THE COHESIVE ENERGIES OF IONIC CRYSTALS
POSSESSING THE FLUORITE STRUCTURE

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ABSTRACT
The theoretical cohesive energies of the fluorides CaF$_2$, SrF$_2$, and BaF$_2$ are calculated using relationships based on the Born and Mayer model of an ionic crystal. The computed values of the theoretical cohesive energies are compared with the experimental values of the cohesive energies based on the Born-Haber cycle and thermochemical data.

INTRODUCTION
Using a theoretical approach, proposed by Born and Mayer (2), the cohesive energy of ionic crystals can be determined by summing the electrostatic energy, the first and second van der Waals energies, the repulsive energy and the zero-point energy. The theoretical cohesive energy, obtained using the Born and Mayer model, can be compared to an experimental value based on the Born-Haber cycle (4) and thermochemical data.

The idealized model of an ionic crystal consists of positive and negative ions having charges that are multiples of the electronic charge. The interaction between ions is assumed to be primarily electrostatic interactions between spherical charge distributions. The ions attract or repel one another by coulomb attraction of their charges. Attraction also occurs from the van der Waals interactions between the two ions resulting from the polarization of each ion in the field of the other. As the ions are brought closer together their outer electron shells begin to overlap and a characteristic repulsive force resists the overlap of the electron distributions with the neighboring ion cores. The repulsive force opposes the electrostatic attractive force and causes the ions to come to equilibrium at a finite value of the interionic distance. The ions form a stable crystal because the electrostatic attraction between unlike ions is larger than the repulsion between like ions. An additional energy term, referred to as the zero-point energy, can be obtained from the Debye limiting frequency.

THEORETICAL COHESIVE ENERGY EQUATIONS
The energy, $U_T$, for the formation of one mole of an ionic crystal may be expressed as

$$ U_T = U_e + U_{es} + U_{re} + U_R + U_z $$  (1)

where $U_e$ is the electrostatic energy term, $U_{es}$ and $U_{re}$ are the first and second van der Waals energy terms, $U_R$ is the repulsive energy term and $U_z$ is the zero-point energy term.

The electrostatic contribution to the cohesive energy is

$$ U_e = -Z^2e^4NAR^{-3} $$  (2)

where $Z$ is the largest common factor of the positive and negative ions, $e$ is the charge on the electron, $N$ is Avogadro's number, $A$ is the Madelung constant for the structure and $r$ is the separation between nearest neighbor ions in the structure.

The first and second van der Waals energy terms are given by the equations

$$ U_{es} = -ND_1R^{-6} $$  (3)

and

$$ U_{re} = -ND_2R^{-8} $$  (4)

where

$$ D_1 = 0.5(S_1^2S_2^2C_{++}^6 + S_2^2C_{--}^6) + S_4^2C_{+-}^6 $$  (5)

and

$$ D_2 = 0.5(S_1^2S_2^2C_{++}^8 + S_2^2C_{--}^8) + S_4^2C_{+-}^8 $$  (6)

The values of $S_1^2$, $S_2^2$, $S_4^2$, and $S_4^2$ for the fluorite structure, have been computed by Benson and Dempsey (1) and their values are given in Table I. The formulae for the constants $C_{ij}^6$ and $C_{ij}^8$ are given by Mayer (10) as

$$ C_{ij}^6 = \frac{2}{3} \alpha_i \alpha_j \left( \frac{p_i p_j}{p_i + p_j} \right) $$  (7)

and

$$ C_{ij}^8 = \frac{9}{4} \alpha_i \alpha_j \left( \frac{p_i p_j}{p_i + p_j} \right) $$  (8)

where $\alpha_i$ is the polarizability of the ion $i$, $e_i$ is an energy characteristic of the ion $i$, and $p_i$ is the effective number of electrons in the outermost shell and was taken as 5.5 after Huggins and Sakamoto (8).

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The repulsive term can be expressed as

$$ U_R = U_{1} + U_{2} + U_{3} + U_{4} $$  (9)

where

$$ U_1 = \frac{N \beta}{r_{+}} \ln \left( \frac{r_{+}}{r_{-}} \right) $$

$$ U_2 = 0.5 \beta \ln \left( \frac{r_{+}}{r_{-}} \right) $$

$$ U_3 = 0.5 \beta \ln \left( \frac{r_{+}^2}{r_{-}^2} \right) $$

$$ U_4 = 0.5 \beta \ln \left( \frac{r_{+}^4}{r_{-}^4} \right) $$

In these expressions $\beta = \exp (r_{+}/r_{-})$ and $\beta = \exp (r_{-}/r_{+})$, $n_{11}$ are the numbers of nearest neighbors of the positive and negative ions and $n_{-}$ is the number of next nearest
neighbors of the negative ion, \( v \) and \( v' \) are the charges on the positive and negative ions, \( \sigma_1 \) are the Pauling factors and \( k_1 \) and \( k_2 \) are constants for the structure. Born and Mayer (2) have shown that the repulsive parameters, \( b \) and \( \rho \), can be determined by solving the equations

\[ r_0 \left( \frac{dU_T}{dr} \right) r_0 = 5.7 V_m \alpha/\beta \]  
\[ r_0^2 \left( \frac{d^2 U_T}{dr^2} \right) r_0 = 9 V_m / \beta \]

where \( \beta \) is the compressibility, \( \alpha \) is the volume coefficient of expansion, \( V_m \) is the volume per molecule and \( r_0 \) is the separation of nearest neighbors at room temperature. A computer program was written to solve the set of equations (10) and (11), using a numerical method of iteration until the values of \( b \) and \( \rho \) were determined correct to four decimal places.

The zero-point energy is the energy of the lattice vibrations at absolute zero and is given by

\[ U_Z = 9 N \left( v' + v \right) \hbar \frac{\hbar}{\text{max} / 8} \]

where \( v' \) and \( v \) are the numbers of positive and negative ions per molecule and \( \text{max} \) is the Debye limiting frequency.

### Calculation of the Theoretical Cohesive Energy

The theoretical cohesive energy at absolute zero can be determined by summing the electrostatic energy term, the two van der Waals energy terms, the repulsive energy term and the zero-point energy term. The values of \( b \) and \( \rho \), determined from equations (10) and (11), were used to find the separation of nearest neighbors at absolute zero, \( r_{0} \), using the equation

\[ r_{0} \left( \frac{dU_T}{dr} \right) r_{0} = 0 \]

This separation of nearest neighbors at absolute zero was used in the calculation of the individual energy terms. The equations for the energy terms were programmed in the fortran language and the energies were computed using an IBM 1620 computer. All of the constants used in the calculations are shown in Table I. The Madelung constant for the fluorite structure was taken from Johnson and Templeton (9). Values of the calculated values of \( C_{66}^t \) and \( C_{66}^s \). The polarizabilities are due to Tessman, Kahn and Shockley (14), e. was taken as 0.75 of the third ionization potential of the positive ion after Mayer (10) and e. is due to Tousey (15). The values of each of the energy terms and the total theoretical cohesive energy, calculated in this work, for CaF\(_2\), SrF\(_2\), and BaF\(_2\), are summarized in Table IV and

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* Not calculated by Harries and Morris
** Included in \( U_{60} \) by Harries and Morris

parameters for CaF\(_2\), SrF\(_2\), and BaF\(_2\), used in the calculations, are given in Table II. The values of \( r_0 \) are from

\[ \text{Table II} \]

\begin{align*}
\text{CaF}_2 & \quad \text{SrF}_2 & \quad \text{BaF}_2 \\
\alpha & \quad 2.565 & \quad 2.560 & \quad 2.563 \\
\beta & \quad 1.17 & \quad 1.17 & \quad 1.17 \\
r_0(\text{A}) & \quad 1.05 & \quad 1.05 & \quad 1.05 \\
\rho_{60}(\text{cm}^3) & \quad 2.555 & \quad 2.683 & \quad 2.769 \\
10^{12} \sigma_{60}(\text{cm}^3) & \quad 61.64 & \quad 51.67 & \quad 42.66 \\
10^{12} \sigma_{60}(\text{cm}^3) & \quad 22.0 & \quad 22.0 & \quad 22.0 \\
10^{12} \sigma_{60}(\text{cm}^3) & \quad 44.25 & \quad 87.077 & \quad 186.616 \\
10^{12} \sigma_{60}(\text{cm}^3) & \quad 18.063 & \quad 25.533 & \quad 40.123 \\
10^{12} \sigma_{60}(\text{cm}^3) & \quad 9.505 & \quad 9.505 & \quad 9.505 \\
10^{12} \sigma_{60}(\text{cm}^3) & \quad 94.550 & \quad 250.216 & \quad 629.040 \\
10^{12} \sigma_{60}(\text{cm}^3) & \quad 24.640 & \quad 45.860 & \quad 85.503 \\
10^{12} \sigma_{60}(\text{cm}^3) & \quad 5.630 & \quad 5.630 & \quad 5.630 \\
\end{align*}
Calculation of the Experimental Cohesive Energy

The experimental cohesive energy can be obtained from thermochemical data by means of the Born-Haber (4) relationship

\[ U_{\text{exp}} = -\Delta H + L + D + I - 2E \]  \hspace{1cm} (14)

where \( \Delta H \) is the heat of formation of the solid fluoride, \( L \) is the heat of atomization of the metal, \( D \) is the dissociation energy of the fluorine, \( I \) is the sum of the first two ionization potentials of the metal and \( E \) is the electron affinity of fluorine. The experimental cohesive energies of \( \text{CaF}_2 \), \( \text{SrF}_2 \), and \( \text{BaF}_2 \) have been calculated by Sherman (13), designated (S), and Harries and Morris (7), designated (H.M.). The results of their work are shown in Table V together with the theoretical cohesive energies calculated by Froumokker (F) (6) and Harries and Morris (H.M.) for comparison.

Summary and Discussion

Using a method based on the Born and Mayer model (2) the theoretical cohesive energies, \( U_T \), of \( \text{CaF}_2 \), \( \text{SrF}_2 \), and \( \text{BaF}_2 \) were determined as \(-625.0\), \(-587.0\), and \(-553.3\) kcal per mole, respectively. The theoretical cohesive energies, calculated in this work, can be compared with the theoretical energies determined by Harries and Morris (7). For all three materials, the energies calculated by Harries and Morris are smaller than the energies computed in this work. The smaller energies obtained by Harries and Morris are due, in part, to holding \( \rho \) fixed at 0.3333 and using the separation of nearest neighbors at room temperature instead of at absolute zero. It may be noted from Table V that the experimental cohesive energies for \( \text{CaF}_2 \), \( \text{SrF}_2 \), and \( \text{BaF}_2 \), calculated by Harries and Morris, using the Born-Haber cycle, are \(-617\), \(-584\), and \(-549\) kcal per mole, respectively. For all three materials the theoretical cohesive energy is greater than the experimental cohesive energy. This is generally attributed to a departure from the ideal ionic bonding assumed in the Born and Mayer model. Deviation between the theoretical and experimental energies is an indication that the structure is not composed purely of spherically symmetrical ions, but that the bonds may have the character of electron-bond pairs.

LITERATURE CITED

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6. R. E. Froumokker, Marquette University, M.S. Thesis (1963)

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