

ANISOTROPY OF (1×1)-SURFACE FREE ENERGIES OF CRYSTALS

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The surface free energy (SFE) of (1×1)-surfaces of crystals, without reconstruction and adsorption, is calculated using a bond-broken mode. In the mode, the potential energy of the crystals is treated as a sum of the energies of the bonds connecting pair-wise atoms (\vec{u} -bonds). The SFE is calculated based on the bond energy and the area density of dangling bonds which depends on the structure of the surface. The results provide a general expression for the SFE in terms of the bond energy (E) and the bond length (d_0) of the crystal and Miller indices hkl . The anisotropy of the SFE is therefore completely determined with the expression. As the examples, considering the nearest-neighboring bonding, the SFEs of sc, fcc, bcc and cth (cubic tetrahedral) crystals are discussed, respectively. Wulff plots of bcc and fcc crystals are then obtained. The equilibrium forms (EFs) of these crystals are consequently got from their Wulff plots, respectively. It is found that the EFs of bcc and fcc are respectively the rhombic dodecahedron and the truncated-octahedron that are their first Brillouin zones, respectively.

KEY WORDS surface free energy, crystal, geometrical thermodynamics

1. Introduction

Interest in the surface free energy (SFE) of crystals is increasing as a consequence of modern experiments in the fields such as crystal growth, crystalline morphology, equilibration of grain boundaries, sintering, adsorption and surface catalysis and etc^[1-2].

It is well known that the SFE of a crystal is generally dependent on the orientation of the surface^[3]. Some previous works have been done to calculate and measure the SFE^[4-8]. But, a generally theoretical method is still needed to describe and compute the SFE. The starting point in present work is the definition of the SFE of a crystal face. By dividing in vacuum a crystal along a plane (hkl), there is to spend the work $W_{hkl}(rev.)$ in order to separate to infinity both parts of the crystal during an isothermal ($\Delta T=0$) and reversible process, creating a surface area $2A_{hkl}$. The per unit area SFE, γ_{hkl} , is that

$$\gamma_{hkl} = W_{hkl}(rev.) / 2A_{hkl}. \quad (1)$$

It is obvious that the work done for dividing crystal is that needed for breaking the bonds of the crystal. In the present paper, it is neglected that surface reconstruction, thermal vibration of atoms, any foreign atoms at surface. The SFE is then simply equal to that

$$\gamma_{hkl} = \sum n(\vec{u})E(\vec{u})/2, \quad (2)$$

where $E(\vec{u})$ is the potential energy of interaction of a pair of atoms separated by a vector \vec{u} , *i.e.* bond energy, and $n(\vec{u})$ is the number per unit area of such bonds broken when the crystal is separated, *i.e.* the area density of dangling bonds.

2. Theoretical Aspects

When an infinite crystal is divided into two parts by a plane $\vec{h}(hkl)$, the two new surfaces is described as atomically flat surfaces indicated as (hkl) and $(\bar{h}\bar{k}\bar{l})$. 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 is occupied on the other side. If a bond is represented by a line with atoms at each end, it must be broken when the surface is formed.

2.1 Interaction between \vec{u} -bonds and dividing plan $\vec{h}(hkl)$

Any bond associated with a given atom is defined as a vector \vec{u} , which contains the components u , v and w in the primitive space, going from this atom to neighboring atoms. Such a bond is called \vec{u} -bond in this paper. Any \vec{u} -bond corresponds to its own coordination, n_i . For instance, when $u \neq v = w = 0$, $n_i=6$; while when $u = v \neq w = 0$, $n_i = 12$, and so on. The \vec{u} -bonds with same components (uvw) are called \vec{u}_i -bond set or \vec{u}_i -bonds ($i = 1, 2, \dots, n_i$). Table 1 lists six possible components of the \vec{u} -bonds and their coordinations. It is evident that the crystalline structure of crystal can be described by the \vec{u}_i -bonds. For example, the first three \vec{u}_i -bonds in the table 1 correspond to sc, fcc, bcc and cth (cubic tetrahedral or diamond) structures with respect to the first neighboring \vec{u}_i -bonds in crystal, respectively. It is obvious that the nearest \vec{u}_i -bond set is essentially a vectorial representation for Bravais lattices.

Table 1 The \vec{u}_i -bonds and their coordination

$\vec{u}(uvw)$ -bond	Coordination	Lattice with respect to the nearest neighboring bonds
1. $u \neq v = w = 0$	6	sc
2. $u = v = w \neq 0$	8 or 4	bcc or cth
3. $u = v \neq w = 0$	12	fcc
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	

On the other hand, an atomically flat surface is specified by a vector \vec{h} which contains the components of h , k and l in the reciprocal lattice. The components are defined as Miller indices of the surface. In the case of cubic symmetry, the \vec{h} is orthogonal to the surface. It is obvious that a process of creating a new surface $\vec{h}(hkl)$ is equivalent to that of cutting crystal by the plane \vec{h} . Fig.1 shows schematically the geometrical relation between \vec{h} and \vec{u} while surface \vec{h} is formed. If \vec{h} is assumed to have a direction towards the outside of the crystal, the \vec{u} -bonds is broken when $\vec{h} \cdot \vec{u}_i > 0$, the \vec{u}_i -bonds is unbroken when $\vec{h} \cdot \vec{u}_i < 0$. In the case when $\vec{h} \cdot \vec{u}_i = 0$, the \vec{u} -bonds lie in the surface and can be understood as being bonds unbroken or bonds broken with zero density.

2.2 The number of the \vec{u}_i -bonds broken while a surface $\vec{h}(hkl)$ is formed

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

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

where d_{hkl} denotes the spacing between adjacent planes of $\vec{h}(hkl)$. It is obvious that $|\vec{h}| d_{hkl} = 1$, and therefore Eq.(3) can be rewritten as

$$N(\vec{u}_i) = \vec{h} \cdot \sum \vec{u}_i \quad \text{when } \vec{h} \cdot \vec{u}_i > 0. \quad (4)$$

In a \vec{u}_i -bond set, one finds that $\sum \vec{u}_i = 0$ ($i = 1, 2, \dots, n_i$) by crystalline symmetry. In principle, the n_i \vec{u}_i -bonds can be divided into two parts as \vec{u}_j ($j = 1, 2, \dots, n_j$) and \vec{u}_k ($k = 1, 2, \dots, n_k$), resulting $\sum \vec{u}_j = -\sum \vec{u}_k$. Generally, the crystalline symmetry follows that $n_j = n_k = n_i/2$. The number of dangling bonds per surface atom is thus given by

$$N(\vec{u}_j) = \vec{h} \cdot \sum \vec{u}_j \quad (j = 1, 2, \dots, n_i/2). \quad (5)$$

Fig.2 gives two cases in which different \vec{u}_i -bonds are broken. When a \vec{u}_i -bond spans two planes, *i.e.* one spacing unit (Fig.2a), it is easy to show that Eq.(3) gives exactly the number of broken \vec{u}_i -bonds. In general, however, when the \vec{u}_i -bond spans more than two planes (Fig.2b) the number of the unit spacings of (hkl) through that the \vec{u}_i -bond passes is equal to the number of the \vec{u}_i -bonds which are cut by one of those planes. If Ω denotes the crystalline volume per atom, then Ω/d_{hkl} is an area of the surface \vec{h} per atom. An area density of the dangling bonds, $n(\vec{u}_i)$, is thus determined by $N(\vec{u}_i)/(\Omega/d_{hkl})$, *i.e.*

$$n(\vec{u}_j) = \vec{h} \cdot \sum \vec{u}_j / (\Omega |\vec{h}|) \quad (j = 1, 2, \dots, n_i/2), \quad (6)$$

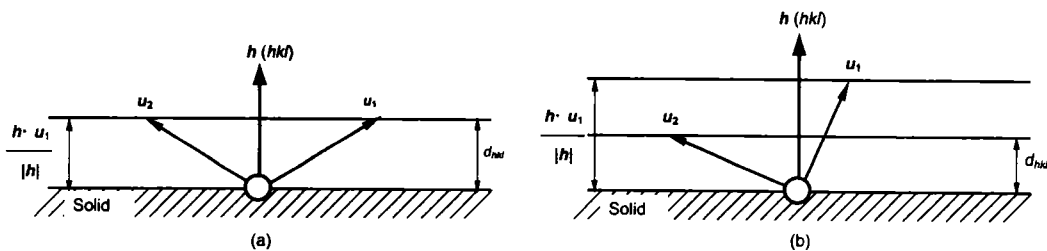


Fig.2 Different \vec{u} -bonds are broken when a surface \vec{h} is formed: (a) \vec{u}_1 and \vec{u}_2 span respectively one unit spacing of $\vec{h}(hkl)$; (b) \vec{u}_1 spans two unit spacings of $\vec{h}(hkl)$ and \vec{u}_2 spans one unit spacing of $\vec{h}(hkl)$.

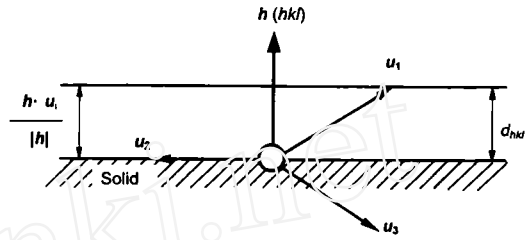


Fig.1 Interaction between $\vec{h}(hkl)$ and $\vec{u}_i(uvw)$ while the surface \vec{h} is formed. $\vec{h} \cdot \vec{u}_i > 0$ implies that the \vec{u}_i -bond is broken; $\vec{h} \cdot \vec{u}_i < 0$ implies that the \vec{u}_i -bond is unbroken and $\vec{h} \cdot \vec{u}_i = 0$ that the \vec{u}_i -bond is unbroken or broken with zero density.

In Eq.(5), it is easy to find that $\Omega|\vec{h}|$ represents a area of surface $\vec{h}(hkl)$ per atom and that $\Omega|\vec{h}|=a^2(h^2+k^2+l^2)^{1/2}/n$ in which n denotes a number of atoms per unit cell.

2.3 The SFE of the crystal

The SFE of (1×1) surface $\vec{h}(hkl)$, without reconstruction and relaxation, is as mentioned above half the energy per unit area required to separate the crystal along the plane $\vec{h}(hkl)$. The energy, $E(\vec{u})$, is bond energy indeed. It follows that

$$\gamma_{hkl} = \sum n(\vec{u})E(\vec{u})/2 = \sum [\vec{h} \cdot \sum \vec{u}_j / (\Omega|\vec{h}|)] E(\vec{u})/2. \quad (7)$$

The term $\vec{h} \cdot \sum \vec{u}_j / |\vec{h}|$ in Eq.(7) is a function of orientation only, while the term $E(\vec{u})/\Omega$ depends on the nature of the crystal. A physical interpretation for Eq.(7) is that the SFE of crystal is dependent on both the orientation of the surface $\vec{h}(hkl)$ and the nature of the crystal, the bond structure and the bond energy.

3. Procedure of Calculation for SFE

In general, the Eq.(7) can be used to compute the SFE of any crystal whose structure is known as a cubic lattice. The procedure for calculating the SFE is the following:

- (1) Calculate the number of dangling bonds per surface atom using Eq.(5),
- (2) Calculate area density of dangling bonds at the surface using Eq.(6),
- (3) Find the \vec{u}_i -bond sets in the crystal, and then calculate the SFE using Eq.(7).

The creation of a new surface, $\vec{h}(hkl)$, is equivalent to a process in which the crystal is cut by a plane $\vec{h}(hkl)$. The number of the \vec{u}_i -bonds broken depends on the cut plane and the \vec{u}_i -bonds. In present paper three different cases in which the plane \vec{h} cuts the crystal are taken in to account.

3.1 Case I: \vec{h} cuts the $\langle 100 \rangle$ -bonds

It is evident that the $\vec{u}_i=\langle 100 \rangle$ represents the sc crystal with respect to the nearest neighboring bonds. For this kind of bond, the coordination is six as shown in Fig.3a:

$$\vec{u}_1 = [100], \quad \vec{u}_4 = -\vec{u}_1, \quad \vec{u}_2 = [010], \quad \vec{u}_5 = -\vec{u}_2, \quad \vec{u}_3 = [001], \quad \vec{u}_6 = -\vec{u}_3$$

Any plane in the first quadrant separates the bond set onto two halves, $\vec{u}_j(\vec{u}_1, \vec{u}_2, \vec{u}_3)$ and $\vec{u}_k(\vec{u}_4, \vec{u}_5, \vec{u}_6)$, giving $\sum \vec{h} \cdot \vec{u}_j > 0$. One therefore finds that $\sum \vec{u}_j = \vec{u}_1 + \vec{u}_2 + \vec{u}_3 = [111]$. The number of the \vec{u}_i -bond broken per atom according to Eq.(6) is thus given by

$$N(\vec{u}_j) = \vec{h} \cdot \sum \vec{u}_j = (hkl) \cdot [111] = h + k + l. \quad (8)$$

3.2 Case II: \vec{h} cuts the $\langle 110 \rangle$ -bonds

The $\langle 110 \rangle$ bond set corresponds to the fcc crystal with respect to nearest neighboring bonds as shown in Fig.3b.

Its coordination is twelve:

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

Any plane $\vec{h}(h \geq k \geq l \geq 0)$ separates the bond set onto two halves, $\vec{u}_j(\vec{u}_1, \vec{u}_2, \vec{u}_3, \vec{u}_4, \vec{u}_5, \vec{u}_6)$ and $\vec{u}_k(\vec{u}_7, \vec{u}_8, \vec{u}_9, \vec{u}_{10}, \vec{u}_{11}, \vec{u}_{12})$, giving $\sum \vec{h} \cdot \vec{u}_j > 0$. It can easily be shown that $\sum \vec{u}_j = [210]$. The number of the \vec{u}_i -bonds broken per atom according to Eq.(6) is thus given by

$$N(\vec{u}_j) = \vec{h} \cdot \sum \vec{u}_j = (hkl) \cdot [210] = 2h + k. \quad (9)$$

It is obvious that Eq.(9) is valid only in the case of $h \geq k \geq l \geq 0$. Furthermore, it can be easily shown that $\sum \vec{u}_j = [120]$ when $k \geq h \geq l \geq 0$, while $\sum \vec{u}_j = [021]$ when $k \geq l \geq h \geq 0$ and $\sum \vec{u}_j = [012]$ when $l \geq k \geq h \geq 0$, etc. Thus, in general the number of \vec{u}_i -bonds broken is

$$N(\vec{u}_j) = 2\lambda + \eta, \quad (10)$$

where λ and η are, respectively, the largest and middle ones of Miller indices (hkl) .

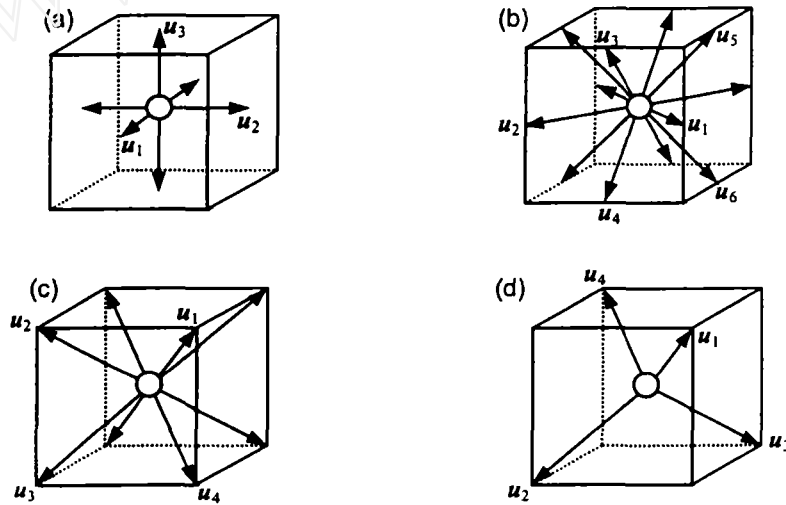


Fig.3 Nearest neighbor bond sets in various lattices: (a) sc lattice: $\vec{u}_i = \langle 100 \rangle$, $n_i = 6$, (b) fcc lattice: $\vec{u}_i = \langle 110 \rangle$, $n_i = 12$, (c) bcc lattice: $\vec{u}_i = \langle 111 \rangle$, $n_i = 8$, (d) cth lattice: $\vec{u}_i = \langle 111 \rangle$, $n_i = 4$.

3.3 Case III: \vec{h} cuts the $\langle 111 \rangle$ -bonds

The $\langle 111 \rangle$ -bonds correspond to two crystalline lattices, bcc and cth, with respect to different coordinations as shown in Fig.3c and 3d. When its coordination is eight:

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

it represents the bcc lattice. Any plane $\vec{h}(h \geq k \geq l \geq 0)$ in region I as shown in Fig.4 separates the bond set onto two halves, $\vec{u}_j(\vec{u}_1, \vec{u}_2, \vec{u}_3, \vec{u}_4)$ and $\vec{u}_k(\vec{u}_5, \vec{u}_6, \vec{u}_7, \vec{u}_8)$, giving $\sum \vec{h} \cdot \vec{u}_j > 0$ and $\sum \vec{u}_j = [200]$. The planes in region II, however, separate the bonds other two halves as $\vec{u}_j(\vec{u}_1, \vec{u}_2, \vec{u}_3, \vec{u}_8)$ and $\vec{u}_k(\vec{u}_5, \vec{u}_6, \vec{u}_7, \vec{u}_4)$, giving $\sum \vec{h} \cdot \vec{u}_j > 0$ and $\sum \vec{u}_j = [211]$. Thus the number of the \vec{u}_i -bonds broken per atom is

$$N(\vec{u}_j) = 2h \quad (\text{in region I}), \quad (11-1)$$

$$N(\vec{u}_j) = h + k + l \quad (\text{in region II}). \quad (11 - 2)$$

On the other hand, the coordination of the \vec{u}_i -bond set can be four:

$$\vec{u}_1 = [111]/4, \quad \vec{u}_2 = [\bar{1}\bar{1}\bar{1}]/4,$$

$$\vec{u}_3 = [\bar{1}1\bar{1}]/4, \quad \vec{u}_4 = [\bar{1}\bar{1}1]/4.$$

which corresponds to the cth lattice with respect to the nearest neighboring bonds. It can be easily found that

$$N(\vec{u}_j) = \lambda/2. \quad (12)$$

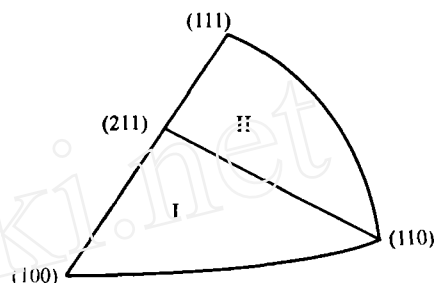


Fig.1 The regions in which the surfaces $h \geq k \geq l$ are divided into part I and park II when $\langle 111 \rangle$ -bond set is considered.

Table 2 lists the summary of the numbers of the \vec{u}_i -bonds per surface atom broken when the plane \vec{h} cut the bonds.

Table 2 The numbers of the \vec{u}_i -bonds broken per surface atom when the plane \vec{h} cut the bonds

\vec{u}_i -bond	$\langle 100 \rangle$	$\langle 110 \rangle$	$\langle 111 \rangle$		
			Coordination is eight		Coordination is four
			Region I	Region II	
$N(\vec{u}_i)$	$h + k + l$	$2\lambda + \eta$	$2h$	$h + k + l$	$\lambda/2$

4. Results and Discussion

In the present calculation for the SFE of crystal, only the first neighboring bonds are taken into account. For instance, for the sc crystal the first and second neighboring bonds are six $\langle 100 \rangle$ -bonds. Its SFE is then determined by

$$\gamma_{hkl} = \frac{h + k + l}{(h^2 + k^2 + l^2)^{1/2}} \frac{E}{2d_0^2}, \quad (13)$$

where E and d_0 denote the bond energy and the bond length, respectively. In Eq.(13), $a=d_0$ in the sc lattice is taken into account. One special case of Eq.(13) is exactly the same as the formula given by Mullins^[4]. It is easy to see that the SFE consists of two parts, one of them determines the orientation of the SFE and other does the magnitude of the SFE. Similarly, one finds the SFEs for the fcc, bcc and cth crystals as shown in Table 3.

To illustrate the mode, typical cth crystals such as silicon and diamond are chosen. The SFE of the cth crystal is given by

$$\gamma_{hkl} = \frac{2\lambda + \eta}{(h^2 + k^2 + l^2)^{1/2}} \frac{3E}{8d_0^2}, \quad (14)$$

where λ is the largest one of Miller indices. For Si, the bond energy (E) is 42.2kcal/mol and the bond length is 0.234nm^[9,10]. Eq.(14) yields $\gamma_{111} = 1160\text{erg/cm}^2$, which is almost

the same as the value of $1240\text{erg}/\text{cm}^2$ measured by Gilman using a cleavage method^[7]. For diamond, the bond energy is $83.1\text{kcal}/\text{mol}$ and the bond length is 0.154nm ^[9,10]. Eq.(14) yields $\gamma_{111}=5277\text{erg}/\text{cm}^2$, which is almost exactly the same as the value calculated by Harkins^[5] and Ramasesham^[6]. Furthermore, Eq.(14) shows that $\gamma_{100} : \gamma_{110} : \gamma_{111} = 1 : 1/\sqrt{2} : 1/\sqrt{3}$.

Table 3 The values $\Omega|\vec{h}|$ and SFE of various crystals with respect to the 1st neighboring bonds

Crystal	$\Omega \vec{h} $	γ_{hkl}^*	
		Region I	Region II
sc	$a^2(h^2 + k^2 + l^2)^{1/2}$	$\frac{h+k+l}{(h^2+k^2+l^2)^{1/2}} \frac{E}{2d_0^2}$	
fcc	$\frac{a^2(h^2+k^2+l^2)^{1/2}}{4}$	$\frac{2\lambda+\eta}{(h^2+k^2+l^2)^{1/2}} \frac{3E}{2d_0^2}$	
bcc	$\frac{a^2(h^2+k^2+l^2)^{1/2}}{2}$	$\frac{h}{(h^2+k^2+l^2)^{1/2}} \frac{3E}{2d_0^2}$	$\frac{h+k+l}{(h^2+k^2+l^2)^{1/2}} \frac{3E}{4d_0^2}$
ctn	$\frac{a^2(h^2+k^2+l^2)^{1/2}}{8}$	$\frac{\lambda}{(h^2+k^2+l^2)^{1/2}} \frac{3E}{8d_0^2}$	

Note: In the expressions of the SFE (γ_{hkl}), $a = d_0$, $a = \sqrt{2}d_0$, $a = (2/\sqrt{3})d_0$ and $a = (4/\sqrt{3})d_0$ are taken into account for sc, fcc, bcc and ctn lattices, respectively.

For the fcc crystal, the SFE is given by

$$\gamma_{hkl} = \frac{2\lambda + \eta}{(h^2 + k^2 + l^2)^{1/2}} \frac{3E}{2d_0^2} \quad (15)$$

The directional factor of the SFE is $(2\lambda + \eta)/(h^2 + k^2 + l^2)^{1/2}$, implying that $\gamma_{100} : \gamma_{110} : \gamma_{111} = 2 : \sqrt{3} : 3/\sqrt{2}$. Based on the directional factor, the Wulff plots of the fcc crystal can be easily found. And the equilibrium form (EF) of this crystal is then constructed from the Wulff plots. Fig.5 shows the Wulff plots and the EF. It is found that the EF is a truncated octahedron which is the same shape as 3D Brillouin zone of the crystal^[11].

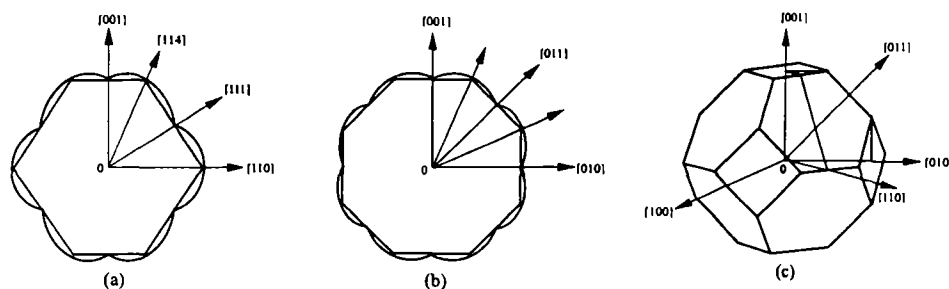


Fig.5 Calculated Wulff plots for fcc crystal: (a) for all planes parallel to the $[110]$ axes, (b) parallel to the $[100]$ axes, (c) the EF of fcc crystal, octahedron, is obtained from the Wulff plots.

For the bcc crystal, furthermore, the directional factors of the SFE are $h/(h^2 + k^2 + l^2)^{1/2}$ and $(h + k + l)/(h^2 + k^2 + l^2)^{1/2}$ in regions I and II respectively, implying that $\gamma_{100} : \gamma_{110} : \gamma_{111} = 2 : \sqrt{2} : \sqrt{3}$. Its EF is a rhombic dodecahedron as shown in Fig.6. It is evident that the EF and its 3D Brillouin zone^[11] are the same in shape.

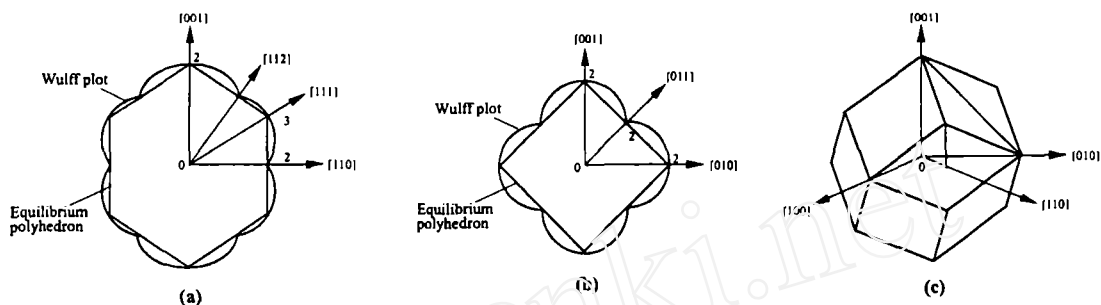


Fig.6 Calculated Wulff plots for bcc crystal: (a) for all planes parallel to the $[110]$ axes, (b) parallel to the $[100]$ axes, (c) the EF of fcc crystal, a rhombic dodecahedron, is obtained from the Wulff plots.

5. Conclusions

(1) The SFE of an ideal surface of crystal is determined by

$$\gamma_{hkl} = \sum [\vec{h} \cdot \sum \vec{u}_j / (\Omega |\vec{h}|)] E(\vec{u}) / 2,$$

which depends on the orientation of the surface, the crystalline structure and the bond energy of the crystal.

(2) The anisotropy of SFE of crystal is represented in terms of the Miller indexes. For fcc crystal, as example, the SFE is that

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

(3) The equilibrium forms of bcc and fcc crystals are rhombic dodecahedron and truncated octahedron, respectively. The shape of the equilibrium forms coincide that of their Brillouin zones, respectively.

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