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 interaction between spherical charge distributions. The ions attract or repel one another by coulomb interaction of their charges. Attraction also occurs from the van der Waals interactions between the 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 overlapping 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 internuclear 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

$$U_T = U_E + U_{D6} + U_{D8} + U_R + U_Z \tag{1}$$

where U_E is the electrostatic energy term, U_{D6} and U_{D8} 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

$$U_E = -Z^2 e^2 N A r^{-1} \tag{2}$$

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

$$U_{D6} = -N D_6 r^{-6} \tag{3}$$

and

$$U_{D8} = -N D_8 r^{-8} \tag{4}$$

where

$$D_6 = 0.5 \, (S_6''' C_{++}{}^6 + S_6'' C_{--}{}^6) + S_6' C_{+-}{}^6 \tag{5}$$

and

$$D_8 = 0.5 \, (S_8''' C_{++}{}^8 + S_8'' C_{--}{}^8) + S_8' C_{+-}{}^8 \tag{6}$$

The values of S_6', S_6'', S_6''' and S_8', S_8'', S_8''', 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

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

and

$$C_{ij}{}^8 = \frac{9 \, C_{ij}{}^6}{4 \, e^2} \left(\frac{\alpha_i e_i}{p_i} + \frac{\alpha_j e_j}{p_j} \right) \tag{8}$$

where α_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).

TABLE I

$N = 6.02472 \times 10^{23}$	$A = 5.03878$	$e = 4.80288 \times 10^{-10}$ e.s.u.
$V_+ = 1.0$	$V_- = 2.0$	$Z = 1.0$
$f_{++} = 1.5$	$f_{+-} = 1.125$	$f_{--} = 0.75$
$n_{++} = 12.0$	$n_{+-} = 8.0$	$n_{--} = 6.0$
$n'_{--} = 12.0$	$k_1 = 1.63299$	$k_2 = 1.15470$
$S_6' = 8.708806$	$S_6'' = 7.089124$	$S_6''' = 0.762218$
$S_8' = 8.157501$	$S_8'' = 4.395594$	$S_8''' = 0.253163$

The repulsive term can be expressed as

$$U_R = U_1 + U_2 + U_3 + U_4 \tag{9}$$

where

$$U_1 = N \, b \, v_+ \, b_+ \, b_- \, f_{+-} \, n_{+-} \exp(-r/\rho)$$

$$U_2 = 0.5 \, N \, b \, v_- b_-^2 \, f_{--} n_{--} \exp(-k_2 r/\rho)$$

$$U_3 = 0.5 \, N \, b \, v_- b_-^2 \, f_{--} n'_{--} \exp(-k_1 r/\rho)$$

$$U_4 = N \, b \, v_+ b_+^2 \, f_{++} n_{++} \exp(-k_1 r/\rho)$$

In these expressions $b_+ = \exp(r_+/\rho)$ and $b_- = \exp(r_-/\rho)$, n_{ij} 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, f_{ij} 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 ρ, can be determined by solving the equations

$$r_0 \; (dU_T/dr)r_0 = 3 \; T \; V_m \; \alpha/\beta \qquad (10)$$

and

$$r_0^2 \; (d^2U_T/dr^2)r_0 = 9 \; V_m/\beta \qquad (11)$$

where β is the compressibility, α 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 ρ 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

$$U_z = 9 \; N \; (v_+ {}^+ v_-) \; h \; \nu_{max}/8 \qquad (12)$$

where v_+ and v_- are the numbers of positive and negative ions per molecule and ν_{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 ρ, determined from equations (10) and (11) were used to find the separation of nearest neighbors at absolute zero, r_{oo}, using the equation

$$r_{oo} \; (dU_T/dr) \; r_{oo} = 0 \qquad (13)$$

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

TABLE II

	CaF$_2$	SrF$_2$	BaF$_2$
r_0 (Å)	2.365	2.509	2.683
r_+ (Å)	1.17	1.31	1.46
r_- (Å)	1.05	1.05	1.05
V_m (Å^3)	40.74	48.63	59.47
$10^5\alpha$(deg^{-1})	5.69	5.69	5.69
$10^{12}\beta$(dyne^{-1}cm^2)	1.23	1.61	1.97
$10^{13}\nu_{max}$(s^{-1})	0.99	0.74	0.59

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

Donnay and Nowack (5) and the values of r_+ and r_- are due to Pauling (11). The molecular volume was calculated from r_0, the compressibilities are due to Bridgman (3), the volume coefficient of expansion for the calcium salt has been measured by Sharma (12) and was assumed to have the same value for the other two salts. The values of ν_{max} were taken from Benson and Dempsey (1). The polarizabilities and energy characteristics of the crystals are shown in Table III with the

TABLE III

	CaF$_2$	SrF$_2$	BaF$_2$
$\alpha +$ (Å^3)	0.979	1.499	2.428
$\alpha -$ (Å^3)	0.759	0.759	0.759
$10^{12}e+$(erg)	61.54	51.67	42.66
$10^{12}e-$(erg)	22.0	22.0	22.0
$10^{60}C_{++}{}^6$(erg cm^6)	44.23	87.077	188.616
$10^{60}C_{+-}{}^6$(erg cm^6)	18.063	26.333	40.123
$10^{60}C_{--}{}^6$(erg cm^6)	9.505	9.505	9.505
$10^{76}C_{++}{}^8$(erg cm^8)	94.530	239.216	629.940
$10^{76}C_{+-}{}^8$(erg cm^8)	24.649	43.969	85.583
$10^{76}C_{--}{}^8$(erg cm^8)	5.630	5.630	5.630

calculated values of $C_{ij}{}^6$ and $C_{ij}{}^8$. 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

TABLE IV

	(CaF$_2$)		(SrF$_2$)		(BaF$_2$)	
	(F)	(H.M.)	(F)	(H.M.)	(F)	(H.M.)
r_0(Å)	2.365	2.360	2.509	2.505	2.683	2.679
r_+(Å)	1.17	1.17	1.31	1.31	1.46	1.46
r_-(Å)	1.05	1.05	1.05	1.05	1.05	1.05
r_{oo}(Å)	2.355	*	2.499	*	2.672	*
ρ(Å)	0.2962	0.3333	0.3218	0.3333	0.3292	0.3333
$10^{12}b$(erg mole^{-1})	1.1293	1.21	1.1021	1.13	1.0967	1.10
U_E (kcal mole^{-1})	-710.35	-708.7	-669.42	-667.9	-626.08	-624.4
U_{D6} (kcal mole^{-1})	-17.54	-21.5	-17.50	-19.3	-17.99	-18.8
U_{D8} (kcal mole^{-1})	-3.43	**	-3.80	**	-4.42	**
U_R(kcal mole^{-1})	103.08	116.8	100.73	103.2	93.32	91.1
U_Z (kcal mole^{-1})	3.19	3.1	2.58	2.4	1.90	2.3
U_T (kcal mole^{-1})	-625.0	-610.0	-587.6	-562.0	-553.3	-550.0

* Not calculated by Harries and Morris

** Included in U_{D6} by Harries and Morris

designated (F). Values of the energy terms calculated by Harries and Morris (7), designated (H.M.) are shown in Table IV for comparison.

CALCULATION OF THE EXPERIMENTAL COHESIVE ENERGY

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

$$U_{exp} = -\Delta H + L + D + I - 2E \qquad (14)$$

where ΔH 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 CaF_2, SrF_2, and 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 Frounfelker (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 CaF_2, SrF_2, and BaF_2 were determined as -625.0, -587.6 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 ρ 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 CaF_2, SrF_2, and 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.

TABLE V

(Values in kcal per mole)

	CaF_2	SrF_2	BaF_2
U_T (F)	-625.0	-587.6	-553.3
U_T (H.M.)	-610.0	-532.0	-550.0
U_{Exp} (H.M.)	-617.0	-584.0	-549.0
U_{Exp} (S)	-617.2	-580.2	-547.0

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