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An Approximate Calculation of Attachment Energies for Ionic Crystals

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Some formulas for an approximate calculation of electrostatic potentials at the surface of ionic crystals are given, based on previous work of Madelung and Kleber. It is concluded that for an infinite crystal the value of this potential is infinite when, parallel to the crystal face, layers of positive ions alternate with layers of negative ions. However, the attachment energy of neutral molecules for such faces is finite.

The formulas are applied to sphalerite to calculate the attachment energies of molecules ZnS on (111), (110) and (001). These energies, expressed in units e^2/a (where a is the unit cell edge) are: $E_{111} = -2{\cdot}583$; $E_{110} = -2{\cdot}711$ and $E_{001} = -6{\cdot}189$.

Introduction

Recently, the study of the relations between crystal structure and crystal morphology lead to the working hypothesis that the morphological importance of a crystal face decreases with increasing attachment energy (Hartman & Perdok, 1955). The attachment energy was defined as the bond energy released when one building unit is attached to the surface of the crystal face concerned. With ionic crystals this attachment energy can be calculated if the ions are considered as point charges. To this end the electrostatic potential at the point of attachment of the ion should be known. It can be calculated conveniently when the structure is divided into periodic bond chains with stoichiometric composition. First, the electrostatic potential of one chain is calculated; then the potential of a layer of chains parallel to the crystal face; and finally the potentials of all layers are added together to obtain the potential of the crystal face.

(a) Electrostatic potential of a chain A^+B^-

Fig. 1(*a*) represents an infinite chain of ions with period p and total charge zero. The x axis is taken parallel to the chain direction; in general it lies outside the plane of the ion chain. All positive ions lie at the same distance y_+ and all negative ions at the same distance y_- from this axis. The electrostatic potential in the point $P(0, 0)$ can be given by applying twice the formula of Madelung (1918) for the potential of a row of equally charged ions. We then find:

$$V_0 = \frac{4e}{p}\left[\sum_{l=1}^{\infty} K_0\left(\frac{2\pi l y_+}{p}\right)\cos\left(\frac{2\pi l x_+}{p}\right) - \sum_{l=1}^{\infty} K_0\left(\frac{2\pi l y_-}{p}\right)\cos\left(\frac{2\pi l x_-}{p}\right)\right] + \frac{2e}{p}\ln\frac{y_-}{y_+}, \quad (1)$$

or

$$V_0 = \frac{4e}{p}A_0 + \frac{2e}{p}B_0. \quad (2)$$

In this formula K_0 represents the Hankel cylinder function of order zero. This expression for V_0 has been shown by Kleber (1939) to be convergent.

(b) Electrostatic potential of a layer of chains of composition A^+B^-

Fig. 1(*b*) represents a layer, parallel to a crystal face, consisting of parallel chains seen end on. The electrostatic potential of this layer can be found by adding together the potentials of all chains in the layer. Thus, if V_n is the electrostatic potential in point P with regard to the nth chain,

$$V_1 = \sum_{-\infty}^{+\infty} V_n,$$

or substituting (2),

$$V_1 = \frac{4e}{p}\sum_{-\infty}^{+\infty} A_n + \frac{2e}{p}\sum_{-\infty}^{+\infty} B_n, \quad (3)$$

where

$$A_n = \sum_{l=1}^{\infty} K_0\left(\frac{2\pi l y_{n+}}{p}\right)\cos\left(\frac{2\pi l x_{n+}}{p}\right) - \sum_{l=1}^{\infty} K_0\left(\frac{2\pi l y_{n-}}{p}\right)\cos\left(\frac{2\pi l x_{n-}}{p}\right) \quad (4)$$

and

$$B_n = \ln\frac{y_{n-}}{y_{n+}},$$

y_{n+} and x_{n+} being the coordinates of the positive ions with respect to the point P as origin; similarly y_{n-} and x_{n-} are the coordinates of the negative ions.

The term A_n in expression (3) decreases rapidly with increasing y, so that it need be calculated only for the first few chains. In order to find a convenient expression for the term B_n, we put (see Fig. 1(*b*)):

$$y_{n+} = \{(nq-u+h\cos\delta)^2+(v-h\sin\delta)^2\}^{\frac{1}{2}}$$

and

$$y_{n-} = \{(nq-u-h\cos\delta)^2+(v+h\sin\delta)^2\}^{\frac{1}{2}},$$

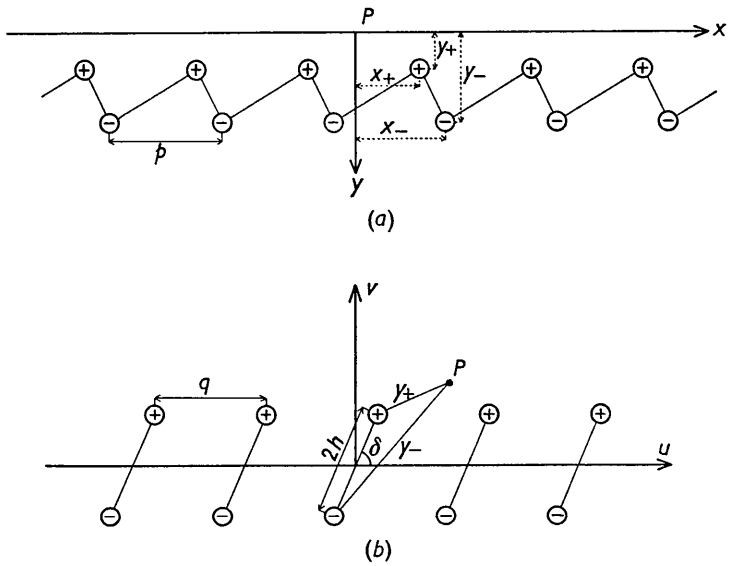

Fig. 1. (*a*) Infinite chain of ions, with coordinates used in the calculation of the electrostatic potential in P. The coordinates y_+ and y_- are measured radially out from the x axis, which in general does not lie in the plane of the chain.
(*b*) Layer, consisting of infinite chains of ions seen end on, with coordinates used in the calculation of the electrostatic potential in the point P. The x axis of Fig. 1(*a*) is perpendicular to the plane of the drawing and goes through P.

where δ is the angle between the positive u axis and the direction from the origin towards the positive ion.

Taking together the terms for $+n$ and $-n$, we obtain:

$$B_n+B_{-n} = \tfrac{1}{2}\ln\frac{1+z_n}{1-z_n} = \tanh^{-1}z_n\,, \qquad (5)$$

with

$$z_n = \frac{\begin{array}{l}4n^2q^2(vh\sin\delta-uh\cos\delta)\\ +4(u^2+v^2+h^2)(vh\sin\delta+uh\cos\delta)\end{array}}{\begin{array}{l}n^4q^4+2n^2q^2(v^2-u^2+h^2\sin^2\delta-h^2\cos^2\delta)\\ +(u^2+v^2+h^2)^2+4(vh\sin\delta+uh\cos\delta)^2\end{array}}\,. \qquad (6)$$

When n is large enough, an approximate power series of n can be used. If we put

$$z_n = \frac{an^2+b}{n^4+cn^2+d}\,,$$

then

$$B_n+B_{-n} = \tanh^{-1}z_n \approx an^{-2}+n^{-4}(b-ac) +n^{-6}\{c(ac-b)-ad\}+n^{-8}\{(b-ac)(c^2-d)+acd\}+\ldots. \qquad (7)$$

The summation in (3) is then readily done, taking into account that

$$\sum_1^\infty n^{-2} = \frac{\pi^2}{6}\,;\quad \sum_1^\infty n^{-4} = \frac{\pi^4}{90}\,;$$

$$\sum_1^\infty n^{-6} = \frac{\pi^6}{945}\,;\quad \sum_1^\infty n^{-8} = \frac{\pi^8}{9450}\,.$$

The calculation of V_1 is thus carried out according to the formula

$$V_1 = \frac{4e}{p}\sum_{-\infty}^{+\infty}A_n+\frac{2e}{p}B_0+\frac{2e}{p}\sum_1^\infty(B_n+B_{-n})\,. \qquad (8)$$

(c) Electrostatic potential of a crystal face

To obtain this potential the potentials of all layers must be calculated and then added together. The distance between two consecutive layers being denoted by d, the coordinate v can be put into the form

$$v = v_0+md, \text{ where } m \text{ is an integral number.}$$

For a certain value of n, the quantity B_n+B_{-n} can be developed into a power series of m:

$$B_n+B_{-n} = \frac{4h\sin\delta}{md} +\text{terms with higher negative powers of } m.$$

The first term is independent of the coordinates of the point P and when m tends to infinity it causes the potential of the face to be infinite, as the first term of the sum

$$\sum_{m=\mu}^\infty(B_n+B_{-n}) = \frac{4h\sin\delta}{d}\sum_{m=\mu}^\infty\frac{1}{m}+\ldots$$

becomes infinite.

A finite attachment energy results only when: (1) $\delta = 0$; (2) neutral molecules attach themselves to the crystal face; (3) the dimensions of the crystal remain finite, but the potential is then very high.

(d) Electrostatic potential in the site of an ion in a layer

For the calculation of the lattice energy, the potential in the site of an ion in a layer must be known. Suppose this site coincides with a positive ion (see Fig. 1(*b*)), then in this case $u=h\cos\delta$, $v=h\sin\delta$, $x_+=0$, $y_+=0$.

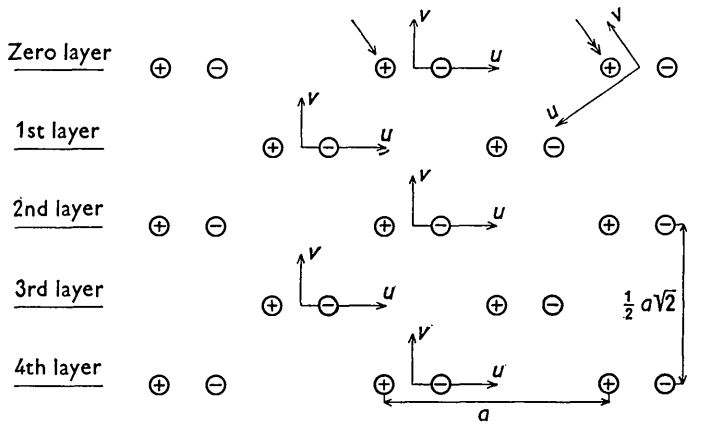

Fig. 2. Projection of the sphalerite structure on $(\bar{1}10)$. Five layers parallel to (110) are shown and for each layer the coordinate axes u and v are drawn. These are also drawn for the zero layer of (111) which runs from the top right corner to the bottom left corner.

Table 1. *Calculation of the attachment energy on* (110) *of sphalerite*

	1st layer	2nd layer	3rd layer	4th layer
q	a	a	a	a
h	$a/8$	$a/8$	$a/8$	$a/8$
$\sin\delta$	0	0	0	0
$\cos\delta$	-1	-1	-1	-1
u	$3a/8$	$-a/8$	$3a/8$	$-a/8$
v	$\frac{1}{4}a\sqrt{2}/2$	$\frac{1}{2}a\sqrt{2}/2$	$\frac{3}{4}a\sqrt{2}/2$	$a\sqrt{2}/2$
A_{-1}	Negligible	$\frac{1}{2}\pi\times+0{\cdot}00003$	Negligible	Negligible
A_0	$\frac{1}{2}\pi\times-0{\cdot}01001$	$\frac{1}{2}\pi\times+0{\cdot}00097$	$\frac{1}{2}\pi\times-0{\cdot}00002$	Negligible
A_1	$\frac{1}{2}\pi\times-0{\cdot}00163$	$\frac{1}{2}\pi\times+0{\cdot}00001$	$\frac{1}{2}\pi\times-0{\cdot}00001$	Negligible
B_0	$-0{\cdot}34657$	$+0{\cdot}05889$	$-0{\cdot}07330$	$+0{\cdot}01538$
B_1+B_{-1}	$+0{\cdot}13219$	$-0{\cdot}01319$	$-0{\cdot}01150$	$+0{\cdot}00711$
B_2+B_{-2}	$+0{\cdot}04406$	$-0{\cdot}01082$	$+0{\cdot}02007$	$-0{\cdot}00343$
B_3+B_{-3}	$+0{\cdot}02030$	$-0{\cdot}00590$	$+0{\cdot}01446$	$-0{\cdot}00361$
B_4+B_{-4}	—	—	$+0{\cdot}00956$	$-0{\cdot}00270$
B_5+B_{-5}	—	—	—	$-0{\cdot}00197$
B_6+B_{-6}	—	—	—	$-0{\cdot}00147$
Rest	$\sum_4^\infty (B_n+B_{-n})$	$\sum_4^\infty (B_n+B_{-n})$	$\sum_5^\infty (B_n+B_{-n})$	$\sum_7^\infty (B_n+B_{-n})$
	$=+0{\cdot}05290$	$=-0{\cdot}01707$	$=+0{\cdot}03943$	$=-0{\cdot}00915$
V_{layer}	$\frac{e}{p}\times-0{\cdot}26738$	$\frac{e}{p}\times+0{\cdot}03017$	$\frac{e}{p}\times-0{\cdot}00275$	$\frac{e}{p}\times+0{\cdot}00032$

Expression (1) now becomes (cf. Madelung, 1918; Kleber, 1939)

$$V_0' = \frac{e}{p}\left[1{\cdot}15443 - 4\sum_{l=1}^{\infty} K_0\left(\frac{2\pi l y_-}{p}\right) \times \cos\left(\frac{2\pi l x_-}{p}\right) - 2\ln\frac{2p}{y_-}\right], \quad (1a)$$

and (6) reduces to

$$z_n = \frac{4n^2q^2h^2(\sin^2\delta-\cos^2\delta)+8h^4}{n^4q^4+4n^2q^2h^2(\sin^2\delta-\cos^2\delta)+8h^4}, \quad (6a)$$

while (8) changes into

$$V_1 = V_0' + \frac{4e}{p}\sum_1^\infty (A_n+A_{-n}) + \frac{2e}{p}\sum_1^\infty (B_n+B_{-n}). \quad (8a)$$

(e) Example: sphalerite

The structure can be divided into an infinite set of periodic bond chains in the direction $[\bar{1}10]$ and of composition ZnS. Fig. 2 gives a projection of the structure on $(\bar{1}10)$; the chains are seen end-on. The attachment energies of ZnS molecules (treated as a pair of ions) on the faces (110), (111) and (001) will now be calculated.

(α) *Attachment energy on* (110)

The electrostatic potential in the site of the Zn ion indicated by the single arrow (Fig. 2) is calculated, assuming for the present the charges of the ions to be $+1$ and -1.

The period of the chains is $p = \frac{1}{2}a\sqrt{2}/2$, where a is the unit-cell edge. For the term A_0 of the nearest

chain in the first layer we find, with $y_+ = \frac{1}{4}a\sqrt{6}$, $x_+ = \frac{1}{2}p$, $y_- = \frac{1}{4}a\sqrt{3}$ and $x_- = 0$, applying formula (2): $A_0 = -\frac{1}{2}\pi \times 0{\cdot}01001$. The factor $\frac{1}{2}\pi$ comes in here because the *Funktionentafeln* of Jahnke & Emde (1933) have tabulated $iH_0^{(1)}(ix) = (2/\pi)K_0(x)$.

The values of the other A-terms and of the B-terms have been summarized in Table 1, together with the values for the other layers.

The rest-terms in this table have been calculated from formula (7), beginning with the term that showed no difference whether calculated exactly (equation (5)) or approximately (equation (7)). The potentials of the layers have been calculated by applying formula (8).

Now $V_{110} = (e/p) \times -0{\cdot}23964$. The electrostatic potential in the site of the S-ion is the same, so that, for doubly charged ions the attachment energy per molecule is found to be:

$$E_{110} = \frac{8e^2}{p} \times -0{\cdot}23964 = -2{\cdot}711e^2/a\,.$$

(β) *Attachment energy on other faces*

In order to find the attachment energy for the other faces, the lattice energy is calculated. This involves the calculation of the electrostatic potential in the site of an ion in the zero layer of (110). For the positive ion $y_+ = 0$, $x_+ = 0$, $y_- = \frac{1}{4}a$, $x_- = \frac{1}{2}p$, $u = -a/8$ and $v = 0$. Equations (1a), (4), (6a), (7) and (8a) then give:

$$V_0' = \frac{e}{p} \times -1{\cdot}98842;$$
$$A_{-1} = \tfrac{1}{2}\pi \times +0{\cdot}00004;\ A_1 = \tfrac{1}{2}\pi \times +0{\cdot}00043;$$
$$B_1 + B_{-1} = -0{\cdot}06454;\ B_2 + B_{-2} = -0{\cdot}01575;$$
$$\sum_3^\infty (B_n + B_{-n}) = -0{\cdot}02472\,.$$

From this it follows that $V_0 = \frac{e}{p} \times -2{\cdot}19549$.

The lattice energy is then:

$$E_{\mathrm{ZnS}} = 8e(\tfrac{1}{2}V_0 + V_{110}) = -15{\cdot}131e^2/a\,.$$

The literature value is $-15{\cdot}13168e^2/a$ (cf. Pauling (1948, p. 338); the value quoted there assumes single-charged ions Zn^+S^-).

(γ) *Attachment energy of a molecule on* (111)

The attachment energy of a molecule on the (111) face can now be found by subtracting half the electrostatic potential of a molecule in the zero layer of (111) from the lattice energy (see Fig. 2):

$$E_{111} = E_{\mathrm{ZnS}} - \tfrac{1}{2}E_0(111)\,.$$

For the positive ion indicated by the double arrow $q = \frac{1}{4}a\sqrt{6}$, $h = a/8$, $\sin\delta = 1/\sqrt{3}$ and $\cos\delta = \frac{1}{3}\sqrt{6}$.

Equations (1a), (4), (6a), (5), (7) and (8a) then give:

$$V_0' = \frac{e}{p} \times -1{\cdot}98842;$$
$$A_{-2} = \tfrac{1}{2}\pi \times +0{\cdot}00001;\ A_{-1} = \tfrac{1}{2}\pi \times -0{\cdot}00163;$$
$$A_1 = \tfrac{1}{2}\pi \times -0{\cdot}01001;\ A_2 = \tfrac{1}{2}\pi \times +0{\cdot}00003;$$
$$B_1 + B_{-1} = -0{\cdot}04350;\ B_2 + B_{-2} = -0{\cdot}01319;$$
$$\sum_3^\infty (B_n + B_{-n}) = -0{\cdot}0217\,3\,.$$

These values give $V_0(111) = \frac{e}{p} \times -2{\cdot}21814$, from which $E_{111} = -2{\cdot}583e^2/a$.

(δ) *Attachment energy of a molecule on* (001)

Similarly the attachment energy of a molecule on the (001) face can be calculated by:

$$E_{001} = E_{\mathrm{ZnS}} - \tfrac{1}{2}E_0(001)\,.$$

For the positive ion $q = \frac{1}{2}a\sqrt{2}$, $h = a/8$, $\sin\delta = 1$ and $\cos\delta = 0$.

$$V_0' = \frac{e}{p} \times -1{\cdot}98842;$$
$$A_{-1} = A_1 = \tfrac{1}{2}\pi \times +0{\cdot}00097;$$
$$B_1 + B_{-1} = +0{\cdot}11778;\ B_2 + B_{-2} = +0{\cdot}03077;$$
$$B_3 + B_{-3} = +0{\cdot}01379;$$
$$\sum_4^\infty (B_n + B_{-n}) = +0{\cdot}03542;$$
$$V_0(001) = \frac{e}{p} \times -1{\cdot}58071\,,$$

from which $E_{001} = -6{\cdot}189e^2/a$.

(ε) *Conclusion*

Two assumptions have been made: (1) the sphalerite structure can be treated as a purely ionic structure, (2) the building units in the crystallization process are ion pairs ZnS. The attachment energies are found to be:

$$E_{111} = -2{\cdot}583;\ E_{110} = -2{\cdot}711;\ E_{001} = -6{\cdot}189\,e^2/a.$$

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