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Structural Considerations and Polarization Energy of Some PbFCl-Type Compounds

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Some ionic compounds *MXY* of the matlockite family (PbFCl) are characterized by the symmetry of the anions *X* and *Y* surroundings. If the cage around the ions *X* and *Y* are regular, the crystal is said to be "regular" and these conditions of symmetry give four equations adequate to compute the lattice parameters. Moreover, the symmetries play a decisive part on some physical properties because they are at the origin of electronic distorsions that produce dipolar moments. More precisely, it should be mentioned that *X* has no dipolar moment because the field acting on *X* is zero and that only the cation *M* and the anion *Y* may have dipolar moments. Both the interactions of the induced moments as well as the polarization energy contribute to stabilize the lattice. Relations between local symmetries and polarization energy and its variation with pressure will be investigated. In the case of PbFI, with an increase in pressure the ion I moves in the cell which becomes more regular. At the same time, opposite variations of the fields and of the induced moments on the ions I and Pb occur so that the polarization energy decreases. This effect is only observable with the highly polarizable ion I and is negligible for Cl.

INTRODUCTION

Ionic mixed halide crystals of the tetragonal PbFCl-type structure with the space group $P4/nmm$ (D_{4h}^7, no. 129) (Fig. 1) form a wide family of ternary compounds MXY, where M is a metal and X and Y are the anions. This study concerns only some fluoro-halide compounds. Their crystallographic data a, c, e $(=c/a)$, $z(M)$ and $z(Y)$ are summarized in Table 1 (1). The atomic positions are X at 000 and 1/2, 1/2, 0; M at 0 1/2 $z(M)$ and 1/2 0 $\bar{z}(M)$; and Y at 0 1/2 $z(Y)$ and 1/2 0 $\bar{z}(Y)$. Both in the matlockite (PbFCl) and in the fluorite (CaF_2) structures, each ion X is surrounded by M_4X tetrahedron of M ions. In the matlockite, ionic layers perpendicular to the C_4 axis contain these tetrahedra sandwiched between a double layer of Y ions. Each atom Y is located in the cavity of the metallic adjacent layer which forms the square base of the surrounding M_5Y pyramid. Moreover two adjacent pyramids are top to bottom (2).

Haberkorn (1) has given a qualitative hard-sphere model (HSM) which explains the structural characteristics of most fluoro-, hydro-, and oxide-halides, except a number of compounds including PbFI which will be the subject of a special study.

In another way Beck (3) and Haberkorn (1) argued about an electronic deformation of the ions Y owing to the displacement of the ions M along C_4. The extra cohesive energy due to the interaction of the induced dipoles can contribute to the stabilization of some crystals, particularly PbFI.

As a matter of fact, Bertaut (5) has pointed out that the interaction energy between charges and induced dipoles stabilizes the structure and that this energy can also be at the origin of displacive transitions.

More generally, if an ion shifts from a more symmetrical surrounding to a less symmetrical one, i.e. if the crystal becomes less "regular", then the induced moment of the ion increases. The polarization energy increases consequently and reinforces the structural stability.

In this respect the influence of the polarization energy in the compounds of the matlockite family is more complicated. Indeed two opposite effects which are linked to the shift of the ion Y are active. The effects are especially well illustrated in the case of PbFI when it is submitted to external stresses. Then the ion I takes up a more symmetrical position. This has for consequence the decrease of the polarization energy. But at the same time the electrical field and the moment induced by the I ions on the Pb ions increase because in the Pb cage all the distances between I and Pb tend to become the same. Then the polarization energy tends to increase.

Finally, on account of the polarizabilities, the effect on I surpasses the effect on Pb and the polarization energy diminishes.

At normal pressure, the shift of I induces a stabilizing polarization energy of the order of 100 kJ mol^{-1}, which is

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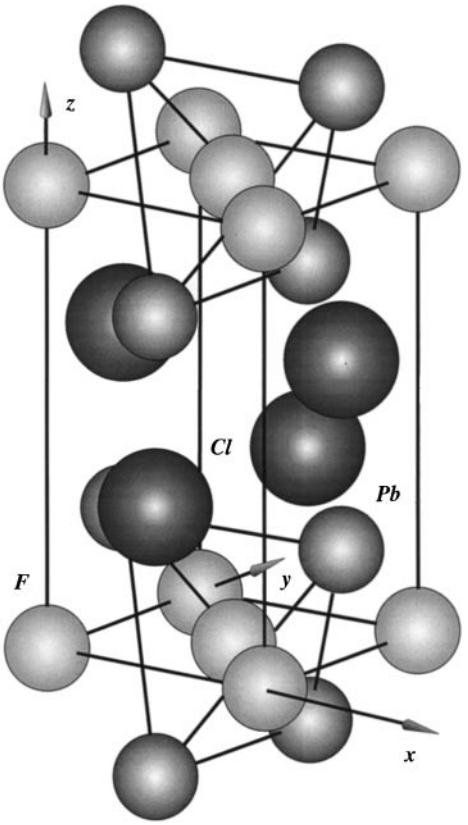

FIG. 1. Structure of the matlockite (PbFCl) with F in 000, 1/2, 1/2, 0; Pb in 0, 1/2, z(Pb), 1/2, 0, $\bar{z}$(Pb); Cl in 0, 1/2, z(Cl), 1/2, 0, $\bar{z}$(Cl); z(Pb) = 0.204, and z(Cl) = 0.648.

higher than the energy which would appear in the "regular" crystal.

In these conditions the total lattice energies including the polarization energy are computed for a number of ionic crystals, on the basis of a classical ionic model. Such calculations taking into account the electrostatic, repulsive and dispersive energies have been given for several compounds, namely SrFCl and BaFCl (4). But until now the polarization energy which can stabilize the crystal has been disregarded in these crystals, but its stabilizing role has been emphasized previously by Bertaut (5).

Let us notice, however, that for the two crystals above, the contribution of this energy plays an unimportant role, as we shall see later (Table 2).

The Coulomb contributions are evaluated with the method of Bertaut (6) in the parabolic approximation. Moreover, the accurate structural data allow to follow the variations with the pressure (up to 5 GPa) of crystallographic parameters and consequently of the various energies for the typical cases of BaFCl and PbFI (7).

As a complement, the entropy of SrFCl and BaFCl has been computed in two separate ways and a Grüneisen constant has been assigned to BaFCl, PbFCl, and PbFBr.

In the second part the relations between the geometrical properties of the crystals and the polarization energy are analyzed.

Firstly, by direct inspection, the point groups of the sites (8) furnish the non-zero components of the Coulomb field acting on the ions. Then a relation between e and $z(M)$ is established if the tetrahedron around X is completely symmetrical. The equidistance between the atom Y and the atoms M which belong to the coordination polyhedron of Y leads to another relation between $z(Y)$, $z(M)$, and e. This relation agrees generally for the fluoro-halides with a low polarization energy. If both relations are fulfilled then all the electrostatic energies depend solely on the parameter e.

In a given crystal the four relations of ionic contiguity and compactness give as many relations as unknown crsytallographic parameters following the construction of a "regular" crystal.

In the last part, the various energy terms of a number of compounds are examined and compared. Most of the discussion is devoted to BaFCl and PbFI because in these cases it is easy to correlate the different energies, especially the polarization energy, with the crystallographic data for pressures increasing up to 5 GPa and to support it stabilizing contribution.

I. LATTICE ENERGY, ENTROPY, AND MODE GRÜNEISEN PARAMETERS

The classical total lattice energy U_{pot} is given by the sum of several contributions (9):

$$U_{\text{pot}} = U_{\text{M}} - U_{\text{R}} + U_{\text{dd}} + U_{\text{dq}} + U_{\text{zp}} + U_{\text{pol}} + U_{\text{cr}} + (PV), \quad [1]$$

where U_{M}, U_{R}, U_{dd}, U_{dq}, U_{zp}, U_{pol}, U_{cr}, and (PV) are electrostatic, repulsive, dipole–dipole, dipole–quadrupole, zero point, polarization, creation of multipoles (dipoles, quadrupoles, etc.), and mechanical energies, respectively. The sum of the dipole–dipole and dipole–quadrupole energies is called the dispersive energy U_{d}.

1. Methods of Calculation

The field strength, the electrostatic and polarization energies have been derived by means of the Bertaut (6) formulae in the parabolic approximation. The dipolar and polarization energy have the same (negative) sign. Polarizability values of Tessman *et al.* (10) were used. For the repulsive part of the lattice energy the formulae by Narajan and Ramaseshan (11) have been used and have been given in a previous paper (4). Only the nearest neighbors of the ions in the unit cell are taken into account. The advantage of this approach is that the same repulsion parameters can be used for ions under different pressures. The dispersive energy

TABLE 1
Experimental and Computed Parameters of MFX Crystals

Compound	a (Å) (1)	c (Å) (1)	e (1)	$z(Y)$ (1)	$z(M)$ (1)	$z(M)e$	α	$d(MY_a)$ (Å)	$r_M + r_Y$ (Å)	$\delta = d(SY_c) - d(MY_a)$ (Å)	$a^{(i)}$ (Å)	$c^{(i)}$ (Å)	$z^{(i)}(Y)$	$z^{(i)}(M)$	$e^{(i)}$
CaFCl	3.894	6.818	1.75	0.6432	0.1962	0.343	34.45	2.963	2.89	0.08	3.853	6.577	0.646	0.207	1.70
CaFBr	3.883	8.05	2.07	0.67	0.17	0.35	35.0	3.033	3.03	1	—	7.079	0.619	0.192	1.83
SrFCl	4.129	6.958	1.68	0.6429	0.2015	0.338	34.05	3.111	3.02	− 0.04	4.066	6.819	0.652	0.21	1.67
SrFBr	4.218	7.337	1.74	0.6479	0.1859	0.323	32.86	3.222	3.16	0.16	—	7.346	0.624	0.195	1.80
SrFI	4.253	8.833	2.07	0.657 (estim.)	0.167 (estim.)										
BaFCl	4.391	7.225	1.64	0.6472	0.2049	0.336	33.90	3.285	3.19	− 0.09	4.343	7.122	0.662	0.215	1.64
BaFBr	4.503	7.441	1.65	0.6495	0.1923	0.315	32.21	3.400	3.33	0.01	—	7.687	0.631	0.199	1.77
BaFI	4.654	7.962	1.71	0.6522	0.1704	0.291	30.2	3.581	3.54	0.25	—	8.371	0.605	0.183	1.92
SmFCl	4.133	6.99	1.69	0.6446	0.2051	0.346	34.58	3.109	2.86	− 0.04	3.804	6.52	0.644	0.206	1.71
EuFCl	4.118	6.969	1.69	0.646	0.199	0.343	34.45	3.106	3.02	0.01	4.066	6.82	0.653	0.21	1.67
YbFCl	3.94	6.825	1.73	0.6436	0.2023	0.35	35.0	2.973	2.93	0.04	3.919	6.652	0.648	0.208	1.69
PbFCl	4.110	7.230	1.75	0.65	0.205	0.36	35.75	3.099	3.08	0.15	4.164	6.928	0.656	0.212	1.66
PBFBr	4.190	7.591	1.81	0.65	0.195	0.353	35.22	3.18	3.22	0.27	—	7.467	0.628	0.197	1.79
PbFI	4.238	8.80	2.07	0.657	0.167	0.346	34.68	3.36	3.43	0.95	—	8.133	0.602	0.181	1.95

terms U_{dd} and U_{dq} have been calculated in the usual way (12) from the characteristic energies and polarizabilities of the ions.

For the sake of completeness the entropy S for SrFCl and BaFCl has been computed from the data of the phonon density of states (13):

$$S = 3nN_A k \int_0^{\omega_L} \left\{ \frac{\hbar\omega}{2kT} \coth \frac{\hbar\omega}{2kT} - \ln\left[2 \sinh \frac{\hbar\omega}{2kT} \right] \right\} \times g(\omega) \frac{d\omega}{2\pi}. \quad [2]$$

In this expression n is the number of atoms in the chemical formula, N_A is the Avogadro number, $\hbar$ is the Planck constant h divided by 2π, k is the Boltzmann constant, T is the temperature in degrees Kelvin, ω is the phonon frequency, ω_L is the maximum lattice vibrational frequency, and $g(\omega)d\omega$ is the fraction of frequencies in the interval $(\omega, \omega + d\omega)$. These computed values are in good agreement with the thermochemical values estimated from the entropy contributions of the ions in solid compounds (14, 15). Encouraged by this, the thermochemical entropies of a number of other compounds of the matlockite were determined (16).

TABLE 2
Computed Energies, Electric Fields, and Moments of MFX Crystals

Compound	U_M (kJ mol^{-1})	U_R (kJ mol^{-1})	U_d (kJ mol^{-1})	U_{pol} (kJ mol^{-1})	U_{pot} (kJ mol^{-1})	$T\Delta S$ (kJ mol^{-1})	M	$E(M)$ (V Å^{-1})	$E(Y)$ (V Å^{-1})	Moment $\mu(M)$ (D)	Moment $\mu(Y)$ (D)
CaFCl	2701.1	369.6	89.1	11.7	2431.7	48.2	7.5709	1.386	0.855	0.50	0.84
CaFBr	2663.7	373.5	126.7	62.3	2479.2	48.1	7.445	1.566	1.741	0.57	2.41
SrFCl	2570.1	332.6	88.3	6.6	2323.9	48.1 44.5*	7.638	1.071	0.452	0.57	0.44
SrFBr	2517.0	345.0	138.2	16.6	2319.6	47.9	7.642	1.203	0.933	0.64	1.29
BaFCl	2431.4	327.8	90.1	7.1	2193.8	48.8 44.4*	7.6848	0.902	0.225	0.75	0.22
BaFBr	2383.4	331.5	139.8	7.4	2193.3	48.9	7.725	0.903	0.47	0.75	0.65
BaFI	2312.3	335.4	77.6	22.0	2071.4	47.8	7.7461	0.961	0.90	0.49	1.93
SmFCl	2560.2	—	—	10.4	—	—	7.6165	1.097	0.504	0.91	0.49
YbFCl	2668.9	—	—	10.8	—	—	7.569	1.321	0.68	0.70	0.67
PbFCl	2544.0	393.6	231.0	28.0	2403.8	47.4	7.5207	1.21	1.166	1.97	1.15
PbFBr	2499.3	413.2	335.3	40.8	2458.2	47.3	7.5302	1.441	1.338	2.35	1.85
PbFI	2423.5	398.8	209.7	99.0	2330.1	46.2	7.3806	1.135	1.82	1.85	3.90

*Computed from the phonon density of states.

2. Results

Table 2 shows the computed values for U_{pot}, U_M, U_R, U_d, U_{pol}, $T\Delta S$, M (Madelung constant), $\vec{E}$ (electrostatic field at a site), and $\vec{\mu}$ (induced dipole moment) of some fluorohalides. Madelung constants and cohesive energies of SrFCl and BaFCl are in good agreement with earlier investigations (4).

The field $\vec{E}$ is zero on the X ions and is collinear to the C_4 axis for the Y and M ions. The discrepancies with calculations by Weenk and Harwig (17) of $\vec{E}$ of PbFCl and PbFBr arise from the initial crystallographic data which are used in the various computations.

For a number of compounds, namely the iodides, the extra cohesive energy due to the induction of dipoles is not negligible and contributes to stabilize the structure. It seems instructive to follow the change with the pressure of the polarization energy and of the Helmholtz free enthalpy G of BaFCl and PbFI (Table 3). The entropy expression $T\Delta S^{(0)}$ remains approximately invariable and equal to 50 kJ mol^{-1} for the fluorides. The magnitude of the pressure correction to S has been calculated (18) through the Maxwell relationship,

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p. \qquad [3]$$

It is negligible for BaFCl up to 6 GPa. We will allow that the same holds true for PbFI. The values of the mode Grüneisen parameters γ,

$$\gamma = \left(\frac{\partial \ln \nu_j}{\partial \ln V}\right)_T, \qquad [4]$$

related to the vibrational frequency ν_j of the jth oscillator have been calculated for PbFCl and PbFBr (19). For BaFCl, the thermodynamic Grüneisen parameter γ_{th} is given by (15)

$$\gamma_{th} = \frac{\alpha_t V}{\chi C_V}, \qquad [5]$$

where α_t is the thermal expansivity calculated from (17), χ is the compressibility (20), and C_V is the heat capacity (21).

All the results are summarized in Table 4.

II. STRUCTURAL INVESTIGATIONS

The electric fields which induce the dipoles at the various nuclei depend on the site symmetries the effects of which are at first applied to the ions X and Y. Then some expressions which depend on the symmetry of the coordination polyhedra around X and Y are established. Finally, "regular"

TABLE 3
Variation with the Pressure of Crystallographic Parameters, Energies, Fields, and Moments of BaFCl and PbFI

Compound	P (GPa)	a (Å) (1)	c (Å) (1)	e (1)	$z(Y)$ (1)	$z(M)$ (1)	$d(MY_a)$ (Å)	$d(SY_c)$ (Å)	$\delta = d(SY_c) - d(MY_a)$ (Å)	$z(M)e$	α	$z(Y)$ rel. (15)	U_M (kJ mol^{-1})	U_R (kJ mol^{-1})	U_d (kJ mol^{-1})	U_{pol} (kJ mol^{-1})	U_{pot} (kJ mol^{-1})	M	$E(M)$ (V Å^{-1})	$E(Y)$ (V Å^{-1})	Moment $\mu(M)$ (D)	Moment $\mu(Y)$ (D)	$G = U_{pot} + PV - TS$ (kJ mol^{-1})
PbFI	0	4.231	8.770	2.073	0.657	0.167	3.36	4.30	0.94	0.346	34.68	0.588	2435.5	398.8	209.7	99.0	2330.0	7.3806	1.135	1.82	1.85	3.90	2376
	2.38	4.262	7.969	1.870	0.658	0.177	3.29	3.83	0.54	0.332	33.58	0.614	2464	469.0	242.7	64.7	2299.2	7.5590	1.408	1.553	2.30	3.33	2353
	2.91	4.27	7.844	1.837	0.649	0.184	3.29	3.65	0.36	0.339	34.13	0.62	2450	462.2	242.9	57.9	2285.5	7.5301	1.423	1.496	2.32	3.20	2344
	3.89	4.26	7.730	1.815	0.652	0.186	3.26	3.60	0.34	0.339	34.13	0.624	2464.9	486.1	253.1	54.1	2283.0	7.5583	1.492	1.443	2.44	3.09	2348
	4.37	4.254	7.684	1.807	0.652	0.192	3.24	3.54	0.30	0.348	34.84	0.626	2461.7	490.3	256.0	49.9	2274.6	7.5378	1.557	1.362	2.54	2.92	2344
	4.55	4.245	7.674	1.808	0.642	0.193	3.26	3.45	0.19	0.35	35.0	0.626	2455.7	487.5	256.5	48.9	2270.3	7.5036	1.458	1.40	2.38	3.00	2342
BaFCl	0	4.391	7.23	1.646	0.647	0.2049	3.285	3.195	−0.09	0.337	33.98	0.661	2431.4	327.8	90.1	7.1	2193.8	7.6848	0.905	0.231	0.75	0.23	2242
	0.65	4.374	7.16	1.644	0.651	0.2049	3.260	3.194	−0.066	0.336	33.90	0.662	2445.4	346.5	93.5	8.04	2193.4	7.6992	0.954	0.197	0.79	0.19	2235.1
	1.95	4.334	7.09	1.637	0.647	0.2067	3.235	3.121	−0.114	0.338	34.05	0.664	2465.8	369	98.9	7.48	2196.2	7.6923	0.913	0.159	0.76	0.16	2241.8
	3.05	4.307	7.05	1.638	0.648	0.2075	3.211	3.105	−0.106	0.339	34.13	0.663	2479.5	388	102.6	8.08	2195.2	7.6868	0.943	0.147	0.78	0.14	2244.6
	4.10	4.282	7.04	1.645	0.648	0.2094	3.190	3.087	−0.103	0.344	34.52	0.662	2487.3	399.9	104.2	8.70	2194.4	7.6664	0.97	0.126	0.80	0.12	2248.5
	5.46	4.254	7.00	1.646	0.647	0.2105	3.169	3.055	−0.114	0.346	34.68	0.661	2501.3	418.8	109.2	8.85	2193.6	7.6590	0.97	0.108	0.80	0.10	2262
	6.51	4.229	6.98	1.652	0.651	0.2097	3.144	3.080	−0.064	0.346	34.68	0.66	2514.5	443	112.6	10.3	2187.5	7.6543	1.06	0.159	0.88	0.15	2255.8

TABLE 4

(a) Thermodynamical Grüneisen Parameter of BaFCl [relation [5]] and (b) Raman Frequencies (cm^{-1}) for PbFCl and PbFBr and Their Mode Grüneisen Constants [relation [4]]

(a) BaFCl	$\alpha_t = 1/3\alpha_v = 2.58 \times 10^{-5}$		$\chi^{-1} = 62 \times 10^9$ Pa			$\gamma = 0.9$
(b)		$E_g(1)$	B_{1g}	$A_{1g}(1)$	$E_g(2)$	$A_{1g}(2)$	$E_g(3)$
PbFCl[II] (17)	$P = 0$ GPa mode (cm^{-1})	240.5	225.5	164	133	106.5	43.5
γ		1.03	0.83	1.45	1.66	1.03	1.87
PbFBr (17)	$P = 0$ GPa mode (cm^{-1})	—	—	116	93	89	39
γ		—	—	1.62	2.32	2.09	3.95

crystals which take into account all the symmetry conditions are constructed.

1. Coulomb Field and Site Symmetry

The site groups are tabulated in the "International Tables for X-Ray Crystallography" (8). The operators of the site group leave the site invariant, whereas the atoms of the other sites are permuted. In the same way the field at the site should remain invariant under these operators which provide its zero components.

Let us, for example, consider the sites of BaFCl, namely ($2a$) of X ($\equiv$F) and ($2c$) of Y ($\equiv$Cl), with the point groups D_{2d} ($\bar{4}m2$) and D_{4h} ($4mm$), respectively.

The effect of the operators of these groups applied to the field $\vec{E}$ leads to

$$\vec{E}(\mathrm{F}) = 0,$$

$$\vec{E}(\mathrm{Cl}) = E\vec{z},$$

where $\vec{z}$ is a unit vector collinear to C_4.

The same process applies to the tensor products of two or more vectors.

2. Cage Around X

Let us choose the following cation positions: X in 0, 0, 0; M in 0, 1/2, $z(M)$; and Y in 0, 1/2, $z(Y)$.

The cation coordination tetrahedron M_4X around X is schematized in Fig. 2a. Haberkorn [1] has remarked that the atoms M and X are generally adjacent:

$$d(MX) = r_M + r_X \equiv x, \qquad [6]$$

where $d(MX)$ is the distance between M and X; r_M and r_X are the Pauling ionic radii of M and X, respectively. For example, for PbFI, the used ionic radii are 1.31, 1.24, and 2.12 Å for Pb^{2+}, F^-, and I^-, respectively.

Moreover for a regular cage:

$$d^2(M_1M_2) = a^2 = d^2(M_1M_3) = \frac{a^2}{2} + [2z(M)c]^2$$

or

$$z(M)e = \frac{1}{2\sqrt{2}} \approx 0.353. \qquad [7]$$

To interprete formula [7], let us define by α the angle (Fig. 2a):

$$\alpha = (XM_2, M_1M_2);$$

then

$$tg\,\alpha = 2z(M)e, \qquad [8]$$

and in this case of a regular cage,

$$tg\,\alpha_0 = \frac{1}{\sqrt{2}} \quad \text{or} \quad \alpha_0 = 35^\circ 15'. \qquad [9]$$

If

$$\alpha < \alpha_0,$$

the pyramid is compressed along C_4 in such a manner that the M and X ions are more contiguous. So formula [7] accounts for the compactness of M toward the X ions. Equation [7] generalizes a remark of Flahaut (22) which had previously noticed that for series MXY with the same M and X atoms, α remains nearly constant.

Generally speaking, the cage M_4X is rather regular with a distorsion for α less than 10%. Moreover, an increase of the pressure (23) has little effect on α (Table 3).

3. Cage Around Y

The cation coordination polyhedron M_5Y around Y is a right polyhedron with a squared base and the top ion on C_4 (Fig. 2b).

If the basal atoms M and Y are adjacent,

$$d(MY_a) = r_M + r_Y \equiv y, \qquad [10]$$

where $d(MY_a)$ is the distance between Y and a basal ion M and r_Y is the Pauling ionic radius of Y. This condition is satisfied better than 10% (Table 1).

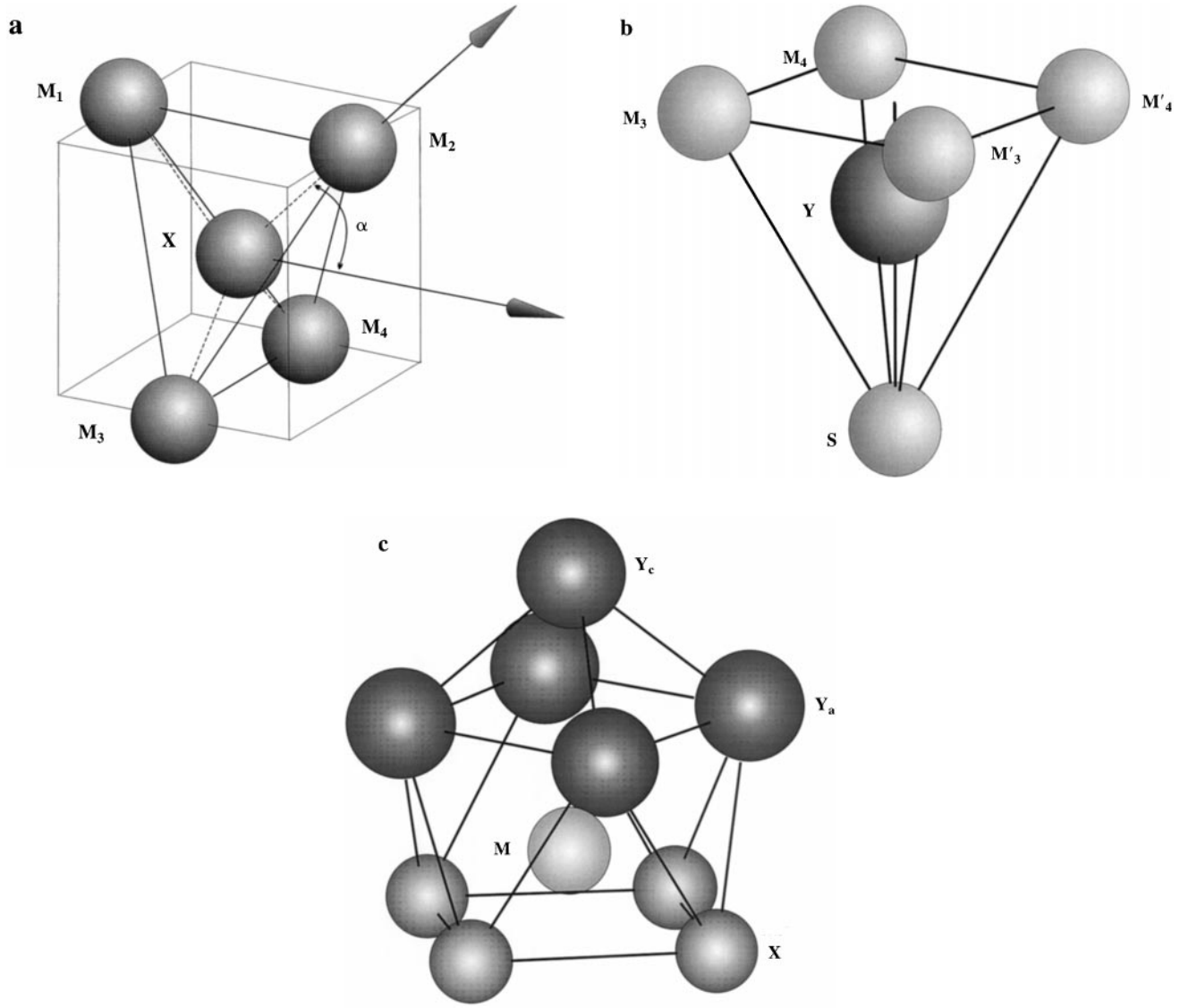

FIG. 2. Coordination polyhedrons (a) of X, (b) of Y, and (c) of M.

Let us design by $d(SY_c)$ the distance between Y and the top atom S of the pyramid. In general $d(MY_a)$ and $d(SY_c)$ are not equal:

$$d^2(MY_a) = \frac{a^2}{2} + [1 - z(M) - z(Y)]^2 c^2, \qquad [11]$$

$$d(SY_c) = [z(Y) - z(M)]c. \qquad [12]$$

Let us define

$$\delta = d(SY_c) - d(MY_a). \qquad [13]$$

If $\delta \geq 0$, one obtains a formula representing the compactness around Y:

$$z(Y) \geq \frac{1}{2} + \frac{1}{4e^2}\frac{1}{1 - 2z(M)}. \qquad [14]$$

If the polyhedron around Y is regular and $\delta = 0$,

$$z(Y) = \frac{1}{2} + \frac{1}{2\sqrt{2e}[e\sqrt{2} - 1]}. \qquad [15]$$

Let us remark that Eqs. [14] and [15] are independent of Eq. [10]. The computations using Eq. [15] are listed in Table 1.

4. "Regular" Crystals

Let us define as "regular" crystal anyone which fulfills at the same time the conditions [6], [7], [10], and [15]. Then the lattice parameters $a^{(i)}$, $c^{(i)}$, $z^{(i)}(M)$, and $z^{(i)}(Y)$ are solely functions of the ionic radii r_M, r_X, and r_Y:

$$a^{(i)} = x\sqrt{\frac{8}{3}}, \qquad [16]$$

$$c^{(i)} = \sqrt{\frac{2}{\sqrt{3}}x + y}\left\{\sqrt{y + \frac{2}{\sqrt{3}}x} + \sqrt{y - \frac{2x}{\sqrt{3}}}\right\} \equiv a^{(i)}e^{(i)}, \qquad [17]$$

$$z^{(i)}(Y) = \frac{1}{2} + \frac{1}{2\sqrt{2}e^{(i)}[e^{(i)}\sqrt{(2)} - 1]}, \qquad [18]$$

$$z^{(i)}(M) = \frac{1}{2\sqrt{2}e^{(i)}}. \qquad [19]$$

Comparison between the "regular" and real crystal brings out the correlation between the symmetries and the polarization energy (Tables 1 and 2).

Useful remark. Combination of the Eq. [18] and [19] gives

$$z^{(i)}(M) + z^{(i)}(Y) = \frac{1}{\sqrt{2}}\frac{e^{(i)}}{e^{(i)}\sqrt{2} - 1}.$$

Taking into account the ionic radii of the fluorides—and, in fact, of most of the matlockite series—$e^{(i)}$ lies between 1.6 and 2.1. Using the mean value 1.85 for $e^{(i)}$, one finds

$$z^{(i)}(M) + z^{(i)}(Y) \cong 0.81.$$

This useful formula is satisfied to a value of better than 5% for the matlockite family. Consequently, $z(M)$ can be used as the single variable parameter in the case of a simulation, for example.

5. Cage around M

The M ion is enclosed in a polyhedron with four X ions and five Y ions at its corners (Fig. 2c). The distances $d(MX)$ and $d(MY)$ are very different. In the case of BaFCl, for example,

$$d(\mathrm{BaF}) = 2.649\ \text{Å},$$

$$d(\mathrm{BaCl}_a) = 3.285\ \text{Å},$$

$$d(\mathrm{BaCl}_c) = 3.195\ \text{Å}.$$

In a number of compounds such as PbFI, the distances $d(MY_a)$ and $d(SY_c)$ are very different (Table 1).

III. DISCUSSION

The crystallographic data and the various energies are now discussed.

1. Crystallographic Properties

(a) Lattice parameter a. The computation of the lattice parameter a builds on the assumption of the ionic contiguity.

It depends therefore on the sum x of the ionic radii r_M and r_F [Eq. [16]]. The accuracy with respect to the experimental values is better than 7%. The shifts in a set MFY with M constant or under an external stress (1, 23) (Tables 1 and 3) are small.

Owing to the symmetry of the tetrahedron M_4F, the electric field at F is zero and the anion does not undergo any electronic distortion. Therefore a is a function of x, independent of $\vec{E}$.

(*b*) *Regularity of M_4X and $z(M)$.* All crystals, except BaFI, satisfy Eq. [7] which is based on the regularity of the tetrahedron M_4X (Table 1). Therefore $z(M)$ is fundamentally a function of e. Later on it is inferred that relation [7] is always true.

(*c*) *Regularity of M_5Y and $z(Y)$.* Allowing that the pyramid M_5Y is regular, relation [15] gives the value of $z(Y)$ with an accuracy better than 8%. Consequently $z(Y)$ is a function of e as well of the electric field $\vec{E}(Y)$ which can slightly change Eq. [15].

(*d*) *Lattice parameter c.* Equation [17] gives directly the parameter c. In short, Eqs. [16], [17], [18], and [19] give the crystallographic parameters satisfactorily except for PbFI on account of its high e value.

It seems therefore interesting to follow the change of its crystallographic properties with external stresses and the possibility to return to the normality. Concurrently the same study is devoted to the "normal" compound BaFCl.

(*e*) *Pressure changes of the crystallographic parameters of BaFCl and PbFI.* Let us first consider BaFCl (Table 3). At atmospheric pressure its crystallographic parameters are correctly deduced from those of the "regular" crystal. At pressure up to 6 GPa (21), the parameters a, e, $z(M)$, $z(Y)$, and the angle α, characteristic of the compactness around X, show small variations. The symmetries of such a crystal are maintained.

Let us now investigate the case of PbFI. The parameter a and the angle α remain invariable at any pressure. Relation (7) is satisfied better than 3%. This reflects the good contact between the atoms Pb and F. In another respect

relation [7] reduces the number of independent parameters to e and $z(Y)$.

At pressure zero the value of e is much higher than the one expected by the HSM; consequently relations [14] and [15] do not agree with the experimental value of $z(Y)$. At increasing pressure (1) e diminishes rapidly and tends approximately to the value predicted by the HSM.

Let us observe that $z(Y)$ remains practically constant. This fact is not at variance with Eq. [14] since the term constant (0.5) is preponderant.

2. *Energies*

The total lattice energy U_{pot} lies in between 2000 and 2500 kJ mol^{-1}, in order of the corresponding metallic fluorides (9). Calculations on SrFCl and BaFCl are in good agreement with previous investigations (4).

For a number of compounds the contribution of entropy to the lattice energy is in the order of 50 kJ mol^{-1}. For SrFCl and BaFCl these values are in good agreement with those computed from the phonon density of states (24).

Let us now relate in detail the contribution of the polarization energy. For some bromides and iodides U_{pol} may be of the same order of magnitude as U_d if the difference δ has a significant value in the order of 1 Å. It is not the case for SrFCl and BaFCl for which U_{pol} is small and shows only small variations with pressure. But for PbFI where δ is in the order of 1 Å at pressure zero (1), U_{pol} shows big variations with the pressure and drops quickly with e following an approximately linear variation (Fig. 3):

$$U_{pol} = 174.4(e - e_0), \qquad [20]$$

$$e_0 \sim 1.5. \qquad [21]$$

Let us now go into more detail of the polarization energy in the case of PbFI. It can be firstly observed that the crystal has gained in stability owing to the polarization energy (Table 3), but it is more interesting to inspect the two contributions (5) of the interaction charge (q)–dipole (m), $W(q, m)$, energy which comes from the moments induced on I and Pb.

At atmospheric pressure the main part of U_{pol}, of the order of 90 kJ mol^{-1}, is due to the moment induced on I. But for increasing pressure, the two contributions vary in opposite directions. For example, at 4.37 GPa they are nearly the same, of the order of 20 kJ mol^{-1}.

These variations are connected with the shifting of I. Let us examine the evolution of the interatomic ranges when the pressure increases to 4.55 GPa (Table 3). The length d(PbF) remains nearly invariable and the length $d(PbI_a)$ shows little modification from 3.36 to 3.26 Å. At the same time $d(PbI_c)$ is submitted to variations of about 20% and the difference δ varies from 0.94 to 0.19 Å. The shifting of I has significant consequences on the polarization (and the field) of the ions I and Pb because it leads to the crystal becoming more or less regular. Consequently the surroundings of the ions become more or less symmetrical. In the case of I, because the difference δ decreases at increasing pressure, the crystal becomes more regular, the cage becomes more symmetrical and the induced moment decreases. Consequently the contribution of I to $W(q, m)$ is reduced.

On the contrary, for the surrounding cage of Pb (Fig. 2c), the I_c ion draws near to the I_a ions and leads to an increase of the field acting on Pb. So the moment induced on Pb and $W(q, m)$ increases. This effect counterbalances partially the decrease of the polarization energy due to I.

Finally, the shift of I induces two opposite effects on U_{pol}, but the changes due to the moment induced on I become greater than that due to Pb owing to the higher polarizability of I.

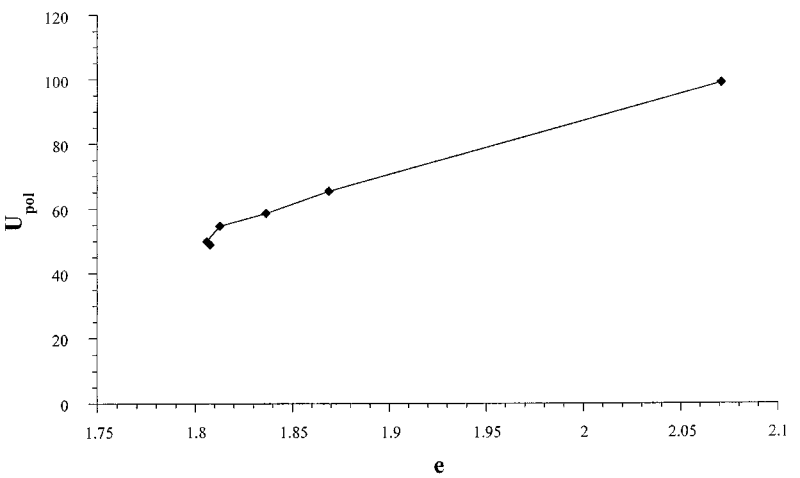

FIG. 3. Variation of U_{pol} with e(P) for PbFI.

This research confirms the observations of Bertaut (5) on the part and the importance of U_{pol} on the stabilization of the lamellar structures.

Other crystals such as the hydro-halides of calcium or oxy-halides of bismuth have also a significant polarization energy. But any information on the stabilizing role of U_{pol} is not yet available for these compounds, as for example the evolution of the crystal data and energies under external stresses.

On the contrary some highly regular compounds as CaFCl, SrFCl, BaFCl, and BaFBr have a negligible polarization energy and are stable up to more than 20 GPa (7).

Remarks on SrFI. Let us now examine the particular case of SrFI of which only the lattice parameters a and c are presently known (Table 1). In spite of the lack of information concerning $z(M)$ and $z(Y)$, a striking resemblance between SrFI and PbFI is to be noticed. In particular, $e\,(=c/a)$ is the same for the two crystals. On the other hand, the ionic radii of Pb^{2+} and Sr^{2+} are very similar.

Let us now assume that the F^- and Sr^{2+} ions are adjacent. Then using the value

$$r_{Sr^{2+}} = 1.27 \text{ Å}$$

for the ionic radius of Sr^{2+} with 8-fold coordination, formulae [16]–[19] give the lattice parameters of the corresponding regular crystal (Table 1). This estimate of the lattice parameters can only be rough. Nevertheless, because of the high value of e, it suggests that the polarization energy arising principally from the I^- ion plays an important role and contributes to the stabilization of the lattice. In consequence, one may expect that SrFI and PbFI have similar behaviours under external pressure.

Finally, admitting that the lattice parameters $z(M)$ and $z(Y)$ are equal for both SrFI and PbFI, one finds for SrFI a polarization energy of the order of

$$U_{pol}(\text{SrFI}) \approx 81 \text{ kJ mol}^{-1}.$$

CONCLUSION

Equation [7] expresses the symmetry and the compactness of the tetrahedral cage around the X atom. Equation [14] takes into account for the equidistance of the atom Y with the various atoms M of the cage M_5Y and for the compactness between M and Y. Symmetry considerations show that the Coulomb field is zero at X. When the crystal is clearly less symmetrical than the regular one, a significant polarization energy occurs. It contributes to the lattice stabilization but does not lead to a displacive phase transition as in the case of $RbAlF_4$ mentioned by Bertaut (5).

Remark on the charge–quadrupole and dipole–quadrupole interactions energies. In quadratic crystals, one of the principal axes of the induced quadrupole tensor is the C_4 axis, the other two axes being orthogonal. Consequently, the charge–quadrupole and dipole–quadrupole interaction energies are equal to zero.

Let us now investigate the physical properties which depend mainly on the interactions between the atoms M and X. In another paper (25) it has been shown that scaling factors are able to infer several physical properties linked to the phonons, as for example the elastic constants of a number of MXY compounds of the matlockite family obtained from those of the similar MX_2 compounds of the fluorite family in which the tetrahedra surrounding and the length $d(MX)$ are identical. But this procedure fails for the elastic constant C_{33} of BaFI and SrFBr and for the Debye temperature of SrFI, PbFBr, and PbFI, for example. One can make the supposition that these discrepancies arise from the deviation with respect to the regular crystal. Direct measurements of C_{33} on compressed crystals would confirm this conjecture.

On the contrary, phase transitions of BaFCl and BaFBr created with pressures higher than 20 GPa are not connected with U_{pol} and probably have a purely structural origin.

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