) as the actual bulk crystal; but of course, not the same parameters  $V_{11}, W_{11}, W_{12}$  and  $W_{13}$ , since these are density dependent.

The theoretical determination of  $\phi_{1s}$  is therefore as follows: we must again solve equations (2.4) to (2.10) of section II in order to determine new EAM parameters for the equivalent crystal solid, remembering to replace  $a$  and  $r_1$ , wherever they occur, by the equivalent crystal values of  $a_s$  and  $r_{1s} (= a_s/\sqrt{2})$ , respectively. Then

$$6\phi_{1s} = U_0 - F_s(\rho) \quad (3.7)$$

where  $F_s(\rho_e)$  is the equilibrium value of the embedding function of the equivalent crystal. Taking into account (3.7), the new formula for the (111) surface energy of the fcc crystal within a nearest neighbour model, now takes the form

$$\Gamma_{111} = \frac{4}{\sqrt{3}a^2} \left( F_b \left( \frac{9}{12} \rho_e \right) + \frac{9}{12} \{ U_0 - F_s(\rho_e) \} - U_0 \right) \quad (3.8)$$

The extension of (3.6) to any other metallic surface or defect region is straight forward. (3.6) simplifies tremendously the steps advocated by Smith et al [12] for determining the lattice constant of the equivalent crystal. Yet the values of  $a_s$  calculated from (3.6) differ by only a few percent from what one would obtain from the work of Smith et al [12].

Before ending this section we must emphasize that in passing from the bulk to the surface defect region, the only function that has not been properly handled in all applications of the EAM that we are aware of, is the pair potential function  $\phi$ . There is no problem with the embedding  $F(\rho)$  since this function is

always correctly evaluated at any position with the density at the given position. The prescription given in this section for the evaluation of  $\phi$  in the defect region, will be shown in the next section to lead to substantially higher surface energies. Results will be exhibited for both the old EAM and the new GEAM.

#### IV RESULTS

In this section we exhibit surface energy results for four fcc metals – Al, Au, Pd and Pt. Table 1 contains pure metal properties used as input for the determination of the EAM parameters. The lattice constant  $a$  and the cohesive energy ( $= -U_0$ ) are taken from the compilation of pure metal properties by Kittel [18]. The vacancy formation energies are taken from Smith et al [12], while the elastic constants and the bulk modulus are taken from the compilation of Foiles et al [7] for Au, Pd and Pt and from Baskes and Melius [19] for Al.

Calculated EAM parameters for the pure bulk solid (i.e. a solid without defects) are collected together in Table 2a, while calculated EAM parameters for the equivalent crystal modeling the (111) surface defect region are exhibited in Table 2b. The results in both Tables were got using the computational algorithm of Appendix 1

Table 4 contains various results of (111) surface energies. The surface energies obtained from the data in Table 2a and equation (3.5) are shown in the 2<sup>nd</sup> column of Table 4. The 3<sup>rd</sup> column of Table 4 contains surface energies obtained from equation (3.8) using data from Tables 2a and 2b. The results in the 2<sup>nd</sup> and 3<sup>rd</sup> columns of Table 4 have been reported previously [11] and clearly the surface energies in column 3 are much higher than those in column 2. However, when the results in column 3 are compared with experiment (last column), we find that while the result for Al is in good agreement with experiment, the results for the other three fcc elements, though better than the results from previous studies [6-10], are still much lower than experimental data. The purpose of this work is to resolve this discrepancy. To better appreciate what is happening we must, in the subsequent discussion, pass to the much richer context of the GEAM.

In the light of this study, the results in columns 2 and 3 of Table 4 may be viewed as GEAM results obtained from equations (3.5) and (3.8), respectively, with the parameter choice  $t_1=t_2=1$  for all four fcc metals. Since the Cauchy relation  $C_{12}=C_{44}$  is not fulfilled for actual metals, and the GEAM parameter  $t_2$  is clearly connected with the Cauchy discrepancy, as evident from (2.8) and (2.9), it was felt that a relaxation of the constraint  $t_2=1$  for all metals ought to improve the surface energy results. The practical implementations of this idea encounters the nontrivial problem of determining the various unknown parameters in the general theory. To cope with this problem the value of  $\alpha_f$  was held constant for the four fcc metals. The goodness of the surface energy result for Al from previous work [11] and in this study, suggested that the constant value of  $\alpha_f$  be chosen around 0.45, the value for Al. For this study  $\alpha_f = 0.4$  was chosen. With  $\alpha_f = 0.4$ , an



appropriate value of  $t_2$  and other relevant GEAM parameters were then determined for each pure bulk metal, using the computational algorithm in Appendix 2. This provided the calculated GEAM parameters displayed in Table 3a. The re-calculated GEAM parameters for the equivalent crystal modelling the (111) surface defect region are exhibited in Table 3b. They have been obtained with the computational algorithm of Appendix 1. The surface energy results obtained from equation (3.8), using the data from Tables 3a and 3b, are displayed in column 4 of Table 4. Columns 5 and 6 contain the EAM surface energy calculations of other workers, while column 7 is a first principles calculation [15] and the last column (column 8) is experimental data [16]. A comparison of the various EAM calculations with first principles calculation and experiment shows clearly the goodness of the results obtained in this study.

**TABLE 1** Pure metal properties used as input for the determination of the EAM functions.  $a$  is the equilibrium lattice constant;  $-U_0$  is the cohesive energy per atom;  $C_{11}$ ,  $C_{12}$ ,  $C_{44}$  are the elastic constants;  $B_0$  is the bulk modulus; and  $E_{IV}^f$  is the monovacancy formation energy.

	Al	Au	Pd	Pt
$a[\text{\AA}]$	4.05	4.08	3.89	3.92
$-U_0[\text{ev}]$	3.39	3.81	3.89	5.84
$E_{IV}^f[\text{ev}]$	0.66	0.96	1.40	1.30
$C_{11}[10^{12} \text{ ergs/cm}^3]$	1.12	1.86	2.341	3.467
$C_{12}[10^{12} \text{ ergs/cm}^3]$	0.66	1.57	1.760	2.507
$C_{44}[10^{12} \text{ ergs/cm}^3]$	0.279	0.42	0.712	0.765
$B_0[10^{12} \text{ ergs/cm}^3]$	0.80	1.70	1.95	2.83

**TABLE 2a** . Calculated EAM parameters for the bulk solid without defects.

	Al	Au	Pd	Pt
$a \equiv a_b [\text{\AA}]$	4.05	4.08	3.89	3.92
$\alpha_f$	0.4551	1.3344	1.3739	0.6965
$\lambda_f$	$\frac{8}{11}$	$\frac{8}{11}$	$\frac{8}{11}$	$\frac{8}{11}$
$f_1[\text{ev}]$	23.5877	2.8419	2.1984	21.9674
$F \equiv F_b(\rho_e) [\text{ev}]$	-6.6721	-4.5170	-3.8956	-9.5050
$F'_b(\rho_e) [\text{ev}/\rho_e]$	-3.8317	-1.5668	-1.3192	-4.7826
$F''_b(\rho_e) [\text{ev}/\rho_e^2]$	2.5690	2.2946	1.9799	4.2333
$V_{11}[\rho_e]$	1.2399	1.2305	2.2049	1.9666
$\phi_1 \equiv \phi_{1b} [\text{ev}]$	0.5470	0.1178	0.00094	0.6108
$F_b(\frac{9}{12} \rho_e) [\text{ev}]$	-5.6257	-4.0424	-3.4941	-8.1623

**TABLE 2b.** Calculated EAM parameters for the equivalent crystal modeling the (111) surface defect region.  $a_s$  is the lattice constant of the fcc equivalent crystal

	Al	Au	Pd	Pt
$a=a_s$ [Å]	4.4576	4.4906	4.2815	4.3145
$\alpha_f$	0.3962	1.2460	1.2810	0.6363
$\lambda_f$	$\frac{8}{11}$	$\frac{8}{11}$	$\frac{8}{11}$	$\frac{8}{11}$
$f_1$ [ev]	29.7045	3.3479	2.6037	26.0964
$F \equiv F_s(\rho_e)$ [ev]	-6.9719	-4.6566	-4.0186	-9.8457
$F'_s(\rho_e)$ [ev/ $\rho_e$ ]	-4.1322	-1.7040	-1.4398	-5.1224
$F''_s(\rho_e)$ [ev/ $\rho_e^2$ ]	2.5556	2.3570	2.0379	4.2587
$V_{11}$ [ $\rho_e$ ]	1.4354	2.6257	2.5096	2.2641
$\phi_1 \equiv \phi_{1s}$ [ev]	0.5970	0.1411	0.0214	0.6676

**TABLE 3a.** Calculated GEAM parameters for the bulk solid without defects

	Al	Au	Pd	Pt
$t_1$	1	1	1	1
$t_3$	0	0	0	0
$\alpha_f$	0.4	0.4	0.4	0.4
$\lambda_f$	$\frac{8}{11}$	$\frac{8}{11}$	$\frac{8}{11}$	$\frac{8}{11}$
$t_2$	1.1332	5.0874	5.4247	1.8171
$f_1$ [ev]	29.2451	31.0271	25.7693	58.8547
$F \equiv F_b(\rho_e)$ [ev]	-6.9516	-7.2571	-6.3404	-11.5605
$F'_b(\rho_e)$ [ev/ $\rho_e$ ]	-4.1118	-4.2925	-3.7503	-6.8379
$F''_b(\rho_e)$ [ev/ $\rho_e^2$ ]	2.5567	2.6691	2.3320	4.2519
$V_{11}$ [ $\rho_e$ ]	1.1675	0.9474	0.8723	1.4557
$\phi_1 \equiv \phi_{1b}$ [ev]	0.5936	0.5745	0.4084	0.9534
$F_b\left(\frac{9}{12}\rho_e\right)$ [ev]	-5.8357	-6.0922	-5.3226	-9.7047



**Table 3b** Calculated GEAM Parameters for the equivalent crystal modeling the (111) surface defect region.  $a_s$  is the lattice constant of the fcc equivalent crystal.

	Al	Au	Pd	Pt
$a \equiv a_s$ [Å]	4.4576	4.4906	4.2815	4.3145
$t_1$	1	1	1	1
$t_3$	0	0	0	0
$\alpha_f$	0.3433	0.3383	0.3362	0.3487
$\lambda_f$	$\frac{8}{11}$	$\frac{8}{11}$	$\frac{8}{11}$	$\frac{8}{11}$
$t_2$	1.1332	5.0874	5.4247	1.8171
$f_1$ [ev]	37.3535	40.5497	34.0070	72.9235
$F \equiv F_s(\rho_e)$ [ev]	-7.2709	-7.6217	-6.6705	-12.0379
$F'_s(\rho_e)$ [ev/ $\rho_e$ ]	-4.4321	-4.6582	-4.0814	-7.3168
$F''_s(\rho_e)$ [ev/ $\rho_e^2$ ]	2.5346	2.6435	2.3086	4.2194
$V_{11}$ [ $\rho_e$ ]	1.3540	1.0992	1.0123	1.6874
$\phi_1 \equiv \phi_{1s}$ [ev]	0.6468	0.6353	0.4634	1.0330

**Table 4.** (111) Surface energies in ergs/cm<sup>2</sup>

Metal	a	b	c	d	e	f	g
Al	510	1017	1049	524	618	1270	1160
Au	662	895	1282	618	886	1610	1500
Pd	978	1204	1596	1074	1381	1880	2050
Pt	1027	1642	1887	1120	1656	2350	2480

- a. EAM using eqn. (3.5) [Ref.11]      e. Modified EAM [Ref. 13]  
 b. EAM using eqn (3.8) [Ref.11]      f. 1<sup>st</sup> Principles calculation [Ref.15]  
 c. GEAM using eqn (3.8) [This study]      g. Experiment [Ref.16]  
 d. EAM [Ref. 10]

## V CONCLUSION

We have, in this study, employed the concept of an equivalent crystal within a generalized embedded – atom method (GEAM) to calculate the (111) surface energies of four fcc metals. The four selected fcc metals are typical of the different physics one is likely to encounter in the fcc metals. It is therefore noteworthy that the surface energy results obtained for all four fcc metals, in this study, are comparable to the results from first principles calculations [15] and experiment [16]. Zypman and Ferrante [14] have also sought to improve EAM surface energies via a tight –binding surface correction to the embedding function. In their approach they employed available first –principles results for the (111) plane to determine the various tight binding parameters in their theory

This done, they then predict surface energies for the (100) and (110) planes. The reliance on another theoretical effort in order to determine the parameters in their theory is, in our thinking, the greatest defect in the work of Zypman and Ferrante. The work reported in this paper furnishes an alternative route for the solution of the same problem. Work is in progress to extend the method outlined in this paper, to other metals and also to other low index surfaces

**Appendix 1: Algorithm for determining the GEAM**

Parameters for an fcc metal if  $t_1$ ,  $t_2$  and  $t_3$  are known or specified, and if  $w_{13} = w_{12}$

**Step 1:** Supply known experimental values for the input parameters  $a$ ,  $C_{11}$ ,  $C_{12}$ ,  $C_{44}$ ,  $U_o$ , and  $E_{IV}^F$  of the selected fcc metal, and note that

$$\Omega_o = a^3/4 \text{ and } r_1 = a/\sqrt{2}$$

**Step 2:** Next calculate  $C_1$  and  $\lambda_f$ , where

$$C_1 = \frac{a^3}{64} [-3B_o + 10C_{11} - 4C_{12} - 12C_{44}] \tag{A1.1}$$

$$\lambda_f = \frac{8t_1 - 8t_3}{8t_1 - 8t_3 + 3} \tag{A1.2}$$

**Step 3:** Next guess a trial value for  $\alpha_f$ , some number between 0 and 2. Then use this trial value to calculate the following in the order written

$$X = \left[ \left( e^{\alpha_f} - 1 \right) / \left( e^{\alpha_f} - e^{\alpha_f/12} \right) \right]^2 \tag{A1.3}$$

$$F(\rho_e) = X(u_o + E_{IV}^F) / (12 - 11X) \tag{A1.4}$$

$$F'(\rho_e) = F(\rho_e) \lambda_f \alpha_f / (e^{\alpha_f} - 1) \tag{A1.5}$$

$$F''(\rho_e) = (1 - e^{\alpha_f} / \lambda_f) [F'(\rho_e)]^2 / F(\rho_e) \tag{A1.6}$$

$$f_1 = [-F(\rho_e)]^{1/\lambda_f} / (e^{\alpha_f} - 1) \tag{A1.7}$$

**Step 4:** Next calculate  $V_{11}$  from the formula

$$V_{11} = \pm \sqrt{\frac{\Omega_o(C_{12} - C_{44})}{(t_2 - t_3)F''(\rho_e)}} \tag{A1.8}$$

This gives two possible values for  $V_{11}$  – one positive and the other negative

**Step 5:** Next cross – check self – consistency condition on  $\alpha_f$  by calculating  $\alpha_f$  from the formula

$$\alpha_f = \ln \left[ \lambda_f \left\{ 1 + \frac{3F''(\rho_e)V_{11}^2}{16(F'(\rho_e)V_{11}/4 + c_1)} \right\} \right] \tag{A1.9}$$

The two possible values for  $V_{11}$  from (A1.8) will lead to two possible values for  $\alpha_f$ . If the calculated  $\alpha_f$  is not equal to the guessed  $\alpha_f$ , then



repeat steps 3 to 5 with another trial guessed  $\alpha_f$ . Continue this iteration until

guessed  $\alpha_f$  = calculated  $\alpha_f$  (A1.10)

**Step 6** Having got a self consistent  $\alpha_f$  from the above steps, then (A1.4) to A1.7 provide the values of  $F(\rho_e)$ ,  $F'(\rho_e)$ ,  $F''(\rho_e)$ , and  $f_1$  respectively. The value of  $V_{11}$  is that one out of the two possible values from (A1.8), which leads to self-consistency for  $\alpha_f$  in (A1. 9).

The remaining GEAM parameters can now be easily determined. From (2.4) to (2.10) in the text, we get

$$\phi_1 = [U_0 - F(\rho_e)]/6 \quad (\text{A1.11})$$

$$\phi_1' = -F'(\rho_e)V_{11}/2r_1 \quad (\text{A1.12})$$

$$\phi_1'' = \frac{a}{8}(3B_0 - 2C_{11} + 4C_{12} + 4C_{44}) - \frac{3F'(\rho_e)V_{11}}{2r_1^2} \quad (\text{A1.13})$$

$$\begin{aligned} \frac{a}{4\Omega_0}F'(\rho_e)W_{11} &= \frac{a}{16}(-B_0 + 6C_{11} - 4C_{12} + 4C_{44}) + \frac{F'(\rho_e)V_{11}}{r_1^2} \\ &\quad - \frac{a}{4\Omega_0}t_1F''(\rho_e)V_{11}^2 \end{aligned} \quad (\text{A1.14})$$

$$\begin{aligned} \frac{a}{4\Omega_0}F'(\rho_e)W_{12} &= \frac{a}{16}\left(-\frac{3}{2}B_0 + C_{11} + 2C_{12} - 2C_{44}\right) - \frac{F'(\rho_e)V_{11}}{4r_1^2} \\ &\quad - \frac{a}{4\Omega_0}t_2F''(\rho_e)V_{11}^2 \end{aligned} \quad (\text{A1.15})$$

$W_{11}$  and  $W_{12}$ , if desired, can be easily determined from (A1,14) and (A1.15)

## Appendix 2: Algorithm for determining the GEAM

Parameters for an fcc metal if  $t_1$ ,  $t_3$  and  $\alpha_f$  are known or specified, and if  $W_{13} = W_{12}$

Step 1: same as in Appendix 1

Step 2: same as in Appendix 1

Step 3: The known value of  $\alpha_f$  is employed to calculate  $X$ ,  $F(\rho_e)$ ,  $F'(\rho_e)$ ,  $F''(\rho_e)$ , and  $f_1$  using equation (A1.3) to (A1,7) of Appendix 1.

Step 4:  $V_{11}$  is calculated from the quadratic equation

$$V_{11}^2 - \frac{4}{3} \frac{F'(\rho_e)}{F''(\rho_e)} \left( \frac{e^{\alpha_f}}{\lambda_f} - 1 \right) V_{11} - \frac{16}{3} \frac{C_1}{F''(\rho_e)} \left( \frac{e^{\alpha_f}}{\lambda_f} - 1 \right) = 0 \quad (\text{A2.1})$$

(A2.1) gives two possible values for  $V_{11}$

step 5: Next,  $(t_2 - t_3)$  is determined from the equation.

$$t_2 - t_3 = \frac{\Omega_o(C_{12} - C_{44})}{F''(\rho_c)V_{11}^2} \quad (A.2.2)$$

Step 6: Our experience with the above equations reveal that the positive value of  $v_{11}$  from (A2.1) leads to physically sensible results. Hence, by (A2.2) the physically sensible result for  $t_2$  is the one corresponding to positive  $V_{11}$ . The remaining GEAM parameters  $(\phi_1, \phi_1', \phi_1'', W_1 \text{ and } W_{12})$  can now be easily determined from (A1.11) to (A1.15) of Appendix 1

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