Analysis of cohesive energy and bulk modulus of diatomic solids

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Empirical relationships studied by Verma and Bhardwaj [J Phys: Condens Matter, 18 (2006) 8603] have been found to be simplified forms of the Born-model with the power law and exponential potential functions. Values of cohesive energy and bulk modulus in case of NaCl under the effect of pressure have also been obtained. It has been found that the exponential potential function gives better agreement with the available experimental data as compared to the inverse power form.

Keywords: Interatomic distances, Cohesive energy, Bulk modulus, Diatomic solids

1 Introduction

Verma and Bhardwaj have studied a number of empirical relationships for the cohesive energy and bulk modulus of diatomic solids formulated by earlier researchers. They proposed the following simple relationships for the cohesive energy:

\[ E_{\text{coh}} = \frac{Z_1 Z_2 \text{constant}}{d} \]  \( \ldots (1) \)

and bulk modulus

\[ B = (Z_1 Z_2)^A N d^{-3} \]  \( \ldots (2) \)

where \( Z_1 \) and \( Z_2 \) are valencies of the cation and anion respectively, and \( d \), the bond length of diatomic solids. The constant in Eq. (1) for the rocksalt type solids was taken as 520. Values of \( A \) and \( N \) in Eq. (2) were found to be 0.75 and 550 for the rocksalt type compounds, and 0.2 and 750 for the zinc-blende type compounds, respectively.

In the present study, it has been shown that Eqs (1) and (2) are simplifications of the Born-model for interatomic potentials. To substantiate this statement the Born-model formulations given by Smith and Cain is used, and present an analysis with the help of experimental data for alkali halides based on ultrasonic measurements. The assumptions which lead to Eqs (1) and (2) have been discussed and analyzed.

2 Analysis based on the Born – model

According to the Born – model, the lattice potential energy \( U \) is written as:

\[ U = -\frac{\alpha_M Z_1 Z_2 e^2}{r} + \phi(r) \]  \( \ldots (3) \)

where \( r \) is the nearest neighbour interatomic distance, \( Z_1 \) and \( Z_2 \) are the ionic valences, \( \alpha_M \) is the Madelung constant, \( e \) is the electronic charge and \( \phi(r) \) is the overlap repulsive potential energy. The first term of right side of Eq. (3) is the Madelung energy arising from the Coulombian interactions between points like charges. The last term, a result of overlap repulsion arising from the Pauli’s exclusion principle being operative in the region of overlap of outermost electrons of the neighbouring atoms \( \phi(r) \), is a short range energy term which increases very fast with the decrease in interatomic distance and vice-versa. In the Born-model, \( \phi(r) \) is represented by an inverse power form or alternatively by an exponential form as follows :

\[ \phi(r) = \frac{B}{r^n} \]  \( \ldots (4) \)

or

\[ \phi(r) = C \exp\left(-\frac{r}{\rho}\right) \]  \( \ldots (5) \)

where \( B, n, C \) and \( \rho \) are the parameters which are determined from the lattice equilibrium condition and the bulk modulus using the following relationships:

\[ \left(\frac{dU}{dR}\right)_{r=R_0} = 0 \]  \( \ldots (6) \)
and

$$K_T = \frac{1}{x r_0} \left( \frac{d^2 U}{dr^2} \right)_{r=r_0} \quad \ldots(7)$$

where \( r_0 \) is the equilibrium value of the interatomic distance \( r \) and \( x \) is a geometrical factor depending on the type of crystal structure. In fact, the volume per unit cell \( V = x r^3 \). With the help of Eqs (3)-(7) the following relationships are obtained:

**Inverse Power Forms** :

$$\frac{\alpha_M Z_1 Z_2 e^2}{r_0^2} = \frac{n B}{r_0^{n+1}} \quad \ldots(8)$$

and

$$K_T = \frac{1}{9x} \frac{\alpha_M Z_1 Z_2 e^2}{r_0^4} (n-1) \quad \ldots(9)$$

**Exponential Forms** :

$$\frac{\alpha_M Z_1 Z_2 e^2}{r_0^2} = \frac{C \exp \left( -\frac{r_0}{\rho} \right)}{\rho} \quad \ldots(10)$$

and

$$K_T = \frac{1}{9x} \frac{\alpha_M Z_1 Z_2 e^2}{r_0^4} \left( \frac{r_0}{\rho} - 2 \right) \quad \ldots(11)$$

Reliable and accurate experimental values of \( r_0 \) and \( K_T \) have been measured ultrasonically by Smith et al.\(^{16-19}\) for sixteen alkali halides. Using these values of \( r_0 \) and \( K_T \), the parameters \( B, n, C \) and \( \rho \) are determined with the help of Eqs (8)-(11). These are given in Table 1. Values of lattice potential energy at equilibrium are then obtained using the following relationships :

$$U_0 = \left[ U \left( r \right) \right]_{r=r_0} = -\frac{\alpha_M Z_1 Z_2 e^2}{r_0^2} \left( 1 - \frac{1}{n} \right) \quad \ldots(12)$$

for the inverse power form, and

$$U_0 = -\frac{\alpha_M Z_1 Z_2 e^2}{r_0^2} \left( 1 - \frac{\rho}{r_0} \right) \quad \ldots(13)$$

for the exponential form.

### Table 1 — The Born-model Parameters and interatomic distance based on ultrasonic measurements\(^{16-18}\) for alkali halides

<table>
<thead>
<tr>
<th>Solids</th>
<th>( r_0(\text{Å}) )</th>
<th>( \rho (\text{Å}) )</th>
<th>( n )</th>
<th>( r_0/\rho )</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>2.013</td>
<td>0.271</td>
<td>6.44</td>
<td>7.43</td>
</tr>
<tr>
<td>LiCl</td>
<td>2.570</td>
<td>0.290</td>
<td>7.85</td>
<td>8.86</td>
</tr>
<tr>
<td>LiBr</td>
<td>2.751</td>
<td>0.294</td>
<td>8.37</td>
<td>9.35</td>
</tr>
<tr>
<td>LiI</td>
<td>3.006</td>
<td>0.300</td>
<td>9.03</td>
<td>10.02</td>
</tr>
<tr>
<td>NaF</td>
<td>2.317</td>
<td>0.267</td>
<td>7.68</td>
<td>8.65</td>
</tr>
<tr>
<td>NaCl</td>
<td>2.820</td>
<td>0.290</td>
<td>8.73</td>
<td>9.72</td>
</tr>
<tr>
<td>NaBr</td>
<td>2.989</td>
<td>0.293</td>
<td>9.21</td>
<td>10.20</td>
</tr>
<tr>
<td>NaI</td>
<td>3.236</td>
<td>0.300</td>
<td>9.79</td>
<td>10.79</td>
</tr>
<tr>
<td>KF</td>
<td>2.674</td>
<td>0.271</td>
<td>8.88</td>
<td>9.87</td>
</tr>
<tr>
<td>KCl</td>
<td>3.146</td>
<td>0.290</td>
<td>9.86</td>
<td>10.85</td>
</tr>
<tr>
<td>KBr</td>
<td>3.300</td>
<td>0.300</td>
<td>10.01</td>
<td>11.00</td>
</tr>
<tr>
<td>KI</td>
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<td>0.310</td>
<td>10.39</td>
<td>11.39</td>
</tr>
<tr>
<td>RbF</td>
<td>2.826</td>
<td>0.263</td>
<td>9.73</td>
<td>10.75</td>
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<tr>
<td>RbCl</td>
<td>3.291</td>
<td>0.284</td>
<td>10.57</td>
<td>11.59</td>
</tr>
<tr>
<td>RbBr</td>
<td>3.445</td>
<td>0.291</td>
<td>10.82</td>
<td>11.83</td>
</tr>
<tr>
<td>RbI</td>
<td>3.671</td>
<td>0.299</td>
<td>11.26</td>
<td>12.28</td>
</tr>
</tbody>
</table>

The cohesive energy \( E_{\text{coh}} \) per mole for a solid can be written as:

$$E_{\text{coh}} = -N_A U_0 \quad \ldots(14)$$

where \( N_A \) is the Avogadro number.

### 3 Results and Discussion

The results for the Born – model parameters in case of sixteen alkali halides are given in Table 1. On the basis of these parameters it is possible to make an assessment of the empirical Eqs (1) and (2) proposed by Verma and Bhardwaj\(^1\). The interatomic distance \( d \) in Eqs (1) and (2) is identical with \( r_0 \) in the Born-model formulation. Equations (12) and (14) give:

$$E_{\text{coh}} = \frac{N_A \alpha_M Z_1 Z_2 e^2}{r_0} \left( 1 - \frac{1}{n} \right) \quad \ldots(15)$$

whereas Eqs (13) and (14) give

$$E_{\text{coh}} = \frac{N_A \alpha_M Z_1 Z_2 e^2}{r_0} \left( 1 - \frac{\rho}{r_0} \right) \quad \ldots(16)$$

It is evident that Eqs (15) and (16) can lead to Eq. (1) only if it is assumed that \( n \) or \( r_0/\rho \) is constant universally for different types of solids. However, this is not true. Even within a family of alkali halides \( n \) and \( r_0/\rho \) change significantly from one crystal to the other (Table 1). From LiF to RbI, \( n \) changes from 6.44
to 11.26, and \( r_0/\rho \) from 7.43 to 12.28. For different types of families of solids, the variations in the values of parameters may be even larger.

Eq. (2) for the bulk modulus proposed by Verma and Bhardwaj\(^1\) reveals that bulk modulus changes with interatomic distance as \( r_0^{-3} \). On the other hand, the Born – model formulations for bulk modulus [Eqs (9) and (11)] do not reveal such an explicit dependence on \( r_0 \). Eqs (9) and (11) can be made to yield \( r_0^{-3} \) dependence for the bulk modulus only when the parameters satisfy the following relationships:

\[
\frac{n-1}{r_0} = c_1
\]

and

\[
\frac{1}{r_0} \left( \frac{r_0}{\rho} - 2 \right) = c_2 \]

These two conditions are same particularly when Eqs (9) and (11) are used to determine the parameters using the same value of bulk modulus for each solid based on the experimental data. \( n+1=r_0/\rho \) is obtained when Eqs (9) and (11) are compatible with each other. Thus Eqs (17) and (18) are also identical with each other (\( c_1 = c_2 \)). Figure 1 is the plot of \( n-1 \) versus \( r_0 \). Most of the points lie on the straight line revealing that Eqs. (17) and (18) are approximately valid. This would imply the approximate validity of Eq. (2) for the dependence of bulk modulus on \( d^{-3} \) or \( r_0^{-3} \). Since unit cell volume for a solid is directly proportional to \( r_0^{-3} \), this gives the simple results that the product of bulk modulus and volume remains nearly constant for a family of diatomic solids. Thus, it can be concluded that the Eqs (1) and (2) are the simplified results of the formulation based on the Born-model.

Values of cohesive energy and bulk modulus in case of NaCl under the effect of pressure have also been obtained and presented in Table 2. It is found that the exponential potential function gives better agreement with the available experimental data as compared to the inverse power form. The Born-model parameters are found to be independent of interatomic distance as judged from the comparison with the experimental \( P-V \) data\(^{20-22}\).

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### References