

Determination of Surface Energies and Equivalent-Crystal Theory Constants of Face-Centred Cubic Metals Using Equivalent Crystal Theory Method

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Abstract

The equivalent-crystal theory (ECT) method is used in this study to calculate the unrelaxed surface energies and ECT constants of the three low-index faces of thirteen FCC metals. The faces are the (111), (110) and (100) faces. The results are compared with those of first principles calculation, the tight-binding (TB) method, the embedded-atom method (EAM), the modified embedded-atom method (MEAM), and experiment. It is found that the surface energy results obtained using the ECT method are very close to first principles calculation and experiment. It is, however, found that the ECT results are uniformly higher than those obtained using the tight-binding (TB) method, the embedded-atom method (EAM), and the modified embedded-atom method (MEAM).

Keywords: Surface energy, perturbation series, lattice constant, nearest neighbour distance, equivalent crystal

INTRODUCTION

Surface energy is a physical quantity that is difficult to measure directly for solid metals, and numerous models have been presented with the aim of obtaining reliable estimates of it. A popular theoretical approach is the use of interatomic pair potentials, but this approach suffers from the drawback that it neglects many-body interactions, which obviously play a role in many interesting physical phenomena. On the experimental front, in spite of considerable experimental efforts, it appears that for many metals the recommended values of surface energies have uncertainties of unknown magnitude. This is, for instances, true for the surface energies derived from the surface tension of liquid metals and listed by Deboar et al., (1988). Nonetheless, according to Skriver and Rosengaard (1992), the compilation by de Boer et al., (1988) represents the most consistent choice of surface energies in existence at present. In this situation one may turn again to theoretical models and in particular to ab initio calculations as a guide especially since the accuracy of such calculations has recently improved considerably.

The embedded-atom method (EAM) developed by Daw and Baskes (1984) has its foundation in some earlier works by Stott and Zarembor (1980), Norskov and Lang (1980) and Kress et al., (1988). Since its introduction, the EAM has been applied to treat successfully several diverse problems in condensed matter physics. The case for semi-empirical models like the EAM rests on the need to circumvent the practical problems posed by ab initio or first principles method.

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However, a fundamental problem with the EAM at present is that it predicts surface energies that are usually too low compared to first principles and experimental values. The reasons for these relatively low values are not yet clear (Rose et al., 1983; Foiles, 1986). Thus, there is need for more intensified work to formulate a better Semi empirical model. At this point the equivalent-crystal theory (ECT) method readily comes to mind (Smith et al., 1991).

Although the accuracy of the ECT method has been demonstrated by Smith et al. (1991), with the successful prediction of surface energies, found on the average to be within 10% of first - principles calculations, these authors have only applied the method to 4 FCC metals. The predicted results are in good agreement with both first-principles calculations and experiments.

METHODOLOGY

Consider a localized structural defect in a solid such as the surface or vacancy shown in the upper diagram of Figure 1.

We would like to compute the energy to form the defect in the single crystal. The local defect represents a substantial increase in complexity relative to single crystal, and so theorists in modelling surfaces and defects have attempted to retain single-crystal simplicity on a local level. In the local density approximation (LDA), the electronic exchange - correlation potential at a particular point in space is assumed to be that of a uniform, free - electron gas whose electron density is the same as the actual electron density evaluated at the same point (Kittel, 1976). The free - electron gas is the simplest model for the single Crystal and, in a sense the LDA assumes that each point in space is represented by such a single crystal. Each different point is represented by a different single crystal, i.e. the constant electron density or the lattice constant of the single crystal is different for each point represented (Cai and Ye, 1996; Polatoglou et al., 1993).

For a theory that hopes to describe successfully both simple metals, transition metals, and covalent solids like semiconductors the free-electron gas model of a single crystal cannot be relied upon (Rose and Shore, 2000). Rather an effective single crystal only is relied upon in the sense that its lattice constant may be different from the ground - state value. Consider M atoms encompassing the range of the local defect. Firstly, replace those M atoms with M atoms of an effective crystal whose lattice constant a is yet to be specified. Next, the energy to form the defect is computed via perturbation theory, where the perturbation arises from the difference in the ion core electronic potentials of the actual defect solid and those of the effective bulk single crystal.

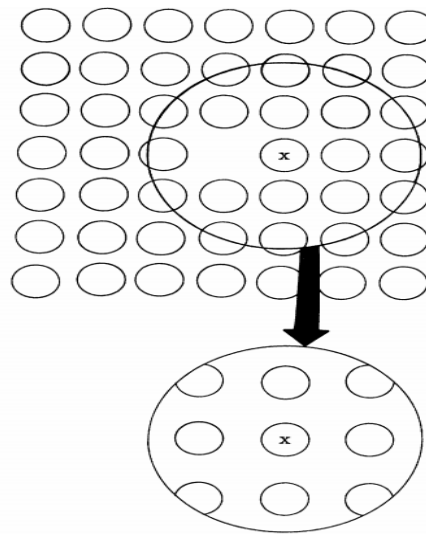


Figure 1 A vacancy in a two-dimensional square lattice as an example of a crystal defect. A vacancy nearest neighbour is indicated by an X. The local environment of the vacancy nearest neighbour is indicated by the circular area. In the upper diagram we have the actual atomic array while an equivalent – crystal representation of that environment is depicted in the lower circular diagram(Smith et al., 1991).

Let ϵ be the total energy to form the defect or surface, Then

$$\epsilon = M[E_c(a) + E_p(a) - E_c(a_m)], \quad (1)$$

where a_m is the equilibrium lattice constant, i.e. the minimum in Figure 2, $E_c(a)$ is the total energy per atom of the effective bulk single crystal, $E_c(a_m)$ is the total energy per atom of the actual crystal, M is the number of atoms in the range of local defect and $E_p(a)$ is the sum of the perturbation series.

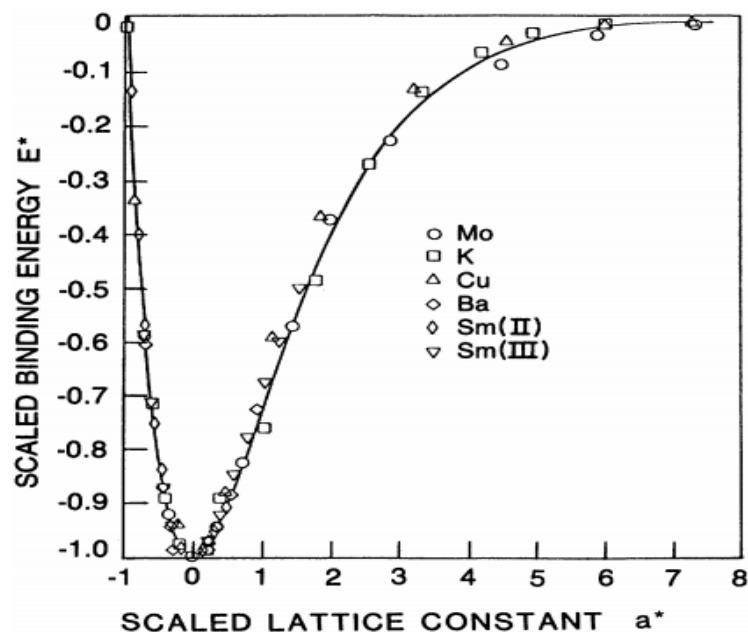


Figure 2 Scaled cohesive energy E^* per atom of a crystal plotted against interatomic separation a^* for representative solids. The solid line is a plot of the Rydberg function(Eq.9).(Rose et al.,1983).

The rate of convergence of the perturbation series is important because typically it is difficult to evaluate high-order perturbation terms. Thus it would be desirable to adjust the lattice constant a of the effective crystal so that the perturbation is minimized and thereby hopefully the perturbation series is rapidly convergent. Now if the crystal structure of the actual single crystal is that of the lowest – energy phase, and if its lattice constant is at the ground-state value a_m , then forming the defect or surface must raise the energy of the system above the minimum in the cohesive energy curve.

There must be a value a of the lattice constant of the effective crystal such that

$$\varepsilon \equiv M[E_c(a) - E_c(a_m)], \quad (2)$$

so that

$$E_p(a) = 0 \quad (3)$$

Since the excitation energy of the effective crystal relative to the ground – state crystal is equal to the total energy to form the local defect or surface [Eq.(2)], the crystal of lattice constant a is called an *equivalent crystal*. Note that we have not only minimized the perturbation series, we have been able to make it sum to zero. Further, while a defect in a solid is a complicated many – atom and many – electron problem, it has been reduced formally to the solution of one equation, Eq.(3), for the one unknown a . Once a is known, then the energy of the solid containing a defect can be immediately found from Eq(2), since $E_c(a)$ is known for many single crystals.

In practice, one finds an equivalent – crystal of lattice constant a with corresponding energy change ε_i by solving Eqs. (2) and (3) for each atom (i) near the surface or defect. If

$$\varepsilon_i = E_c(a(i)) - E_c(a_m) \quad (4)$$

then

$$\varepsilon = \sum_i \varepsilon_i \quad (5)$$

For Metals only a few neighbours contribute significantly to Eq. (5).

There is a simple, universal form for $E_c(a)$ which can be obtained by a simple scaling of the total energy. Let L be the scaling length and let r_{ws} be the Wigner Seitz radius of equilibrium value r_{WSE} . Then according to Smith et-al, 1991,

$$E^*(\alpha^*) = E(a)/\Delta E \quad (6)$$

where $\alpha^* = (r_{ws}-r_{wse})/L \quad (7)$

and $L = (\Delta E/12\pi B r_{wse})^{1/2} \quad (8)$

B is the equilibrium bulk modulus and ΔE is the cohesive energy. A simple analytic form which accurately represents the universal energy relation is the Rydberg function given by

$$E^*(\alpha^*) = - (1+\alpha^*) e^{-\alpha^*} \quad (9)$$

Taking into account Eqs. (6) and (9) we get

$$E(a) = -\Delta E (1+\alpha^*)e^{-\alpha^*} \quad (10)$$

and $\varepsilon_i = - \Delta E F^*(\alpha^*(i)) \quad (11)$

where

$$F^*[a^*(i)] = 1 + E^*(a^*(i)) = 1 - (1 + a^*(i)) e^{-a^*(i)} \quad (12)$$

In fact, a number of other methods also rely on the universal nature of the cohesive energy relation in different ways (Banerjee et al., 1990). For metals Daw and Baskes (1984), Daw (1989), Daw and Johnson, (1989), employed the universal energy relation in their widely used embedded-atom method. The universal energy relation is also found in the semiconductor method of Tersoff (1988), Baskes, Nelson, and Wright, (1989), and Dodson, (1987).

This study is focussed on unrelaxed (i.e. rigid) surface energies of FCC metals. The important equation that needs to be solved for each metal is given by Smith et-al., 1991 as

$$N_1 R_{ec}^P e^{-\alpha R_{ec}} + N_2 (C_2 R_{ec})^P e^{-(\alpha+1/\lambda) C_2 R_{ec}} - \sum_{defect NN} R_j^P e^{-\alpha R_j} - \sum_{defect NNN} R_j^P e^{-(\alpha+1/\lambda) R_j} = 0 \quad (13)$$

where

$$R_j \equiv |\vec{R}_j - \vec{R}_l|, \quad (14)$$

$$\text{and for FCC metals} \quad R_{ws} = R_{ec}/c \quad (15)$$

$$\text{with} \quad c = \sqrt{2}(2\pi/3)^{1/3} \quad (16)$$

N_1 and N_2 are respectively the number of equivalent-crystal nearest and next-nearest neighbours, R_{ec} is the equivalent - crystal nearest neighbour distance that is to be determined from Eq. (13), C_2 is the ratio between the next - nearest - neighbour distance and the nearest - neighbour distance in the undistorted crystal and λ is the electronic screening length.

$$R_j \equiv |\vec{R}_j - \vec{R}_l|, \lambda = \lambda_{Na} (I/I_{Na}) = 2.81 \quad (17)$$

$$P = 2n - 2 \quad (18)$$

where n is the atom principal quantum number. The sums in Eq. (13) are over the actual defect crystal, the first is over nearest neighbours and the second over next - nearest neighbours, to atom i . Values of i , λ , P , α and all the other parameters in the equations are given in Table 1. They are computed from input data listed in Table 2 for the FCC metals. One solves Eq. (13) for R_{ec} , obtains $a^*(i)$ from Eq. (7), and then obtains $F^*[a^*(i)]$ via Eq. (12).

If a crystal were cleaved to produce a high-index plane, it is possible for a plane of atoms deeper than the surface plane to be missing nearest neighbours. In this case even nearest - neighbour removal could be screened out with the enhanced screening factor, exponential $(-R/\lambda)$. One example of this is found in the FCC (110) surface where the second layer is missing a nearest neighbour and so for this layer the term $N_1 R_{ec}^P e^{-\alpha R_{ec}}$ in Eq. (13) is replaced by $(N_1 - 1) R_{ec}^P e^{-\alpha R_{ec}} + R_{ec}^P e^{-(\alpha+1/\lambda) R_{ec}}$. This is a small change ($\sim 8\%$ decrease of the surface energy of Cu (110)], but it is technically more correct. For the lower - index (100) or (111) metal surfaces, the second layer is not missing any nearest neighbours, and so Eq. (13) applies as written. Eq. (13) is unaltered in application to point defects as well, because there the screening charge decays essentially readily, completely consistent with the form of the equation (Rose et al. 1984). The value of α is determined for metals so that the energy to form a rigid or unrelaxed vacancy is equal to the experimental value, (Soderling et al. 1993; Anderson et al. 1994).

IMPLEMENTATION OF THE METHOD FOR SURFACE DEFECT

In the case of FCC metals, the basic equations that must be solved in order to determine the nearest neighbour distance (R_{ec}) for the equivalent-crystal, are as follows for the different surfaces.

(111) Surface:

$$12R_{ec}^P e^{-\alpha R_{ec}} + 6(\sqrt{2}R_{ec})^P e^{-(\alpha+1/\lambda)\sqrt{2}R_{ec}} - 9(a/\sqrt{2})^P e^{-\alpha\frac{a}{\sqrt{2}}} - 3(a)^P e^{-(\alpha+1/\lambda)a} = 0 \quad (19)$$

(110) Surface:

$$12R_{ec}^P e^{-\alpha R_{ec}} + 6(\sqrt{2}R_{ec})^P e^{-(\alpha+1/\lambda)\sqrt{2}R_{ec}} - 7(a/\sqrt{2})^P e^{-\alpha\frac{a}{\sqrt{2}}} - 4(a)^P e^{-(\alpha+1/\lambda)a} = 0 \quad (20a)$$

and

$$11R_{ec}^P e^{-\alpha R_{ec}} + R_{ec}^P e^{-(\alpha+1/2)R_{ec}} + 6(\sqrt{2}R_{ec})^P e^{-(\alpha+1/2)\sqrt{2}R_{ec}} - 11(\alpha/\sqrt{2})^P e^{-\alpha\frac{a}{\sqrt{2}}} - 4(a)^P e^{-(\alpha+1/2)a} = 0 \quad (20b)$$

(100) Surface:

$$12R_{ec}^P e^{-\alpha R_{ec}} + 6(\sqrt{2}R_{ec})^P e^{-(\alpha+1/\lambda)\sqrt{2}R_{ec}} - 8(a/\sqrt{2})^P e^{-\alpha\frac{a}{\sqrt{2}}} - 5(a)^P e^{-(\alpha+1/\lambda)a} = 0 \quad (21a)$$

$$12R_{ec}^P e^{-\alpha R_{ec}} + 6(\sqrt{2}R_{ec})^P e^{-(\alpha+1/\lambda)\sqrt{2}R_{ec}} - 12(a/\sqrt{2})^P e^{-\alpha\frac{a}{\sqrt{2}}} - 5(a)^P e^{-(\alpha+1/\lambda)a} = 0 \quad (21b)$$

Once one knows the R_{ec} value, then $F^*[a^*(i)]$ and $a^*(i)$ can be calculated directly from Eqs. (12) and (7) and the surface energy Γ from the formula

$$\Gamma = (\Delta E/A) \sum F^*[a^*(i)] \quad (22)$$

where A is the surface Area per atom. For the various surfaces we get

$$\Gamma_{111} = \left(\frac{4}{a^2\sqrt{3}} \Delta E\right) \sum_i F^*(a^*(i)) \quad (23)$$

$$\Gamma_{110} = \left(\frac{\sqrt{2}}{a^2} \Delta E\right) \sum_i F^*[a^*(i)] \quad (24)$$

$$\Gamma_{100} = \left(\frac{2}{a^2} \Delta E\right) \sum_i F^*[a^*(i)] \quad (25)$$

The sum over i includes only one atom per atomic layer for a (1 x 1) surface structure and usually only two to three layers need to be included for metal low index planes.

RESULTS AND DISCUSSION

In this section we report unrelaxed surface energies for thirteen FCC metals. The ECT method requires as experimental input, the three bulk elastic constants, the bulk cohesive energy, the bulk lattice constant and the vacancy formation energy. These are shown in Table 1 and they have been employed to compute the ECT constants in Table 2.

Results of surface energies for four FCC metals are shown in Table 2. Essentially this Table provides a comparison of our work with the work of Smith et-al., 1991 whose ECT method we have employed in this study. Clearly the two studies are in excellent agreement. This agreement gave us the confidence to extend the work of Smith et al. to other FCC metals.

The surface energies obtained for the three low index faces of thirteen FCC metals are presented in Table 4, and compared with the results from first principles calculations, the tight-binding (TB) method, the embedded - atom method (EAM), the modified embedded - atom method (MEAM), and experiment.

For all the theoretical models whose result are presented in Table 4, the closed packed (111) face has the lowest energy. For the (100) and (110) faces the situation is not clear. While some models predict the (100) surface energy to be less than the (110) surface energy, others give an opposite picture. This is an outstanding problem in the theory of metallic cohesion that needs to be properly addressed. Unfortunately, experimental studies have not been of much assistance with this problem since experimental surface energies are average values of all crystalline faces.

To further illustrate the effectiveness of the ECT method, we present in Table 5 surface energy results of MEAM and ECT (This study) for three FCC metals, using the same vacancy formation energy as used by Baskes (1992). Clearly the predicted results from ECT are still closer to both experimental and ab initio results than the MEAM results.

EXPERIMENTAL INPUTS FOR FCC METALS.

The following are used as experimental inputs for FCC metals. Lattice constants (in Å), Bulk modulus (in 10^{12} erg/cm³) and cohesive energies (in eV) are from Kittel, 1976 and Rose et al., 1984, elastic constant (in 10^{12} erg/cm³) are from Rose et al., 1983, and metal vacancy formation energies (in eV) are from Smith et al. 1991, except Rh and Pb which are from Polatoglou, 1993. For Ca, Sr, Ir, and Th, the vacancy - formation energy, in the absence of experiment values, has been assumed to be approximately 1/3 of cohesive energy. They are shown in Table 1.

TABLE 1 EXPERIMENTAL INPUTS FOR FCC METALS

	Coh. Energy ΔE	Lattice const. a	Vac form. Energy E_{IV}^f (eV)	Elastic constants			Bulk mod. B
				C_{11}	C_{12}	C_{44}	
Ni	4.44	3.51	1.60	2.612	1.508	1.317	1.876
Pd	3.94	3.89	1.40	2.341	1.761	0.712	1.955
Pt	5.85	3.92	1.30	3.580	2.536	0.774	2.884
Cu	3.50	3.61	1.30	1.762	1.249	0.818	1.420
Ag	3.96	4.08	1.19	1.314	0.973	0.511	1.087
Au	3.78	4.07	0.96	2.016	1.697	0.454	1.803
Al	3.34	4.04	0.66	1.143	0.619	0.316	0.794
Pb	2.04	4.95	0.5	0.466	0.392	0.144	0.488
Rh	5.75	3.80	1.71	4.13	1.94	1.84	2.704
Ca	1.84	5.58	0.6	0.228	0.16	0.14	0.152
Sr	1.72	6.08	0.6	0.147	0.0574	0.099	0.116
Ir	6.94	3.84	2.35	6.0	2.6	2.7	3.704
Th	6.20	5.08	2.0	0.753	0.489	0.478	0.543

ECT CONSTANTS FOR FCC METALS

The constants P , l , a , and λ are the computed ECT constants for FCC and are shown in Table 2. The constant P is $2n - 2$, where n is the atomic principal quantum number, l (in Å) is computed from Eq. (8) and λ (in Å) from Eq. (17). For metals, α (in Å⁻¹) is computed by requiring agreement with the experimental vacancy formation energy (listed in Table 2).

TABLE 2 COMPUTED ECT CONSTANTS FOR FCC METALS

Element	P	L	α	λ
Ni	6	0.27079	3.01330	0.76093
Pd	8	0.23736	3.61090	0.66670
Pt	10	0.23722	4.53410	0.66659
Cu	6	0.27249	2.93410	0.76570
Ag	8	0.26941	3.33410	0.75705
Au	10	0.23668	4.33570	0.66508
Al	4	0.33650	2.10410	0.94557
Pb	10	0.30305	3.53920	0.85158
Rh	8	0.24669	3.72580	0.69320
Ca	6	0.48572	1.86390	1.36487
Sr	8	0.51499	2.16000	1.44712
Ir	10	0.23035	4.41720	0.64729
Th	12	0.49440	3.61730	1.38927

SURFACE ENERGIES, IN erg/cm² FOR SOME SELECTED FCC METALS

Energies have been computed in a "rigid" configuration, in which the surface atoms are held in the same relative locations they would have had in the bulk. ECT predictions of Smith et al., 1991 are rounded to the nearest 10 erg/cm², while the energies obtained in this work have been rounded to the nearest one erg/cm². Table 3 shows the surface energies for the three low-index faces for selected FCC metals.

TABLE 3 SURFACE ENERGIES IN erg/cm² FOR SELECTED FCC METALS

Element	Crystal face	ECT (rigid) Smith et al., 1991)	ECT (rigid) present
Cu	(111)	1830	1835
	(100)	2380	2385
	(110)	2270	2275
Ag	(111)	1270	1266
	(100)	1630	1631
	(110)	1540	1542
Ni	(111)	2400	2398
	(100)	31200	3123
	(110)	2980	2986
Al	(111)	920	922
	(100)	1290	1289
	(110)	1310	1309

SURFACE ENERGIES OF FCC METALS USING THE DIFFERENT METHODS

The surface energies of the thirteen FCC metals are computed using ECT method, ab initio method, TB, EAM, MEAM methods and experiment. The results are shown in Table 4. Note that there are two columns for the EAM method since two sets of researchers, namely Foiles et al., 1986; Cai and Ye, 1996 have used the method.

TABLE 4: SURFACE ENERGIES IN erg/cm² USING THE DIFFERENT METHODS

Element	Crystal face	ECT (present)	Abinitio ^a	TB ^b	EAM ^c	MEAM ^d	EAM ^e	Expt. ^f
Ni	(111)	2398	2630		1450	2036	1540	2450
	(100)	3123			1580	2435	1654	
	(110)	2986			1730	2384	1786	
Pd	(111)	1752	1880	1570	1220	1381	1074	2050
	(100)	2302	1900	1750	1370	1659	1157	
	(110)	2206		1860	1490	1670	1240	
Pt	(111)	1791	2350	2510	1440	1656	1120	2480
	(100)	2457	2480	2830	1650	2167	1228	
	(110)	2448		2970	1750	2131	1309	
Cu	(111)	1835	1960	1730	1170	1409	1180	1830
	(100)	2385	2090	1930	1280	1651	1261	
	(110)	2275	2310	2040	1400	1642	1361	
Ag	(111)	1266	1120	1140	620	1089	765	1250
	(100)	1632	1200	1290	705	1271	821	
	(110)	1542	1290	1420	770	1222	883	
Au	(111)	1193	1610	1480	790	886	616	1500
	(100)	1620	1710	1690	918	1084	683	
	(110)	1596	1790	1850	980	1115	728	
Al	(111)	922	1270			618	524	1160
	(100)	1289				897	579	
	(110)	1309				969	617	
p ^b	(111)	419				366		
	(100)	568				424		
	(110)	501				431		
	(111)	2333	2780	2460		2598		
	(100)	311	2900	2500		2902		
Rh	(110)	3027		2710		2921		
Ca	(111)	355	352					490
	(100)	463						
	(110)	455						
Sr	(111)	278	287					410
	(100)	356						
	(110)	338						
Ir	(111)	2972	3410	2590		2835		3000
	(100)	3899	3810	2950		2907		
	(110)	3739		3190		3058		
Th	(111)	1156						
	(100)	1445						
	(110)	1365						

a. : see Skriver and Rosengaad, 1992

b. : see Mehel and Papaconstantopoulos, 1996

c. : see Foiles et al., 1986

d. : see Baskes, 1992

e. : see Cai and Ye, 1996

f. : see deBoer et al., 1988

TABLE 5: SURFACE ENERGIES IN erg/cm² USING THE SAME VACANCY FORMATION ENERGY AS IN Baskes, 1992

Element	Crystal face	ECT (PRESENT)	MEAM (Baskes, 1992)	E_{IV}^f	Expt.(Deboer et al., 1988)
Ni	(111)	2256	2036	1.46	2450
	(110)	2968	2435		
	(100)	2861	2384		
Rh	(111)	3144	2598	2.70	2700
	(110)	2984	2902		
	(100)	3714	2921		
Ir	(111)	3820	2835	3.50	3000
	(110)	4790	2907		
	(100)	4430	3058		

CONCLUSION AND RECOMMENDATION

We have used the equivalent – Crystal Theory (ECT) method of Smith et al., 1991 to calculate the unrelaxed surface energies of thirteen FCC metals. This has greatly extended the work of Smith et-al who presented results for only four FCC metals. Like in the work of Smith et-al, the surface energies are in good agreement with the results from first principles calculations and experiment. In both cases, we find the ECT energies to be uniformly higher than the corresponding results from the EAM, MEAM and the tight-binding model. It is our belief that unrelaxed surface energies have to be correctly calculated in any theoretical model, before including relaxation effects. In view of the excellent agreement of our unrelaxed results with experiment, one wonders whether relaxation effects for surface energy studies are really important for FCC metals.

This study has been carried out on FCC metals. It is suggested that similar study should be carried out on BCC as well as HCP metals.

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