

Perovskite-Like Fluorides. I. Structures of KMnF_3 , KFeF_3 , KCoF_3 , KNiF_3 and KZnF_3 . Crystal Field Effects in the Series and in KCrF_3 and KCuF_3 *

BY KERRO KNOX

Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey, U.S.A.

(Received 20 February 1960 and in revised form 22 August 1960)

The structures of KMnF_3 , KFeF_3 , KCoF_3 , KNiF_3 and KZnF_3 have been shown to be ideal perovskite by powder and single crystal data. The lattice constants are: KMnF_3 (4.182), KFeF_3 (4.120), KCoF_3 (4.071), KNiF_3 (4.012) and KZnF_3 (4.055). Powder photographs of KCrF_3 and KCuF_3 can be indexed on a tetragonal basis; the lattice constants for the sub-cells have $c/a = 0.940$ for KCrF_3 and 0.947 for KCuF_3 . The structures and ionic sizes in the series are discussed in terms of crystal-field theory and Jahn-Teller distortions.

Introduction

That many alkali metal-divalent metal-fluorides crystallize with perovskite-like structures has been known for many years, but their structures have not been refined because of lack of single crystal data. In view of the increased current interest in the physical properties of these compounds, single crystals of the series KMnF_3 , KFeF_3 , KCoF_3 , KNiF_3 , KCuF_3 and KZnF_3 have been grown, and optical and X-ray diffraction studies have been carried out. The complete refinement of the KCuF_3 structure is given in the following paper of this series; the lattice constants are reported here for discussion purposes. In addition, powder data on KCrF_3 have been gotten.

Experimental

Preparation of samples

Many perovskite-like fluorides can be precipitated from aqueous solution (see e.g., Palmer (1954)), but samples prepared in this way are seldom stoichiometric. Preparations in these laboratories have always shown a deficiency of potassium and fluorine. Therefore, single crystals were prepared in the following manner: (1) material precipitated from aqueous solution was heated to about 500 °C in anhydrous HF and cooled below 200 °C. in dry pure nitrogen, (2) the product was mixed with sufficient KHF_2 to bring the potassium-divalent metal ratio to 1:1, and (3) single crystals were made by melting and slow-cooling in an inert atmosphere. The crystal growth can be accomplished in a number of ways: (1) using an open graphite crucible in a nitrogen atmosphere, (2) sealing the compound (in this case, addition of KHF_2 is omitted because of the pressure it develops) in a platinum tube, a technique developed by Guggenheim (1959), or (3) zone refining in an inert atmosphere. The lattice constants of the crystals agree with those

of the powders, prepared both here and by others. Generally, only small ($\sim 1 \text{ mm.}^3$) crystals were made for X-ray purposes, but large crystals of KMnF_3 have been made with the following analysis: K, obs. 25.72%, calc. 25.89; Mn, obs. 35.68, calc. 36.37; F, obs. 37.11, calc. 37.74.

Structure determination

Powder photographs of precipitated KMnF_3 , KFeF_3 , KCoF_3 , KNiF_3 and KZnF_3 show only the lines due to a one-formula cubic unit cell. The same photographs for KCrF_3 and KCuF_3 can be indexed on a tetragonal basis with a one-formula unit cell, but the copper, and presumably the chromium, compound prepared by us is more complicated, as will be shown in a subsequent paper in this series. For the cubic compounds, the ions are in the following positions of space group $O_h^1-Pm\bar{3}m$:

1 K in (a): 0, 0, 0.

1 Me^{II} in (b): $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$; $Me^{II} = \text{Mn, Fe, Co, Ni, Zn}$.

3 F in (c): 0, $\frac{1}{2}, \frac{1}{2}$; $\frac{1}{2}, 0, \frac{1}{2}$; $\frac{1}{2}, \frac{1}{2}, 0$.

The lattice constants for the cubic KMeF_3 are: Mn, 4.182; Fe, 4.120; Co, 4.071; Ni, 4.012; Zn, 4.055. For the tetragonal compounds, the sub-cell lattice constants are: Cr, $a = 4.274$, $c = 4.019$; Cu, $a = 4.140$, $c = 3.922$. Semi-quantitative comparison shows the observed and calculated intensities to be in good agreement. The lattice constants are in agreement with most previously published values; see for example, Martin, Nyholm & Stephenson (1956).

Since perovskites are seldom found to have a simple cubic structure (Wells (1950), Geller (1956), Geller & Wood (1956), Geller & Bala (1956), Gilileo (1957), Geller (1957)), single crystal analysis of these compounds was undertaken. Optical examination of KMnF_3 , KFeF_3 , KCoF_3 , KNiF_3 and KZnF_3 showed them to be isotropic and, hence, cubic. Rotation and precession photographs showed no indication of superstructure, either ordered or disordered, even on long time exposures. Thus, the compounds are proved to

* Presented at 1959 Annual Meeting of the American Crystallographic Association, Ithaca, New York, July 1959.

have one-formula cubic unit cells. Results with which these are in agreement for the cubic compounds have recently been reported by Okazaki, Suemune & Fuchikami (1959). They did not, however, report the superstructure in KCuF_3 , which will be discussed in a subsequent article to be published in this series; recently they have found it (Okazaki (1960)).

Hoppe (1959) and Edwards & Peacock (1959) have also reported what we call the sub-cell lattice constants for KCuF_3 and KCrF_3 , with which ours are in agreement. When single crystals which show the superstructure reflections are ground up, the extra lines are too weak to be observed in the powder pattern.

Discussion

It is of interest to consider the theoretical aspects of the structures of this series of perovskite-like fluorides. Crystal field theory (see e.g., Moffitt & Ballhausen (1956); Dunitz & Orgel (1957); McClure (1959)) together with the theory of Jahn & Teller (1937) predict that ions with orbitally degenerate electron configurations distort their environments so as to remove the degeneracy. For transition-metal ions, the d orbitals are split by an octahedral field into a lower triplet, t_{2g} , and an upper doublet, e_g . When the degeneracy occurs in the antibonding e_g , the distortions from cubicity will be large; when in the non-bonding t_{2g} , small. More refined treatments of Fe^{II} and Co^{II} by Opik & Pryce (1957) and by van Vleck (1958) show that the strong spin-orbit coupling reduces the degeneracy for Co^{II} to a Kramers doublet (Jahn, 1938) which cannot be split by a configurational distortion of the Jahn-Teller type, and that the coupling stabilizes the symmetrical octahedral configuration for Fe^{II} by reducing the Jahn-Teller distortion. The first approximations to the electron configurations and the distortions for these compounds are given in Table 1.

Table 1. *Electron configurations and distortions*

Ion	Electron configuration	Predicted distortion	Observed distortion
Cr^{II}	$(t_{2g})^3(e_g)^1$	large	large
Mn^{II}	$(t_{2g})^3(e_g)^2$	0	0
Fe^{II}	$(t_{2g})^4(e_g)^2$	small or 0	0
Co^{II}	$(t_{2g})^5(e_g)^2$	0	0
Ni^{II}	$(t_{2g})^6(e_g)^2$	0	0
Cu^{II}	$(t_{2g})^6(e_g)^3$	large	large
Zn^{II}	$(t_{2g})^6(e_g)^4$	0	0

It is seen that the observed static distortions follow the theoretical calculations. A dynamical distortion for $\text{Fe}(\text{II})$ and $\text{Co}(\text{II})$ might be observed in the infrared absorption spectrum in a manner similar to that shown for some transition-metal hexafluorides by Weinstock & Claassen (1959). They found a special vibronic coupling in ReF_6 , OsF_6 and IrF_6 due to Jahn-Teller instability in the absence of a static configurational distortion.

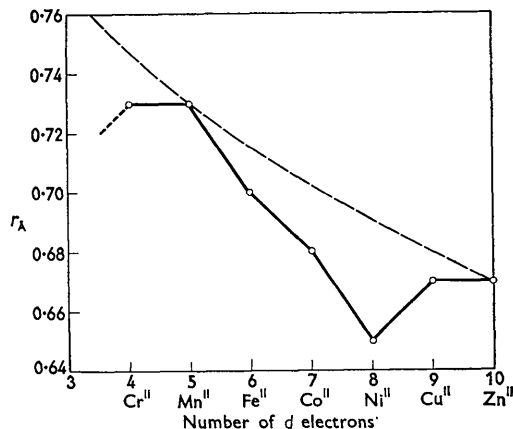


Fig. 1. Radii of Me^{II} versus number of d electrons.

A further comparison can be made between the radii of the transition-metal ions in the fluoride-perovskite series and theories of the relative sizes of transition-metal ions (van Santen & van Wieringen (1952); Hush & Pryce (1957, 1958); Hush (1958)). Using 1.36 \AA for the radius of the fluoride ion and taking the weighted average of the lattice constants for KCrF_3 and KCuF_3 (a very close approximation in the copper case in spite of the complexity of the structure), the radii in Table 2 are obtained; they are plotted versus number of d electrons in Fig. 1. A similar plot is obtained if the molecular volumes are used.

Table 2. *Ionic radii in fluoride-perovskites*

Cr^{II} *	0.73 Å	Ni^{II}	0.65 Å
Mn^{II}	0.73	Cu^{II} *	0.67
Fe^{II}	0.70	Zn^{II}	0.67
Co^{II}	0.68		

* Weighted average from lattice constants only; see text.

The smooth curve through d^5 and d^{10} shows the expected decrease with increasing nuclear charge in the absence of crystal-field effects. These have been shown in the above-mentioned work to decrease further the sizes, with marked contractions when electrons are added to the t_{2g} orbitals, and with lesser decrements when these are added to the e_g orbitals. Similar effects have been shown for other compounds; they are especially evident in this structurally similar series. The drop from Fe^{II} to Co^{II} is not so great as those from Mn^{II} to Fe^{II} and Co^{II} to Ni^{II} because in Co^{II} a small part of the 5 t_{2g} electrons is promoted to e_g , resulting in a slight repulsion as shown by van Santen & van Wieringen (1952). The dotted line shows the expected drop going back to V^{II} ; it should be possible to make KVf_3 and perhaps KTiF_3 , probably cubic at room temperature. Lastly, it is seen that the contractions for Cr^{II} and Cu^{II} are not so large as might be expected from the work of Hush & Pryce (1957, 1958) and Hush (1958), a difference undoubtedly due to the Jahn Teller distortion which was not included in their

considerations. It is interesting that distortions in these cases have led to larger average volumes for the ions.

The author is grateful to S. Geller for his help in all phases of this work. Thanks are also due A. D. Liehr for discussion of the theoretical aspects, R. G. Treuting for the use of his computation programs, E. A. Wood and W. L. Bond for assistance with the optical observations, J. P. Wright for the chemical analysis and H. Guggenheim, W. Masterson and D. W. Mitchell for help with the experiments.

References

- DUNITZ, J. D. & ORGEL, L. E. (1957). *J. Phys. Chem. Solids*, **3**, 20.
 EDWARDS, A. J. & PEACOCK, R. D. (1959). *J. Chem. Soc.* p. 4126.
 GELLER, S. (1956). *J. Chem. Phys.* **24**, 1236.
 GELLER, S. (1957). *Acta Cryst.* **10**, 243.
 GELLER, S. & BALA, V. B. (1956). *Acta Cryst.* **9**, 1019.
 GELLER, S. & WOOD, E. A. (1956). *Acta Cryst.* **9**, 563.
 GILLES, M. A. (1957). *Acta Cryst.* **10**, 161.
 GUGGENHEIM, H. (1960). *J. Phys. Chem.* **64**, 938.
 HOPPE, R. (1959). *Angew. Chem.* **71**, 457.
 HUSH, N. S. (1958). *Disc. Faraday Soc.* **26**, 145.
 HUSH, N. S. & PRYCE, M. H. L. (1957). *J. Chem. Phys.* **26**, 143.
 HUSH, N. S. & PRYCE, M. H. L. (1958). *J. Chem. Phys.* **28**, 244.
 JAHN, H. A. (1938). *Proc. Roy. Soc. A*, **164**, 117.
 JAHN, H. A. & TELLER, E. (1937). *Proc. Roy. Soc. A*, **161**, 220.
 MARTIN, R. L., NYHOLM, R. S. & STEPHENSON, N. C. (1956). *Chem. and Ind.*, p. 83.
 MCCLURE, D. S. (1959). *Solid State Physics*, **9**, 400.
 MOFFITT, W. & BALLHAUSEN, C. J. (1956). *Ann. Rev. Phys. Chem.* **7**, 107.
 OKAZAKI, A. (1960). *J. Phys. Soc. Japan.* (To be published.)
 OKAZAKI, A., SUENUME, Y. & FUCHIKAMI, T. (1959). *J. Phys. Soc., Japan*, **14**, 1823.
 OPTIK, U. & PRYCE, M. H. L. (1957). *Proc. Roy. Soc. A*, **238**, 425.
 PALMER, W. G. (1954). *Experimental Inorganic Chemistry*, p. 556. Cambridge: University Press.
 SANTEN, J. H. VAN, & WIERINGEN, J. S. VAN (1952). *Rec. Trav. Chim. Pays-Bas*, **71**, 420.
 VLECK, J. H. VAN (1958). *Disc. Faraday Soc.* **26**, 96.
 WEINSTOCK, B. & CLAASSEN, H. W. (1959). *J. Chem. Phys.* **31**, 262.
 WELLS, A. F. (1950). *Structural Inorganic Chemistry*, 2nd ed., p. 375. Oxford: University Press.

Acta Cryst. (1961). **14**, 585

On the Polyhalide Ions*

BY R. E. RUNDLE

Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa, U.S.A.

(Received 16 August 1960)

Experimental evidence is cited to show that cation size is responsible for variation of the structure of the triiodide ion, I_3^- , and that in an isolated state the ion is probably linear and symmetrical with an over-all length, D , similar to the shortest distances found in crystals. The applicability of a simple molecular orbital description of the bonding without the use of outer d -orbitals is shown to be in keeping with most of the observed facts for polyhalides and polyhalogens. Where modification is necessary it is shown that a contribution of outer d -orbitals to σ -bonding, and to π -bonding can be added naturally to the MO description. These contributions can, in an MO description, be made large or small to minimize the energy of the system, and seem preferable to the valence bond, hybrid orbital description in its usual form since the latter description seems to require an arbitrarily high contribution of outer d -orbitals.

Introduction

The nearly linear triiodide ion, I_3^- , varies in structure with its environment, and an increase in asymmetry of the bonds accompanies an increase in the total length, D , of the ion (Table 1) (R. Slater, 1959). This behavior parallels the theoretically predicted behavior for H_3 (Hirschfelder, Diamond & Eyring, 1937), and using this analogy J. Slater (1959) has

suggested that in its lowest state the isolated I_3^- ion may have a length, D , comparable with the largest D observed in crystals, but in certain crystals 'pressure' may force the ion to have a shorter length until at some critical D the ion may become symmetrical.

The nature of the triiodide ion and its variation with environment is an interesting question related to the more general question of the nature of polyhalide ions. A number of suggestions have been made, and these have been evaluated by Havinga (1957). In this paper a wider range of experimental information is used as

* Contribution No. 926. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.