

APPLICATION OF EQUIVALENT CRYSTAL THEORY TO BCC METAL SURFACES: SURFACE RELAXATION CALCULATION.

E. AGHEMENLOH

Department of Physics, Ambrose Alli University, Ekpoma Nigeria.
And

J.O.A. IDIODI

Department of Physics, University of Benin, Benin City, Nigeria.
e-mail: idijohn@uniben.edu

ABSTRACT

The surface energy and surface relaxation for three low-index surfaces of nine bcc metals are calculated using the equivalent crystal theory. The results for changes in the first interlayer spacing (Δ_{12}) and the ensuing surface energies are discussed and then compared with other theoretical results and available experimental data.

1. INTRODUCTION

It is now well established that metal surfaces undergo relaxation [1]. The experimental results are mainly obtained by low-energy electron diffraction [1,2] (LEED) and ion scattering studies [3].

These experimental studies have shown that multilayer relaxation is a rather common phenomenon and that the relaxation profile varies dramatically from one surface to another. Moreover, for unsymmetrical surfaces (i.e., surfaces for which there does not exist at least two mirror planes) the relaxation would have parallel as well as perpendicular components [4,5].

Theoretically, Allan and lannoo [6] predicted a long time ago a contraction of the first interlayer distance using a second-moment approximation of the tight-binding Scheme. The same model was used to study monolayer relaxations of the (100), (110), and (111) surfaces of fcc transition metals [7], the (100) surface of bcc Mo and W [8], and stepped surfaces of fcc transition metals [9]. Similar studies for low-index surfaces of bcc and fcc transition metals have also been done [10,11].

Other semi-empirical approaches like the electrostatic model of Finnis and Heine [12], which was later improved upon by Jiang et al. [13,14], have also been developed for surface relaxation studies. However, the Finnis-Heine approach requires an experimental input for its effective implementation. Other theoretical works include the total energy calculations of Ho and Bohnen [15], Fu et al [16], Equiluz [17], Davenport and Weinert [18], Hamann and Feibelman

[19,20], and Methfessel et al [21]. A study of six lower index surfaces of Nb, Ta, Mo, and W, has also been done by Luo and Legrand [22], using the "quenched molecular - dynamics" approach, and it examined the face - dependent profiles of perpendicular relaxations, from total energy minimizations in a tight-binding frame work.

In this present work, we use the "equivalent crystal theory" method to find the top-layer relaxation of three surfaces, (110), (100), and (111), for nine bcc metals. We also calculate the relaxed surface energies for these metals. Although the equivalent crystal theory of Smith et al [23], has been used extensively for the calculation of surface energies and surface relaxations for face-centered cubic metals [23,24], it has seen limited application to body - centered cubic metals. To fill this gap, we recently reported unrelaxed surface energies for twelve bcc metals [25]. We therefore extend our previous effort by including the effect of relaxation on the calculated surface energies of Nb, Ta, Mo, W, Li, Na, K, Rb, and Cs. In this study, we considered only perpendicular relaxation.

The summary of this paper is as follows: in section 2, we give a brief discussion of the ECT method, and in section 3 we discuss the ECT method of calculating the surface energies of bcc metals. Results of surface energies and the top-layer relaxation are reported in section 4, along with results obtained by other workers. Concluding remarks are given in section 5.

2. EQUIVALENT CRYSTAL THEORY

Equivalent crystal theory [23-25] 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. Rose et al. [26] found that the cohesive energy of metals and covalent solids as a function of the lattice parameter could be represented by a simple relationship:

$$E = \Delta E \cdot E^*(a^*) \quad (1)$$

Where ΔE is the cohesive energy and $E^*(a^*)$ is a universal shape for the curve, which can be well represented by the Rydberg function Thus,

$$E^*(a^*) = -(1 + a^*) \exp(-a^*) \quad (2)$$

and

$$a^* = (r_{WS} - r_{WSE})' / l \quad (3)$$

where r_{WS} is the Wigner - Seitz radius, r_{WSE} is the corresponding equilibrium value and l is given by

$$l = [\Delta E / (d^2 E / da^2) a = a_m]^{1/2} \quad (4)$$

where a_m is the equilibrium value of the lattice parameter a . The parameter l can also be written in terms of known experimental quantities as

$$l = [\Delta E / 12\pi B r_{WSE}]^{1/2} \quad (5)$$

where B is the bulk modulus. The energy of the equivalent crystal as a function of its lattice constant can therefore be given by the universal binding energy relation (UBER) in Eq. (1).

Let's consider a certain arbitrary defect and let ϵ be the total energy to form the defect or surface, then

$$\epsilon = \sum_i \epsilon_i \quad (6)$$

where ϵ_i is the contribution from an atom i close to the defect or surface.

ECT is based on the concept that for each atom i a certain perfect, equivalent crystal exists with its lattice parameter fixed at a value so that the energy of atom i in the equivalent crystal is also ϵ_i . This equivalent crystal differs from the actual ground - state crystal only in that its lattice constant may be different from the ground-state value. We compute ϵ_i via perturbation theory, where the perturbation arises from the difference between the ion core electronic potentials of the actual defect solid and those of the effective bulk single crystal. The

problem of finding ϵ_i , and hence ϵ , is reduced to finding for each atom i an effective equivalent single crystal and calculating the energy of the atom i in it.

Many body terms contribute to the energy of each atom in real systems. Hence,

ϵ_i is written as a sort of perturbation series of one-, two-, three- and four-body terms, each of which is obtained by considering a different effective perfect equivalent single crystal. In this approximation [23], ϵ_i takes the form:

$$\epsilon_i = \Delta E [F^*(a_1^*(i)) + \sum_j F^*(a_2^*(i,j)) + \sum_{j,k} F^*(a_3^*(i,j,k)) + \sum_{p,q} F^*(a_4^*(i,p,q))] \quad (7)$$

where

$$F^*(a^*) = 1 - (1 + a^*) \exp(-a^*) \quad (8)$$

The first term in Eq. (7), $F^*(a_1^*(i))$, contributes when average neighbor distances are altered via defect or surface formation. It can be thought of as representing local atom density changes. In most cases, this 'volume' term is the leading contribution to ϵ_i and in the case of isotropic volume deformations; it gives ϵ_i to the accuracy of the UBER. The value of $a_1^*(i)$, the lattice parameter of the first equivalent crystal associated with atom i , is chosen so that the perturbation (the difference in potentials between the solid containing the defect and its bulk, ground- state equivalent crystal) vanishes. Within the framework of ECT, this requirement translates into the following condition from which $a_1^*(i)$ is determined:

$$N_1 R_{ec}^p \exp(-\alpha R_{ec}) + N_2 (C_2 R_{ec})^n \exp[-(\alpha + 1/\lambda) C_2 R_{ec}] - \sum_{\text{defectNN}} R_j^p \exp(-\alpha R_j) - \sum_{\text{defectNNN}} R_j^p \exp[-(\alpha + 1/\lambda) R_j] = 0 \quad (9)$$

where

$$R_j \equiv |\bar{R}_j - \bar{R}_i| \quad (10)$$

Eq. (9) is the same as Eq. (26) of Ref. [23] and it is just the mathematical representation for local atom density changes in the defect region. In Eq. (9), R_j is the distance between the atom located at position \bar{R}_j and a reference atom

located at position \bar{R}_i ; N_1 and N_2 are, respectively, the number of nearest neighbors (NN) and next-nearest neighbors (NNN) in the equivalent crystal; and finally, C_2 is the ratio between the NNN distance and the NN distance in the undistorted actual crystal. The electronic screening length λ in Eq. (9) is chosen after Smith et al. [23], to be of the form:

$$\lambda = 2.81 l \quad (11)$$

and the ECT parameter p is defined by

$$p = 2n - 2 \quad (12)$$

where n is the atom principle quantum number. The two summations in Eq. (9) are over the actual defect crystal - the first over nearest neighbors and the second over next - nearest neighbors to atom i . The values of the ECT parameters l , λ , and p for each metal can be determined via their defining equations as given in the above presentation. Table 1 displays the values of these parameters for the bcc elements used in this work. The ECT parameter α in Eq. (9), primarily reflects the structure of the electron density in the overlap region between two neighboring atoms, and it is determined via the requirement that the energy to form a rigid or unrelaxed monovacancy be equal to the experimental vacancy formation energy E_{iv}^f . The equivalent lattice parameter a_1 , is thus related to the scaled quantity a_1^* via

$$a_1^* = (R_{ec} / c - r_{WSE}) / l \quad (13)$$

where l is a scaling length and c is the ratio between the equilibrium lattice constant and r_{WSE} . Thus, the determination of the energy for an ion in or near a defect amounts to solving a simple transcendental equation for the equivalent lattice parameter.

The higher order terms are relevant for the case of anisotropic deformations. The linear independence attributed to these four terms is consistent with the limit of small perturbations, which is assumed for the formation of the ECT. The second term, $F^*(a_2^*(i, j))$, is a two-body term which accounts for the increase in energy when NN bonds are compressed below their equilibrium value. This effect is also modelled with an equivalent crystal, whose lattice parameter is obtained by solving the perturbation equation given by

The fourth term, $F^*(a_4^*(i, p, q))$, describes face diagonal anisotropies. The perturbation equation is

$$N_1 R_{ec}^p \exp(-\alpha R_{ec}) - N_1 R_0^p \exp(-\alpha R_0) + A_4 R_0^p |d_p - d_q| / d \exp[-\alpha (R_j + R_k + R_l + R_m - 4R_0)] = 0 \quad (20)$$

where d is the face diagonal of the undistorted cube and A_4 is a constant adjusted to reproduce the experimental shear elastic constants. Finally, the scaled lattice parameter for the fourth term is given by

$$a_4^* = (R_{ec} / c - r_{WSE}) / l \quad (21)$$

3. SURFACE ENERGY CALCULATION

RELAXED SURFACE

In this study, we provide a simple application of the ECT method to bcc metallic surfaces, in contrast to our previous work [25], where we considered only a rigid surface. The assumption here is that only the surface plane is allowed to relax, and perpendicular relaxation was considered in this study.

Letting the plane 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 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 right - hand side of Eq. [7]) are necessary but, in the case of surface energy calculations of metals, of very little relevance. As have been shown [23,24], in other previous ECT works, they introduce a small correction, usually of the order of 1% of the leading term in

Equations (22-24) 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

$$\sigma_1 = \frac{\Delta E}{A} \sum_{j=1}^3 F^*(a_{1,j}^*(x)) \quad (29)$$

where

$$a_{1,j}^* = (R_{ec}^{(j)} / c - r_{WSE}) / l \quad (30)$$

A is the surface area and F^* is given by Eq. (8).

In order to compute the bond-compression contribution within the ECT framework, we need to solve the following transcendental equation in order to find the equivalent crystal associated with this effect:

$$8R_{ec}^p \exp(-\alpha R_{ec}) - 8R_o^p \exp(-\alpha R_o) + 4A_2 R_o^p (r_x - R_o) \exp[-\beta(r_x - R_o)] = 0 \quad (31)$$

Equation (31) is then solved with respect to R_{ec} and the energy contribution is then

$$\sigma_2 = \frac{\Delta E}{A} F^*(a_2^*(x)) \quad (32)$$

where a_2^* is given by Eq. (17).

The third term in Eq. (7) deals with bond-angle anisotropies. Contributions to σ_3 come from atoms for which the angle between the nearest neighbors departs from its equilibrium value θ_o ($\theta_o = 70.5^\circ$ for bcc metals). We shall adopt the convention described in Ref. [23], i.e., if an atom is missing one or more nearest neighbors then $F^*(a_3^*(i, j, k)) = 0$ for that atom and the atoms in the top layer do not contribute to σ_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

$$8R_{cc}^p \exp(-\alpha R_{cc}) - 8R_o^p \exp(-\alpha R_o) + A_3 R_o^p \exp[-\alpha(r_x - R_o)] \sin|\theta - \theta_o| = 0 \quad (33)$$

where

$$\theta = \cos^{-1} \left[\frac{r_x^2 + R_o^2 - S_x^2}{2r_x R_o} \right] \quad (34)$$

Equation 33 is solved with respect to R_{cc} and the bond-angle contribution is then

$$\sigma_3 = \frac{4\Delta E}{A} F^*(a_3^*(x)) \quad (35)$$

where a_3^* is given by Eq. (19).

Summarizing, the surface energy of a bcc (100) face, where the top layer is allowed to relax, is given by

$$\sigma = \frac{\Delta E}{A} \left[\sum_{j=1}^3 F^*(a_{1,j}(x)) + F^*(a_2^*(x)) + 4F^*(a_3^*(x)) \right] \quad (36)$$

The calculation of the contribution to the defect energy from a_4^* has been ignored in this study. Equations similar to Eq. (22-36) can also be written down for the (111) - (110) - faces. Such details are ignored here.

4. RESULTS

The different contributions of surface energy arising from the ECT formalism are displayed in Table 2, the surface energy results are both for the rigid and relaxed case. From Table 2, it can be seen that the contributions from the bond-angle term σ_3 , are very small when compared to the first two terms of the ECT expansion. This, further establishes the fact known from previous ECT works [23,24], that the many-body anisotropies (bond-angle, face-diagonal) that appear in the ECT formalism are not of great relevance for the calculation of surface energies.

The surface energies obtained from the three low-index faces of the nine bcc metals are summarized in Table 3, and are compared with the results from the embedded atom method (EAM) [27], first principles calculations [16,21,28,29], the modified embedded atom method (MEAM) [30], the Tight-binding (TB) method [31], the Jellium model [32], and experiment [33]. The

ECT surface energies are uniformly larger, and closer to experiment than those obtained by the EAM[27], which is known to underestimate surface energies in fcc metals. From Table 3, it can be seen that our ECT surface energy results are uniformly larger and closer to experiment and first principles calculations. Our relaxed surface energy results like the unrelaxed surface energies [25], consistently support the trend $\sigma_{110} < \sigma_{111} < \sigma_{100}$, which shows that relaxation effects do not affect the ordering of the (100), (110) and (111) surface energies of the ECT.

Our results for the top-layer relaxations are presented in Table 4, and are compared with the results from first-principles calculations [21], the Tight-binding quenched molecular - dynamics calculation [22], and experiment [34-39]. Our relaxation results of the (100) and (110) faces of Nb, Ta, Mo and W compare favourably well with the work of Luo and Legrand [22]. The only discrepancy is the rather too high contractions predicted for the (111) faces compared to our low values. Our ECT values are also in good agreement with the first-principles calculation of Methfessel et al. [21]. The first -layer contraction determined experimentally for the (100) surface of Mo (Ref.[35]) is in reasonable agreement with our value. The agreement with experiment is rather good considering the experimental uncertainties, for instance experimental $\Delta d_{12}/d$ is between - 3% and - 10% for the most studied surface, W (100)[37].

All the result presented here are obtained for the unreconstructed surfaces, i.e., we allow only rigid translation of the surface layers. However, it is well known that W (100) and Mo (100) are reconstructed at low temperature [22].

5. CONCLUSION

We have presented an ECT study of surface energy and surface relaxation in nine bcc metals. This has greatly extended the work of Smith et al. [23] and other workers [24,25] on bcc metals. 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 also good too, as it gives the correct sign and magnitude of the top-layer relaxations compared to theories [21,22] and experiment [34-39].

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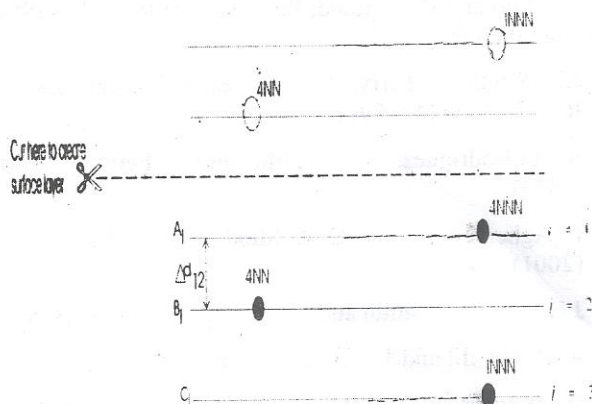


Fig. 1. The bcc (100) plane and the neighbor atoms in each plane. The index j labels the planes, starting with $j = 1$ for the surface plane, and 4NNN indicates that the plane $j = 1$ has 4 next nearest neighbors, etc.

Table 1. Computed ECT Constants and Experimental input for bcc metals.

| Element | P | l (\AA^0) | α (\AA^{0-1}) | $\lambda(\text{\AA}^0)$ | $10^{-2} A^2/D$ |
|---------|----|------------------------|---------------------------------|-------------------------|-----------------|
| Nb | 8 | 0.341 | 3.353 | 0.958 | 4.374 |
| Ta | 10 | 0.326 | 4.069 | 0.915 | 4.374 |
| Mo | 8 | 0.262 | 3.598 | 0.736 | 4.582 |
| W | 10 | 0.271 | 4.243 | 0.760 | 4.568 |
| Li | 2 | 0.589 | 1.063 | 1.656 | 4.135 |
| Na | 4 | 0.578 | 1.374 | 1.625 | 3.416 |
| K | 6 | 0.694 | 1.524 | 1.951 | 2.762 |
| Rb | 8 | 0.652 | 1.930 | 1.831 | 2.584 |
| Cs | 10 | 0.758 | 2.105 | 2.129 | 2.388 |

Table 1. Ctd

| Elements | 10^{-2} A3/D | 10^{-1} A4/D | 10^{-4} D | $\Delta E(\text{eV})$ | $a (\text{\AA}^0)$ |
|----------|-------------------|----------------|-------------|-----------------------|--------------------|
| Nb | 9.560 | 0.729 | 8.728 | 7.57 | 3.30 |
| Ta | 8.568 | 1.402 | 1.161 | 8.10 | 3.30 |
| Mo | 12.431 | 1.238 | 7.936 | 6.82 | 3.15 |
| W | 11.697 | 1.468 | 1.168 | 8.66 | 3.16 |
| Li | 5.248 | 2.247 | 3903.951 | 1.63 | 3.491 |
| Na | 4.287 | 1.896 | 538.857 | 1.113 | 4.225 |
| K | 4.930 | 1.776 | 72.532 | 0.934 | 5.225 |
| Rb | 4.440 | 1.851 | 9.427 | 0.852 | 5.585 |
| Cs | 2.041 | 1.466 | 1.336 | 0.804 | 6.045 |

APPLICATION OF EQUIVALENT.....

Tables 3. Surface Energies (in erg/cm²) for bcc metals

| Element | Crystal face (hkl) | ECT Present | EAM Ref.[27] | LDA | MEAM Ref.[30] | TB Ref. [31] | JELLI UM Ref. [32] | Expt. Ref. [33] |
|---------|--------------------|-------------|--------------|-------------------------------------|---------------|--------------|--------------------|-----------------|
| Nb | (100) | 3967 | 1970 | 3100 ^a 2860 ^b | 2788 | 2370 | | 2700 |
| | (110) | 2110 | 1810 | 1640 ^c 2360 ^b | 1868 | 1540 | | |
| | (111) | 2809 | | | 2018 | 2440 | | |
| Ta | (100) | 4121 | 1990 | | 3292 | 3000 | | 3190 |
| | (110) | 2217 | 1800 | 1790 ^c | 2173 | 2050 | | |
| | (111) | 2944 | | | 2305 | 3140 | | |
| Mo | (100) | 4778 | 2280 | 3520 ^b | 2122 | 2120 | | 3000 |
| | (110) | 2598 | 2130 | 3180 ^c 3140 ^b | 1930 | 3040 | | |
| | (111) | 3384 | | | 1861 | 2840 | | |
| W | (100) | 5819 | 2810 | 5100 ^d | 2646 | 6700 | | 3680 |
| | (110) | 3293 | 2600 | 3840 ^c | 2232 | 4300 | | |
| | (111) | 4227 | | | 2247 | 6750 | | |
| Li | (100) | 636 | | 436 ^c | 431 | | 371 | 525 |
| | (110) | 314 | | 458 ^c | 202 | | 326 | |
| | (111) | 425 | | | 279 | | 433 | |
| Na | (100) | 391 | | 236 ^c | 288 | | 216 | 260 |
| | (110) | 218 | | 307 ^c | 169 | | 190 | |
| | (111) | 280 | | | 202 | | 252 | |
| K | (100) | 207 | | 129 ^c | 182 | | 115 | 130 |
| | (110) | 122 | | 116 ^c | 110 | | 111 | |
| | (111) | 154 | | | 125 | | 134 | |
| Rb | (100) | 145 | | 107 ^c | | | 98 | 110 |
| | (110) | 79 | | 92 ^c | | | 86 | |
| | (111) | 104 | | | | | 114 | |
| Cs | (100) | 109 | | 92 ^c | | | 79 | 95 |
| | (110) | 63 | | 72 ^c | | | 69 | |
| | (111) | 82 | | | | | 92 | |

E. AGHEMENLOH AND J.O.A. IDIODI

a Full – Potential LAPW calculation, using nine-layer slabs (Ref.28)

b FP LMTO calculation, using seven – layer slabs (Ref. 21)

c Green's function LMTO – ASA calculations (Ref. 29)

d Local – density functional calculation with full – potential LAPW total – energy calculation (Ref. 16).

Table 4. Top – layer relaxation in percent of the unrelaxed layer spacing d_{12}/d (%) for the three symmetrical surfaces, d is the bulk interlayer distance.

| Element | (hkl) | ECT | LDA Ref. [21] | TB Ref. [22] | Expt. |
|---------|-------|-------|------------------|-----------------|------------------------|
| Nb | (100) | -5.5 | -9.3 | -6.3 | |
| | (110) | -3.6 | -3.7 | -3.6 | |
| | (111) | -7.3 | | -21.5 | |
| Ta | (100) | -4.2 | | -6.3 | -11a |
| | (110) | -3.0 | | -3.8 | |
| | (111) | -6.1 | | -21.6 | |
| Mo | (100) | -5.1 | -9.0 | -6.9 | -9 ^b |
| | (110) | -3.2 | -3.9 | -3.3 | -1.6 ^c |
| | (111) | -7.0 | | -19.7 | |
| W | (100) | -3.8 | | -3.5 | -3 to -10 ^d |
| | (110) | -3.2 | | -1.4 | <2 ^e |
| | (111) | -5.7 | | -16.3 | |
| Li | (100) | -14.9 | | | |
| | (110) | -9.7 | | | |
| | (111) | -22.9 | | | |
| Na | (100) | -8.5 | | | |
| | (110) | -6.2 | | | |
| | (111) | -13.7 | | | |
| K | (100) | -6.1 | | | |
| | (110) | -4.6 | | | |
| | (111) | -10.0 | | | |
| Rb | (100) | -5.4 | | | |
| | (110) | -3.9 | | | |
| | (111) | -7.9 | | | |
| Cs | (100) | -4.3 | | | |
| | (110) | -3.3 | | | |
| | (111) | -6.6 | | | |

a From Ref. 34

b From Ref. 35

c From Ref. 36

d From Ref. 37 and 22

e From Ref. 38 and 39