JOURNAL OF SOLID STATE CHEMISTRY **57**, 379–385 (1985)

A Theoretical Study on the Cohesive Properties of SrFCl and BaFCl

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Received July 5, 1984

Using an ionic model and partitioning the lattice energy into electrostatic, repulsive, and dispersive (van der Waals) contributions, the energetics of SrFCl and BaFCl, having PbFCl structure, are studied by varying the internal parameters. For the calculation a minimization procedure was used based on an expansion of the electrostatic energy in terms of all lattice parameters not fixed by symmetry. The lattice energies of SrFCl and BaFCl are found to be 2300.5 and 2178.5 kJ/mole and the Madelung constants of some isostructural crystals are reported. © 1985 Academic Press, Inc.

Introduction

In this paper the energetics of the mixed halide compounds SrFCl and BaFCl, having PbFCl structure, are studied on the basis of an ionic model. Although some of these compounds have been known for a long time, precise structural information has become available only during the last decade (*1–4*). SrFCl and BaFCl have been chosen for the present investigation, because for these crystals also elastic constants have been published (*5*) allowing an accurate determination of the repulsive energy.

First, the lattice energies of the two crystals were calculated using a minimization procedure (*6*) based on the expansion of the electrostatic energy in terms of the axial ratio and the internal parameters of the ions that are not fixed by symmetry (*7*). Such an expansion, giving the electrostatic energy as a function of all lattice parameters, can easily be used to calculate all the derivatives needed for the minimization and also to evaluate the Madelung constants of a series of isostructural crystals. From the calculated lattice energies the heats of solution, for infinite dilution, were evaluated for SrFCl and BaFCl.

The parametrization of the repulsive energy obtained for the equilibrium cell lengths was then used to calculate the total lattice energy and its components within the electrostatic model (i.e., the electrostatic, the repulsive, and the dispersive energies) as functions of the internal parameters of the alkaline earth and chloride ions. Plots of the resulting energy surfaces are presented which can help to get a qualitative understanding of the differences in the structural parameters between SrFCl and BaFCl. Furthermore, it is shown that the influence of changes of the ionic radii on the lattice parameters can be predicted correctly within this model.

Method of Calculation

The total lattice energy of the crystal is

0022-4596/85 $3.00

given by

$$U_{\mathrm{POT}} = U_{\mathrm{E}} - U_{\mathrm{R}} + U_{\mathrm{dd}} + U_{\mathrm{dq}}, \quad (1)$$

where U_{E}, U_{R}, U_{dd}, and U_{dq} are the electrostatic, the repulsive, and the dipole–dipole and dipole–quadrupole contributions to the dispersive energy, respectively.

The electrostatic energy of a tetragonal crystal with two internal lattice parameters, u_{M} and u_{X}, can be expanded as (*7*)

$$U_{\mathrm{E}}(a, c, u_{\mathrm{M}}, u_{\mathrm{X}}) = \frac{K}{a} \sum_{L} \left(\frac{c/a}{c_0/a_0} - 1\right)^{L} \sum_{l} \left(\frac{u_{\mathrm{M}}}{u_{0\mathrm{M}}} - 1\right)^{l} \sum_{l'} \left(\frac{u_{\mathrm{X}}}{u_{0\mathrm{X}}} - 1\right)^{l'} \times \left(\frac{c/a}{c_0/a_0}\right)^{l+l'} M_{\mathrm{a}}^{(l,l',L)}, \quad (2)$$

where the origin of the expansion is given by a_0, c_0, $u_{0\mathrm{M}}$, and $u_{0\mathrm{X}}$, the factor $K = 1389.30$ converts the units $\mathrm{e}^2\ \text{Å}^{-1}$/molecule into kJ/mole, and $M_{\mathrm{a}}^{(l,l',L)}$ are the coefficients that can be calculated according to Ref. (*7*).

For the repulsive part of the lattice energy the formula by Huggins and Mayer (*8*) is used

$$U_{\mathrm{R}} = \frac{b}{a} \sum_{k} \sum_{k'} C_{kk'} e^{(\bar{r}_{\mathrm{k}} + \bar{r}_{\mathrm{k'}})/\rho} \sum_{j} \exp(-|\mathbf{r}_j - \mathbf{r}_{\mathrm{k}} + \mathbf{r}_{k'}|/\rho), \quad (3)$$

where b is constant (10^{-12} erg/molecule) and

$$C_{kk'} = \left(1 + \frac{q_k}{p_k} + \frac{q_{k'}}{p_{k'}}\right), \quad (4)$$

q_k being the charge of the kth ion and p_k its electron number. The positions of the ions k and k' in the unit cell are defined by the vectors $\mathbf{r}_{\mathrm{k}}$ and $\mathbf{r}_{\mathrm{k'}}$ and their basic radii are designated by $\bar{r}_{\mathrm{k}}$ and $\bar{r}_{\mathrm{k'}}$. The repulsion constant ρ, the so-called hardness parameter, is obtained (*6*) from the compressibilities derived from the elastic constants (*5*).

The dispersive energy terms were computed in the usual way (see, e.g., Ref. (*9*)) from the polarizabilities and characteristic energies of the ions.

In the present case the equilibrium conditions used are

$$\left(\frac{\partial U_{\mathrm{POT}}}{\partial a}\right)_0 = 0; \left(\frac{\partial U_{\mathrm{POT}}}{\partial c}\right)_0 = 0;$$
$$\left(\frac{\partial U_{\mathrm{POT}}}{\partial u_{\mathrm{M}}}\right)_0 = 0; \left(\frac{\partial U_{\mathrm{POT}}}{\partial u_{\mathrm{X}}}\right)_0 = 0. \quad (5)$$

The subscript 0 indicates that the partial derivatives are calculated for the equilibrium lattice parameters.

The derivatives of the repulsive energy, and hence the unknown basic radii, can be derived from the equilibrium conditions (Eq. (5)), and from the calculable derivatives of the electrostatic and dispersive energies. In the present calculation two different variable basic radii were used for the chloride ion depending on which of the two nonequivalent *M*–Cl interactions were considered. In one case the metal ion lies just above (or below) the chloride ion (in the direction of the *c*-axis), in the other case the chloride ion is surrounded by four metal ions slightly above (or below) the *ab*-plane. For the Cl–Cl and the F–Cl interactions, whose contribution to the repulsive energy is only small, the mean value of the two basic radii was taken. In this way one allows for an unisotropic *M*–Cl repulsion due to the relatively high polarizability of the chloride ion.

The derivatives of the repulsive and dispersive energy contributions were calculated by differentiating the respective formulae by a, c, u_{M}, or u_{X} and by summing over the direct lattice until the required accuracy was obtained.

Results and Discussion

SrFCl and BaFCl crystallize in the PbFCl structure and have a tetragonal unit cell, shown in Fig. 1, which contains two formula units. A detailed discussion of the structure has been given by Beck (*3*, *10*).

Table I lists the data used for the present calculation. Table II shows the calculated coefficients $M_a^{(l,l',L)}$ for the PbFCl structure. The origin of the expansion was chosen such that the Madelung constants (or electrostatic energies) of most of the ionic compounds of this structural type can be calculated. For some of these compounds, for which accurate structural information is available, the Madelung constants M_a are displayed in Table III. Although they were evaluated using the expansion in Eq. (2), they are accurate to the number of figures given.

Table IV shows the calculated partial derivatives of U_E, U_{dd}, and U_{dq} together with the basic radii and the repulsion constant ρ for SrFCl and BaFCl. Of the two different basic radii for the chloride ion, $\bar{r}'_{Cl}$ is the one which parametrizes the M–Cl repulsion in direction of the c-axis. As can be seen from Table IV relatively large differences between the corresponding basic radii of SrFCl and of BaFCl occur. They can probably be explained by the fact that in the present investigation as many as four different basic radii were determined from the equilibrium conditions making their actual values strongly dependent on the parametrization and on the fortuitousness of the model without affecting the repulsive energy. It can be shown that basic radii similar to those obtained for SrFCl lead to the correct repulsive energy for BaFCl, but do not accurately satisfy the equilibrium conditions. Therefore the basic radii determined for these compounds should only be taken as parameters and should not be interpreted physically.

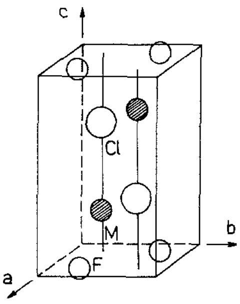

FIG. 1. The unit cell of SrFCl and BaFCl.

The lattice energies and calculated heats of solution, for infinite dilution, are listed in

TABLE I

DATA USED FOR THE CALCULATION OF THE LATTICE ENERGIES OF SrFCl AND BaFCl

Quantity			SrFCl	BaFCl	References and remarks
Lattice parameters	a	(Å)	4.1259	4.3939	(*1*)
	c	(Å)	6.9579	7.2248	
	u_M		0.2015	0.2049	
	u_X		0.6429	0.6472	
Elastic constants	c_{11}	(10^{11} dynes/cm^2)	10.61	9.08	(*5*)
	c_{12}		3.32	2.67	
	c_{13}		4.58	4.16	
	c_{33}		8.29	6.00	
Polarizabilities	$\alpha_{M^{2+}}$	(Å^3)	0.86	1.55	(*11*)
	α_{F^-}		1.04	1.04	
	α_{Cl^-}		3.66	3.66	
Characteristic energies	$\varepsilon_{M^{2+}}$	(10^{-12} erg)	62.9	51.2	**90% of ionization potential**
	ε_{F^-}		18.5	19.0	RbF, CsF (*12*)
	ε_{Cl^-}		15.7	16.0	RbCl, CsCl (*12*)

TABLE II

COEFFICIENTS $M_a^{(l,l',L)}$ FOR THE PbFCl Structure[a]

L	l	l'	$M_a^{(l,l',L)}$
0	0	0	7.634339
	0	1	0.813896
	1	0	−0.607068
	0	2	−4.315437
	1	1	−8.916691
	2	0	−1.489188
	0	3	−30.851020
	1	2	−10.731583
	2	1	−4.487238
	3	0	−0.117651
	0	4	56.124560
	1	3	−14.666764
	2	2	5.475761
	3	1	−1.253184
	4	0	0.520463
1	0	0	−2.489538
	0	1	8.460584
	1	0	−0.156167
	0	2	−20.534523
	1	1	14.373137
	2	0	−0.426342
	0	3	28.459073
	1	2	−11.467240
	2	1	3.543648
	3	0	0.416445
2	0	0	0.657629
	0	1	−4.938556
	1	0	1.224370
	0	2	65.157410
	1	1	−23.248469
	2	0	6.797078
3	0	0	−3.268922
	0	1	0.720309
	1	0	−1.853634
4	0	0	5.047900

[a] $c_0/a_0 = 1.70$, $u_{0M} = 0.19$, $u_{0X} = 0.65$.

Table V. The enthalpies for the process $MFX \rightarrow M^{2+} + F^- + X^-$, at standard temperature, were calculated using the estimated values of $H_{298}^\circ - H_0^\circ = 14$ and 15 kJ/mole for SrFCl and BaFCl, respectively. The lattice energies, which have not been calculated before for these crystals, lie in between the theoretical or thermochemically derived values for SrF_2 and $SrCl_2$, and for BaF_2 and $BaCl_2$, respectively (*13*).

TABLE III

MADELUNG CONSTANTS M_a FOR SOME COMPOUNDS HAVING PbFCl STRUCTURE

	c/a	u_M	u_X	Ref.	M_a
CaFCl	1.7509	0.1962	0.6432	(*2*)	7.52920
SrFCl	1.6864	0.2015	0.6429	(*1*)	7.61002
SrFBr	1.7394	0.18594	0.64791	(*3*)	7.58553
BaFCl	1.6443	0.2049	0.6472	(*1*)	7.66353
BaFBr	1.6506	0.1911	0.6497	(*2*)	7.70363
	1.6511	0.19229	0.64952	(*3*)	7.69897
BaFI	1.7108	0.1704	0.6522	(*2*)	7.67168

The calculated values of the heats of solution are certainly not very accurate, because they are relatively small quantities compared with the lattice energies and the heats of solvation. However, since experimental values have not yet been published, they are included in the present paper.

The parameters of Table IV were used to calculate U_E, U_R, U_D $(=U_{dd} + U_{dq})$, and the total lattice energy as functions of the

TABLE IV

PARTIAL DERIVATIVES OF THE ELECTROSTATIC AND DISPERSION ENERGIES (kJ/mole/Å), BASIC RADII, AND REPULSION CONSTANTS ρ (Å)

	SrFCl	BaFCl
$(\partial U_E/\partial a)_0$	−405.522	−365.609
$(\partial U_E/\partial c)_0$	−127.819	−113.037
$(\partial U_E/\partial u_M)_0$	−1199.327	−1259.199
$(\partial U_E/\partial u_X)_0$	143.170	−82.729
$(\partial U_{dd}/\partial a)_0$	−76.469	−76.179
$(\partial U_{dd}/\partial c)_0$	−22.793	−23.262
$(\partial U_{dd}/\partial u_M)_0$	−70.755	−82.375
$(\partial U_{dd}/\partial u_X)_0$	−1.502	12.495
$(\partial U_{dq}/\partial a)_0$	−11.128	−12.869
$(\partial U_{dq}/\partial c)_0$	−3.324	−3.912
$(\partial U_{dq}/\partial u_M)_0$	−12.235	−18.797
$(\partial U_{dq}/\partial u_X)_0$	−3.377	−0.537
$\bar{r}_M$	1.1561	1.7023
$\bar{r}_F$	1.2062	0.8222
$\bar{r}_{Cl}$	1.4823	1.1825
$\bar{r}'_{Cl}$	1.5734	1.2584
ρ	0.31993	0.33930

TABLE V

CALCULATION OF THE LATTICE ENERGIES AND HEATS OF SOLUTION OF SrFCl AND BaFCl (kJ/mole)

	SrFCl	BaFCl	Ref.
U_E	2562.5	2423.1	
U_R	349.6	339.0	
U_{dd}	79.0	83.8	
U_{dq}	8.6	10.6	
U_{POT}	2300.5	2178.5	
$\Delta H(MFX \rightarrow M^{2+} + F^- + X^-)$	2305.1	2182.1	
$\Delta H^0_{hyd}(M^{2+})$	−1520.9	−1378.6	*(14)*
$\Delta H^0_{hyd}(F^-)$	−474.0	−474.0	*(14)*
$\Delta H^0_{hyd}(Cl^-)$	−340.2	−340.2	*(14)*
$\Delta H^0_{solu}(MFX)$	−30.0	−10.7	

internal parameters u_M and u_X. The plots of the energy surfaces thus obtained are shown in Fig. 2 for SrFCl and in Fig. 3 for BaFCl.

This investigation is intended to supplement the one by Beck *(10)* where only the electrostatic energy was taken into account. In agreement with his results, the electrostatic energy does not shown a maximum but, neglecting the other energy terms, u_X would become larger and u_M smaller, so that the most favorable arrangement (keeping c/a constant) would be the one where both the alkaline earth and the chloride ions lie in the layer formed by the fluoride ions. One also notices that for the experimentally found internal parameter u_M the electrostatic energy is almost independent of u_X showing that this parameter is not at all determined by electrostatic interactions, especially with regard to the fact that the variations in u_X are much less pronounced than the variations in u_M if a series of isostructural compounds is considered.

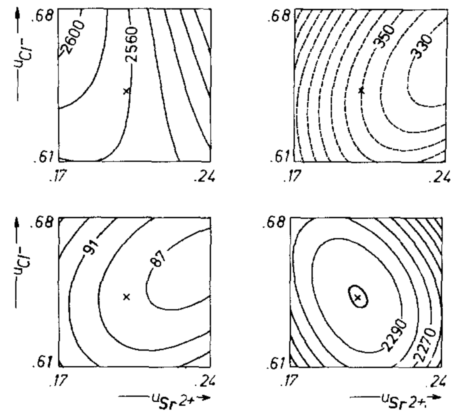

FIG. 2. Contour plots of the electrostatic energy (top left), the repulsive energy (top right), the dispersive energy (bottom left), and the total lattice energy (bottom right) of SrFCl as functions of the internal parameters u_{Sr} and u_{Cl}.

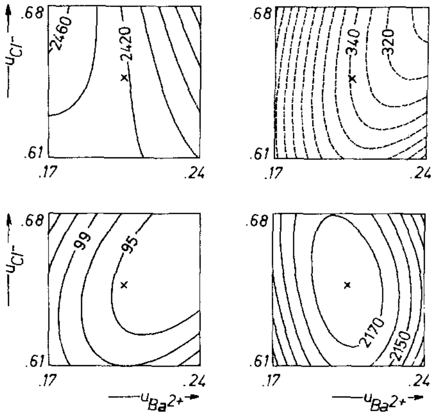

FIG. 3. Contour plots of the electrostatic energy (top left), the repulsive energy (top right), the dispersive energy (bottom left), and the total lattice energy (bottom right) of BaFCl as functions of the internal parameters u_{Ba} and u_{Cl}.

An inspection of the plots reveals that for the repulsive energies the situation is different: the repulsion has a minimum for u_M and u_X both larger than the experimental values. Going from SrFCl to BaFCl one sees that the minimum in the repulsion moves to larger values of u_M and u_X, an effect which, to a smaller extent, is also recognized in the internal parameters determined experimentally. The general appearance of the repulsive energy surface is easy to understand: The cation–fluoride ion interaction represents the largest contribution and the cation–chloride ion interaction the second largest contribution to the overall repulsion, whereas the chloride–fluoride interaction is smaller by about an order of magnitude. Therefore, considering the repulsion on its own, the chloride ions are pushed toward the (nearest) fluoride layer while the alkaline earth ions are pushed away from it. These effects are more pronounced for BaFCl than for SrFCl, because the metal–halide repulsion decreases compared with the other repulsions going from the Ba to the Sr salt.

The dispersive energy only contributes less than 10% of the total lattice energy and, in a qualtitative discussion, its influence on u_M and u_X is therefore relatively unimportant.

U_{POT}, of course, shows a maximum for the experimental internal parameters, since it was assumed, right from the beginning, that the cations and the chloride ions be in their equilibrium positions.

As can be seen from Fig. 2 for SrFCl and from Fig. 3 for BaFCl, the positional parameter for the chloride ion is mainly determined by a minimum in the repulsive energy (for constant u_M), whereas electrostatic and repulsive interactions are almost equally important for the equilibrium position of the metal ion.

In an earlier stage of the work only the two equilibrium conditions

$$\left(\frac{\partial U_{POT}}{\partial a}\right) = 0; \left(\frac{\partial U_{POT}}{\partial c}\right) = 0$$

were taken and a fixed value for the basic radius of the cation was assigned. The basic radii of fluorine and chlorine were determined by the equilibrium conditions. The interesting result was that, assuming a spherical chloride ion, it was impossible to get a maximum of U_{POT} at or even near the experimental internal parameters. The cation–chloride ion repulsion in direction of the c-axis was found to be too small compared with the other cation–chloride interactions which can be explained by assuming the chloride ion to be elongated by polarization effects in direction of the c-axis. Taking into account that the present calculation only allows for a distortion of the chloride ion, this finding corresponds to what Beck (*3*) describes as a movement of the cation out of the electrostatic center of the coordination polyhedron in the positive c-direction which was correlated by him with the product of the polarizabilities $\alpha_M \alpha_X$.

Finally, the influence of an increase or a decrease of a particular basic radius on the first derivatives of the lattice energy was studied. In such a way one can simulate the effect caused by replacing an ion of the crystal by a larger or smaller ion. If one takes, e.g., BaFCl and replaces $\bar{r}_{Ba}$ = 1.7023 by 1.50, it is found that all four lattice parameters (a, c, u_M, and u_X) become smaller, a behavior which is actually found if one goes from BaFCl to SrFCl. On the other hand, if the chloride basic radius of BaFCl is increased by 10% the result is that a, c, and u_X become larger and u_M decreases which again is confirmed experimentally if chlorine is substituted by bromine or by iodine.

It is hoped that the present investigation of the mixed halide compounds SrFCl and BaFCl demonstrates the usefulness of the expansion of the electrostatic energy in terms of the lattice parameters. This technique facilitates the interpretation of the stability of ionic and molecular crystals insofar as the electrostatic interactions for a whole series of isostructural compounds can be described with a single set of parameters which can be readily computed.

In a recent paper by Sieskind and Ayadi (*15*) Madelung constants and cohesive energies of a series of compounds with PbFCl structure, including SrFCl and BaFCl, are given. Their results are in good agreement with the present investigation taking into account that different models for the repulsive interactions have been used and that dispersive energies are not considered in Ref. (*15*).

Acknowledgments

The author is grateful to Professor A. Neckel for many helpful discussions and to Dr. J. Redinger for the preparation of the computer plots.

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