



## Surface relaxation and surface energy of face –centered Cubic metals

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**ABSTRACT:** Surface relaxation and surface energy are calculated for Rh, Ir, Pb, Ca, Sr, and Th, for three low-index surfaces, using the equivalent crystal theory (ECT) method. The surfaces are the (100), (110) and (111) faces. In this study, we only considered perpendicular relaxation where the relaxation was determined by the minimization of the total energy. The results obtained are analyzed with good agreement to experiment and first – principles calculations where available. .@JASEM

The phenomena of reconstruction and relaxation of metal surfaces has received considerable attention. Considerable experimental data indicate multilayer oscillatory relaxation of surfaces. Two methods, the Embedded Atom Method (EAM), based on density functional theory, and Equivalent Crystal Theory, ECT (Smith et al 1991), based on perturbation theory, have been extensively used to describe the energetics of defects in metals. Both methods have also been applied to the study of surface relaxation (Smith et al 1991). Surface energy is another surface property of great interest. The energy of a free surface plays an important role in several physical and chemical processes such as fracture, catalysis, etc. Experimental measurements of the surface energy are usually at high temperatures and are subject to errors due to surface – active contaminants and thus have a degree of uncertainty. Early theoretical calculations were based on perturbation theory or non-perturbative variational methods. Over the years, there has been an increasing effort on first-principles calculations as well as in the area of Semi-empirical methods: EAM and ECT have been applied to this and other surface properties (Smith et al 1991), with the latter method providing excellent agreement with available experimental data and first-principles calculations. Finally the work of Methfessel, Hennig and Scheffler (1992) discusses trends in surface energies as well as different models that relate the surface energies to other crystal properties.

In this paper, we extend our previous application of ECT to surface energy calculation (Aghemenloh and Idiodi 1998), and in order to improve on our previous calculated results; we here include the effect of relaxation in the calculated surface energies. Several studies of surface phenomena have been done with the ECT on Al, Ni, Pd, Cu, Pt, Ag and Au (Smith et al 1991; Rodriguez et al.1993) obtaining remarkable

agreement with experimental results. At the present time none has been performed to the author's knowledge for Rh, Ir, Pb, Ca, Sr and Th metal surfaces. To fill this gap, we present in this paper the first ECT calculation of surface energy and surface relaxation for the three low-index faces (100), (110) and (111) of these metal surfaces. In this study, we ignore parallel relaxation as well as surface reconstruction and dealt only with rigid perpendicular translations of the near-surface planes. With these restrictions, we apply ECT and discuss the different contributions to the surface energy.

*Equivalent crystal theory:* Equivalent crystal theory is based on an exact relationship between the total energy and atomic locations and applies to surfaces and defects in both simple and transition metals as well as in covalent solids. Lattice defects and surface energies are determined via perturbation theory on a fictitious, equivalent single crystal whose lattice constant is chosen to minimize the perturbation. The energy of the equivalent crystal, as a function of its lattice constant is given by a Universal binding energy relation (Smith et al 1991). The method has been applied previously to calculate surface energies (Rodriguez et al 1993; Aghemenloh and Idiodi 1998), surface reconstructions and bulk distortions of metals and semiconductors (Smith et al 1991). Since the details of the ECT method may be found in other previous works (Smith et al 1991; Rodriguez et al 1993; Aghemenloh and Idiodi 1998), we shall here restrict ourselves to the calculation of relaxed surface energies only. As given in section three of this work.

*Surface energy calculation:* In a previous study (Aghemenloh and Idiodi 1998), we considered a rigid surface where no interlayer relaxation was allowed, hence all bond lengths and angles, retained their bulk equilibrium values, thus,

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$F^*(a_2^*) = F^*(a_3^*) = F^*(a_4^*) = 0$ . The surface energy was therefore obtained by solving for the ‘volume’ term represented by  $F^*(a_1^*)$  only. If we now consider the simplest surface relaxation, that is, a rigid displacement of the surface layer towards the bulk, the contribution from the higher order anisotropic terms must be included. Letting the planes close to the surface relax turns on the other three contributions to the energy. Some bonds are compressed, contributing to  $F^*(a_2^*)$ , the bond angles near the surface as well as the difference between face diagonal are distorted, generating an increase of energy via  $F^*(a_3^*)$  and  $F^*(a_4^*)$ . Also, allowing the atoms in the surface region to relax introduces the additional complexity of including in the calculation more nonequivalent atoms, located in deeper layers. Many – atom effects, which are represented in the ECT by the inclusion of the three – atom bond – angle anisotropy and the four – atom face diagonal distortion terms (see the third and fourth term in the RHS of Eq. (2) of Rodriguez et al 1993) are necessary but, in the case of surface energy calculations of metals, of very little relevance. As have been shown in other previous ECT works, they introduce a small correction, usually of the order of

1% of the leading term in Eq. (2) of Rodriguez et al (1993). This is however not the case for semiconductors, where angular anisotropies are a significant contribution to the surface energy.

*Calculation of relaxed surface energy for (100) surface:* This subsection provides an application of the ECT method to an fcc (100) metallic surface, where only the surface plane is allowed to relax. All atoms in a given plane are identical; therefore we only need to evaluate the contribution of a single nonequivalent atom per plane. Moreover, only two to three planes have to be considered in this calculation: atoms in the fourth plane and below find themselves in equilibrium, bulk-like environment. The data by Bozzolo et al (1993) shows the (100) surface of Fcc metals. Let assume that the top plane ( $j = 1$ ) is lightly contracted by a distance  $x$  towards the first plane below the surface ( $j = 2$ ), but both the  $j = 2$  and  $j = 3$  planes as well as any other plane below are at equilibrium positions. The rigid inter-planar spacing is  $d = a/2$  ( $a$  is the equilibrium lattice parameter); therefore, the distance between  $j = 1$  and  $j = 2$  is  $a/2 - x$ . Following the labeling of Bozzolo et al 1993, we write the ECT equations for the atoms  $A_1$ ,  $B_1$  and  $C_1$  in terms of the distances between atoms of nearest and next nearest neighbors:

$$12R_{ec}^p \exp(-\alpha R_{ec}) + 6(\sqrt{2}R_{ec})^p \exp[-(\alpha + 1/\lambda)\sqrt{2}R_{ec}] - 4r_{A_1A_2}^p \exp(-\alpha r_{A_1A_2}) - 4r_{A_1B_1}^p \exp(-\alpha r_{A_1B_1}) - 4r_{A_1A_3}^p \exp[-(\alpha + 1/\lambda)r_{A_1A_3}] - r_{A_1C_1}^p \exp[-(\alpha + 1/\lambda)r_{A_1C_1}] = 0 \quad (j = 1) \quad (1)$$

$$12R_{ec}^p \exp(-\alpha R_{ec}) + 6(\sqrt{2}R_{ec})^p \exp[-(\alpha + 1/\lambda)\sqrt{2}R_{ec}] - 8r_{B_1B_2}^p \exp(-\alpha r_{B_1B_2}) - 4r_{B_1A_1}^p \exp(-\alpha r_{B_1A_1}) - 5r_{B_1B_3}^p \exp[-(\alpha + 1/\lambda)r_{B_1B_3}] = 0 \quad (j = 2) \quad (2)$$

$$12R_{ec}^p \exp(-\alpha R_{ec}) + 6(\sqrt{2}R_{ec})^p \exp[-(\alpha + 1/\lambda)\sqrt{2}R_{ec}] - 12r_{C_1C_2}^p \exp(-\alpha r_{C_1C_2}) - 5r_{C_1C_3}^p \exp[-(\alpha + 1/\lambda)r_{C_1C_3}] - r_{C_1A_1}^p \exp[-(\alpha + 1/\lambda)r_{C_1A_1}] = 0 \quad (j = 3) \quad (3)$$

where

$$r_{A_1A_2} = r_{B_1B_2} = r_{C_1C_2} = R_o = a / \sqrt{2} \quad (4)$$

$$r_{A_1B_1} = r_{B_1A_1} = r_x = \sqrt{a^2 / 2 + x^2 - a.x} \quad (5)$$

$$r_{A_1A_3} = r_{B_1B_3} = r_{C_1C_3} = S_o = a \quad (6)$$

and

$$r_{A_1C_1} = r_{C_1A_1} = S_x = a - x \quad (7)$$

Equations (1-3) are then solved, for each value of  $x$ , for the equivalent crystal nearest neighbor distance  $R_{ec}$ . Finally, the ‘volume’ contribution to the surface energy is

$$\sigma_1 = \frac{\Delta E}{A} \sum_{j=1}^3 F^*(a_{1,j}^*(x)) \quad (8)$$

where

$$a_{1,j}^* = (R_{ec}^{(j)} / c - r_{WSE}) / l \quad (9)$$

A is the surface area and  $F^*$  is given by Eq. (3) of Rodriguez et al. (1993).

Next, we compute the bond length anisotropy contribution to the surface energy (for atoms  $A_1$  and  $B_1$ ) associated with this defect:

$$12R_{ec}^p \exp(-\alpha R_{ec}) - 12R_o^p \exp(-\alpha R_o) + 4A_2 R_o^p (r_x - R_o) \exp[-\beta(r_x - R_o)] = 0 \text{ (atom } A_1) \quad (10)$$

The equation for atom  $B_1$ , for this particular case is identical to Eq. (10). Eq. (10) is then solved with respect to  $R_{ec}$  and the energy contribution is then

$$\sigma_2 = \frac{\Delta E}{A} F^*(a_2^*(x)) \quad (11)$$

where  $a_2^*$  is given by Eq. (7) of Rodriguez et al (1993)

The third term in the ECT expansion deals with bond – angle anisotropies. Contributions to  $\sigma_3$  comes from atoms for which the angle between the nearest neighbours departs from its equilibrium value  $\theta_0$  ( $\theta_0 = 90^\circ$  for fcc metals). Following the conversion described by Smith et al (1991), i.e., if an atom is missing one or more nearest neighbours then  $F^*(a_3^*(i, j, k)) = 0$  for that atom and the atoms in the top layer do not contribute to  $\sigma_3$ . The only contribution then arises from the atoms in the first layer below the surface ( $j = 2$ ), for which we solve the transcendental equation

$$12R_{ec}^p \exp(-\alpha R_{ec}) - 12R_o^p \exp(-\alpha R_o) + A_3 R_o^p \exp[-\alpha(r_x - R_o)] \text{Sin}|\theta - \theta_0| = 0 \quad (12)$$

where

$$\theta = \text{Cos}^{-1} \left[ \frac{r_x^2 + R_o^2 - S_x^2}{2r_x R_o} \right] \quad (13)$$

Equation (12) is solved with respect to  $R_{ec}$  and the bond – angle contribution is then

$$\sigma_3 = \frac{4\Delta E}{A} F^*(a_3^*(x)) \quad (14)$$

Summarizing, the surface energy of an fcc (100) face, where only the top layer is allowed to relax, is given by

$$\sigma = \Delta E \left[ \sum_{j=1}^3 F^*(a_{1,j}^*(x)) + F^*(a_2^*(x)) + 4F^*(a_3^*(x)) \right] \quad (15)$$

The calculation of the contribution to the defect energy from  $a_4^*$  has been ignored in this study. Equations similar to Eq. (1-15) can also be written down for the (111) - (110) – faces. Such details are ignored here.

**Table 1.** Experimental input for fcc metals.

Element	Cohesive Energy $\Delta E$	Lattice constant $a$	Vac. Form. Energy $E_{iv}^f$	Elastic Constants			Bulk modulus B
				$C_{11}$	$C_{12}$	$C_{44}$	
Rh	5.75	3.80	1.71	4.13	1.94	1.84	2.704
Ir	6.94	3.84	2.35	6.0	2.6	2.7	3.704
Pb	2.04	4.95	0.5	0.466	0.392	0.144	0.488
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
Th	6.20	5.08	2.0	0.753	0.489	0.478	0.543

## RESULTS AND DISCUSSIONS

In this section we report surface energies for six fcc metals. The ECT method requires as experimental input, the three bulk elastic constants, the bulk cohesive energy, the bulk lattice constants and the vacancy formation energy. These are collected together in Table 1 above and they have been employed to compute the ECT constants in Table 2. The different contributions of surface energy arising from the ECT expansion are displayed in Table 3, the surface energy are both for the rigid and relaxed case.

From Table 3, it can be seen that the contributions from the bond – angle term  $\sigma_3$ , are very small when compared to the ‘volume’ and bond – compression term. It has been shown else where (Rodriguez et al. 1993; Bozzolo et al. 1993), that the bond-angle and the face – diagonal term of the ECT represents only 1 to 2% of the total energy, hence they are not of great relevance for the calculation of surface energies.

**Table 2.** Computed ECT Constants for Rh, Ir, Pb, Ca, Sr and Th

Element	P	$l(\text{\AA})$	$\alpha(\text{\AA})$	$\lambda(\text{\AA})$	$\times 10^{-4}$	$\times 10^{-4}$	$\times 10^{-4}$	$\times 10^{-4}$
					$A_2$	$A_3$	$A_4$	D
Rh	8	0.247	3.726	0.693	0.336	0.938	2.979	10.835
Ir	10	0.230	4.417	0.647	0.0273	0.082	0.253	0.890
Pb	10	0.303	3.539	0.852	0.0284	0.0448	0.216	1.195
Ca	6	0.486	1.864	1.365	2.196	6.692	33.2.65	103.98
Sr	8	0.515	2.160	1.447	2.773	12.099	4.406	3
Th	12	0.494	3.617	1.389	0.0629	0.182	0.0848	14.307 0.271

**Table 3.** Rigid and relaxed surface energies (in erg cm<sup>-2</sup>) for Rh, Ir, Pb,Ca,Sr and Th surfaces.

Element	Crystal face (hkl)	Rigid	Relaxed		
			$\sigma_1$	$\sigma_2$	$\sigma_3$
Rh	(100)	3112.37	2956.21	39.90	3.49
	(110)	3251.56	3016.62	59.82	1.39
	(111)	2332.82	2258.82	22.10	0.00
Ir	(100)	3898.17	3742.10	41.10	3.94
	(110)	4040.15	3796.42	67.08	1.65
	(111)	2971.46	2883.82	35.52	0.00
Pb	(100)	568.30	531.21	8.18	0.12
	(110)	599.39	553.87	11.75	0.05
	(111)	418.86	403.20	5.62	0.00
Ca	(100)	486.57	443.90	4.79	0.25
	(110)	482.70	453.70	7.33	0.10
	(111)	356.19	346.24	3.43	0.00
Sr	(100)	355.10	344.93	2.37	0.21
	(110)	369.05	352.36	3.96	0.09
	(111)	277.48	271.83	1.88	0.00
Th	(100)	1442.76	1419.69	6.16	0.31
	(110)	1510.56	1472.75	9.28	0.12
	(111)	1155.45	1143.50	3.36	0.00

The surface energies obtained from the three low – index faces of the six fcc metals are summarized in

Table 4, and are compared with the results from first – principles calculations (Methfessel et al 1992;

Skriver and Rosengaard 1992), the Tight – binding (TB) method (Mehl and Papaconstantopoulos 1996), the modified embedded atom method (MEAM) (Baskes 1992), and experiment (de Boer et al 1988). In all cases we find  $\sigma_{111} < \sigma_{100} < \sigma_{110}$ . Thus close packed surfaces are the most stable for the fcc metals. The ECT surface energies are uniformly larger and closer to experiment, than those obtained by TB. Our surface energies are generally closer to experiment than those obtained by the MEAM and in good agreement with first – principles calculations for the surface energy of Ca (111) and Sr (Skriver and

Rosengaard 1992). Our results for the top-layer relaxations are presented in Tables 5, and are compared with the results of other theoretical calculations and experiment of which the authors are aware. Table 5 shows that our ECT values are in good agreement with the first– principles calculation of Methfessel et al (1992) for the (100) and (111) faces of Rh. The ECT value of the (110) face of Rh are also in better agreement with experiment (Begley et al 1993) than the theoretical calculations of Sinnott et al. (1991) and Methfessel et al (1992).

**Table 4.** Surface energies (in erg cm<sup>-2</sup>) for fcc metals

Element	Crystal face (hkl)	ECT (Present)	First – Principles Calculations	TB <sup>c</sup>	MEAM <sup>d</sup>	Expt <sup>e</sup> .
Rh	(100)	3000	2810 <sup>a</sup> 2900 <sup>b</sup>	2570	2900	2700
	(110)	3078	2880 <sup>a</sup>	2710	2920	
	(111)	2281	2530 <sup>a</sup> 2780 <sup>b</sup>	2460	2600	
Ir	(100)	3787	3810 <sup>b</sup>	2950	2910	3000
	(110)	3865		3190	3060	
	(111)	2919	3410 <sup>b</sup>	2590	2840	
Pb	(100)	546			424	
	(110)	566			431	
	(111)	409			366	
Ca	(100)	449				490
	(110)	461				
	(111)	350	352 <sup>b</sup>			
Sr	(100)	348				410
	(110)	356				
	(111)	274	287 <sup>b</sup>			
Th	(100)	1426				
	(110)	1482				
	(111)	1147				

a: FP LMTO calculations (Methfessel et al. 1992); b: LMTO – ASA calculations (Skriver and Rosengaard 1992); c: Tight-binding total ; energy calculations (Mehl and Papaconstantopoulos 1996); d: Modified embedded atom calculations (Baskes 1992); e: Experimental surface energies tabulated by deBoer et al. (1988).

**Conclusion:** We have in this study extended the surface energy results of Aghemenloh and Idiodi (1998), by including the effect of relaxation on the calculated surface energy of Rh, Ir, Pb, Ca, Sr and Th. Very generally, the surface energies are found to be in good agreement with the results from first principles calculation and experiment. Our work on relaxation is good, as it gives the correct sign and magnitude of the top-layer relaxations where experimental and first – principles calculations are available.

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**Table 5.** The top-layer relaxation in percent of the unrelaxed layer spacing  $\Delta_{12}/d$  (%) for some metals.

Element	Crystal face (hkl)	Changes in spacing (%)		Other method (Theoretical)	Experiment
		X (Å)	$\Delta_{12}/d$		
Rh	(100)	-0.07	-3.7	-3.2 <sup>a</sup> -3.5 <sup>b</sup>	-1.16±1.6 <sup>c</sup>
	(110)	-0.08	-4.2	-7.8 <sup>a</sup> -7.5 <sup>b</sup>	-3.3±1.5 <sup>d</sup>
	(111)	-0.04	-2.1	-2.3 <sup>a</sup> -2.5 <sup>b</sup>	-1.6±0.8 <sup>d</sup>
Ir	(100)	-0.06	-3.1		
	(110)	-0.07	-2.1		
	(111)	-0.04	-3.6		
Pb	(100)	-0.08	-2.1		
	(110)	-0.09	-3.2		
	(111)	-0.05	-3.6		
Ca	(100)	-0.13	-4.7		
	(110)	-0.15	-5.4		
	(111)	-0.08	-2.9		
Sr	(100)	-0.11	-3.6		
	(110)	-0.13	-4.3		
	(111)	-0.07	-2.3		
Th	(100)	-0.07	-2.8		
	(110)	-0.08	-3.2		
	(111)	-0.04	-1.6		

$d$  is the bulk interlayer distance. The calculated absolute changes are also given in  $\text{Å}$ ;

a: Corrected effective-medium calculations (Sinnott et al. 1991).

b: FP LM TO calculation, using seven-layer slabs (Methfessel et al 1992)

c: Experimental result for the (100) surface (Begley et al. 1993)

d: LEED experimental result (Rodriguez et al.1993).

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