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Influence of High Hydrostatic Pressure on the Crystal Structure of BaFCl in the Pressure Range up to 6·5 GPa

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Abstract

High-pressure X-ray diffraction measurements were made with BaFCl single crystals (space group *P*4/*nmm*) using a diamond-anvil cell on a four-circle diffractometer (six data sets, 30 to 50 reflections, *R* values ranging from 2·5 to 5·0%). This compound does not show a pressure-induced phase transition up to 6·5 GPa at ambient temperatures. At lower pressures the compressibility of the *c* axis is larger than that of the *a* axis. At 2 GPa the compressibility becomes isotropic and at higher pressures again anisotropic, but now with an increasing *c*/*a* ratio. Such effects of pressure and the changes in positional parameters are discussed in comparison with the known structural data for a whole series of PbFCl-type compounds. Changes in the ion 'size' are accompanied by distortions of the structural framework leading to a more efficient packing. While the Madelung number decreases during this process, the relative loss of ionic lattice energy is compensated for by an increase in interactions due to polarization, which can be traced by the movement of the Ba^{2+} ions within their coordination sphere.

Introduction

It is remarkable that mixed-anion compounds *MFX* with larger cations *M* mostly crystallize with the same structural arrangement regardless of the large differences in size and polarizability of the atoms found in such compounds. It has been stated that this variety in constituents leads to different 'branches' of the structure type, of which one – the PbFCl type (Fig. 1) – contains compounds with mainly ionic interactions, whereas another – coined as anti-Fe_2As type – is encountered with compounds showing strongly covalent character, *e.g.* UPS (Flahaut, 1974; Johnson & Jeitschko, 1973).

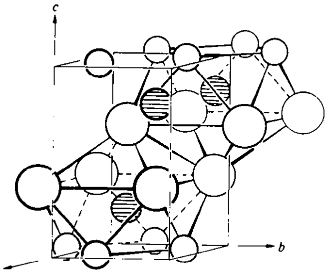

Fig. 1. Coordination polyhedra and unit cell of the PbFCl-type structure. Cl^- ions are given as large spheres, F^- ions as smaller spheres and Pb^{2+} ions as hatched spheres.

We have emphasized that, within its field of existence, the PbFCl type itself shows marked variations with respect to crystal geometry and even bonding. The structural differences within this arrangement, ranging from a coordination lattice (found with *M*OCl, *M*FCl and *M*HCl compounds) to a layer structure (*M*OI, *M*FI, *M*HI), have been discussed by Bärnighausen, Brauer & Schultz (1965).

A detailed analysis of well refined structures of fluorohalides (Beck, 1979) has shown an interesting correlation between positional parameters and the polarizability of the constituent ions. In the course of these studies it was our aim to trace the changes in bonding type induced by higher pressures by the same minute analysis of structural details.

High-pressure X-ray investigations using powder specimens of fluorochlorides and -bromides of Eu, Sm, Pb and alkaline earths have shown no structural rearrangement up to pressures between 5 and 10 GPa (1 GPa = 10 kbar) (Beck, 1978*a*). The lattice constants of these compounds decrease linearly with pressure except for BaFCl, which was therefore chosen for further studies under high pressure using single crystals.

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Experimental

BaFCl crystals were prepared by sintering of the binary compounds (Beck, 1976). A single crystal 100 × 100 × 60 μm was transferred into a hole about 210 μm diameter in an Inconel gasket, which had been compressed to 150 μm, together with a CsCl crystal of similar dimensions for pressure calibration. A 4:1 methanol/ethanol mixture was taken as the pressure-transmitting agent (Piermarini, Block & Barnett, 1973).

The diamond-anvil cell used has been described by Keller & Holzapfel (1977). It was adjusted on a Philips four-circle diffractometer (PW 1100, Mo $K\alpha$ radiation, graphite monochromator) (Denner, Dietrich, Schulz, Keller & Holzapfel, 1978). For data collection a measuring procedure was used which allows automatic measurements of reflection intensities in the largest possible areas of reciprocal space and correction for systematic errors due to absorption effects of the high-pressure cell (Denner, Schulz & d'Amour, 1978).

After data reduction with the program *PROMETHEUS* (Zucker, Perenthaler, Kuhs, Bachmann & Schulz, 1983) reflections with $I > 3\sigma$ were used for least-squares refinements with the program *CRYLSQ* of the XRAY system (Stewart, Kundell & Baldwin, 1970). Scattering factors have been taken from Cromer & Mann (1968).

This procedure was repeated for a total of six different pressures, which were attained successively by increasing the force in the anvil device. The pressures were determined by evaluating the changes of the lattice constant of the CsCl crystal (Decker, 1971).

With a good CsCl crystal the accuracy of the pressure calibration is estimated to be ±0·1 GPa. We have been able to confirm this by using the pressure shift of ruby luminescence (Barnett, Block & Piermarini, 1973) in comparison, since a second run with another BaFCl crystal proved necessary after the first crystal had broken at about 5·6 GPa.

The results of the refinements are presented in Tables 1 and 2. The high standard deviations for the c constants and for the z parameters are due to the fact that the reflections were limited to low l indices. The plate-like crystal could only be adjusted with the c axis in the direction of the primary beam with small maximum ω angles (20–22°) because of the geometry of the high-pressure cell.

Table 1. *Unit-cell parameters for* BaFCl *in the pressure range up to* 6·5 GPa

Pressure (GPa)	a (Å)	c (Å)	c/a	V (Å^3)
0·0001	*4·391 (3)	7·226 (4)	1·646	139·3
	†4·3939 (6)	7·2248 (9)	1·644	139·5
0·65	4·374 (6)	7·16 (6)	1·638	137·1
1·95	4·334 (3)	7·09 (3)	1·637	133·2
3·05	4·307 (3)	7·05 (3)	1·638	130·9
4·10	4·282 (4)	7·04 (4)	1·645	129·1
5·46	4·254 (9)	7·00 (4)	1·646	126·7
5·92	4·242 (6)	6·99 (5)	1·650	125·9
6·51	4·229 (5)	6·98 (5)	1·652	124·9

* Cell constants taken from Beck (1976).
† Cell constants taken from Sauvage (1974).

Table 2. *Atom parameters and isotropic temperature factors* (Å^2) *of* BaFCl *in the pressure range up to* 6·5 GPa

Space group: $P4/nmm$
Point site: Ba [2(c)] $\frac{1}{4}, \frac{1}{4}, z$; Cl [2($c$)] $\frac{1}{4}, \frac{1}{4}, z'$; F [2($a$)] $\frac{1}{4}, \frac{3}{4}, 0$

The temperature factor expression is $\exp(-B\sin^2\theta/\lambda^2)$.

Pressure (GPa)	z_{Ba}	z'_{Cl}	B(Ba)	B(Cl)	B(F)
0·0001	0·2049 (1)	0·6472 (7)	0·83 (4)	1·2 (2)	1·1 (4)
0·65	0·2049 (11)	0·6506 (57)	0·31 (22)	0·8 (4)	0·9 (9)
1·95	0·2067 (6)	0·6467 (27)	0·32 (6)	0·8 (2)	0·2 (3)
3·05	0·2075 (7)	0·6478 (29)	0·35 (7)	0·5 (2)	0·5 (4)
4·10	0·2094 (6)	0·6480 (26)	0·37 (9)	0·4 (2)	0·4 (5)
5·46	0·2105 (11)	0·6465 (45)	0·52 (12)	0·9 (3)	−0·3 (6)
6·51	0·2097 (9)	0·6509 (37)	0·23 (9)	0·5 (2)	0·0 (4)

Thermal parameters proved to be especially uncertain, indicating that even this elaborate measuring routine cannot eliminate the severe systematic errors caused by absorption in the high-pressure cell.

R values ($R = \sum||F_o| - |F_c||/\sum|F_o|$) in the refinements range from 2·5 to 5% on the basis of 30 to 50 reflections in the different data sets.*

Results and discussion

The total compressibility of crystalline matter is due to changes in the volume of the individual atoms – resulting in smaller interatomic distances and eventually in a different coordination – and to geometric distortions of the structural framework enhancing the packing efficiency of the structure.

Both changes will affect the lattice energy, the bonding character and more or less the electronic state of the crystal. This study traces the geometric effects of increasing pressure in BaFCl.

Fig. 2 presents the proportional decrease of the lattice constants. Initially the structure is compressed mainly along the c axis. At pressures of about 2 GPa the compressibility becomes isotropic and in the pressure range above again anisotropic, but now with an increasing c/a ratio. An analysis of the lattice constants of all known fluorohalides MFX of alkaline earths and divalent rare earths (Beck, 1976, 1978b) has

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* Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38409 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

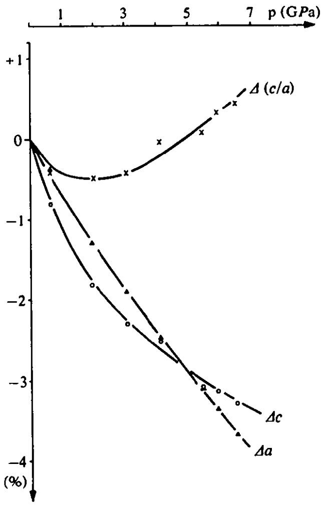

Fig. 2. Plot of the proportional change of lattice constants and c/a ratio of BaFCl *versus* pressure.

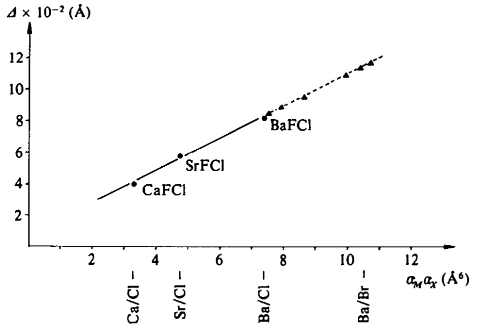

Fig. 3. Deviations of cation positions from the electrostatic centre of the anion polyhedron (Δ) *versus* the products of polarizabilities $\alpha_M\alpha_X$ (taken from Tessman, Kahn & Shockley, 1953). The corresponding values for Ba at the different pressures are plotted with triangles.

shown a specific correlation between the c/a ratios and the cell volume of these compounds. The volume reduction in going to compounds with smaller anions X is always combined with a decrease of the c/a ratio, whereas a corresponding substitution of the cation leads to an increase in c/a. At first the volume reduction under pressure mimics a compression of the 'softer' anions. Once the anion lattice has 'stiffened', further volume reduction is achieved especially at the cost of the Ba^{2+} ions.

Such changes in ion size are accompanied by distortions of the structural framework leading to a more efficient packing of the atoms. The initial anisotropy of compression can also be understood as a consequence of the layer-like structure of BaFCl. The layers shift at first closer together and in doing so the Ba^{2+} ion moves into the chlorine layer. This movement is reflected in the corresponding z parameters (Table 2). z_{Cl} does not change significantly in the whole pressure range; z_{Ba}, however, has increased about 2·5% at 6 GPa. The Madelung number of this structural arrangement is now considerably smaller [Madelung numbers for this structure type as a function of the positional parameters have been discussed earlier (Beck, 1976)]. The relative loss of bonding energy must be compensated by other effects.

The classification of these MXY compounds, as mentioned in the *Introduction*, can also be given on the basis of the z_M parameter. In PbFCl-type compounds z_M is smaller than 0·23, and $z_M > 0{\cdot}25$ is usually encountered in anti-Fe_2As-type compounds, in which nonionic interactions prevail. To a certain extent such interactions also play a role among the PbFCl-type compounds themselves. In oxyhalides MOX partial covalent bonding between the metal atoms and the O atoms is reflected in smaller z_M values. In fluorohalides MFX, however, the interaction with the fluorine layer is weakened in comparison and the metals move away. In the fluorochlorides, and even more in the fluorobromides (parameter refinements of comparable accuracy are not yet available for all fluoroiodides), this tendency clearly increases when going from CaFX to SrFX and finally to BaFX.

Beck (1979) has correlated this movement out of the electrostatic centre of the coordination polyhedron with the product of the polarizabilities $\alpha_M\alpha_X$, which may be taken as a representative measure for the increasing tendency to form nonionic interactions. The movement of the Ba^{2+} ion in BaFCl under pressure is indicative for the increase in interactions due to polarization, which will become more important as distances are shortened. If it is accepted that the linear correlation can be extrapolated (Fig. 3), the geometric effect may be interpreted on the $\alpha_M\alpha_X$ scale. It can be stated that at 5 GPa $\alpha_{Ba}\alpha_{Cl}$ has reached a value which is comparable with the product of polarizabilities of Ba and Br at normal pressure, and these contributions to the lattice energy may well compensate for the loss in Madelung energy.

Gutmann & Mayer (1976) have pointed out that the effect of high pressure can be discussed in comparison with donor–acceptor interactions. The electron density between non-bonded atoms is increased by applying pressure, and it is reduced between bonded ones. The bonding interactions are therefore weakened, but at the same time new bonds are formed, and coordination numbers tend to increase. The subtle structural changes in BaFCl are a good example to illustrate this general rule.

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Anisotropic Mean-Square Displacements (MSD) in Single Crystals of $2H$- and $3R$-MoS_2

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Abstract

Integrated intensities for $h0.l$ reflections in single crystals of $2H$- and $3R$-MoS_2 have been measured both to refine the c-axis structural parameter (z) and to determine the vibrational amplitude for the Mo and S atoms. It was found that the MSD for the Mo atom along the c axis is distinctly larger than for the S atom ($7{\cdot}6\times10^{-3}$ Å^2 *versus* $5{\cdot}0\times10^{-3}$ Å^2), independent of the polytype studied. Within the basal plane the amplitudes of $2H$-MoS_2 are both smaller and more equal ($4{\cdot}8\times10^{-3}$ Å^2 for Mo and $3{\cdot}8\times10^{-3}$ Å^2 for S). Both polytypes gave a z parameter for the S atom of $z=0{\cdot}127_4$.

I. Introduction

MoS_2 belongs to the layered dichalcogenides of transition metals of Groups IVb, Vb and VIb, which have attracted interest on account of their highly anisotropic properties. A review of these materials may be found in Wilson & Yoffe (1969). The metal dichalcogenide layer consists of one plane of hexagonally packed metal atoms between two planes of chalcogenide atoms. In these layers the chalcogen array around each metal atom is typically octahedral or trigonal prismatic and MoS_2 belongs to the latter group. The metal dichalcogenide layers may be stacked in different ways (polytypism). Thus, MoS_2, either natural or synthetic, may be $2H$ or $3R$ or a mixture of both. In nature, $2H$-MoS_2 is dominant (Frondel & Wickman, 1970). Further polytypic structures in molybdenite, other than $2H$ or $3R$, have been derived analytically (Zvyagin & Soboleva, 1967) but have not yet been observed experimentally.

Recently, calculations to determine the mean-square displacements (MSD) of $2H$-MoS_2 have been made by Feldman & Boyer (1981). In the present paper, we compare these calculations with experimental findings and refine the structural z parameter which is half the height of the MoS_6 prism studied earlier by Dickinson & Pauling (1923) and Takéuchi & Nowacki (1964).

II. Theory

The structures of the $2H$ and $3R$ polytypes of MoS_2 are easily visualized by starting from the unit structure of an MoS_2 plane sandwich (Zvyagin & Soboleva, 1967). This unit structure is shown in Fig. 1, with the S atoms at $(0,0,\pm z)$, the Mo atom at $(\frac{2}{3},\frac{1}{3},0)$ and with the nomenclature for the different lattice sites A, B and C. We obtain the $2H$ polytype by stacking this unit structure along the c axis (leaving a van der Waals gap

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