

## Interionic forces in AgF, AgCl and AgBr crystals

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**Abstract.** An interionic force model has been used in which the short range nearest neighbour and the next nearest neighbour repulsive interactions and the van der Waals' interactions are balanced by the long range electrostatic forces. The nearest neighbour and the next nearest neighbour interactions are derived from the overlap integrals for outer shell electrons. The van der Waals' interactions are estimated from the Slater-Kirkwood variational method. The cohesive energy, the bulk modulus and its pressure dependence for AgF, AgCl and AgBr crystals have been calculated and compared with experimental data.

**Keywords.** Alkali halides; overlap integrals; cohesive energy; bulk modulus.

### 1. Introduction

Silver halides particularly AgF, AgCl and AgBr crystallise in NaCl structure but are not as highly ionic as alkali halide crystals (Pauling 1960; Phillips 1970). Interesting deviations from alkali halide like behaviour have been found. The simple Born model of the cohesive energy, which is successful for alkali halides, does not work so well for silver halide crystals (Tosi 1964). This is because the contribution from the van der Waals' (VDW) interactions in silver halides seems to be quite large (Mayer 1933; Bakhshi *et al* 1977). The difference between low and high frequency dielectric constants in silver halides is larger than that observed in alkali halides (Lowndes and Martin 1969). The presence of outermost *d* electrons in Ag<sup>+</sup> ion seems to be responsible for the changing nature of chemical bond and anomalous behaviour in silver halide crystals.

In the present paper we derive the repulsive interactions in AgF, AgCl and AgBr directly from the values of overlap integrals for outer *s*, *p* and *d* electrons reported by Hayns and Calais (1972). It is evident from recent calculations based on Lowdin's LCAO method (Hayns and Calais 1972, 1973; Castman *et al* 1971; Calais *et al* 1971; Froman and Lowdin 1962; Mansikka and Bystrand 1966; Petterson *et al* 1967 that the next nearest neighbour (NNN) interactions are quite important. We therefore consider both the nearest neighbour (NN) and NNN interactions. In silver halides the VDW interactions also contribute significantly to the binding of these crystals (Bakhshi *et al* 1977). We have estimated the magnitude of these interactions using the variation method (Slater and Kirkwood 1931).

## 2. Method of analysis

The crystal energy of an ionic crystal can be written as

$$W = W_e + W_R + W_V, \quad (1)$$

$$\text{where } W_e = -a_M e^2/r. \quad (2)$$

$a_M$  is the Madelung constant and  $r$  is the NN separation. The repulsive energy can be related to the overlap integrals

$$W_R = C \lambda_{AB}, \quad (3)$$

$$\text{and also } W_R = C' (\lambda_{AB}/r). \quad (4)$$

$A$  and  $B$  correspond to two types of ions.  $C$  and  $C'$  are the constants of proportionality and  $\lambda_{AB}$  are the sum of the squares of overlap integrals given as follows (Hafemeister and Flygare 1965)

$$\begin{aligned} \lambda_{AB} = & 2[S^2(ns_i, n's_j) + S^2(ns_i, n'p_{\sigma j}) \\ & + S^2(np_{\sigma i}, n's_j) + S^2(np_{\sigma i}, n'p_{\sigma j}) \\ & + 2S^2(np_{\pi i}, n'p_{\pi j}) + S^2(nd_{\sigma i}, n's_j) \\ & + S^2(nd_{\sigma i}, n'p_{\sigma j}) + 2S^2(nd_{\pi i}, n'p_{\pi j})] \end{aligned} \quad (5)$$

where  $S$  is the overlap integral. The two forms for  $W_R$  have been proposed by Hafemeister and Flygare (HF) (1965) and Hafemeister and Zahrt (HZ) (1967), respectively. The factor  $r^{-1}$  in HZ form arises from the interaction of exchange charges and effective nuclear charges. The repulsive energy extended upto second neighbours can be written as follows (HF form)

$$W_R = C_{AB} \lambda_{AB} + C_{AA} \lambda_{AA} + C_{BB} \lambda_{BB}, \quad (6)$$

and (HZ form)

$$W_R = C'_{AB} \frac{\lambda_{AB}}{r_{AB}} + C'_{AA} \frac{\lambda_{AA}}{r_{AA}} + C'_{BB} \frac{\lambda_{BB}}{r_{BB}}. \quad (7)$$

For NaCl structure  $r_{AA} = r_{BB} = \sqrt{2} r_{AB}$ .  $\lambda_{AA}$  and  $\lambda_{BB}$  are the sums of the squares of the overlap integrals given as follows

$$\begin{aligned} \lambda_{AA} = & 2 [S^2 (ns_i, n's_j) + S^2 (ns_i, n'p_{\sigma j}) + S^2 (ns_i, n'd_{\sigma j}) \\ & + S^2 (np_{\sigma i}, n's_j) + S^2 (np_{\sigma i}, n'p_{\sigma j}) + S^2 (np_{\sigma i}, n'd_{\sigma j}) + \end{aligned}$$

$$\begin{aligned}
 & + 2 S^2 (np_{\pi i}, n'p_{\pi j}) + 2 S^2 (np_{\pi i}, n'd_{\pi j}) + S^2 (nd_{\sigma i}, n's_j) \\
 & + S^2 (nd_{\sigma i}, n'p_{\sigma j}) + S^2 (nd_{\sigma i}, n'd_{\sigma j}) + 2 S^2 (nd_{\pi i}, n'p_{\pi j}) \\
 & + 2 S^2 (nd_{\pi i}, n'd_{\pi j}) + 4 S^2 (nd\delta_i, n'd\delta_j)
 \end{aligned} \tag{8}$$

$$\begin{aligned}
 \lambda_{BB} = & 2 [S^2 (ns_i, n's_j) + S^2 (ns_i, n'p_{\sigma j}) \\
 & + S^2 (np_{\sigma i}, n's_j) + S^2 (np_{\sigma i}, n'p_{\sigma j}) \\
 & + 2 S^2 (np_{\pi i}, n'p_{\pi j})].
 \end{aligned} \tag{9}$$

Values of  $\lambda_{AB}$ ,  $\lambda_{AA}$  and  $\lambda_{BB}$  can be calculated from equations (5), (8) and (9) respectively, using the overlap integrals reported by Hayns and Calais (1972). In fact we can represent  $\lambda_{ij}$  in a mathematically convenient form as

$$\lambda_{ij} = a_{ij} \exp(-r_{ij}/\rho_{ij}). \tag{10}$$

Following the procedure adopted by HF (1965) we have computed  $\rho_{ij}$  for various ion pairs. These are given in table 1. Equation (10) holds well in the range  $r_{ij} \pm 0.5 \text{ \AA}$ . The constants  $C_{AB}$ ,  $C_{AA}$  and  $C_{BB}$  can be expressed in terms of ionic radii following the Born-Mayer treatment (Tosi 1964). We can thus obtain for HF form

$$\begin{aligned}
 W_R = & Mb \beta_{AB} \exp(r_A + r_B - r_{AB})/\rho_{AB} \\
 & + \frac{1}{2} M' b [\beta_{AA} \exp(2r_A - r_{AA})/\rho_{AA} + \beta_{BB} \exp(2r_B - r_{BB})/\rho_{BB}],
 \end{aligned} \tag{11}$$

and for HZ form

$$\begin{aligned}
 W_R = & \frac{Mb' \beta_{AB}}{r_{AB}} \exp(r_A + r_B - r_{AB})/\rho_{AB} \\
 & + \frac{1}{2} M' b' \left[ \frac{\beta_{AA}}{r_{AA}} \exp(2r_A - r_{AA})/\rho_{AA} + \frac{\beta_{BB}}{r_{BB}} \exp(2r_B - r_{BB})/\rho_{BB} \right].
 \end{aligned} \tag{12}$$

**Table 1.** Values of  $\rho_{AB}$ ,  $\rho_{AA}$  and  $\rho_{BB}$  in ( $\text{\AA}$ )

Crystal	$\rho_{AB}$	$\rho_{AA}$	$\rho_{BB}$
AgF	0.304	0.195	0.456
AgCl	0.344	0.188	0.472
AgBr	0.366	0.180	0.514

$M$  and  $M'$  are the numbers of NN and NNN respectively;  $b$  and  $b'$  are the repulsive energy parameters.  $\beta_{ij}$  are the Pauling coefficients expressed as

$$\beta_{ij} = 1 + (Z_i/N_i) + (Z_j/N_j), \quad (13)$$

where  $Z_i$  and  $Z_j$  are the valences and  $N_i$ ,  $N_j$  are the numbers of outermost electrons of  $i$  and  $j$  ions. The coefficients  $\beta_{ij}$  were introduced by Pauling (1960) to provide appropriate weightage for repulsive interactions between different ion pairs. The VDW energy can be written as (Tosi 1964).

$$W_V = (C/r^6) - (D/r^8), \quad (14)$$

where  $C$  and  $D$  are the dipole-dipole and the dipole-quadrupole coefficients respectively. The earlier methods (Mayer 1933; Lynch 1967) for determining  $C$  and  $D$  are expressed in terms of excitation energy parameters for ions. The evaluation of these quantities is subjected to considerable uncertainties (Jain *et al* 1976). An alternative approach, based on the Slater-Kirkwood (1931) variational method has recently been developed (Narayan 1977; Jai Shanker *et al* 1978) to evaluate  $C$  and  $D$ . The VDW coefficients can be expressed as (Narayan 1977)

$$C_{ij} = \frac{3}{2} \frac{e\hbar^2}{m^{\frac{1}{2}}} \frac{\alpha_i \alpha_j}{(\alpha_i/N_i)^{\frac{1}{2}} + (\alpha_j/N_j)^{\frac{1}{2}}}, \quad (15)$$

$$d_{ij} = \frac{27\hbar^2}{8m} \alpha_i \alpha_j \frac{[(\alpha_i/N_i)^{\frac{1}{2}} + (\alpha_j/N_j)^{\frac{1}{2}}]^2}{(\alpha_i/N_i) + 20/3 (\alpha_i \alpha_j / N_i N_j)^{\frac{1}{2}} + (\alpha_j/N_j)}. \quad (16)$$

$C$  and  $D$  are evaluated from  $C_{ij}$  and  $d_{ij}$  using the appropriate lattice sums (Tosi 1964). The resulting values of VDW coefficients and energies along with the input data are given in table 2.

Table 2. Input data and calculated values of van der Waals' coefficients and energies.

	AgF	AgCl	AgBr	Reference
$r$ (Å)	2.46	2.772	2.884	Slater (1965)
$r_A$ (Å)	1.26	1.26	1.26	Pauling (1960)
$r_B$ (Å)	1.133	1.648	1.909	Sysio (1969)
$\alpha_+$ (Å <sup>3</sup> )	2.40	2.48	2.44	Tessman <i>et al</i> (1953)
$\alpha_-$ (Å <sup>3</sup> )	0.876	2.87	3.69	Jaswal and Sharma (1973)
$N_+$	27	27	27	
$N_-$	8	17	22	
$C_{+-}$ (10 <sup>-60</sup> erg cm <sup>6</sup> )	82.2	251	319	
$C_{++}$ (10 <sup>-60</sup> erg cm <sup>6</sup> )	243	255	249	
$C_{--}$ (10 <sup>-60</sup> erg cm <sup>6</sup> )	29.2	252	419	
$d_{+-}$ (10 <sup>-76</sup> erg cm <sup>8</sup> )	40.1	137	173	
$d_{++}$ (10 <sup>-76</sup> erg cm <sup>8</sup> )	110	117	113	
$d_{--}$ (10 <sup>-76</sup> erg cm <sup>8</sup> )	14.6	157	259	
$C$ (10 <sup>-60</sup> erg cm <sup>6</sup> )	802	2114	2709	
$D$ (10 <sup>-76</sup> erg cm <sup>8</sup> )	296	952	1214	
$W_V$ (k cal./mole)	55.3	71.0	71.0	

Thus we determine electrostatic, repulsive and van der Waals' contributions to the crystal energy. The repulsive parameter  $b$  or  $b'$  in  $W_R$  (equations (11) and (12)) can be estimated employing the crystal equilibrium condition

$$dW/dr = 0. \quad (17)$$

We can now calculate the cohesive energy by adding all the three contributions  $W_e$ ,  $W_R$  and  $W_v$ . We have also calculated bulk modulus  $B_T$  and its pressure derivative using the following relations which can be derived from the Hildebrand (1931) equation of state

$$B_T = r^2 W''/9V, \quad (18)$$

$$dB_T/dp = 1 - (r^3 W'''/3r^2 W''), \quad (19)$$

where  $W''$  and  $W'''$  are the second and third order derivatives of the potential energy with respect to  $r$ .

### 3. Results and discussion

Values of cohesive energies for AgF, AgCl and AgBr calculated in the present work are compared in table 3 with the corresponding values based on experimental thermodynamic data. Theoretical values obtained by other workers have also been included in table 3. It is observed that the cohesive energies calculated from the HZ form are in better agreement with experiment than those obtained from the HF potential form. The cohesive energies obtained from the HZ potential form are also better than those estimated theoretically by previous investigators (Mayer 1933; Huggins 1951, Ladd and Lee 1958). A feature of the present calculations is that the bulk modulus is not used as input data as has been done by other workers (Mayer 1933; Huggins 1951; Ladd and Lee 1958). Instead, we have derived the repulsive hardness parameters from the values of overlap integrals. We can therefore extend our calculations to evaluate the bulk modulus  $B_T$  and its pressure dependence  $dB_T/dp$ . These quantities have been calculated and compared in table 4 with available experimental data. It is interesting that the HZ potential form again yields better agreement with experiment for  $B_T$  and  $dB_T/dp$ . Although the HZ form seems to be nearer the experimental results considered in the present study,

Table 3. Values of cohesive energy (in kcal/mole)

Crystal	Present study		Other workers			Experimental (Tosi 1964)
	HF Form	HZ Form	Ladd and Lee (1958)	Huggins (1951)	Mayer (1933)	
AgF	-221.2	-228.7	-217	-218	-216	-225.4
AgCl	-201.2	-209.9	-196	-201	-200	-213.6
AgBr	-192.2	-201.3	-192	-195	-194	-210.2

**Table 4.** Values of bulk modulus  $B_T$  (in  $10^{12}$  dynes/cm<sup>2</sup>) and its pressure derivative  $dB_T/dp$

Crystal	Bulk Modulus $B_T$			$dB_T/dp$		
	Present study HF form	HZ form	Experi- mental	Present study HF form	HZ form	Experi- mental
AgF	0.483	0.640	—	4.46	5.09	—
AgCl	0.307	0.435	0.440 <sup>a</sup>	4.10	4.98	6.55 <sup>a</sup>
AgBr	0.244	0.358	0.405 <sup>a</sup>	3.89	4.87	7.03 <sup>a</sup>

<sup>a</sup>Loje and Schuele (1970)

its overall superiority can be established by performing calculations like the pressure derivatives of elastic constants and dielectric constant of the crystals. It is pertinent to mention there that the Born-Mayer (BM) potential, which is similar to the HF potential, has been recently criticised by some workers (Puri 1977; Thakur 1973) that BM or HF repulsive potential does not tend to infinite as interionic distance tends to zero. However, the HZ potential form is free from this criticism.

Finally, the most striking feature in the present paper appears to be the fact that the hardness parameter  $\rho$  is very different for  $AA$ ,  $AB$  and  $BB$  pairs (table 1). The Born-Mayer theory, on the other hand, assumes a constant value of  $\rho$  for different pair interactions. This difference might be the main reason for the improved results obtained in this paper. The discrepancy still existing between our theoretical and experimental results can be ascribed to the presence of many body forces and partial ionic character of silver halides.

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