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The concept of directional binding energy and analysis of the phenomena involving surface and grain boundary

Part I *Theory*

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The concept of directional binding energy (DBE) is proposed to describe the binding energy of the crystal and the ideal direction of the antiaction force against the surface tension, which derives the grain-boundary energy and also energy ratio (γ_{gb}/γ_s). It may provide a simple and lucid way to analyse the surface energy, grain-boundary energy and energy ratio from the correlative view point. It has been found that the grain-boundary energy can be derived only from the conceptual approach of DBE, irrespective of the dislocation model, which also makes it possible to determine the energy ratio with the misorientation angle. That is, the energy ratio (γ_{gb}/γ_s) is proportional to the misorientation angle, $2\sin(k'\theta/2)$ where k' is a constant and θ is the misorientation angle.

1. Introduction

It has been recognized that the surface and the grain boundary of crystalline ceramics affect many important properties, including shape, microstructure and sintering behaviour [1–3]. In sintering, especially it is reported that the dihedral angle concerned with the surface energy and the grain-boundary energy has influence on determining the minimum interfacial energy configuration [4] and the driving force [5]. For these reasons, the surface structure and the composition of the surface regions have been primarily studied using various techniques [6]. Handwerker *et al.* [7] calculated the dihedral angles from surface thermal grooves for MgO and Al_2O_3. They showed that under the force balance, the dihedral angles were usually nearly 105°–113°, indicating the energy ratio (γ_{gb}/γ_{sv}) to be 1.1–1.3. As is well known, the surface energy and the grain-boundary energy can be illustrated by the force balance in the equilibrium state, which leads to the possibility of obtaining the grain-boundary energy when the surface energy and the dihedral angle are known, without the strain energy of the dislocations.

In this work, as a thermodynamic quantity, the formation energy was considered to determine the binding energies of some crystal systems. Because they are, in turn, related to the surface energy, derivation of the surface energies has been discussed. To obtain the grain-boundary energy from the force balance, the ideal direction of the binding energy was proposed to represent the antiaction force against the surface tension. It was found that the grain-boundary energy can be derived by this simple conceptual approach, and to confirm the data calculated by the directional binding energy (DBE) concept, the values of the surface energy, grain-boundary energy and energy ratio have been compared with the previous measurements.

2. Theoretical estimates of surface energy and grain-boundary energy

2.1. Surface energy

The theoretical approaches to the calculation of the surface energy have often deviated from the experiments, not only because the nature of the theoretical approach necessarily varies with the type of solid considered, but also because the theories are so idealized. As a simple example of the covalent bonding, Harkins [8] considered the surface energy of the diamond at 0 K to be simply one-half of the energy to rupture numbers of bonds passing through 1 cm^2, that is

$$\gamma_{sv} = 1/2\,\gamma_{cohesion} \tag{1}$$

where γ_{sv} is the surface energy (hereafter γ_s) and $\gamma_{cohesion}$ is the bonding energy. Although no allowance has been made for surface distortions, it apparently gives the result that surface energy can be related to the bonding energy. For ionic bonding, however, the calculated surface energy is mainly based on the potential energy functions for like or unlike ions [9–13].

Born and Stern [9] considered the surface energy by the hard-shell repulsion and the electrostatic attractions between ions in rock-salt type crystal

$$\gamma_{100} = 0.0145\,[(Ze)^2/r^3]\ \text{(cgs units)} \tag{2}$$

where e is the electron charge, Z is the valance and r is the interionic distance. Better agreement is obtained by the theory of Glauberman [10]

$$\gamma_{100} = 0.0124\,[(Ze)^2/r^3]\ \text{(cgs units)} \tag{3}$$

A similar calculation which used the complete Born–Mayer potential energy equation [11], thereby attempting to include the effects of ionic polarization on the surface energy, was made by Lennard–Jones and Taylor [12].

Direct measurement of the surface tension has been reported to be possible from the work of cleaving a crystal. Gilman *et al.* [13] applied the cleavage technique to a variety of crystals. If a crystal is cleaved, two surfaces will be created by an amount of applied work, so the specific surface energy is

$$\gamma_s = (E/d_0)(a/\pi)^2 \tag{4}$$

where E is Young's modulus, γ_s is the surface energy, d_0 is a normal surface distance, and a is the range of the attraction force.

Previous measurements on the surface energies are given in Table I.

2.2. Grain-boundary energy involving a dislocation array

Grain boundaries are considered to be separate regions of different crystallographic orientation which are therefore thermodynamically unstable due to the misfits in the grain-boundary regions [14]. It is known that the grain-boundary energy consists of two terms, one due to a strain effect (atom displacement to maintain bonds between atoms) and the other a chemical effect (due to the different binding in the vicinity of the grain boundary compared with that occurring in the interior of the grains).

The well-known model of grain-boundary energy is that considered by Read and Shockly [15]. If a crystal is slightly tilted, there is a misfit at the interface equivalent to the insertion of a row of dislocations. Thus, the grain-boundary energy is the extent of the stress field for an edge dislocation as

$$E_{\text{edge}} = [G\boldsymbol{b}^2/4\pi(1-\nu)]\ln R/b + B \tag{5}$$

where E_{edge} is the energy per unit length, G is the shear modulus, $\boldsymbol{b}$ is Burger's vector, ν is Poisson's ratio, R is the distance that the elastic field extends away from the core, and B is the core energy.

TABLE I Surface energies of hallides on the (1 0 0) cleavage plane

Surface	Energy	(erg cm^{-2})	Reference
NaCl	LiF	MgO	
–	340	1200	[13]
150	420	1440	[9]
130	360	1230	[10]
96	···	1360	[12]

2.3. Thermodynamics of the dihedral angle

If the simple situation exists when the surface energy is isotropic ($\partial\gamma_s/\partial\theta = 0$) and grain-boundary energy is a function of grain misorientation but not of the grain-boundary tangent plane ($\partial\gamma_{gb}/\partial\theta = 0$) [16], then from the force balance between two free surfaces and a grain boundary, the dihedral angle is defined as the angle formed between the two free surfaces

$$\gamma_{gb} = 2\gamma_s \cos(\psi/2) \tag{6}$$

where ψ is the dihedral angle, and it is known that the grain boundary to surface energy ratio can be determined from the dihedral angle itself. However, for ceramics, the two conditions for the use of the above equation are not frequently met.

3. Discussion

3.1. The concept of DBE and its measurement

Thermodynamically, the binding energy [17] is associated with the latent heat of fusion, vaporizing or formation which, in turn, is related to the surface energy. In the case of ionic bonding, especially, according to the Born–Harber cycle [18], it is known that the formation of ceramic compounds involves heat of sublimation, heat of dissociation and lattice energy and also is due to the nature of the ionic bonding of ceramic compounds. Thus, to form the new surfaces of ionic compounds, referred to the cleavage experiment [13], the atoms must overcome the coulomic attraction force, which is determined from the potential energy function. Through this approach, Gilman *et al.* obtained surface energies of some halides [13]. However, it is not clear how to apply (or relate) the thermodynamic quantity to the attraction force because it is difficult to measure the heat of sublimation of ceramic compounds or the heat concerned with the potential energy function. Thus, in order to apply the thermodynamic quantity to the attraction energy, there should be a thermodynamic relation between heat and work.

Considering cleavage fracture, to separate the atoms from their original position, the atoms must overcome the attraction force, that is, external stress (or heat) must be applied to the system. At constant temperature, the work done by external pressure can be related by enthalpy. For uniaxial pressure and a linear modulus, the change of stress will be represented as

$$3\,\mathrm{d}\sigma_u = 3E_1\,\mathrm{d}\varepsilon \tag{7a}$$

$$\therefore\ \mathrm{d}\sigma = E\,d\varepsilon \tag{7b}$$

where σ_u is uniaxial stress and ε is strain.

At 298 K, if the reaction is a reversible process, using Maxwell's equation

$$\mathrm{d}S = \frac{DQ}{T} = \left(\frac{\partial V}{\partial T}\right)_P \mathrm{d}P$$

$$= \alpha_V V_0\,\mathrm{d}P \tag{8a}$$

$$\therefore\ DQ = \alpha_V T V_0\, \mathrm{d}P$$
$$= \alpha_V T V_0\, \mathrm{d}\sigma \qquad (8b)$$

where α_v is the bulk thermal expansion coefficient and V_0 is the molar volume at 0 K. From Equations 7 and 8, and because the bulk thermal expansion coefficient, α_v, is about three times the linear thermal expansion coefficient, α_1, and $\mathrm{d}\sigma = E\mathrm{d}\varepsilon = E(\mathrm{d}x/x_0)$, thus

$$DQ \simeq 3\alpha_1 T V_0\, \mathrm{d}\sigma$$
$$= 3\alpha_1 T V_0 E \frac{\mathrm{d}x}{x_0} \qquad (9)$$

If the attraction force is given by a sine function and at the thermodynamically equilibrium state ($\simeq 0$ K), it is considered that, because of the short-range exponential nature of atomic attraction forces, the distance where there is no longer an attraction force will be a small quantity corresponding approximately to r (the interionic distance). Thus, integrating from r_0 to $r_0 + r$, and summing

$$\frac{Q}{V_0} x_0 \simeq 3\alpha_1 T E r \qquad (10)$$

According to cleavage fracture, $\gamma_s = Er/4\pi^2$, therefore

$$\gamma_s = \frac{Er}{4\pi^2} \simeq \left[\frac{1}{(3\alpha_1 T 4\pi^2)}\right] \frac{Q}{V_0} x_0 \qquad (11)$$

where x_0 is the interionic distance (or r_0).

The above equation indicates that the work done by stretching the atoms from r_0 to $r_0 + r$ can be related to the heat of Equation 11. Thus, it is considered that the heat term $(Q/V_0 x_0)$ is the amount of work needed to cleave the crystal at 298 K as shown Fig. 1.

Because it is difficult to obtain the enthalpy breaking the coulomic attraction force for the reaction of Fig. 1, we consider the indirect reaction for MgO as illustrated in Fig. 2, where it is shown that both are associated with the binding energy because of the sublimation reaction.

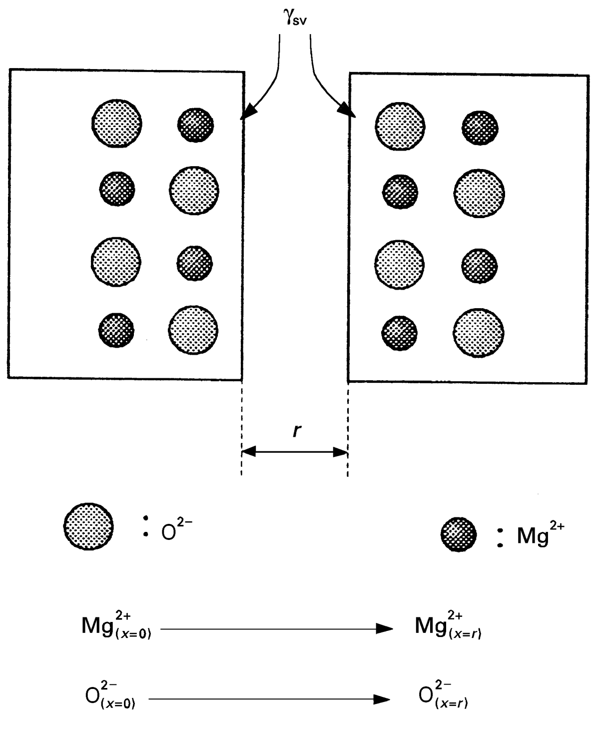

Figure 1 Schematic diagram of the surface energy involving the coulomic attraction force.

Assuming that the binding energy of MgO is associated with the reaction of sublimation as

$$\mathrm{MgO(s)} \rightarrow \mathrm{Mg(g)} + 1/2\mathrm{O_2(g)} \qquad (12a)$$

ΔH_B (binding energy) $= \Delta H_f$ (enthalpy of formation) $+ \Delta H_s$ (enthalpy of sublimation of Mg)

$$\simeq Q_B = 1/1.5 Q_f \qquad (12b)$$

where the enthalpy of formation has a positive value due to the reverse reaction of the formation of compounds.

To remove the ions from their original sites, ions must break (CN-1) bonds, and this involves half the binding energy due to the pair of ions as shown in Fig. 2b (CN is the cordination number). For MgO, because CN is 6, Q of Equation 10 is converted to

$$Q \simeq \frac{1}{15}\frac{1}{5}\frac{1}{2} Q_f \qquad (13)$$

Because the thermal expansion coefficient and temperature are constants, from Equation 10

$$\gamma = k \frac{Q_f}{V_0} x_0 \qquad (14)$$

where k is a constant mainly dependent on the thermal expansion coefficient and the difference between the reaction enthalpies of Figs 1 and 2.

The formation energy, molar volume, interionic distance, r, and derived surface energies are given in Tables II and III.

Because the thermal expansion coefficient of MgO is $13.5 \times 10^{-6}\,\mathrm{K}^{-1}$ and k of Equation 10 is 0.14, the surface energy, γ_s, leads to the value of about $1500\ \mathrm{erg\,cm^{-2}}$. However, this is a slightly higher value than that reported elsewhere [13], and to be an accurate derivation, it must contain surface distortion which is associated with the asymmetrical field at the surface, as well as the tolerance of measured values, such as surface energy and enthalpy of formation. In the case of Al_2O_3, especially, thermal expansion and

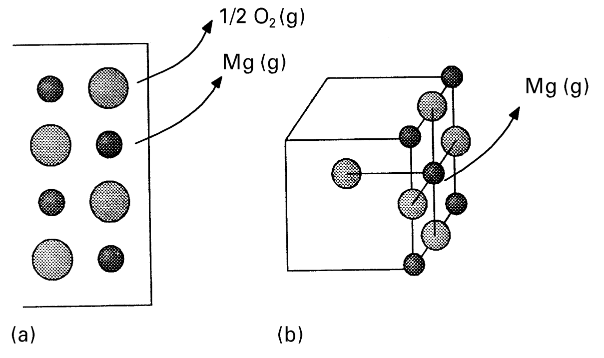

Figure 2 Schematic diagram of the reaction concerning the binding energy: (a) $\mathrm{MgO(s)} \rightarrow \mathrm{Mg(g)} + 1/2\mathrm{O_2(g)}$, $\Delta H = \Delta H_f$ (enthalpy of formation) $+ \Delta H_s$ (enthalpy of sublimation of magnesium); (b) halides structure involving (CN-1) bonds for sublimation of magnesium or $1/2\mathrm{O_2}$.

TABLE II Formation energy, r, molar volume and thermal expansion coefficient of MgO and Al_2O_3 [19]

Material	Formation energy ($kJ\ mol^{-1}$)	r (pm)	Molar volume V_0 (mol)	Thermal expansion coefficient ($10^{-6}\ K^{-1}$)
MgO	601	200	11.248	13.5
Al_2O_3	1675.7	239	25.575	8.8

TABLE III Surface energies and grain-boundary energies according to a concept of DBE and experimental values

Material	DBE ($erg\ cm^{-2}$) ($k = 0.12$)	γ_{sv} ($erg\ cm^{-2}$)		γ_{gb} ($erg\ cm^{-2}$) (derived at $\theta = 20°$)
		Derived	Experimental	
MgO	$\simeq 5400$	1200	1200 (25 °C) – 1440 [9–13]	500
Al_2O_3	$\simeq 2400$	2960	905 (1850 °C) [14] 2600 ($\simeq$ 0 K) [20]	1100

structure anisotropy must be considered. Considering the surface energy of MgO ($1200\ erg\ cm^{-2}$), k is reduced to about 0.12, which is lower than that of Equation 10. As previously mentioned, this may be due to effects such as surface distortion and the difference between reactions as shown in Figs 1 and 2. Applying this value ($k = 0.12$) to the alumina, it seems coincident with the reports as presented in Table III, which implies that the enthalpy of formation contributes to the heat of cleaving the crystals. It may be due to the nature of binding energy originated from potential energy as well as the reaction enthalpy of formation.

In the case of binding energy, assuming that the binding energies of crystals involve the enthalpy of cleaving the crystals, it will be

$$\mathrm{DBE} = 2k\frac{Q_f}{V_0}x_0 \qquad (15)$$

Fig. 3 describes the concept of DBE for two particles (or grains). Physically, the ideal direction of the surface tension in the particles can be represented by the antiaction force against the surface tension, and because the vector addition of 1/2DBE (Fig. 3a) just describes the force acting from one particle to the other, the antiaction force can be given by the vector difference of 1/2DBE (Fig. 3b) whose value is equal to 1/2DBE, impling the grain-boundary energy when the dihedral angle is known.

3.2. Grain-boundary energy and energy ratio according to the DBE concept

As mentioned above, it is considered that grain boundaries are separate regions with different crystallographic orientations, and it was illustrated that the grain-boundary energy increased in proportion to the misorientation angle up to 10°–15° where there is no overlap of dislocation cores [14].

As shown in Fig. 3b, it is noticed that the grain-boundary energy exists due to the force balance when a bonding is formed between two particles (or grains) having free surfaces. However, to determine the grain-boundary energy from the force balance, the dihedral angle and the surface energy must be known. Thus, because the surface energy is obtained by the formation energy approach, the dihedral angle must be given.

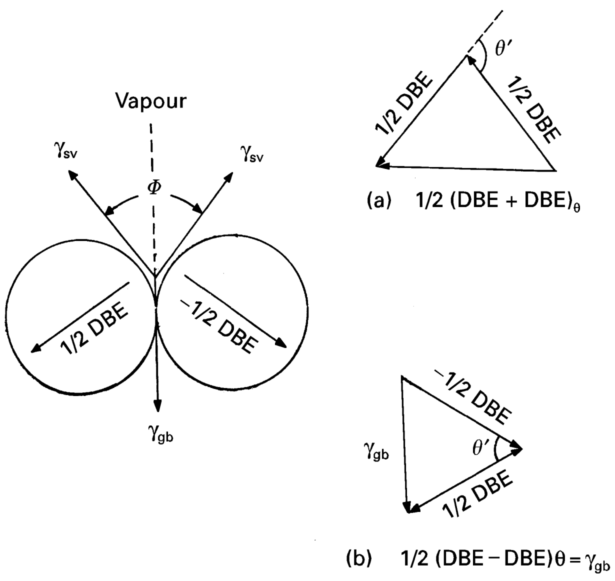

Figure 3 Schematic diagram of the DBE concept for the two particles (or grains): (a) the vector addition of 1/2DBE, impling the force acting on one particle is transferred to the other, (b) the vector difference of DBE, showing the grain-boundary energy (where $\theta' = 180° - \psi$).

It is considered that there is a relation between the dihedral angle and the misorientation angle. The grain-boundary energy can be determined according to the angle θ' where θ' is equal to the $(180° - \psi)$

$$\begin{aligned}\gamma_{gb} &= 1/2\,[\mathrm{DBE} - \mathrm{DBE}]_{\theta'} \\ &= 1/2\,[\mathrm{DBE}]\,[2(1 - \cos\theta')]^{1/2} \\ &= [\mathrm{DBE}]\sin(\theta'/2) \qquad (16)\end{aligned}$$

and the angle θ' must be in the range, $0 \leqslant \theta' < 90°$.

Equation 16 describes the variation of the grain-boundary energy with the angle θ'; it also shows that the grain-boundary energy increases with the angle θ' as in the case of misorientation angle of the grain-boundary energy, and considering that the grain-boundary energy is inversely proportional to the dihedral angle ($\psi = 180° - \theta'$), it is found θ' has the analogous trend with the misorientation angle.

Because it is considered that the angle θ' is proportional to the misorientation angle

$$\theta' = k'\theta (k' \text{ is a constant}) \tag{17}$$

Thus from Equations 16 and 17

$$\gamma_{gb} = [\mathrm{DBE}] \sin(k'\theta/2) \tag{18}$$

Fig. 4b illustrates the plots of the grain-boundary energies with the misorientation angle when the constant k' is 1.1–1.3. It is also found that the grain-boundary energy increases in proportion to the constant k', showing similar trends with the results of the dislocation model given by Read [15].

If the misorientation angle for MgO is 53.1° (when k' is 1.5), according to Equation 18, the grain-boundary energy is $1.6\ \mathrm{J\,m^{-2}}$, which approximately corresponds to Duffy's result ($16\ \mathrm{J\,m^{-2}}$) [21].

Table III gives the grain-boundary energy derived by the DBE concept when the misorientation angle is 20°, indicating that the grain-boundary energies also depend on the surface energy (or 1/2 DBE values) and θ' in Equation 16. Recalling the surface energy is approximately (1/2 DBE), the energy ratio leads to

$$\gamma_{gb}/\gamma_{sv} = \{\sin(\theta'/2\,[\mathrm{DBE}]\}/\{1/2[\mathrm{DBE}]\} = 2\sin(k'\theta/2) \tag{19}$$

Equation 19 indicates that the energy ratio increases in proportion to $2\sin(k'\theta/2)$.

The results of Fig. 5 also conform the assumptions of Equations 17 and 18, because when the constant k' is 1.2, the plot shows very similar results to those of Readey and Jech [22] for NiO, impling that the grain-boundary energy can be determined by the DBE difference when the misorientation angle is known.

However, when the constant k' is 1.2 for MgO, the grain-boundary energy is different from other results [23]. However, when taking k' as 1.7, it is in good coincidence with that reported by Kimura up to 23° for MgO [24], as well as the results of Handwerker *et al.* [7], because the high value of energy ratio (1/2) is shown above 30°. Therefore, it is considered that the constant k' may depend on the material characteristics, such as bonding energy or bonding type of materials. In addition, it is illustrated that the constant k' has an effect on the magnitude of grain-boundary energy and the energy ratio, which implies that the high k' has a relatively larger grain-boundary energy than the surface energy in each case (higher energy ratio).

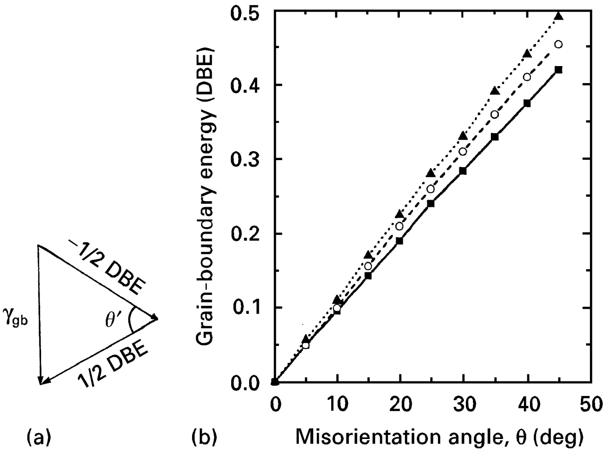

Figure 4 Schematic diagram of the grain-boundary energy: (a) a model of the grain-boundary energy according to the DBE difference, (b) the variation of the grain-boundary energy with the misorientation angle. k': (■) 1.1, (○) 1.2, (▲).

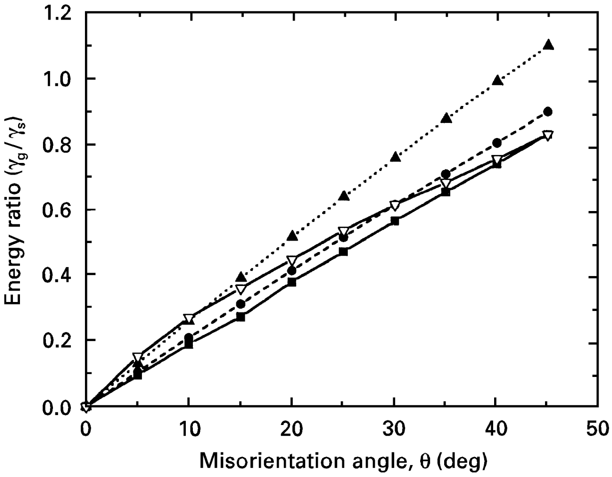

Figure 5 The variation of the energy ratio (γ_{gb}/γ_{sv}) with the misorientation angle. k': (■) 1.1, (○) 1.2, (▼) 1.3. (▽) Readey *et al.* [22].

Although the simple situation, that is, isotropic γ_s and γ_{gb} being a function of the grain-boundary misorientation but not of the boundary plane, is frequently not met in ceramics, it is considered that the grain-boundary energy derived by the DBE concept will provide the thermodynamic excess energy in the grain-boundary region, perhaps due to the change of crystallographic orientation, and thereby may lead to the formation of a dislocation array.

4. Conclusions

The concept of DBE is considered to describe the surface energy and the grain-boundary energy in terms of thermodynamics and force balance.

1. It is found that the thermodynamic quantity (or formation energy) can be related to binding energy and surface energy, and thus the energy ratio.
2. The direction of the DBE vector in the particles is represented by the antiaction force against surface tension whose value is equivalent to 1/2 DBE.
3. Under the force balance, the grain-boundary energy is conceptualized by the DBE difference, irrespective of the dislocation model.
4. It is illustrated that the energy ratio increases in proportion to $2\sin(k'\theta/2)$.

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