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Orientation of (1 × 1)-surface free energies of crystals

Z. Yu *, A. Flodström

Materials Physics, Department of Physics, Royal Institute of Technology, Teknikringen 14, S-100 44 Stockholm, Sweden

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Abstract

The free energy of a (1 × 1)-surface, with no relaxation and no adsorption, is calculated using a bond-breaking mode in which the potential energy of the crystal is treated as the sum of the energy of the bonds connecting pair-wise atoms. Based on a purely geometrical model, the number of broken bonds or dangling bonds per atom is calculated on the surface of the crystal when an atomically flat plane $\boldsymbol{h}(hkl)$ is created. The results provide a general expression of the surface free energy in terms of Miller indices *hkl*. The anisotropy of the surface free energy is completely described in the expression. Considering nearest-neighboring bonding only, the orientation dependence of the surface free energy is discussed for simple cubic (sc) and cubic tetrahedral (cth) crystals, respectively. Wulff plots and the equilibrium forms for the sc and the cth crystals are obtained on the basis of their expressions of the surface free energy, implying the cube and the octahedron are the equilibrium forms for the sc and the cth crystals, respectively. Furthermore a predicted anisotropy of fcc metals is discussed. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Single crystal surface; Surface energy

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1. Introduction

Interest in the surface configuration and surface energy of crystals is increasing as a consequence of modern experiments in fields such as the equilibration of grain boundaries, the oriented growth of crystals, sintering, adsorption and surface catalysis [1]. It can be expected that a perspective on problems in various fields will be gained by investigating the surface energies of the various possible configurations of the surfaces of a crystal.

It is well known that the surface free energy of a crystal is generally dependent on the orientation of the surface [1–5]. Some previous work has been done to calculate and measure the surface free energy [6–8]. A periodic bond chain model has been proposed by Wolff et al. [9] who expect that the specific surface free energy may be derived in terms of the crystallographic indices *hkl*. A vector function model has been proposed by Hoffman et. al. [10] to describe the orientation of surface energy. Mackenzie et al. [11] have presented a theoretical model to determine the distribution of dangling bonds on the atomically flat surfaces. The aim of the work described in this paper has been to determine, on a purely geometrical basis, the surface free energy as a function of orientation by dealing with a bond-breaking mode.

A surface which gives a precise separation of the system into two parts, with homogeneous portions of the two phases located on its opposite sides, was called by Gibbs a dividing surface [12]. The surface tension $\gamma(\boldsymbol{u})$ of a solid–vapor interface

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* Corresponding author. E-mail: ming@matphys.kth.se

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may be defined as the reversible work W_{rev} required to create a surface of area $2A(\boldsymbol{u})$ with an orientation given by the unit vector $\boldsymbol{u}$ normal to the surface [9,13], i.e.

$$\gamma(\boldsymbol{u}) = W_{\text{rev}}/2A(\boldsymbol{u}). \tag{1}$$

The surface tension is usually defined in terms of specific surface free energy [2,14]. The reversibility implies that the atomic configurations everywhere in the system and particularly in the surface region are always those characteristic of equilibrium.

In the present paper, the surface is dealt with in a bond-breaking mode without regard to the surface reconstruction. However, we still use the phrase "surface free energy" in this case. Furthermore, a restriction is imposed in which the potential energy of the crystal is represented as the sum of pair-wise interatomic interactions. The crystal is taken to be semi-infinite and defect-free, and thermal vibrations and any contacting phase are neglected. The specific surface free energy, γ_{hkl}, is then simply equal to half the energy per unit area of surface associated with breaking the bonds which would connect the crystal occupying the other half space [2,9,13]:

$$\gamma_{hkl} = \frac{1}{2}\sum n(\boldsymbol{u})E^0(u) \tag{2}$$

where $E^0(u)$ is the potential energy of interaction of a pair of atoms separated by a vector $\boldsymbol{u}$ and $n(\boldsymbol{u})$ is the number per unit area of such bonds broken when the crystal is separated. It is obvious that $n(\boldsymbol{u})$ is dependent on orientation and that $E^0(u)$ is dependent on the nature of crystal.

2. Theoretical aspects

When an infinite ideal crystal is divided into two parts by a plane (hkl), the two new surfaces may be described as atomically flat surfaces indicated as (hkl) and $(-h-k-l)$. Clearly, a semi-infinite crystal with an atomically flat surface is one in which all possible atomic positions are occupied on one side of the dividing plane but in which none are occupied on the other side. If a bond is represented by a line with atoms at each end, it must be broken when an atomically flat surface is formed.

2.1. Interaction between u-bonds and the dividing plane h(hkl)

Any specific bond associated with a given atom can be defined as a vector $\boldsymbol{u}$, which contains the components u, v and w in the primitive cell, going from this atom to a neighboring atom. Such a bond is called the $\boldsymbol{u}$-bond [11]. Any $\boldsymbol{u}$-bond with components $\langle uvw\rangle$ corresponds to its own coordination, n_i. For instance, when $u \neq v = w = 0$, $n_i = 6$, i.e. $[u00]$, $[-u00]$, $[0u0]$, $[0-u0]$, $[00u]$ and $[00-u]$, while when $u \neq v \neq w \neq 0$, $n_i = 48$, and so on. The $\boldsymbol{u}$-bonds with the same components, u, v and w, are called a $\boldsymbol{u}$-bond set or $\boldsymbol{u}_i$-bonds. Table 1 lists five possible components of the $\boldsymbol{u}$-bonds and their coordination. It is evident that a crystal lattice can be described completely by the $\boldsymbol{u}$-bonds. For example, the first three components of the $\boldsymbol{u}$-bonds in Table 1 correspond to sc, fcc, bcc and cth (cubic tetrahedral or diamond) lattices with respect to first neighbor $\boldsymbol{u}$-bonds, respectively. Table 2 shows the first, second and third $\boldsymbol{u}$-bonds corresponding to sc, bcc, fcc and cth, respectively.

Table 1
The coordination with respect to components of $\boldsymbol{u}_i$-bonds (u, v and w are integral)

$\boldsymbol{u}_i$-bonds ($\langle uvw\rangle$)	Coordination	Lattices with respect to nearest neighboring bonds
1. $u \neq v = w = 0$	6	sc [a]
2. $u = v = w \neq 0$	8	bcc and cth [b]
3. $u = v \neq w = 0$	12	fcc [c]
4. $u \neq v = w \neq 0$	24	
5. $u \neq v \neq w = 0$	24	
6. $u \neq v \neq w \neq 0$	48	

[a] If $u = a$, the $\boldsymbol{u}_i$-bonds become $\langle 100\rangle a$, which are nearest neighbor bonds in the sc crystal with lattice constant a.

[b] If $u = a/2$, the $\boldsymbol{u}_i$-bonds become $\langle 111\rangle a/2$, which are nearest neighbor bonds in the bcc crystal with lattice constant of a; if $u = a/4$, the $\boldsymbol{u}_i$-bonds become $\langle 111\rangle a/4$, which are nearest neighbor bonds in the cth crystal with lattice constant of a.

[c] If $u = a/2$, the $\boldsymbol{u}_i$-bonds become $\langle 110\rangle a/2$, which are nearest neighbor bonds in the fcc crystal with lattice constant of a.

Table 2
The first, second and third nearest neighbor bonds of various cubic crystals

Crystal	Components ($\langle uvw\rangle \times$ bond number)		
	1st neighbor bonds	2nd neighbor bonds	3rd neighbor bonds
sc	$\langle 100\rangle \times 6$	$\langle 110\rangle \times 12$	$\langle 111\rangle \times 8$
fcc	$\langle 110\rangle/2 \times 12$	$\langle 100\rangle \times 6$	$\langle 211\rangle/2 \times 24$
bcc	$\langle 111\rangle/2 \times 8$	$\langle 100\rangle \times 6$	$\langle 110\rangle \times 12$
cth	$\langle 111\rangle/4 \times 4$	$\langle 110\rangle/2 \times 12$	$\langle 100\rangle \times 6$

Furthermore, $\sum \boldsymbol{u}_i = 0$ ($i = 1, 2, \ldots, n_i$), for any ***u***-bond set. It is obvious that the ***u***-bonds are essentially vectorial representation for Bravais lattice.

On the other hand, an atomically flat surface is specified by the vector ***h*** which contains components of h, k and l in the reciprocal cell. The components are defined as Miller indices of the surface. In case of cubic symmetry, the vector $\boldsymbol{h}(hkl)$ is orthogonal to the dividing plane (hkl) in the primitive lattice. Fig. 1 shows schematically the geometrical relation between ***h*** and ***u*** when plane $\boldsymbol{h}(hkl)$ divides the crystal in which the atoms are connected with some kind of ***u***-bonds. If ***h*** is assumed to have direction perpendicular to the surface and towards the outside of the crystal, the ***u***-bond can be broken only if $h \cdot u > 0$. If $h \cdot u < 0$ the ***u***-bond is directed backwards into the crystal and remain unbroken. If $h \cdot u = 0$, the ***u***-bonds lie in the surface $\boldsymbol{h}(hkl)$ and can be understood as being bonds unbroken or bonds broken with zero density (Fig. 1).

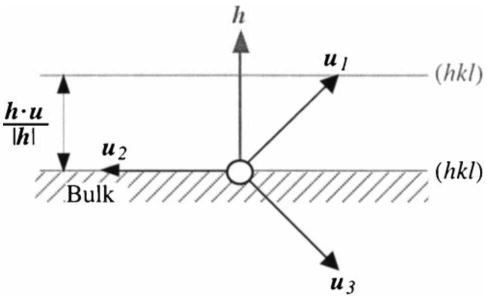

Fig. 1. Geometrical coordination of the dividing plane $\boldsymbol{h}(hkl)$ and the ***u***-bonds. $\boldsymbol{h} \cdot \boldsymbol{u}_1 > 0$ implies that the $\boldsymbol{u}_1$-bond is broken; $\boldsymbol{h} \cdot \boldsymbol{u}_3 < 0$ implies that the $\boldsymbol{u}_3$-bond is not broken and $\boldsymbol{h} \cdot \boldsymbol{u}_2 = 0$ that the $\boldsymbol{u}_2$-bond is unbroken or broken with zero density.

2.2. The number of u-bonds broken when a surface h(hkl) is formed

Since ***u*** is a lattice vector and therefore exactly spans an integral number of lattice planes with normal ***h***, it is found that, when plane $\boldsymbol{h}(hkl)$ divides the crystal, i.e. when the surface hkl is formed, the number of broken $\boldsymbol{u}_i$-bonds or dangling bonds per atom can be given by

$$N(\boldsymbol{u}_i) = \boldsymbol{h} \cdot \sum \boldsymbol{u}_i / |\boldsymbol{h}| d_{hkl}, \quad \boldsymbol{h} \cdot \boldsymbol{u}_i > 0, \tag{3}$$

where d_{hkl} denotes the spacing between adjacent planes (hkl). Fig. 2 gives three cases in which different ***u***-bonds are broken. When the ***u***-bond spans two planes, i.e. one spacing unit between the planes (Fig. 2a), it is easy to show that Eq. (3) gives exactly the number of broken bonds. In general, if the ***u***-bond spans more than two planes (Figs. 2b and c), the number of unit spacings of (hkl) through which ***u*** passes is equal to the number of ***u***-bonds which are cut by one of those planes. If Ω denotes the volume of crystal per atom, then Ω / d_{hkl} is obviously the area of the surface (hkl) per atom. Thus, when the crystal is divided along plane (hkl), i.e. when the surface (hkl) is formed, the areal density of the dangling bonds, $n(\boldsymbol{u})$, can be determined by $N(\boldsymbol{u}_i)/\Omega/d_{hkl}$, i.e.

$$n(\boldsymbol{u}_i) = \boldsymbol{h} \cdot \sum \boldsymbol{u}_i / \Omega |\boldsymbol{h}| \quad \text{when } \boldsymbol{h} \cdot \boldsymbol{u}_i > 0. \tag{4}$$

It is evident that $\Omega |\boldsymbol{h}|$ is the area of the surface (hkl) per atom, s_{hkl}, where $|\boldsymbol{h}| = (h^2 + k^2 + l^2)^{1/2}/a$.

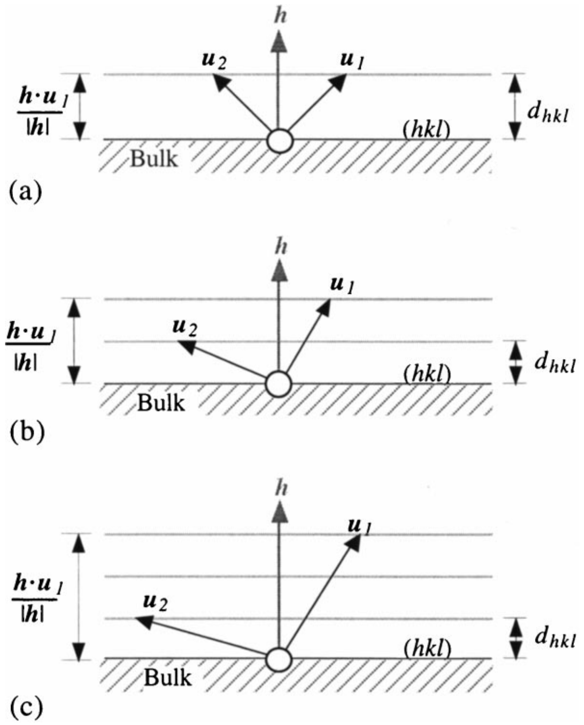

Fig. 2. Division of a crystal into two parts in which different bonds are broken. The number of spacings of (*hkl*) through which $\boldsymbol{u}_i$ passes is equal to the number of $\boldsymbol{u}_i$-bonds which are cut by one of those planes. (a) $\boldsymbol{u}_1$ and $\boldsymbol{u}_2$ span respectively one unit spacing of (*hkl*) and the plane cuts two $\boldsymbol{u}_i$-bonds; (b) $\boldsymbol{u}_1$ spanning two unit spacings of (*hkl*) and the plane cuts two **u**-bonds; (c) $\boldsymbol{u}_1$ spans three unit spacings of (*hkl*) and the plane cuts three **u**-bonds.

In general, this area is given by

$$s_{hkl} = \Omega|\boldsymbol{h}| = a^2(h^2+k^2+l^2)^{1/2}/n \tag{5}$$

where a and n are, respectively, the lattice constant and the number of atoms per unit cell. It follows that the number of the $\boldsymbol{u}_i$-bonds broken per atom is given by

$$N(\boldsymbol{u}_i) = n(\boldsymbol{u}_i)s_{hkl} = \boldsymbol{h}\cdot\sum \boldsymbol{u}_i, \quad \boldsymbol{h}\cdot\boldsymbol{u}_i > 0. \tag{6}$$

One can find easily that, from Eq. (6), the number is dependent on and only on both the dividing plane and the atomic structure of the crystal.

If in a **u**-bond set, n_i $\boldsymbol{u}_i$-bonds are separated into two arbitrary groups n_j and n_k, where $n_j + n_k = n_i$, it can be found that $\sum \boldsymbol{u}_j = -\sum \boldsymbol{u}_k$, since $\sum \boldsymbol{u}_i = 0$ ($i=1, 2, \ldots,$ n_{i}). It follows that

$$\boldsymbol{h}\cdot\sum \boldsymbol{u}_j = -\boldsymbol{h}\cdot\sum \boldsymbol{u}_k. \tag{7}$$

Eq. (7) is independent of **h** and can be rewritten as $\sum \boldsymbol{h}\cdot\boldsymbol{u}_j = -\sum \boldsymbol{h}\cdot\boldsymbol{u}_k$, implying that any $\boldsymbol{h}(hkl)$ can separate the $\boldsymbol{u}_i$-bonds into two equivalent parts in which the **u**-bonds in the one part are broken and the **u**-bonds in the other part remain unbroken. In fact, in most of case these two equivalent parts satisfy $n_j = n_k = n_i/2$, i.e. the plane divides the n_i $\boldsymbol{u}_i$-bonds into two halves. The number of $\boldsymbol{u}_i$-bonds broken per atom, when the crystal is cut by the plane $\boldsymbol{h}(hkl)$, is then given by

$$N(\boldsymbol{u}) = \boldsymbol{h}\cdot\sum \boldsymbol{u}_j \qquad (j=1, 2, \ldots, n_i/2). \tag{8}$$

In the case of $n_j \neq n_k \neq n_i/2$, however, to calculate the number of **u**-bonds broken per atom according to Eq. (8), a special plane $\boldsymbol{h}_0$ ($\boldsymbol{h}_0$ and **h** belong to a same family of planes) can be chosen which divides the n_i $\boldsymbol{u}_i$-bonds into two halves, i.e. $n_j = n_k = n_i/2$.

2.3. The surface free energies of the crystals

The (1×1) surface free energy, γ_{hkl}, is defined as being half the energy per unit area required to separate the crystal along a plane $\boldsymbol{h}(hkl)$ [2,9,13]. For simplicity, as mentioned above, a restriction is imposed in which the pair-wise interatomic interaction is represented as the energy of a bond connecting the pair-wise atoms. This energy is obviously a bond energy. Only half the bond energy, E, is therefore considered to contribute the broken **u**-bond to the specific surface free energy

$$\gamma_{hkl} = n(\boldsymbol{u})(E/2) = \frac{1}{\Omega|\boldsymbol{h}|}\sum_i \boldsymbol{h}\cdot\boldsymbol{u}_j(E/2) \tag{9}$$

since both the crystal surfaces, (*hkl*) and $(-h-k-l)$, created during the dividing process are identical.

In real crystals, any atom is considered to be connected to other atoms by various **u**-bonds. For example, the first, second and third neighboring **u**-bonds of an sc crystal are six ⟨100⟩, twelve ⟨110⟩ and eight ⟨111⟩ bonds. In other cubic crystals, such as fcc, bcc and cth, the first three neighboring bonds are shown in Table 2. If the $\boldsymbol{u}$-bond connecting with the rth neighboring atom has an energy E_r, the specific surface free energy of a crystal, when an atomically flat surface $\boldsymbol{h}$ is created, is equal to

$$\gamma_{hkl} = \frac{1}{\Omega|\boldsymbol{h}|} \sum_r \sum_j \boldsymbol{h} \cdot \boldsymbol{u}_{rj} (E_r/2). \tag{10}$$

It is evident that the term $\boldsymbol{h} \cdot \sum \boldsymbol{u}_{rj}/|\boldsymbol{h}|$ in Eq. (10) is a function of orientation, while the term E_r/Ω depends on the nature of the material. A physical interpretation of Eq. (10) is therefore that the surface free energy is dependent on both the orientation of the cutting plane $\boldsymbol{h}(hkl)$ which defines the surface and the nature of the bond in the crystal, i.e. the bond energy and its geometry.

3. Method of calculation

In general, Eq. (10) can be used to compute the specific surface free energy of any crystal whose structure can be described as a cubic lattice. The procedure for calculating the surface free energy is the following:

(1) Determine the number of $\boldsymbol{u}_i$-bonds broken per atom using Eq. (8).
(2) Determine the contribution of the broken $\boldsymbol{u}_i$-bonds to the surface free energy using Eq. (9).
(3) Find the $\boldsymbol{u}$-bond sets in the crystal and then determine the surface free energy for the crystal using Eq. (10) in combination with Eq. (5).

3.1. *The number of* $\boldsymbol{u}$*-bonds broken per atom*

The creation of a surface $\boldsymbol{h}(hkl)$ is equivalent to a process in which the crystal is cut by the $\boldsymbol{h}(hkl)$ plane. It is evident from Eq. (8) that the number of $\boldsymbol{u}$-bonds broken depends on both the cut plane and the $\boldsymbol{u}$-bonds. In present paper three different possibilities are considered.

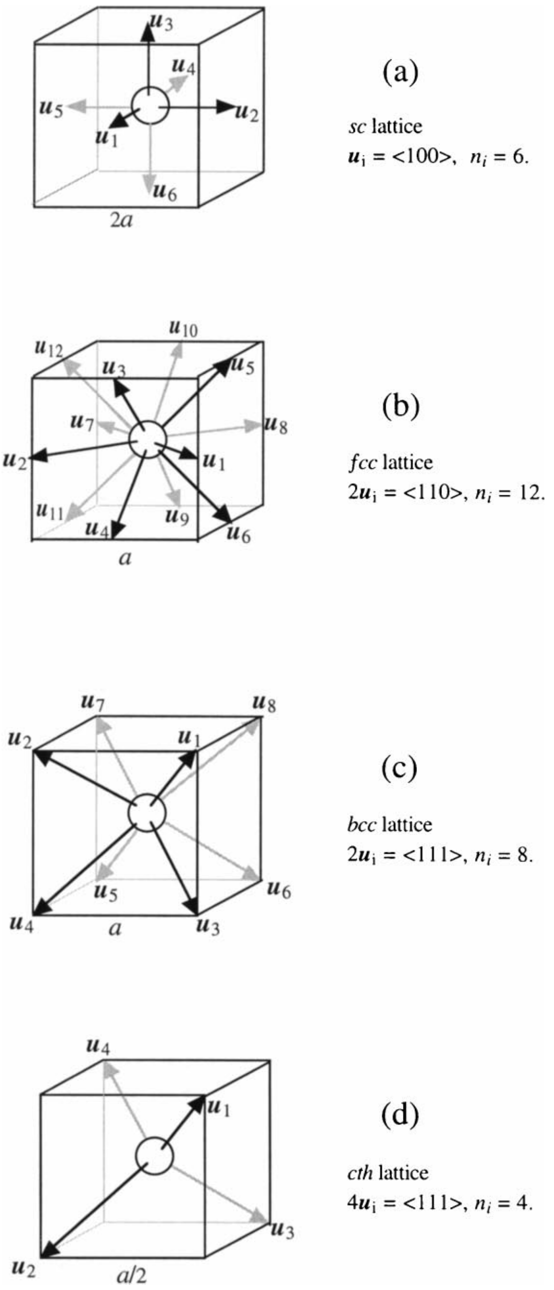

Fig. 3. The regions in which the planes ($h \geq k \geq l \geq 0$) are divided into part I and part II when $\langle 111 \rangle$ bond set is considered.

3.1.1. *Case I:* $\boldsymbol{h}$ *cuts the* $\langle 100 \rangle$*-bonds*

It is evident that $\boldsymbol{u} = \langle 100 \rangle$ represents the first neighbor bonds of the sc lattice with respect to the nearest neighboring bonds as shown in Fig. 3a.

For this kind of bond, the coordination is six,

$$\begin{aligned} &\boldsymbol{u}_1=[100], \quad \boldsymbol{u}_4=[-100],\\ &\boldsymbol{u}_2=[010], \quad \boldsymbol{u}_5=[0-10],\\ &\boldsymbol{u}_3=[001], \quad \boldsymbol{u}_6=[00-1]. \end{aligned} \tag{11}$$

Any plane in the first quadrant separates this $\boldsymbol{u}$-bond set into two halves, $\boldsymbol{u}_j(\boldsymbol{u}_1, \boldsymbol{u}_2, \boldsymbol{u}_3)$ and $\boldsymbol{u}_k(\boldsymbol{u}_4, \boldsymbol{u}_5, \boldsymbol{u}_6)$, giving $\sum \boldsymbol{h}\cdot\boldsymbol{u}_j>0$. Therefore, $\sum \boldsymbol{u}_j=\boldsymbol{u}_1+\boldsymbol{u}_2+\boldsymbol{u}_3=[111]$. The number of the $\boldsymbol{u}$-bonds broken per atom according to Eq. (8) is thus given by

$$N(\boldsymbol{u})=\boldsymbol{h}\cdot\sum \boldsymbol{u}_j=h+k+l. \tag{12}$$

In the case of the planes in other quadrants, considerations of cubic symmetry show that the number of the $\boldsymbol{u}$-bonds broken per atom is given by $N(\boldsymbol{u})=|h|+|k|+|l|$.

3.1.2. Case II: h cuts the ⟨110⟩-bonds

In this case, the $\boldsymbol{u}$-bond set ⟨110⟩ corresponds to fcc lattice with respect to nearest neighbor bonds as shown in Fig. 3b. Its coordination is twelve:

$$\begin{aligned} &\boldsymbol{u}_1=[110]/2, && \boldsymbol{u}_7=[-1-10]/2,\\ &\boldsymbol{u}_2=[1-10]/2, && \boldsymbol{u}_8=[-110]/2,\\ &\boldsymbol{u}_3=[101]/2, && \boldsymbol{u}_9=[-10-1]/2,\\ &\boldsymbol{u}_4=[10-1]/2, && \boldsymbol{u}_{10}=[-101]/2,\\ &\boldsymbol{u}_5=[011]/2, && \boldsymbol{u}_{11}=[0-1-1]/2,\\ &\boldsymbol{u}_6=[01-1]/2, && \boldsymbol{u}_{12}=[0-11]/2. \end{aligned} \tag{13}$$

Any plane $\boldsymbol{h}(h\geq k\geq l\geq 0)$ can separate this set of $\boldsymbol{u}_i$-bonds into two halves, $\boldsymbol{u}_j(\boldsymbol{u}_1, \boldsymbol{u}_2, \boldsymbol{u}_3, \boldsymbol{u}_4, \boldsymbol{u}_5, \boldsymbol{u}_6)$ and $\boldsymbol{u}_k=-\boldsymbol{u}_j$, where $\sum \boldsymbol{h}\cdot\boldsymbol{u}_j>0$. It can then easily be shown hat $\sum \boldsymbol{u}_j=[210]$. Using Eq. (8), the number of $\boldsymbol{u}$-bonds broken per atom in this case is given by

$$N(\boldsymbol{u})=2h+k. \tag{14}$$

It is evident that Eq. (14) is valid only when $h\geq k\geq l\geq 0$. It can be shown that $\sum \boldsymbol{u}_j=[120]$ when $k\geq h\geq l\geq 0$, while $\sum \boldsymbol{u}_j=[021]$ when $k\geq l\geq h\geq 0$ and $\sum \boldsymbol{u}_j=[012]$ when $l\geq k\geq h\geq 0$, etc. Thus, considering the planes in the first quadrant, the number is in general given by the expression

$$N(\boldsymbol{u})=2\lambda+\eta \tag{15}$$

in which λ and η are, respectively, the largest and middle Miller indices (hkl). By symmetry, it is easy to show that, in general, $N(\boldsymbol{u})=2|\lambda|+|\eta|$.

3.1.3. Case III: h cuts the ⟨111⟩-bonds

This kind of $\boldsymbol{u}_i$-bond corresponds to two crystal lattices, bcc and cth, with respect to different coordinations. When the coordination is eight as in the following:

$$\begin{aligned} &\boldsymbol{u}_1=[111]/2, && \boldsymbol{u}_5=[-1-1-1]/2,\\ &\boldsymbol{u}_2=[1-11]/2, && \boldsymbol{u}_6=[-11-1]/2,\\ &\boldsymbol{u}_3=[11-1]/2, && \boldsymbol{u}_7=[-1-11]/2,\\ &\boldsymbol{u}_4=[1-1-1]/2, && \boldsymbol{u}_8=[-111]/2. \end{aligned} \tag{16}$$

The $\boldsymbol{u}_i$-bonds are evidently the nearest neighbor bonds of the bcc crystal as shown is Fig. 3c. In this case, the $\boldsymbol{h}(hkl)$ plane in region I in Fig. 4 separates the $\boldsymbol{u}_i$-bonds into two halves, $\boldsymbol{u}_j(\boldsymbol{u}_1, \boldsymbol{u}_2, \boldsymbol{u}_3, \boldsymbol{u}_4)$ and $\boldsymbol{u}_k=-\boldsymbol{u}_j$, giving $\sum \boldsymbol{h}\cdot\boldsymbol{u}_j>0$ and $\sum \boldsymbol{u}_j=[200]$. The planes in region II, however, separate the $\boldsymbol{u}_i$-bonds into two different halves as $\boldsymbol{u}_j(\boldsymbol{u}_1, \boldsymbol{u}_2, \boldsymbol{u}_3, \boldsymbol{u}_8)$ and $\boldsymbol{u}_k=-\boldsymbol{u}_j$, so that $\sum \boldsymbol{u}_j=[111]$. Thus, the numbers of these $\boldsymbol{u}_i$-bonds broken per atom are determined by

$$N(\boldsymbol{u})=2h \quad \text{(in region I)}, \tag{17a}$$

$$N(\boldsymbol{u})=h+k+l \quad \text{(in region II)}, \tag{17b}$$

where $h\geq k\geq l\geq 0$. Similarly, taking symmetry into account, Eqs. (17a) and (17b) can be rewritten so

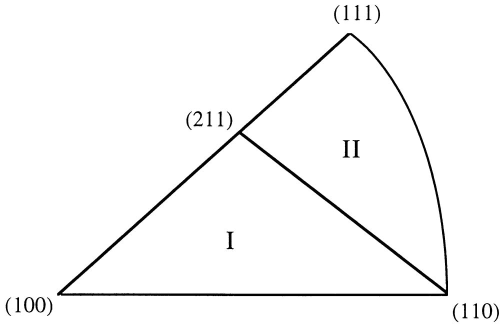

Fig. 4. Nearest neighbor bond sets in various lattices.

that $N(\boldsymbol{u})=2|\lambda|$ and $(|h|+|k|+|l|)$, in regions I and II, respectively.

On other hand, the coordination of this $\boldsymbol{u}_i$-bond set can be four as in the following:

$$\boldsymbol{u}_1=[111]/4, \qquad \boldsymbol{u}_3=[-11-1]/4, \qquad (18)$$

$$\boldsymbol{u}_2=[1-1-1]/4, \quad \boldsymbol{u}_4=[-1-11]/4.$$

which corresponds to the cth lattice with respect to nearest neighboring bonds. Fig. 3d depicts the four-bond set schematically. This bond set can be divided into two parts as $\boldsymbol{u}_j(\boldsymbol{u}_1, \boldsymbol{u}_2)$ and $\boldsymbol{u}_k(\boldsymbol{u}_3, \boldsymbol{u}_4)$ by any plane $\boldsymbol{h}(h \geq k \geq l)$ in region I as shown in Fig. 4. Other planes, as in region II, however, separate these four bonds into two parts which contain respectively one bond and three bonds, i.e. $\boldsymbol{u}_j=\boldsymbol{u}_1$ and $\boldsymbol{u}_k(\boldsymbol{u}_2, \boldsymbol{u}_3, \boldsymbol{u}_4)$, in which $\boldsymbol{u}_j$ and $\boldsymbol{u}_k$ make equivalent contribution to the number of broken bonds. Only planes in region I are therefore considered to calculate the number of the broken bonds using Eq. (8). Thus, $\sum \boldsymbol{u}_j=[1/2\ 0\ 0]$, and the number of this kind of $\boldsymbol{u}$-bond broken by a plane $\boldsymbol{h}$ is then

$$N(\boldsymbol{u})=|\lambda|/2 \qquad (19)$$

in which the symmetry is taken into account.

3.2. Contribution of the broken $\boldsymbol{u}_i$-bonds to the surface free energies.

Eq. (9), which is a general expression representing the surface free energy due to the $\boldsymbol{u}_i$-bonds broken, enables the contribution of the broken $\boldsymbol{u}_i$-bonds to the surface free energy to be calculated. Table 3 shows the results of the contributions when the ⟨100⟩-, ⟨110⟩- and ⟨111⟩-bonds are broken. For the sake of simplicity, the calculation is taken for the surfaces (hkl) in the first quadrant i.e. h, k and l are substituted for their absolute values respectively and so on.

4. Results for some crystals

In the present calculation of surface free energies for real crystals, only the first, second and third neighboring atoms are in general considered and more distant neighbors are neglected. For instance, for the sc crystal the first, second and third neighboring $\boldsymbol{u}$-bonds are six ⟨100⟩-bonds, twelve ⟨110⟩- and eight ⟨111⟩-bonds, respectively, as shown in Table 2. According to Eq. (5) the area of the surface (hkl) per atom, $\Omega|\boldsymbol{h}|$, is $a^2(h^2+k^2+l^2)^{1/2}$. The surface free energy of the sc crystal is therefore given by Eq. (10):

$$\gamma_{hkl}=\frac{(h+k+l)E_1/2+(2\lambda+\eta)E_2+2\lambda E_3}{a^2(h^2+k^2+l^2)^{1/2}} \qquad (20a)$$

(in region I),

$$\gamma_{hkl}=\frac{(h+k+l)(E_1/2+E_3)+(2\lambda+\eta)E_2}{a^2(h^2+k^2+l^2)^{1/2}} \qquad (20b)$$

(in region II).

Table 4 presents the calculated surface free energies of sc, fcc, bcc and cth crystals with respect to first three order of neighboring $\boldsymbol{u}$-bonds.

5. Discussion

In the theory here presented, an important assumption is that the potential energy of the

Table 3
The surface free energy due to the $\boldsymbol{u}_i$-bonds broken by plane $\boldsymbol{h}(hkl)$[a]

$\boldsymbol{u}_i$-bonds	⟨100⟩	⟨110⟩	⟨111⟩		
			Coordination is eight		Coordination is four
			In region I	In region II	
Surface free energy (γ_{hkl})	$\frac{h+k+l}{2\Omega\lvert\boldsymbol{h}\rvert}E_{\langle 100\rangle}$	$\frac{2\lambda+\eta}{2\Omega\lvert\boldsymbol{h}\rvert}E_{\langle 110\rangle}$	$\frac{\lambda}{2\Omega\lvert\boldsymbol{h}\rvert}E_{\langle 111\rangle}$	$\frac{h+k+l}{2\Omega\lvert\boldsymbol{h}\rvert}E_{\langle 111\rangle}$	$\frac{\lambda}{4\Omega\lvert\boldsymbol{h}\rvert}E_{\langle 111\rangle}$

[a] $E_{\langle uvw\rangle}$ denotes the bond energy for $\boldsymbol{u}\langle uvw\rangle$-bonds; λ and η denote the first and second largest Miller indices h, k and l.

Table 4
The surface free energies of various crystals with respect to the first three neighboring **u**-bonds

Crystals	$\Omega\lvert\boldsymbol{h}\rvert$	Surface free energies $\left(\frac{1}{\Omega\lvert\boldsymbol{h}\rvert}\sum_r\sum_j \boldsymbol{h}\cdot\boldsymbol{u}_{rj}(E_r/2)\right)$	
		In region I	In region II
sc	$a^2(h^2+k^2+l^2)^{1/2}$	$\frac{(h+k+l)E_1/2+(2\lambda+\eta)E_2+2\lambda E_3}{a^2(h^2+k^2+l^2)^{1/2}}$	$\frac{(h+k+l)(E_1/2+E_3)+(2\lambda+\eta)E_2}{a^2(h^2+k^2+l^2)^{1/2}}$
fcc [a]	$\frac{a^2(h^2+k^2+l^2)^{1/2}}{4}$	$\frac{2[(2\lambda+\eta)E_1+(h+k+l)E_2+4\lambda E_5]}{a^2(h^2+k^2+l^2)^{1/2}}$	$\frac{2[(2\lambda+\eta)E_1+(h+k+l)(E_2+2E_5)]}{a^2(h^2+k^2+l^2)^{1/2}}$
bcc	$\frac{a^2(h^2+k^2+l^2)^{1/2}}{2}$	$\frac{2\lambda E_1+(h+k+l)E_2+2(2\lambda+\eta)E_3}{a^2(h^2+k^2+l^2)^{1/2}}$	$\frac{(h+k+l)(E_1+E_2)+2(2\lambda+\eta)E_3}{a^2(h^2+k^2+l^2)^{1/2}}$
cth	$\frac{a^2(h^2+k^2+l^2)^{1/2}}{8}$	$\frac{4[(\lambda/2)E_1+(2\lambda+\eta)E_2+2(h+k+l)E_3]}{a^2(h^2+k^2+l^2)^{1/2}}$	

[a] For fcc, the first, second and fifth neighboring **u**-bonds are considered.

crystal can be represented as a sum of pair-wise interatomic interactions, i.e. bond energies. With this restriction, the surface free energy given by Eq. (10) is justifiable for covalently bonded and simple ionic materials since the bond in these materials are strongly oriented. Owing to delocalization of the valence electrons in metals, however, the representation of the binding in terms of a pair-wise interaction is somewhat artificial [12].

It is evident that the cth lattice corresponds to sp^3 bonded materials such as Si and diamond. For these highly covalent bonded materials, it is reasonable to suppose that $E_1 \gg E_2$ and $E_1 \gg E_3$ and therefore to neglect E_2 and E_3. This neglect implies

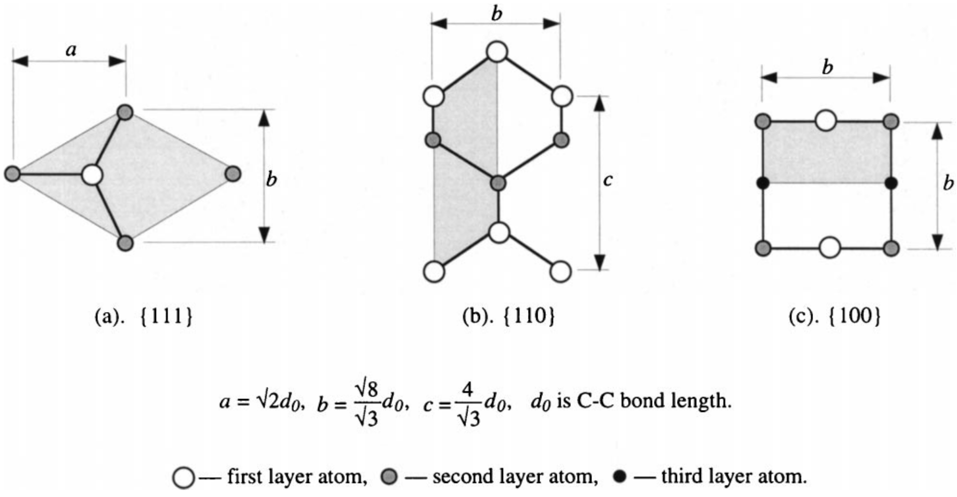

Fig. 5. A schematic drawing of the unit areas containing one bond, A_{hkl} (shaded), in a cubic tetrahedral crystal. (a) $A_{111}=ab=\sqrt{3}[(4/3)d_0^2]$, (b) $A_{110}=bc/2=\sqrt{2}[(4/3)d_0^2]$ and (c) $A_{100}=b^2/2=(4/3)d_0^2$, where d_0 denotes the bond length. The large open, middle shaded and small filled circules denote atoms on the first, second and third layers, respectively.

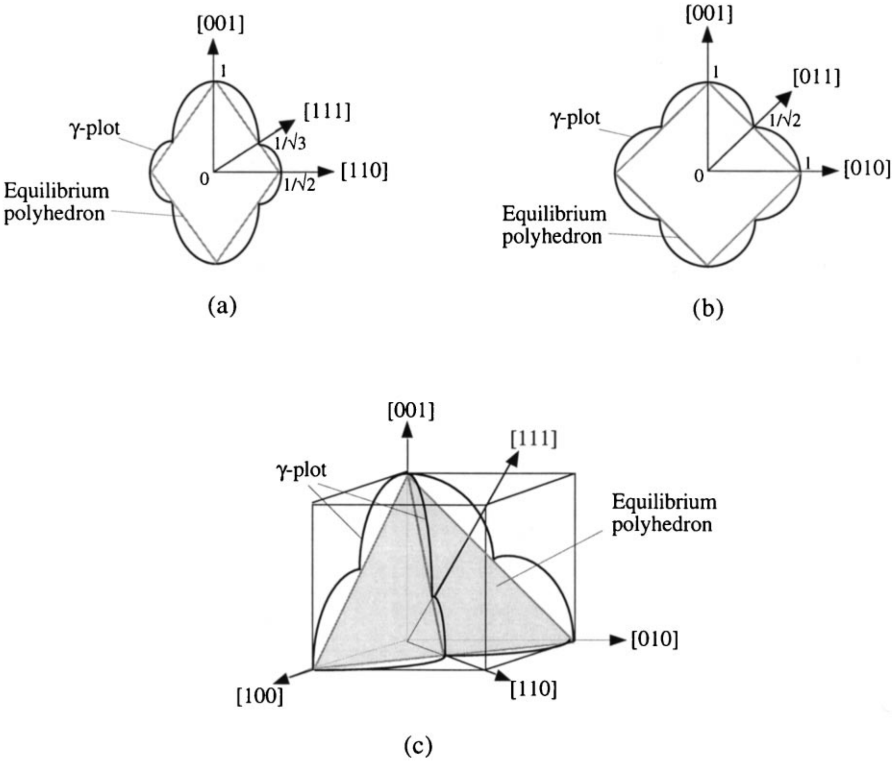

Fig. 6. Wulff plots and equilibrium form of a diamond crystal based on Eq. (22) or Eq. (23). (a) a two-dimensional Wulff plot for a family of planes parallel to [1 − 10]; (b) a two-dimensional Wulff plot for a family of planes parallel to [100]; (c) a three-dimensional Wulff plot in the first quadrant.

that the effect of sub-nearest neighbor atoms on mechanical stability of lattice is consequently ignored. The surface free energy of the cth crystals, shown in Table 4, is therefore simply given by

$$\gamma_{hkl} = \frac{\lambda}{(h^2+k^2+l^2)^{1/2}} \frac{2E}{a^2} \tag{21}$$

where $E = E_1$ is the bond energy.

The validity of Eq. (21) can be shown simply as follows. If a unit area, A_{hkl}, is defined as an area containing only one dangling bond, it can be shown that for the cth crystal $A_{111} = [(4/3)d_0^2]\sqrt{3}$, $A_{110} = [(4/3)d_0^2]\sqrt{2}$ and $A_{100} = (4/3)d_0^2$ (where d_0 denotes the bond length) as shown in Fig. 5. In general, it can be shown that $A_{hkl} = 4(h^2+k^2+l^2)^{1/2}d_0/3\lambda$, where λ is the largest of the Miller indices h, k and l, by derivation using a simple inductive method. Consideration of the fact that $\gamma_{hkl} = (E/2)/A_{hkl}$ then gives immediately that

$$\gamma_{hkl} = \frac{\lambda}{(h^2+k^2+l^2)^{1/2}} \frac{3E}{8d_0^2}. \tag{22}$$

This equation is exactly the same as Eq. (21) since $d_0 = (\sqrt{3}/4)a$ in a cth cell.

To illustrate Eq. (22), typical cth crystals Si and diamond are chosen. For silicon, the bond energy $E = 42.2$ kcal mol^{-1} and the bond length $d_0 = 2.34$ Å [15,16] and Eq. (22) yields $\gamma_{111} = 1160$ erg cm^{-2}, which is almost the same as the value of 1240 erg cm^{-2} measured by Gilman using a cleavage method [7]. For diamond, $E = 83.1$ kcal mol^{-1} and $d_0 = 1.54$ Å [15,16], and the surface free energy calculated according to Eq. (22) is $\gamma_{111} = 5277$ erg cm^{-2}, which is almost exactly the same as the value calculated by Harkins [6] and Ramaseshan [8]. Furthermore Eq. (22)

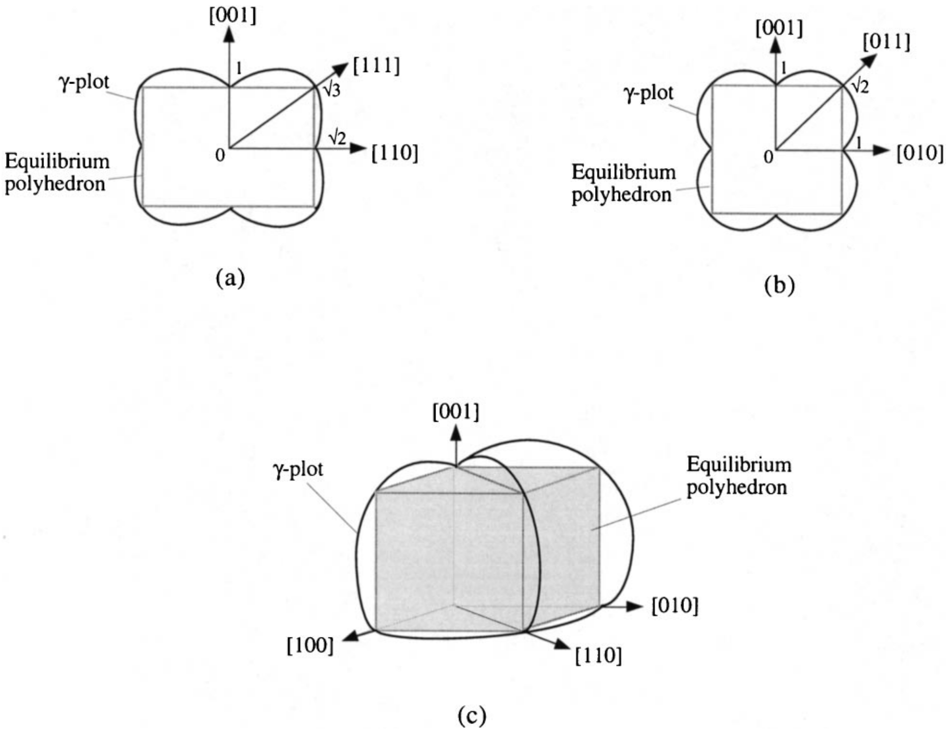

Fig. 7. Wulff plots and equilibrium form of the sc crystal based on Eqs. (24a) and (24b). (a) a two-dimensional Wulff plot for a family of planes parallel to [1 − 10]; (b) a two-dimensional Wulff plot for a family of planes parallel to [100]; (c) a three-dimensional Wulff plot in the first quadrant.

shows that $\gamma_{100}:\gamma_{110}:\gamma_{111} = 1:1/\sqrt{2}:1/\sqrt{3}$. The Wulff plots of the cth crystal from Eq. (22), shown schematically in Fig. 6, imply that the equilibrium form of diamond is an octahedron [9].

On other hand, ionic materials such as the alkali halides with NaCl structure may be constructed by arranging Na^+ and Cl^- ions alternatively at the points of a simple cubic lattice. It is therefore reasonable that only the energy of the first neighboring ***u***-bonds, E, is considered in the calculation [13]. The surface free energy of the simple cubic crystals represented in Eqs. (20a) and (20b) can therefore be simplified to

$$\gamma_{hkl} = \frac{h+k+l}{(h^2+k^2+l^2)^{1/2}} \frac{E}{2a^2}. \tag{23}$$

The Wulff plots for this type of crystal obtained from Eq. (23), as shown in Fig. 7, imply that the cube is the equilibrium form of the such crystals as NaCl and PbS etc. This kind of equilibrium form is proved by Wells [17].

To calculate the surface free energy for metals using this mode, more sub-bond energies (2nd-nearest bond energy E_2, 3rd-nearest bond energy E_3, etc.) should be considered. For example, the anisotropy of the surface free energy of fcc metal is given from Eq. (10):

$$\frac{\gamma_{hkl}}{\gamma_{111}} = \frac{\sqrt{3}[2h+k+(h+k+l)\beta_1+4h\beta_2]}{3(1+\beta_1+2\beta_2)(h^2+k^2+l^2)^{1/2}} \tag{24a}$$

(in region I),

$$\frac{\gamma_{hkl}}{\gamma_{111}} = \frac{\sqrt{3}[2h+k+(h+k+l)(\beta_1+2\beta_2)]}{3(1+\beta_1+2\beta_2)(h^2+k^2+l^2)^{1/2}} \tag{24b}$$

(in region II),

where $\beta_1 = E_2/E_1$ and $\beta_2 = E_5/E_1$. It is reasonable to assure that $1 > \beta_1 > \beta_2$. Fig. 8 gives a comparison

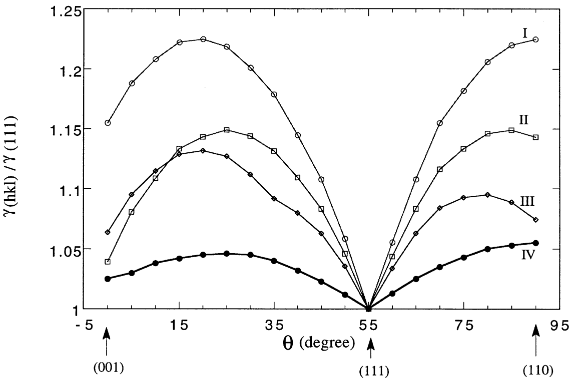

Fig. 8. Comparison of measured anisotropy of the surface free energy with predicted one for fcc metals. The interaction between two atoms is assured to be proportional to r^2, where r is distance between the atoms. When $\beta_1 = \beta_2 = 0$, i.e. only the nearest neighbor atoms are considered, the anisotropy of the surface free energy is shown in curve I. When the first and second neighbor atoms are taken into account, i.e. $\beta_1 = 1/4$, $\beta_2 = 0$, the calculated anisotropy is shown as curve II. When the first, second and fifth neighbor atoms are taken into account, i.e. $\beta_1 = 1/4$, $\beta_2 = 1/6$, the calculated anisotropy is shown as curve III. Curve IV shows measured data given by Heyraud and Metois in Ref. [18] (the data are read from their Fig. 4-b).

of the measured anisotropy of the surface free energy of fcc metals [18] with the predicted anisotropies in various values of β_1 and β_2. It is evident that the latter are closer and closer to the former (curve IV) when the second and further neighbour atoms are considered, as shown in curves II and III, respectively. It indicates that sub-bonds become more important to determine the surface free energy due to the non-directional bonding in a metal. Furthermore, the fcc metal equilibrium form predicted by the mode is the truncated octahedron consisted of {100} and {111} facets. The experimental investigation of the equilibrium form for such fcc metals as Pb, Cu, Ni, Ag and Au [18–20] shows the {100} and {111} facets too.

6. Summary

Based on a bond-breaking mode, a general representation of the anisotropy of the (1×1)-surface free energy is obtained for various materials, particularly oriented bond materials such as cth and sc crystals. The anisotropy of the surface free energies is exactly described in terms of the Miller indices *hkl*. Eqs. (21) and (23) give, respectively, the specific surface free energies of the cth and sc crystals, which have strongly oriented bonds. The ideal surface free energy, with no relaxation and no adsorption, can be calculated from the bond energy and bond lengths using these equations. The Wulff plots obtained from the general representation indicate that the equilibrium forms of the diamond and sc crystals are the octahedron and the cube, respectively. Furthermore, the predicted anisotropy of fcc metals is in agreement with experiment [18].

Acknowledgements

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