



## Surface energies of hcp metals using equivalent crystal theory

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### ABSTRACT

The equivalent crystal theory method of Smith et al. [Phys. Rev. B 44 (1991) 6444] originally formulated for fcc and bcc metals, and semiconductors, is here extended to hcp metals and applied to calculate surface energies. The (0 0 1) surface energies obtained for 22 hcp metals are in good agreement with the results of both experiment and *ab initio* calculations.

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### 1. Introduction

Surface energy is a physical property of great interest [1–18]. 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 more commonly found for polycrystalline materials, and are also usually subject to errors due to surface-active contaminants and thus have a degree of uncertainty. Early theoretical calculations were based on perturbation theory [1] or non-perturbative variational method [2]. In the last few years, there has been an increasing effort on first-principles calculations [3–7], as well as in the area of semi-empirical methods [8–16].

In general, semi-empirical approaches tackle the many-body problem by determining a functional form for the cohesive energy based on some physical model. The functional form often contains one or more parameters which are to be determined by fitting to experimental properties. Once these parameters have been determined, the functional form may then be used to calculate various other properties, such as defect energies, etc. While the various semi-empirical models have been impressively successful in describing a wide variety of metallic properties, a significant short-coming is that the estimate of surface energies from several of these semi-empirical models [8–15] is

considerably lower than experiment and first-principles results. The reasons for this short-coming are not yet clear and current research efforts are in the direction of formulating better semi-empirical models.

A review of recent theoretical efforts dealing with the calculation of properties of materials using semi-empirical methods reveals that four methods are dominant: Finnis–Sinclair method [8], embedded atom method (EAM) [9–14], effective medium theory (EMT) [15], and equivalent crystal theory (ECT) [16,19–24]. The ECT method has been used extensively for both face-centred cubic (fcc) and body-centred cubic (bcc) metals [16,19–24] but has so far not been applied to the hexagonal closed-packed (hcp) metals. The purpose of this study is first, to extend the original ECT method [19] to hcp metals and thereby fill out that gap in the literature, and finally to use the method to study the surface energy problem for these materials. This completes our initial objective of using the ECT method to provide comprehensive surface energy results for fcc [21], bcc [22] and hcp metals. Such extensive results obtained with the same theoretical model, are useful to both theorists and experimentalists.

The remainder of this paper is organized as follows. In Section 2, we give a brief discussion of the ECT method and its appropriate extension to hcp metals. In Section 3, we discuss the ECT method of calculating the surface energies of hcp metals. The results of surface energies for 22 hcp metals are reported in Section 4, along with the results obtained by other workers. Concluding remarks are given in Section 5.

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## 2. The ECT method

In this section a brief operational description of the ECT method is given. Details of its derivation and the rationale behind its development can be found in Ref. [19]. Equivalent crystal theory (ECT) is based on an exact relationship between the total energy of the constituent atoms in a solid and the atomic locations and it 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 minimise the perturbation. The energy of the equivalent crystal, as a function of its lattice constant is given by a universal binding energy relation [25].

Let  $\varepsilon$  be the total energy to form the defect or surface, then

$$\varepsilon = \sum_i \varepsilon_i \quad (1)$$

where  $\varepsilon_i$  is the contribution from an atom  $i$  close to the defect or surface. The linear independence attributed to the terms in Eq. (1) is consistent with the limit of small perturbations which is assumed in the formulation of the ECT. ECT is based on the concept that there exist, for each atom  $i$ , a certain perfect, equivalent crystal with its lattice parameter fixed at a value so that the energy of atom  $i$  in the equivalent crystal is also  $\varepsilon_i$ . This equivalent crystal differs from the ground-state crystal only in that its lattice constant may be different from the ground-state value. We compute  $\varepsilon_i$  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. The problem of finding  $\varepsilon_i$ , and hence  $\varepsilon$ , is reduced to finding for each atom 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,  $\varepsilon_i$  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 [19],  $\varepsilon_i$  takes the form:

$$\varepsilon_i = \Delta E \left[ F^*[a_1^*(i)] + \sum_j F^*[a_2^*(i,j)] + \sum_{i,j} F^*[a_3^*(i,j,k)] + \sum_{p,q} F^*[a_4^*(i,p,q)] \right] \quad (2)$$

where  $\Delta E$  is the equilibrium cohesive energy per atom of the actual crystal, and  $F^*[a^*]$  is the simple analytic function

$$F^*[a^*] = 1 - (1 + a^*) \exp(-a^*) \quad (3)$$

The first term in Eq. (2),  $F^*[a_1^*(i)]$ , contributes when average neighbour distances are altered via defect or surface formation. It can be thought of as representing local atom density changes. The second term,  $F^*[a_2^*(i,j)]$ , is a two-body term which accounts for the increase in energy when nearest neighbour bonds are compressed below their equilibrium value. The third term,  $F^*[a_3^*(i,j,k)]$ , is a three-body term that accounts for the increase in energy which arises when bond angles deviate from their equilibrium values in the undistorted single crystal. Finally, the fourth term,  $F^*[a_4^*(i,p,q)]$ , describes face diagonal anisotropies. A detailed description, for each lattice type, of the structural effect associated with these four terms can be found in Ref. [19].

Now Eq. (2) can be re-written, in an obvious notation, as

$$\varepsilon_i = \Delta E \sum_{k=1}^4 F^*[a_k^*(i)] \quad (4)$$

where the scaled lattice constant  $a^*$  is given in terms of the equivalent crystal nearest-neighbour distance  $R_{ec}$  as

$$a^* = (R_{ec}/c - r_{WSE})/l \quad (5)$$

Eqs. (1)–(3), (and) (5) correspond respectively to Eqs. (5) and (20)–(22) of Smith et al. (1991). However, the fact that the hcp structure has two lattice constants which convention denotes as  $a$  and  $c$  makes it mandatory for us to relabel  $c$  in Eq. (5) as  $c_1$ . Eq. (5) thus becomes

$$a^* = (R_{ec}/c_1 - r_{WSE})/l \quad (6)$$

Let  $r_{WS}$  be the Wigner–Seitz radius in the actual crystal with the equilibrium value  $r_{WSE}$ , then  $c_1$  is the ratio between the nearest-neighbour distance and  $r_{WSE}$  in the undistorted actual crystal. For the hcp crystal,  $r_{WSE} = (3\sqrt{3}a^2c/16\pi)^{1/3}$ , and the scaling length  $l$  takes the form

$$l = (\Delta E/12\pi B r_{WSE})^{1/2} \quad (7)$$

where  $B$  is the equilibrium bulk modulus of the actual crystal.

By intuition rather than a rigorous proof, our work hangs on the assumption, [26,27], that the universal binding energy curve of Rose et al. [25] describes the hydrostatic compression or expansion of a pure hcp crystal by keeping the ratio  $c/a$  constant and using the Wigner–Seitz radius as a reference instead of the lattice constant. Throughout this work it is assumed that the  $c/a$  ratio for the equivalent hcp crystal is the same as that for the actual crystal. Then a knowledge of  $a^*(i)$  for the equivalent crystal implies immediately a knowledge of  $c^*(i)$ , and in what follows we shall be focusing attention on how to determine  $a^*(i)$ . Eq. (2) shows clearly that each atom  $i$  in the defect region has associated with it four different types of equivalent crystals with lattice parameters  $a_1^*$ ,  $a_2^*$ ,  $a_3^*$ , and  $a_4^*$ .

The value of  $a^*$ , the lattice parameter of the first equivalent crystal associated with atom  $i$ , 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 frame work of ECT, this requirement translates into the following equation for the determination of the nearest neighbour distance of the first equivalent crystal,  $R_{ec}$ :

$$N_1 R_{ec}^p \exp(-\alpha R_{ec}) + N_2 (C_2 R_{ec})^p \exp\left[-\left(\alpha + \frac{1}{\lambda}\right) C_2 R_{ec}\right] - \sum_{\text{defect NN}} R_j^p \exp(-R_j) - \sum_{\text{defect NNN}} R_j^p \exp\left[-\left(\alpha + \frac{1}{\lambda}\right) R_j\right] = 0 \quad (8)$$

where

$$R_j = \left| \vec{R}_j - \vec{R}_i \right| \quad (9)$$

Eq. (8) is the same as Eq. (26) of Ref. [19] and it is just the mathematical representation for local atom density changes in the defect region. Once  $R_{ec}$  has been determined from Eq. (8) then  $a_i^*(i)$  can be determined from Eq. (6). In Eq. (8),  $R_j$  is the distance between the atom located at position  $\vec{R}_j$  and a reference atom located at position  $\vec{R}_i$ ;  $N_1$  and  $N_2$  are, respectively, the number of nearest neighbours (NN) and next-nearest neighbours (NNN) in the equivalent crystal; and finally,  $C_2$  is the ratio between the NNN distance and NN distance in the undistorted actual crystal.

The electronic screening length  $\lambda$  in Eq. (8) is chosen, after Smith et al. [19], to be of the form

$$\lambda = 2.81l \quad (10)$$

and the ECT parameter  $p$  is defined by

$$p = 2n - 2 \quad (11)$$

where  $n$  is the atom principle quantum number. The two summations in Eq. (8) are over the actual defect crystal, the first over nearest neighbours and the second over next-nearest neighbours to atom  $i$ .

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