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Study of surface cell Madelung constant and surface free energy of nanosized crystal grain*

Zhang Wei-Jia(张维佳)†, Wang Tian-Min(王天民),
Rong Ai-Lun(戎霭伦), and Cui Min(催 敏)

School of Science, Beijing University of Aeronautics and Astronautics, Beijing 100083, *China*

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Surface cell Madelung constant is firstly defined for calculating the surface free energy of nanosized crystal grains, which explains the physical performance of small crystals and may be greatly beneficial to the analysis of surface states and the study of the dynamics of crystal nucleation and growth. A new approximative expression of the surface energy and relevant thermodynamic data are used in this calculation. New formula and computing method for calculating the Madelung constant α of any complex crystals are proposed, and the surface free energies and surface electrostatic energies of nanosized crystal grains and the Madelung constant of some complex crystals are theoretically calculated in this paper. The surface free energy of nanosized-crystal-grain TiO_2 and the surface electrostatic energy(absolute value) of nanosized-crystal-grain α-Al_2O_3 are found to be the biggest among all the crystal grains including those of other species.

Keywords: Madelung constant, surface free energy, nanosized crystal grain
PACC: 0550, 6840, 6146

Surface energy of crystal grains has a crucial influence on the electrical and mechanical performances of materials, especially those materials made up of nanosized crystal grains because all the outstanding performances of the material may come from its big surface free energy. However, there have been hardly found any papers studying the surface free energy of nanosized crystal grains theoretically. In this paper a detailed study of surface free energy and surface electrostatic energy of nanosized crystal grains has been reported based on the calculation of surface cell Madelung constant.

The Madelung constant, which can be used to calculate lattice energy and so on,[1] is of central importance in the theory of ionic crystal and the study of crystal structures. There is no special difficulty in calculating Madelung constant for one-dimensional lattice. However, for three-dimensional lattice it does present greater difficulty because of very slow convergence and the need of some special mathematical methods.[2−7] Recently, Grosso *et al*[8] computed the Madulung constants of some ionic crystals using the Evjen method,[7] but it is valid only for some simple cubic crystals.

The Madelung constant α may be calculated from electrostatic lattice energy U_C^0 as follows:[9]

$$U_{\rm C}^0 = \frac{1}{2} N_{\rm A} u_{\rm C\,molecule} = \frac{1}{2} N_{\rm A} \frac{u_{\rm C\,cell}}{m} = -\frac{N_{\rm A} e^2 \alpha}{4\pi\varepsilon_0 R_0}, \quad (1)$$

$$u_{\rm C\,cell} = \sum_{1\le j\le k} p_j u_{{\rm C}_j}^{+} + \sum_{k<j\le(k+w)} q_j u_{{\rm C}_j}^{-}. \quad (2)$$

Here $N_{\rm A}$, $u_{\rm C\,molecule}$, $u_{\rm C\,cell}$ and m are respectively the Avogadro's number, the electrostatic energy of the molecule and the cell, and the number of molecules in the cell. The factor 1/2 arises from the fact that in the double summation, each pair of ions is counted twice; if n_1, n_2, n_3 are the serial numbers of cells along the three basic vectors $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$ of the parallelepiped cell's three edges, the $u_{{\rm C}j}^{+}$, $u_{{\rm C}j}^{-}$ and α_j^{+}, α_j^{-} are the electrostatic energies and Madelung constants of the j'th ion in the reference neutral parallelepiped cell (0,0,0) respectively, their expressions are given as follows:

*Project supported by the National Defence Pre-Research Foundation of China (Grant No 413100202).
†E-mail: zwjghx@buaa.edu.cn

$$u_{Cj}^{+} = -\frac{e^2}{4\pi\varepsilon_0 R_0}\alpha_j^{+}, \quad \alpha_j^{+} = -R_0\left\{\sum_{n_1,n_2,n_3}\left(\sum_{1\le i\le k} m_i\frac{(Z_+)_j(Z_+)_i}{r_{ij}} - \sum_{k<i\le(k+w)} l_i\frac{(Z_+)_j(Z_-)_i}{r_{ij}}\right)\right\}, \quad (j=1,2,\cdots,k), \tag{3}$$

$$u_{Cj}^{-} = -\frac{e^2}{4\pi\varepsilon_0 R_0}\alpha_j^{-}, \quad \alpha_j^{-} = -R_0\left\{\sum_{n_1,n_2,n_3}\left(\sum_{1\le i\le k} m_i\frac{-(Z_-)_j(Z_+)_i}{r_{ij}} + \sum_{k<i\le(k+w)} l_i\frac{(Z_-)_j(Z_-)_i}{r_{ij}}\right)\right\}, \quad (j=k+1,k+2,\cdots,k+w), \tag{4}$$

where $j=1,2,\cdots,k$ are the serial numbers for positive ions in a reference parallelepiped neutral cell; $j=k+1,k+2,\cdots,k+w$ are the serial numbers for negative ions in the reference cell(0,0,0); $i=1,2,\cdots,k+w$ are the serial numbers for positive plus negative ions in the cell (n_1, n_2, n_3); p_j and q_j are the fractions of positive and negative ions in the reference cell respectively; for example, the fraction is 1/2 if the ion is situated at the face of the cell; m_i and l_i are fractions of positive and negative ions in the cell (n_1, n_2, n_3) respectively; r_{ij} is the distance between the i'th ion in the computed cell and the j'th ion in the reference cell. The terms for which r_{ij}=0, that is for $i=j$, will be omitted from the summation. Z_+ and Z_- are the valences of the positive and negative ions respectively. On the basis of Eqs.(1)–(4), the Madelung constant α can be written as follows:[9]

$$\alpha = \frac{1}{2m}\left(\sum_{1\le j\le k} p_j\alpha_j^{+} + \sum_{k<j\le(k+w)} q_j\alpha_j^{-}\right). \tag{5}$$

In order to calculate the Madelung constant of any complex crystal easily with accelerated convergence, a new method for calculating Madelung constant α is proposed. Based on the many neutral parallelepiped cells which compose the first, second, third, $\cdots$, Nth shell, made up of 26, 98, 218, $\ldots$, $24N^2+2$ cells respectively, and surround a neutral reference parallelepiped cell, whose center serves as the origin of the coordinate system and is not always occupied by an ion. The three basic vectors along the three edges of the parallelepiped cell and its coordinates in a coordinate system are $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$ and (x,y,z) respectively, by which a mathematical expression of r_{ij} can be built to calculate the Madelung constant $\alpha(N)$. The Madelung constants α of all kinds of complex crystals can be calculated by this method because the repeated parallelepiped cell in any crystal can be found using crystallographic group and structure analysis. The $\alpha(N)$ is a rapidly converging series with increasing

Table 1. Madelung constants of some crystals and surface cell Madelung constants and surface free energies of nanosized crystal grains (N=20).

crystal	α	$\alpha_{\text{literature}}$	α_V	α_S	$\gamma/10^{-7}\text{J}\cdot\text{cm}^{-2}$	$\sigma/10^{-7}\text{J}\cdot\text{cm}^{-2}$
NaCl	1.747564599	1.747564595[8]	11.308026381	9.430743955	670.49241	–24514.892
CsCl	1.762664662	1.76268[10]	2.833799141	2.12211819	508.31011	–8066.071
ZnS	6.552189828	6.55222[10]	37.456847603	32.76639013	199.20870	–110499.100
TiO_2 rutile	19.08705257	19.0803[10]	55.393332044	44.040131793	1433.90821	–247293.639
SnO_2	19.22449867		55.756842074	44.302796577	783.75137	–221833.519
$In(OH)_3$	8.802823161		79.704483466	76.580393276	78.37630	–128460.136
In_2O_3 cubic	24.49846529	24.4984[11]	470.14905311	444.742211696	582.65451	–471405.451
In_2O_3corundum	24.331930758	24.3335[11]	185.995792259	182.501397104		–660782.344
InOOH	10.767829320		30.606008346	24.721202041		–110564.276
Al_2O_3 corundum	24.239936645	24.242[10]	184.669223742	181.240495707	645.16871	–997587.842

Annotation: the cell dimensions of NaCl, CsCl and ZnS are a_0=5.62Å, 4.123Å and 5.406Å respectively; the cell dimensions of TiO_2 and SnO_2 are $a_0=b_0$=4.59Å, c_0=2.958Å, u=0.3053,[12] and $a_0=b_0$=4.7382Å, c_0=3.1871Å, u=0.307,[13] respectively; the cell dimensions of $In(OH)_3$ are a_0=7.979Å, R_0=2.171Å, $(0,y,z)$=(0.0, 0.323, 0.176);[1] the cell dimensions of In_2O_3 cubic are a_0=10.117Å, (x,y,z)=(0.39085, 0.15435, 0.3814), u=0.46655 or 03345;[14] the cell dimensions of In_2O_3 corundum are $a_0=b_0$=5.4870Å, c_0=14.510Å, (x,y,z)=(0.2980, 0.0, 0.35731);[11] the cell dimensions of αAl_2O_3 are $a_0=b_0$=4.7628Å, c_0=13.0082Å, x=0.303, (x,y,z)=(0.303, 0.0, 0.355);[10] the cell dimensions of V_2O_3 are $a_0=b_0$=4.952Å, c_0=14.002Å, (x,y,z)=(0.315, 0.0, 0.3463);[11] Asterisk * denotes our work by using the thermochemical cycle.[15]

N and is easy to calculate. Table 1 shows that the Madelung constants of some crystals calculated by using this method with N=20, are in agreement with the data given in the literature.

In order to study how the surface energy influences the properties of crystals, it is necessary that the electrostatic interactional energies of all the ions in the surface cell and all the ions in the crystal should be defined in term of the electrostatic energy $u^{\mathrm{S}}_{\mathrm{C\,cell}}$ of the surface cell, which may give a definition of surface cell Madelung constant α_{S} according to Eq.(6). The definition of the inner cell Madelung constant α_{V} is analogous, but the cell used is in the interior of the crystal. Surface cell electrostatic energy $u^{\mathrm{S}}_{\mathrm{C\,cell}}$ may be calculated by using Eqs.(6)–(8) if surface reconstruction and relaxation of the crystal are ignored and the surface cells are considered as neutral cells. Serial numbers i and j of the ions in the surface cells are the same as in the inner cell. The factor 1/2 in the following equations arises from the fact that in the double summation each pair of ions in a surface cell is counted twice.

$$\begin{aligned} u^{\mathrm{S}}_{\mathrm{C\,cell}} &= \sum_{1\le j\le k} p_j u^{+}_{\mathrm{C}j} + \sum_{k<j\le(k+w)} q_j u^{-}_{\mathrm{C}j} \\ &= -\frac{e^2}{4\pi\varepsilon_0 R_0}\alpha_{\mathrm{S}}, \end{aligned} \tag{6}$$

$$\begin{aligned} u^{+}_{\mathrm{C}j} =& \frac{1}{2}\frac{e^2}{4\pi\varepsilon_0}\left(\sum_{1\le i\le k} m_i\frac{(Z_+)_j(Z_+)_i}{r_{ij}} - \sum_{k<i\le(k+w)} l_i\frac{(Z_+)_j(Z_-)_i}{r_{ij}}\right)_{\text{surface reference cell}} \\ &+ \frac{e^2}{4\pi\varepsilon_0}\left\{\sum_{n_1,n_2,n_3}\left(\sum_{1\le i\le k} m_i\frac{(Z_+)_j(Z_+)_i}{r_{ij}} - \sum_{k<i\le(k+w)} l_i\frac{(Z_+)_j(Z_-)_i}{r_{ij}}\right)\right\}_{\text{other cell}} \\ =& -\frac{e^2}{4\pi\varepsilon_0 R_0}\left\{\left(\frac{1}{2}\alpha^{+}_j\right)_{\text{surface reference cell}} + \left(\alpha^{+}_j\right)_{\text{other cell}}\right\}, \end{aligned} \tag{7}$$

$$u^{-}_{\mathrm{C}j} = -\frac{e^2}{4\pi\varepsilon_0 R_0}\left\{\left(\frac{1}{2}\alpha^{-}_j\right)_{\text{surface reference cell}} + \left(\alpha^{-}_j\right)_{\text{other cell}}\right\}. \tag{8}$$

When a surface neutral parallelepiped cell is defined as the reference cell, the surface cell Madelung constant α_{S} may be written as follows:

$$\alpha_{\mathrm{S}} = \frac{1}{2}\left(\sum_{1\le j\le k} p_j\alpha^{+}_j + \sum_{k<j\le(k+w)} q_j\alpha^{-}_j\right)_{\text{surface reference cell}} + \left(\sum_{1\le j\le k} p_j\alpha^{+}_j + \sum_{k<j\le(k+w)} q_j\alpha^{-}_j\right)_{\text{other cell}}. \tag{9}$$

Through this reasoning, when the center neutral parallelepiped cell is defined as the reference cell, the inner cell Madelung constant α_{V} may be written as

$$\alpha_{\mathrm{V}} = \frac{1}{2}\left(\sum_{1\le j\le k} p_j\alpha^{+}_j + \sum_{k<j\le(k+w)} q_j\alpha^{-}_j\right)_{\text{center reference cell}} + \left(\sum_{1\le j\le k} p_j\alpha^{+}_j + \sum_{k<j\le(k+w)} q_j\alpha^{-}_j\right)_{\text{other cell}}, \tag{10}$$

where α^{+}_j and α^{-}_j can be computed respectively by using Eqs.(7) and (8). If the shell serial number N is still set at 20, α_{S} and α_{V}, corresponding to the surface reference cell(0, 0, 20) and the center cell(0, 0, 0) respectively, are computed by using Eqs.(9) and (10) respectively, and the results are listed in Table 1.

Surface cell electrostatic energy $u^{\mathrm{S}}_{\mathrm{C\,cell}}$ may be calculated by using Eqs.(6)–(9) and the results obtained are listed in the table too. Inner cell electrostatic energy $u^{\mathrm{V}}_{\mathrm{C\,cell}}$ is calculated analogously. Surface electrostatic energy σ in the table may be calculated by dividing the outside area of surface cell into $u^{\mathrm{S}}_{\mathrm{C\,cell}}$, because only the ion electrostatic energies of outermost surface cells differ from the energies of interior cells.[1] It can be seen from Table 1 that the biggest absolute value among the surface electrostatic energies is that of Al_2O_3 which has a high rigidity, thus it has been applied widely.

Surface free energy of the nanosized crystal grain can be roughly estimated by using α_{S} and α_{V}, for studying the dynamics of nanosized crystal grain growth. We know that Gibbs free energy ΔG for form-

ing a crystal grain in a system is the change of the Gibbs free energy which causes the inner and surface layer molecules of the crystal grain to move from a metastable phase (gaseous or liquid state) to a steady phase(solid state). If g_s and g_v denote the ΔG of the inner and the surface layer of the nanosized crystal grain formed in a unit volume respectively, and $g_s/g_v \approx u_C^S/u_C^V = \alpha_S/\alpha_V = w$, and the thickness of surface layer is assumed to be $d = a_0/2$,[1] the surface free energy γ of a nanosized crystal grain with radius r can be roughly estimated as follows:

$$\begin{aligned}\Delta G(r) =& \frac{4}{3}\pi r^3 g_V + 4\pi r^2 \frac{1}{2} a_0 (g_S - g_V) \\ \approx& \frac{4}{3}\pi r^3 g_V + 4\pi r^2 \frac{1}{2} a_0 (w-1) g_V \\ =& \frac{4}{3}\pi r^3 g_V + 4\pi r^2 \gamma, \qquad (11)\end{aligned}$$

$$\therefore \gamma = \frac{1}{2} a_0 (w-1) g_V. \qquad (12)$$

For a compound formed from the single steady gas phase or solid state materials, g_v may be obtained from Eq.(13) in which the standard Gibbs free energy ΔG_f^0 can be easily found in the chemical handbook.[16]

$$g_V = \frac{\Delta G_f^0}{N_A} \times \frac{m}{v_{cell}}. \qquad (13)$$

Here N_A, m and v_{cell} are Avogadro's number, number of molecules in a cell and the volume of the cell, respectively.

For compounds formed from liquid state materials, g_v may be obtained from Eq.(13) in which ΔG_f^0 can be replaced by the change of the Gibbs energy ΔG_T^0 in a given chemical equilibrium reaction, which is the standard Gibbs free energy $\Delta G_{f,T}^0$ of resultant minus that of the reactant.

Surface free energy γ of nanosized crystal grains may be calculated by using Eq.(12), the results obtained for some ionic crystals are given in Table 1. In this table, γ(ZnS) and γ(In(OH)$_3$) are the surface free energies of the interface between solid and liquid(water), while the others are those of the interface between solid and air. Attention should be paid to the difference between the surface free energies γ of nanosized crystal grains and the block. The γ(NaCl) is 670.5×10^{-7}J/cm^2 for nanosized crystal grains, while it is 310×10^{-7}J/cm^2 for the block,[17,18] because surface layers on the block are of polycrystals actually.

In fact, the data of γ in Table 1 are surface free energies of nanosized crystal grain corresponding to the reference cell(0, 0, 20) with N=20. Distinctly surface free energy corresponding to the reference cell (20, 20, 20) at the top corner of the square shell is the biggest, but there are a few of the cells whose surface free energy is the biggest when N increases. So, it is reasonable that the surface free energy γ of nanosized crystal grains, with a size about 50nm, is calculated according to the reference cell(0, 0, 20). It can be seen from Table 1 that the biggest value of surface free energy γ is that of TiO_2, which is highly surface chemical active and can sterilize bacteria, so the material has been widely used in architecture and environmental protection etc.

Actually this method may be applicable for very small crystal grains also for studying the dynamics of crystal nucleus growth. We might as well look the smaller crystal grain as a cube whose dimension may be estimated by $r = N(a_0^2 + b_0^2 + c_0^2)^{1/2}$, so the relationship between γ and r or N may be built by using Eqs.(12), (9) and (10), and $\bar{\alpha}_S(N)$ ought to be the average of all surface cell Madelung constants of the smaller crystal grains. For example, the $\gamma(r, N)$ of SnO_2 and In(OH)$_3$ are given in Table 2 and Fig.1. It can be seen that the small crystal nucleus can give rise to a big surface free energy γ. Conversely, the bigger the crystal grain, the smaller the γ, and it may tend to a definite value. Corresponding to size 10–20nm of In(OH)$_3$ crystal grain, the calculated γ value is $(100–120)\times10^{-7}$J/cm^2 which is in agreement with the experimental value 108×10^{-7}J/cm^2.[19]

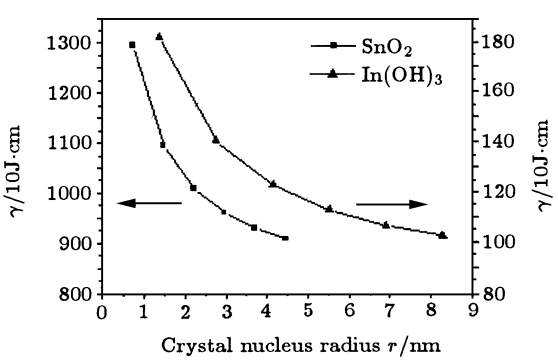


Fig.1. The curves of γ against r.

Generally speaking, the bigger the surface free energy, the more difficult the formation of a crystal nucleus, according to the dynamic theory of nucleation.[20] It can be seen from Table 2 and Fig.1 that the surface free energy γ of SnO_2 crystal nucleus is bigger than that of In(OH)$_3$, so, forming nanosized crystal grain of SnO_2 is more difficult than that of In(OH)$_3$, the latter is formed only at room temperature, while the former formed at high temperature.[21]

In addition, it can be seen from Table 2 that the surface free energy γ of TiO_2 rutile crystal nucleus is bigger than that of SnO_2. So, nanosized rutile crystal grain of TiO_2 is formed at a higher temperature, about 600°C in oxygen gas.[22,23] The calculated surface free energy γ of TiO_2 rutile crystal nucleus is $1433.90821\times10^{-7}\mathrm{J\cdot cm^{-2}}$ $\approx1.4\mathrm{J\cdot m^{-2}}$, which is approximately in agreement with the experimental data $2.2\pm0.2\mathrm{J\cdot m^{-2}}$ of the surface enthalpies of the rutile,[24] the enthalpy approximates free energy when the change of free energy with temperature T is very small. These results agree with experimental phenomena and experimental data.

In this paper, a new formula and a relevant method for calculating Madelung constant α are built on neutral cells among which there are 26 such cells as the first shell directly contacting the reference cell and surrounding it, then 98, 218, $\cdots 24N^2+2$ cells as the second, third, $\cdots N$th shell respectively followed. The $\alpha(N)'$s are rapidly converging series and are calculated very easily. A new surface cell Madelung constant of nanosized crystal grain is defined and a basic hypothesis, that the ratio between the Gibbs free energies for the surface layer and the bulk is approximatively equal to the ratio between the electrostatic energies of surface cell and inner cell, namely the ratio between Madelung constants of surface cell and inner cell might as well be assumed in order to built an approximate expression of surface free energy for nanosized crystal grains and calculate it using the thermodynamic data. These theories may redound to make surface analysis and to study dynamics of growth of crystal nucleus, then proceed to explain physical properties of nanosized crystal grain and so on.

Table 2. Madelung constants (α_S, α_V) for surface and inner cells of SnO_2 and $In(OH)_3$ and their surface free energies γ.

N	$In(OH)_3$				SnO_2			
	radius r/nm	inner cell α_V	surface cell α_S	surface $\gamma/10^{-7}\mathrm{J\cdot cm^{-2}}$	radius r/nm	inner cell α_V	surface cell α_S	surface $\gamma/10^{-7}\mathrm{J\cdot cm^{-2}}$
1	1.382	79.707107251	72.440802212	182.29	0.742	56.102597026	37.06536	1294.57
2	2.764	79.704486906	74.095009664	140.73	1.484	55.790152578	39.78111	1094.74
3	4.146	79.704471185	74.804636738	122.93	2.226	55.773312195	41.02058	1009.14
4	5.528	79.704517971	75.199042895	113.03	2.968	55.766903153	41.72763	960.44
5	6.910	79.704535823	75.450097567	106.73	3.71	55.763511531	42.18432	929.03
6	8.292	79.70460241	75.62393238	102.38	4.452	55.761510888	42.50352	907.08

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