

Structural Relationships in Compounds with $R\bar{3}c$ Symmetry

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A trifluoride series BF_3 ($B = \text{Ru, Co, V, Fe, Ti}$) is related to different perovskite-type series ABO_3 ($A = \text{Bi, Pb, La, Li}$ and $B = \text{Fe, Zr-Ti, Co, Al, Nb, Ta}$) as being based on the same anion framework. This anion framework can be viewed as generated by linear chains of regular octahedra rotated from the ideal close-packed configuration. Experimental data for these compounds are in excellent agreement with the relationships between atomic parameters and the unit-cell dimensions developed from a study of this model possessing $R\bar{3}c$ symmetry.

Introduction

The study of pseudo-symmetric pure compounds or solid-solutions is of considerable interest owing to the unusual physical properties often related to small atomic displacements from a higher symmetry form.

A wide range of atomic structures is based on a framework of regular or slightly distorted octahedra sharing corners. From geometrical considerations of the oxygen framework of LiNbO_3 , Megaw (1968) proposed a model of regular octahedra sharing corners and topologically able to rotate without distortion around their threefold axes. The resulting model, with $R\bar{3}c$ symmetry and anions in the $18(e)$ position of that space group, can be described in terms of a continuous rotation of the oxygen octahedra from two ideal symmetry forms: the hexagonal close-packed and the ideal perovskite configurations.

The magnitude of the distortion can be evaluated by either the angle α of the rhombohedral unit-cell containing two formula units or the corresponding axial ratio c/a in the hexagonal cell.

Our purpose is to establish how the atomic positions are correlated with the unit-cell dimensions and to compare the resulting relationships with the experimental data.

Geometrical relationships

The proposed model can be viewed also as being generated by an array of linear chains of rigid octahedra sharing corners and allowed to rotate around their trigonal axes, Fig. 1. Along this chain, φ is the bond angle metal-anion-metal with the metallic atom at the geometrical center of each octahedron and ω is the rotation angle of the octahedron from the ideal perovskite position.

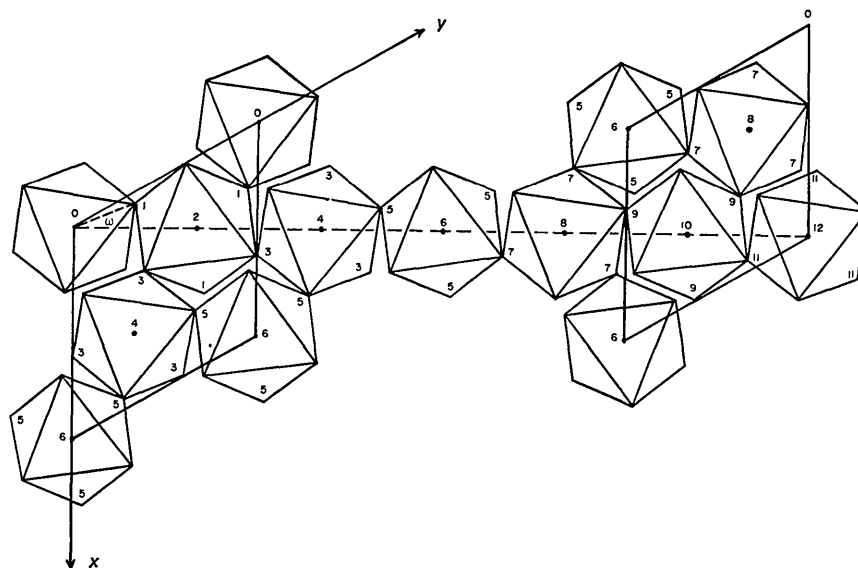


Fig. 1. Three-dimensional framework of regular octahedra sharing corners projected onto (0001). Numbers correspond to the heights of octahedral positions expressed in units of $c/12$. Left-hand solid-line gives lower half of the unit cell, right-hand solid-line the upper half.

A continuous change of the unit-cell volume is associated with the rotation ω of the octahedra around their threefold axes. A parametric relation can be derived between ω and the bimolecular rhombohedral cell angle α or the corresponding hexagonal axial ratio c/a :

$$\left(\frac{c}{a}\right)^2 = \frac{6}{\cos^2 \omega} = \frac{9}{4 \sin^2 \frac{\alpha}{2}} - 3.$$

From the geometry one can also relate ω with the bond angle φ or equivalently with the variable parameter x of the anion $[x 0 \frac{1}{2}]$ in position 18(e) ($R\bar{3}c$, hexagonal) –

$$x = \frac{1}{2} - \frac{\tan \omega}{2\sqrt{3}} \text{ and } \varphi = 2 \arcsin \left(\frac{2 \cos^2 \omega + 1}{3} \right)^{1/2}$$

Thus it is possible to directly relate the atomic parameters x and φ to the rhombohedral cell angle α :

$$\alpha = \arccos \left(\frac{1 + 4(1 - 2x)^2}{2 + 4(1 - 2x)^2} \right) = \arccos \left(\frac{5 + \cos \varphi}{6 - 2 \cos \varphi} \right)$$

Then, by continuity the two high symmetry forms are reached with the following parameters:

For the ideal perovskite configuration,

$$\frac{c}{a} = \sqrt{6}, \quad \alpha = \frac{\pi}{3}, \quad x = \frac{1}{2} \text{ and } \varphi = \pi;$$

For the hexagonal close-packed configuration,

$$\frac{c}{a} = \sqrt{8} \quad \alpha = 2 \arcsin \sqrt{\frac{9}{44}} = 53^\circ 50'$$

$$x = \frac{1}{3} \text{ and } \varphi = 2 \arcsin \sqrt{\frac{5}{8}} = 132^\circ.$$

These relationships are compared graphically with crystallographic data of ABX_3 type compounds where the anion X lies exactly or approximately in the 18(e) position of the $R\bar{3}c$ space group (hexagonal notation).

Crystallographic data

(1) A series of trifluoride compounds, which can be expressed in terms of vacancies \square by: $\square ABF_3$ where B is a transition metal, is first examined. The following classification, due to Hepworth, Jack, Peacock & Westland (1957), is most appropriate.

(a) The group MoF_3 which corresponds to the configuration, $\omega = 0$.

This group forms the series MoF_3 , TaF_3 , NbF_3 isostructural with ReO_3 (Gutmann & Jack, 1951; Ehrlich & Pitzka, 1955). This structure may be described as a cubic close-packing of fluorine atoms in which the octahedral interstices are occupied by metal atoms forming a simple cubic superlattice, and in which one-fourth of the fluorine atom sites, those not adjacent to metal atoms, remain vacant.

(b) The group PdF_3 which corresponds to the configuration $\omega = \pi/6$.

PdF_3 , RhF_3 and IrF_3 are isostructural. The fluorine array is hexagonal close-packed (Hepworth *et al.*, 1957).

(c) The VF_3 group where the fluorine framework is intermediate between the arrangements of type (a) and (b).

This group forms the isostructural series VF_3 , FeF_3 , CoF_3 , RuF_3 , TiF_3 (Gutmann & Jack, 1951; Siegel, 1956; Hepworth *et al.*, 1957).

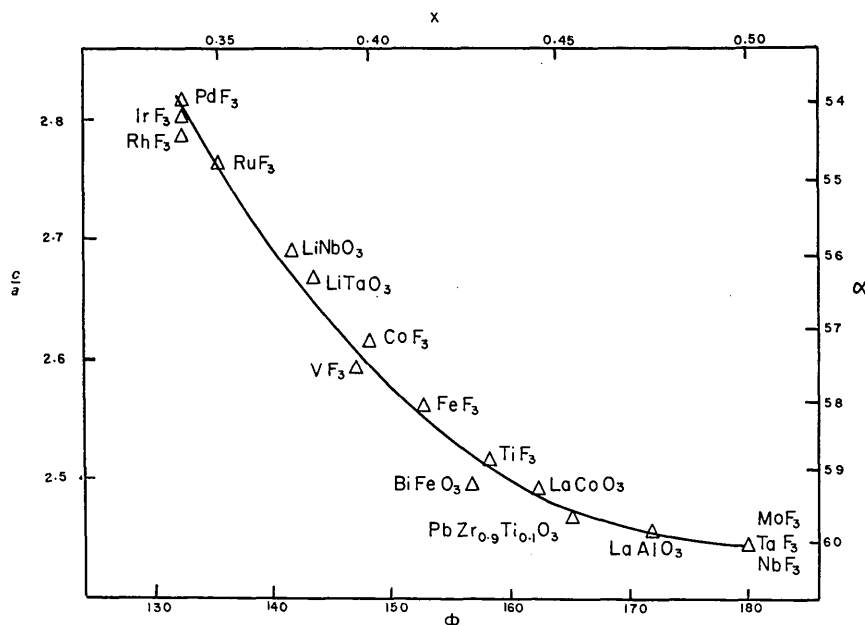


Fig. 2. Plot of c/a or α vs. φ or x . Solid line: theoretical, Δ : experimental values. c/a is the hexagonal axial ratio, α is the rhombohedral angle in the bimolecular unit-cell, φ is the bond angle MOM or MMM where M is a metal atom at the center of each octahedron, x is the octahedral parameter in the hexagonal cell.

The rhombohedral unit-cell is bimolecular. These structures consist of alternately and regularly spaced planes of metal atoms and planes of fluorine atoms perpendicular to the trigonal (hexagonal c) axis. Each octahedron is not perfectly regular but the distortions are negligible for most of the compounds. As suggested by Hepworth *et al.*, the discrepancies from the ideal model may be attributed to variations from stoichiometric composition.

(2) A series of perovskite-type compounds ABO_3 is also examined. $LaCoO_3$ (Menyuk, Dwight & Raccach, 1967) and $LaAlO_3$ (de Rango, Tsoucaris & Zelwer, 1966) are isostructural. The space group is $R\bar{3}c$. The two cations A and B are in special positions while the BO_6 octahedra are slightly rotated from the ideal perovskite-like positions.

(3) The ferroelectric series of $BiFeO_3$ (Michel, Moreau, Achenbach, Gerson & James, 1969), $PbZr_{0.9}Ti_{0.1}O_3$ (Michel *et al.*, 1969); $LiTaO_3$ (Abrahams & Bernstein, 1967); and $LiNbO_3$ (Abrahams, Hamilton & Reddy, 1966; Abrahams, Reddy & Bernstein, 1966). The A and B cations are shifted along the hexagonal c axis from the $R\bar{3}c$ special positions. Consequently the oxygen octahedral framework is more distorted from the idealized model and the space group becomes the noncentrosymmetric $R3c$. Nevertheless the spread of the oxygen distances around the average is still sufficiently small for these octahedra to be considered to be regular to a first approximation.

Table 1. Crystallographic parameters

Compounds	c/a	$\varphi = M-X-M$	α_R	x_H
$LiNbO_3$	2.693	142.00	55.89	0.382
$LiTaO_3$	2.674	143.04	56.17	0.383
$BiFeO_3$	2.488	156.17	59.30	0.445
PZT	2.465	166.33	59.70	0.463
$LaCoO_3$	2.492	163.20	59.23	0.447
$LaAlO_3$	2.462	172.11	59.90	0.475
VF_3	2.592	147.00	57.52	0.395
TiF_3	2.502	158.80	59.07	0.433

Table 1 (cont.)

Compounds	c/a	$\varphi = M-X-M$	α_R	x_H
FeF_3	2.564	153.00	57.99	0.419
CoF_3	2.625	149.00	56.97	0.400
RuF_3	2.769	136.00	54.67	0.350
RhF_3	2.786	132.00	54.42	0.333
PdF_3	2.818	132.00	53.92	0.333
IrF_3	2.797	132.00	54.13	0.333
$(Mo, Ta, Nb)F_3$	2.449	180.00	60.00	0.500

Table 1 lists the different values of φ , x , c/a and α for all the compounds mentioned. The experimental values reported (Fig. 2) are in excellent agreement with the theoretical relationships obtained from the ideal model.

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References

- ABRAHAMS, S. C., HAMILTON, W. C. & REDDY, J. M. (1966). *J. Phys. Chem. Solids*, **27**, 1013.
- ABRAHAMS, S. C., REDDY, J. M. & BERNSTEIN, J. L. (1966). *J. Phys. Chem. Solids*, **27**, 997.
- ABRAHAMS, S. C. & BERNSTEIN, J. L. (1967). *J. Phys. Chem. Solids*, **28**, 1685.
- EHRlich, P. & PIETZKA, G. (1955). *Z. anorg. Chem.* **275**, 121.
- GUTMANN, V. & JACK, K. H. (1951). *Acta Cryst.* **4**, 244.
- JACK, K. H., GUTMANN, V. (1951). *Acta Cryst.* **4**, 246.
- HEPWORTH, M. A., JACK, K. H., PEACOCK, R. D. & WESTLAND, G. J. (1957). *Acta Cryst.* **10**, 63.
- MEGAW, H. (1968). *Acta Cryst.* **A24**, 583.
- MENYUK, N., DWIGHT, K. & RACCAH, P. M. (1967). *J. Phys. Chem. Solids*, **28**, 549.
- MICHEL, C., MOREAU, J. M., ACHENBACH, G., GERSON, R. & JAMES, W. J. (1969). *Solid State Comm.* **7**, 701, 865.
- RANGO, C. DE, TSOUCARIS, G. & ZELWER, C. (1966). *Acta Cryst.* **20**, 590.
- SIEGEL, S. (1956). *Acta Cryst.* **9**, 684.