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The Crystal Structure of KMF_3

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The electron distributions in $KMnF_3$, $KFeF_3$, $KCoF_3$ and $KNiF_3$ have been determined by an X-ray analysis to reveal whether there are any local distortions around the 3*d* metal ions or not. The [001] projection of each compound obtained by Fourier synthesis of the observed structure factor shows that the structure is of the ideal perovskite type at room temperature. In each case, however, the electron distributions around F^- ions are elongated in the direction perpendicular to the 3*d* metal-fluorine-3*d* metal bonds. This elongation has been analyzed by difference Fourier projection along [001] based on each of the following assumptions: i) Anisotropic thermal vibrations of F^- ions due to the tetragonal symmetry of their positions. ii) Isotropic thermal vibrations of F^- ions which occupy such positions as being distributed with uniform probability along a circle, of which axis is along the 3*d* metal-fluorine-3*d* metal bond. The elongation is too small to distinguish which is the better.

In recent years the crystal structures of the antiferromagnets KMF_3, where M indicates the 3*d* transition group elements, have been investigated using single crystals. At room temperature ($> T_N$) the structures of $KMnF_3$, $KFeF_3$, $KCoF_3$ and $KNiF_3$ are of the cubic perovskite type[1),2)], while $KCuF_3$ crystallizes as a tetragonal modification of the perovskite type[3),4)]. The distortion of $KCuF_3$ may be attributed to the co-operative Jahn-Teller effect[3)]. From the view-point of the crystalline field theory it may be expected that the surroundings of Fe^{2+} and Co^{2+} ions in $KFeF_3$ and $KCoF_3$, respectively can distort slightly. Therefore the detailed structure analysis using Fourier methods was undertaken to reveal whether these four compounds have the ideal perovskite structure or not.

Specimens on which the X-ray work was performed were formed into nearly cylindrical shape, about 1 mm in length and about 0.1 mm in diameter, by cutting crystals with a razor blade and by grinding with sand paper. Intensity data for MoKα radiation were obtained from integrating Weissenberg photographs taken about [001] using multiple-film technique. The ranges of the intensities measured were about 10^4 to 1 and reflexions out to $\sin\theta/\lambda = 1.38(\text{Å}^{-1})$ were recorded for each compound. The intensities were corrected for the absorption factor as well as Lorentz and polarization factors. No corrections were made for extinction and dispersion.

The [001] projection of the electron distribution in each compound obtained by the F_o synthesis is shown in Fig. 1, where F_o means the observed structure factor and has a positive value because the origin is chosen at the position of M^{2+} ion. In this figure one fourth of the unit cell is shown. The highest peak represents M^{2+} ion superposed by one of F^- ions, while the medium and two lowest peaks represent single K^+ and F^- ions, respectively, in each case.

It seems that there is no essential difference between these four compounds and that all of these have the ideal perovskite structure except for some considerable elongation of F^- ions. This elongation may be attributed naturally to an anisotropic thermal vibration of F^- ion due to the tetragonal symmetry of its position. But if the centre of F^- ion occupies such positions as being distributed with uniform probability along a circle, of which axis is along the $M^{2+}-F^--M^{2+}$ bond, a similar elongation of F^- peak will be obtained, even though an isotropic thermal vibration is assumed.

The final (F_o-F_c) syntheses of $KNiF_3$ and $KCoF_3$ are shown in Fig. 2. (The following discussions will be concentrated on $KNiF_3$ and $KCoF_3$.) Since M^{2+} ion and one of F^- ions are superposed and then the syntheses are not straightforward, a trial and error method is used. In the case of Fig. 2(a) the calculated structure factor F_c was evaluated by assuming an anisotropic temperature

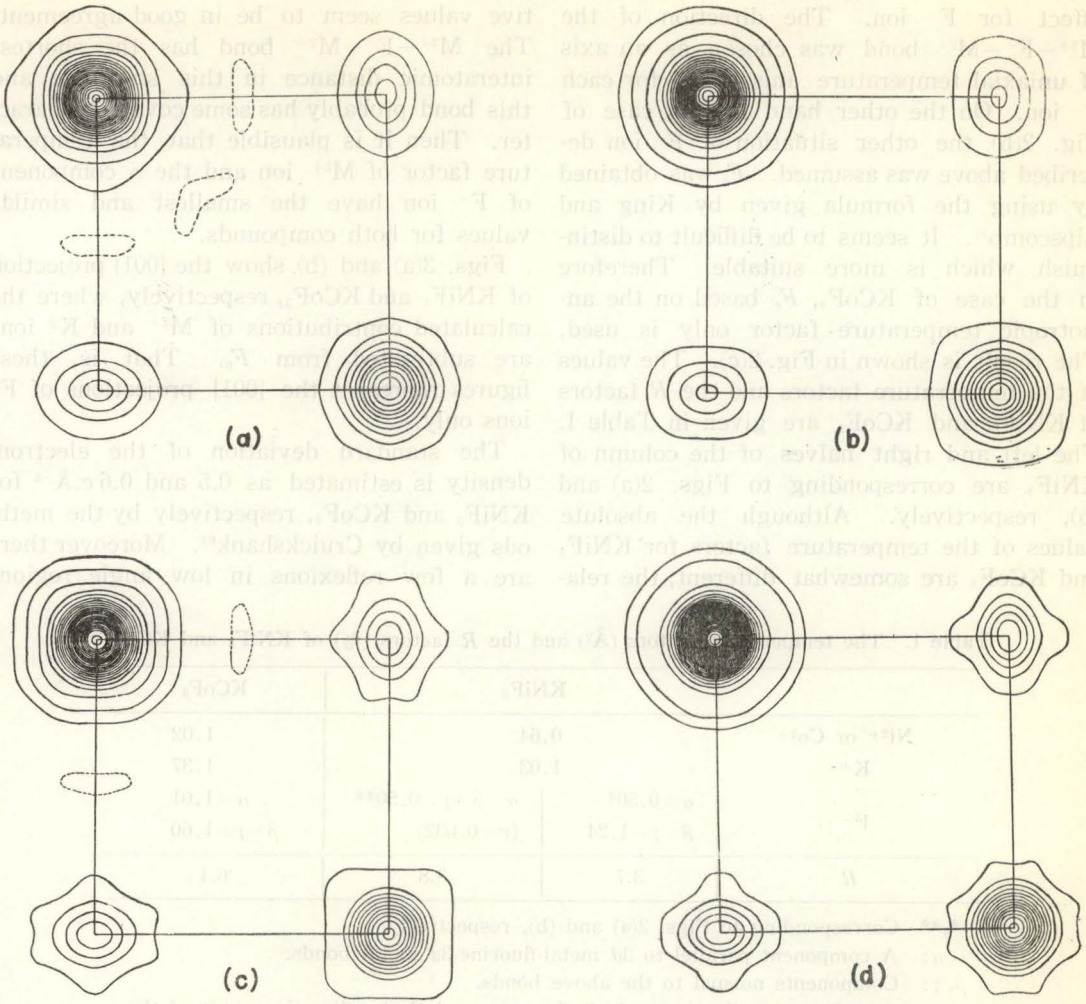
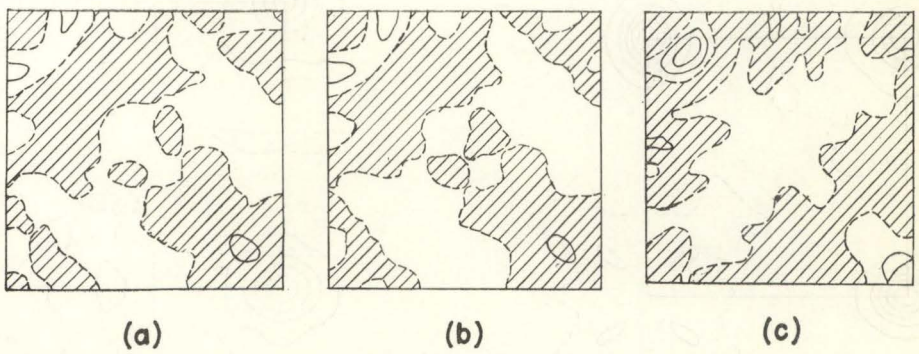


Fig. 1. Electron-density projections along [001] at room temperature, (a): $KMnF_3$, (b): $KFeF_3$, (c): $KCoF_3$ and (d): $KNiF_3$, with contours at intervals of 5 e.Å^{-2}. Dotted lines indicate 0 e. Å^{-2}. One fourth of the unit cell is shown for each compound.



Fig, 2. Final $(F_c - F_c)$ Fourier projections of (a), (b) $KNiF_3$ and (c) $KCoF_3$ along [001], with contours at intervals of 1 e.Å^{-2}. Negative region is shaded. The same region as in Fig. 1 is shown. As for $KCoF_3$, F_c based on the anisotropic temperature factor only is used,

effect for F^- ion. The direction of the $M^{2+}-F^--M^{2+}$ bond was chosen as an axis of uniaxial temperature anisotropy for each F^- ion. On the other hand in the case of Fig. 2(b) the other situation of F^- ion described above was assumed. F_c was obtained by using the formula given by King and Lipscomb[5]. It seems to be difficult to distinguish which is more suitable. Therefore in the case of $KCoF_3$, F_c based on the anisotropic temperature factor only is used. The result is shown in Fig. 2(c). The values of the temperature factors and the R factors of $KNiF_3$ and $KCoF_3$ are given in Table I. The left and right halves of the column of $KNiF_3$ are corresponding to Figs. 2(a) and (b), respectively. Although the absolute values of the temperature factors for $KNiF_3$ and $KCoF_3$ are somewhat different, the relative values seem to be in good agreement. The $M^{2+}-F^--M^{2+}$ bond has the shortest interatomic distance in this structure and this bond probably has some covalent character. Then it is plausible that the temperature factor of M^{2+} ion and the α component of F^- ion have the smallest and similar values for both compounds.

Figs. 3(a) and (b) show the [001] projection of $KNiF_3$ and $KCoF_3$, respectively, where the calculated contributions of M^{2+} and K^+ ions are subtracted from F_o. That is, these figures represent the [001] projections of F^- ions only.

The standard deviation of the electron-density is estimated as 0.5 and 0.6 e.Å^{-2} for $KNiF_3$ and $KCoF_3$, respectively by the methods given by Cruickshank[6]. Moreover there are a few reflexions in low angle regions

Table I. The temperature factors (Å^2) and the R factors (%) of $KNiF_3$ and $KCoF_3$.

	$KNiF_3$		$KCoF_3$
Ni^{2+} or Co^{2+}	0.64		1.02
K^+	1.03		1.37
F^-	$\alpha=0.50$*	$\alpha=\beta=\gamma=0.50$**	$\alpha=1.01$
	$\beta=\gamma=1.24$	($r=0.032$)	$\beta=\gamma=1.60$
R	3.7	3.8	6.4

*,** Corresponding to Figs. 2(a) and (b), respectively.
α: A component parallel to 3d metal-fluorine-3d metal bonds.
β, γ: Components normal to the above bonds.
r: A radius of a circle on which the centre of F^- ion lies (in a unit of the lattice constant).
$R=\Sigma|F_o-F_c|/\Sigma|F_o|$

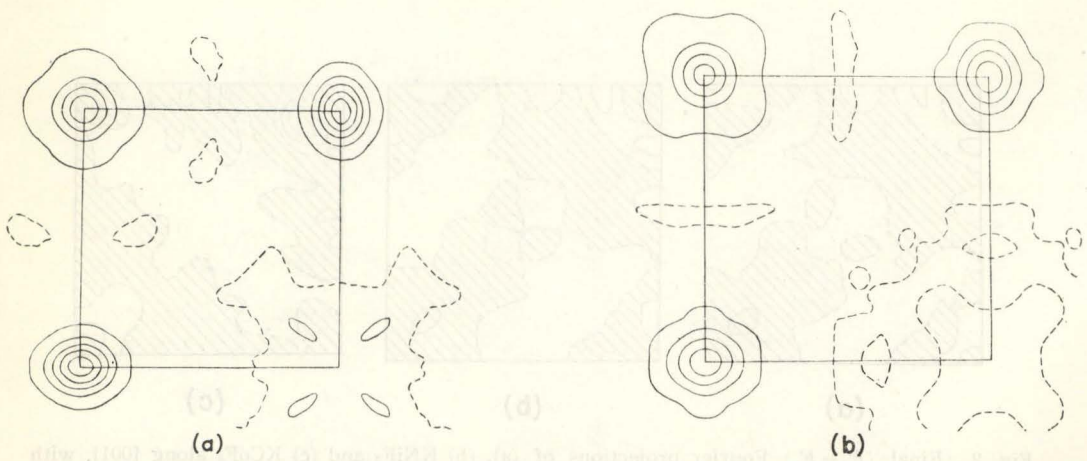


Fig. 3. Projection of electron-density of F^- ions in (a) $KNiF_3$ and (b) $KCoF_3$, with contours at intervals of 5 e. Å^{-2}. Broken lines indicate 0 e. Å^{-2}.

because of the small unit cell size. Therefore it is meaningless to discuss the outer part of the electron distribution of each atom; for example the shape of the outmost contours of F^- ions in Figs. 3(a) and (b). Nevertheless the elongation of F^- ions normal to the $M^{2+}-F^--M^{2+}$ bond is conclusive.

The elongation of F^- ions discussed above seems to be consistent with the following facts. $KMnF_3$ has pseudo-tetragonal lattice below 184°K. Beckman and Knox[7] have reported that the structure of this phase is of gadolinium orthoferrite ($GdFeO_3$) type. In $GdFeO_3$ structure anions are not on the lines connecting two adjacent magnetic cations, but on the planes which are perpendicular to these lines and crossing these lines at the middle points. In the case of $KMnF_3$ the distance between F^- ions and these lines is about 5~8% of the lattice constant. These values may be compared with that of about 3% given in Table I as a radius of a circle on which F^- ion lies. Although the lattice distortion independent of the magnetic order is found only in the case of $KMnF_3$, the elongation of F^- ion suggests some tendency of a similar distortion for the others.

References

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DISCUSSION

S. Iida: According to my feeling, transition metal should attract the electron cloud of fluorine ion more than the potassium ion does. On your electron density map, it seems that the deformation of fluorine ion is larger in the potassium side. Is it related to the presence of a larger amount of fluorine electrons which are distributed mainly on the transition metal ions?

A. Okazaki: The standard deviation of the electron-density is estimated as 0.5 and 0.6 $e.Å^{-2}$ for $KNiF_3$ and $KCoF_3$, respectively. Moreover, the number of reflexion in low angle regions is not large because of the small unit cell size. Therefore it is meaningless to discuss the outer part of the electron distribution of each atom, the shape of the outmost contours, for example.

E. Banks: Were your temperature factors determined experimentally by measurements over a range of temperatures?

A. Okazaki: We determined the temperature factors experimentally only at room temperature.