Magnetic Properties of KMnF₃. I. Crystallographic Studies*

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The lattice parameters for KMnF₃ have been determined by means of an x-ray rotation camera designed for temperatures down to 15°K. The cubic room temperature perovskite structure transforms at 184°K to an orthorhombic phase with $D_{2h}^{16}-Pbnm$ as the most probable space group with a unit cell containing 4 formula units; it has a tetragonal pseudocell with $c/a>1$ in which the fluorine octahedra about the manganese remain essentially regular but tilt relative to the crystal axes. At 84°K, just below the Néel temperature of 88°K, the pure antiferromagnetic also has a tetragonal pseudocell, but with $c/a<1$ and the still essentially regular octahedra rotated as well as twisted. Below a second magnetic transition at 81.5°K, the 65°K structure shows in addition a significant distortion of the regularity of the octahedra.

INTRODUCTION

FLUORIDES of the type KMeF₃, where Me is a $3d$ element, have attracted wide attention because of their interesting magnetic properties. As do several other compounds of similar composition, they crystallize in the perovskite structure (Fig. 1). Antiferromagnetism is common in perovskite-like double oxides of $3d$ ions, and also occurs in the double fluorides.[1]

The fluoride KMnF₃ with the Néel temperature $T_N=88°K$ has a divalent manganese ion with five d electrons. Mn^{+2} is thus in an S state, which excludes any Jahn-Teller type of distortion. For this reason we can expect that KMnF₃ will be only slightly distorted if at all from the cubic perovskite structure. On the other hand, the cubic perovskite structure itself is known to be unstable. These facts contribute to make KMnF₃ an especially interesting compound from a magnetic point of view. Torsion measurements, which will be reported in the second paper in this series,[2] among other things
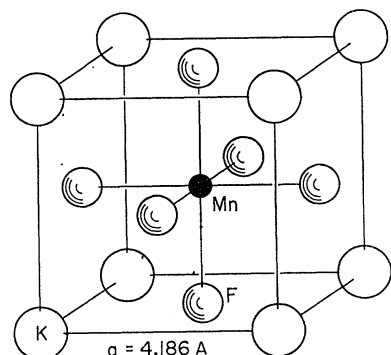

FIG. 1. The unit cell of KMnF₃ at room temperature.

a = 4.186 A

have shown the existence of a second magnetic transition at 81.5°K, not far below the Néel temperature of 88°K. Below 81.5°K the crystal has a weak ferromagnetic moment caused by a canting of the spins. Crystallographic studies of KMnF₃ were undertaken in order to determine the magnitude of the fluorine distortions both above and below the Néel temperature, thereby facilitating the explanation of the magnetic structure.

Scatturin et al.[3] have investigated several of the potassium double fluorides by means of neutron powder diffraction at liquid helium and liquid nitrogen temperatures. At 4.2°K the magnetic structure belongs to the so-called G-type configuration, where the two magnetic sublattices constitute two interpenetrating face-centered lattices of opposite spin. The diffraction pattern reveals some distortion of the fluorines, and the authors show that their data fit reasonably well with the same kind of distortion that was found by Geller[4] in several perovskite crystallizing materials. The same space group $D_{2h}^{16}-Pbnm$ is also applicable to our x-ray data, though we have found a slightly different distortion of the fluorine octahedron and also some distortion of the potassium ions. A difference is further noticed in the ion parameters for the two magnetic states found by the torsion measurements, although the lattice constants do not change noticeably.

At room temperature the fluorides of Mn, Fe, Co, Ni, and Zn have the ideal cubic perovskite structure, while KCrF₃ and KCuF₃ show a considerable distortion.[5,6] Preliminary measurements of KMnF₃ at lower temperatures[7] showed that the cubic structure persists down to

¹ R. L. Martin, R. S. Nyholm, and N. C. Stephenson, Chem. & Ind. (London), No. 3, 83 (1956). R. G. Shulman, K.Knox , and B. J. Wyluda, Bull. Am. Phys. Soc. 4, 166 (1959).
² A. J. Heeger, O. Beckman, and A. M. Portis (to be published).
³ V. Scatturin, L. Corliss, N. Elliott, and J. Hastings, Acta Cryst. (to be published).
⁴ S. Geller, J. Chem. Phys. 24, 1236 (1956).
⁵ K. Knox, Abstracts of the Annual Meeting of the American Crystallographic Association, Ithaca, New York, July, 1959 (unpublished).
⁶ A. Okazaki, Y. Suemune, and T. Fuchikami, J. Phys. Soc. (Japan) 14, 1823 (1959).
⁷ O. Beckman, I. Olovsson, and K. Knox, Acta Cryst. 13, 506 (1960).

FIG. 2. X-ray rotation camera for low temperatures.
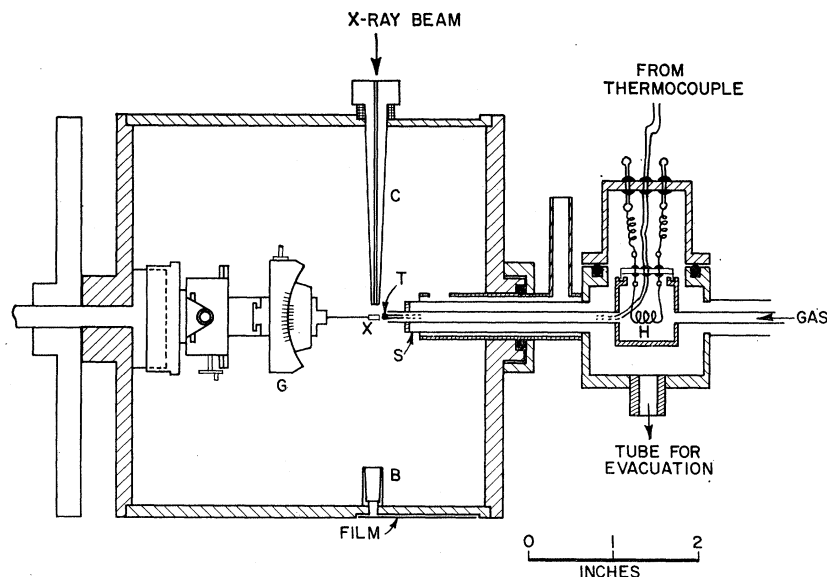
184°K, where a distortion to a tetragonal pseudocell with $c/a>1$ sets in. At the Néel temperature a second change occurs to $c/a<1$. In both temperature regions the true crystallographic cell contains four molecules of KMnF₃. Okazaki et al.[6] have reported lattice parameters at room temperature and 77°K. They report a monoclinic pseudocell at the lower temperature, a phase that we have found in the temperature region 88°K to 105°K, provided the crystal is warmed from the antiferromagnetic region. This intermediate phase does not seem to occur with decreasing temperature.

EXPERIMENTAL

A simple rotation camera (Fig. 2) was designed and built for operation at temperatures down to 15°K. The x-ray beam is directed by the collimator C towards the crystal X and the main beam is then caught by the beam stopper B. A goniometer head G carrying the sample is mounted on an axis through one of the end walls of the camera. The opposite wall supports the double walled stainless steel tubes for transferring the cooling gas from a liquid helium (or nitrogen) Dewar. The current through a resistor dipping into the liquid helium controls the rate of flow of the gas. The temperature is measured by a thermocouple T close to the crystal. A boiling rate of 1 liter of liquid per hour brought the temperature down to 15°K, while only 0.3 liter/hour was needed for temperatures closer to the Néel temperature. A small heater H is placed in the gas stream about four inches from the sample for fine adjustment of the temperature. Owing to the small distance between this heater and the crystal the time constant for the temperature regulation is as short as 2 sec. The temperature could easily be maintained manually within ±2 degrees for several hours and therefore no automatic temperature regulating device was built.

The open circumference of the camera is covered by a thin film of plastic with negligible x-ray absorption in order to prevent heavy icing of the sample. The photographic film in black paper is wrapped from the outside. Notches in the camera circumference give reference marks every 30 degrees.

The single crystal was grown by zone-refining material that had been precipitated from aqueous solution and sintered in anhydrous hydrogen fluoride. In order to reduce oxygen contamination, the material to be zone-refined was placed in a graphite boat in a dry nitrogen atmosphere. An oxygen contamination might be expected to result in some trivalent manganese ions. No Mn^{+3} ions could be detected by analytical methods with an estimated upper limit of 0.06%.

A crystal of the size 0.1×0.3 mm was cut from a sample and mounted in the camera with a $\langle 100 \rangle$ axis parallel to the rotation axis. For the lattice parameter measurements, Cu K radiation was used, while the intensity measurements were made on films exposed with Mo K radiation because of the smaller absorption of this radiation, which made absorption corrections unnecessary. In the cubic room-temperature phase the 0, 1, and 2 layers could be obtained. The relative intensities were estimated visually by comparison with an intensity scale. In order to cover a large intensity range, the multiple-layer film technique was used. Since the absorption in each film is very low, 0.003-in. Mo foils were placed between the films.

CRYSTALLOGRAPHIC DATA

Photographs taken at room temperature show the undistorted cubic perovskite structure with one molecule per unit cell. The lattice constant is 4.186 A, which gives a density of 3.42 g/cm³. Upon lowering the temperature, the spots split at 184°K, indicating a lower

TABLE I. Crystallographic data on KMnF₃.

Temp. (°K)	Lattice constants			Pseudocell (A)
	a(A)	b(A)	c(A)	
293				cubic, $a=b=c=4.186$
95	5.885	5.885	8.376	tetr. $a=b=4.161$, $c=4.188$
65	5.900	5.900	8.330	tetr. $a=b=4.172$, $c=4.165$
92, incr. temp.				monocl. $a=4.169$, $b=4.175$ $c=4.190$, $\beta=89°49'$
	Okazaki et al.[a]			monocl. $a=4.168$, $b=4.171$ $c=4.185$, $\beta=89°51'$

[a] See reference 6.

symmetry. The splitting may in the first approximation be explained by a tetragonal symmetry. At this transition the crystal twins with the crystallites having their main crystallographic axis oriented along any of the three former cube axes. Reflections ($h00$) thus show the largest splitting with an intensity ratio of 2:1 of the two spots. The transition was confirmed by optical measurements, which showed the appearance of optical anisotropy below 184°K.

At low temperatures, long-exposure films show superlattice lines halfway between the cubic layer lines, indicating a larger unit cell containing four molecules. The crystal has orthorhombic symmetry with the a and b axes equal within experimental error and the c axis close to the value $a\sqrt{2}$. The cell constants at 293°K, 90°K, and 65°K are given in Table I, as well as the dimensions of the pseudocell. The variation of the pseudocell with temperature is shown in Fig. 3. As the temperature is lowered from 184°K the c/a ratio of the pseudocell increases to the maximum value $c/a=1.0065$ at the Néel temperature. In the antiferromagnetic state the lattice changes, giving a c/a ratio of 0.9985.

The crystal shows hysteresis in the temperature region immediately above the Néel temperature. On increasing the temperature the crystal goes from the magnetic state to another orthorhombic phase with three different axes. The pseudocell is then monoclinic with axial lengths indicated by black triangles in Fig. 3. These data are consistent with the parameters given by
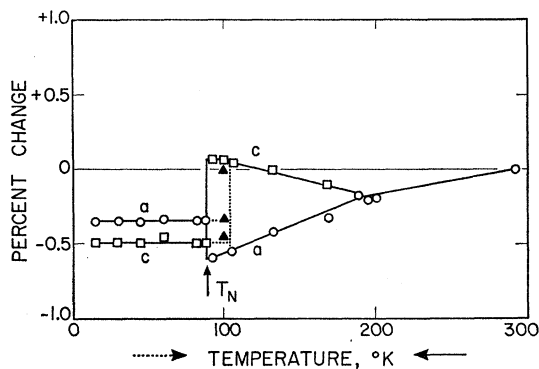

FIG. 3. Pseudocell dimensions of KMnF₃ as a function of temperature.

Okazaki et al.[6] for 77°K. These authors remark, however, that they have taken their picture of KMnF₃ very close to the Néel temperature and the crystal might, in fact, have been above 88°K for most of the exposure time. According to our experience this phase only appears when the crystal warms up from the antiferromagnetic state.

In a single-crystal rotation photograph the intensity of a reflection (in the 0 layer) is expressed by

$$I_{obs} = \mathrm{const}\, p\, |F_{hkl}|^2 LP \exp[-B(\sin\theta/\lambda)^2].$$

LP is the Lorentz and polarization factor for the Bragg angle θ, and p is a multiplicity factor. The structure factor is given by

$$F_{hkl} = \sum_i f_i \exp[2\pi i(hx_i + ky_i + lz_i)],$$

summing over the different ions with the coordinates x_i, y_i, and z_i. The scattering factors f_i for K⁺ and F⁻ were obtained from Freeman[8] and from Thomas and Umeda[9] for Mn⁺².

The temperature factor B, which is proportional to the mean square deviation of the ions from their regular positions, could be expected to be rather small for the high melting crystal KMnF₃. In the first approximation the same factor was assumed for all the ions in the lattice. This resulted in some discrepancies between observed and calculated intensities for reflections of high indices. Reflections with $h+k+l$ odd, where the heaviest ions K⁺ and Mn⁺² scatter with 180° phase difference, were observed to be too strong compared with the reflections $h+k+l$ even, when the scattering factors of K⁺ and Mn⁺² add together. These deviations could be explained by applying a higher temperature factor for the K⁺ ions than for the Mn⁺² and the F⁻ ions. A good fit was obtained for $B=1.3$ A² for potassium and $B=0.5$ A² for the other ions. The assumption is not unreasonable with regard to the sizes of the ions and the crystal structure. The geometrical conditions for the perovskite structure is expressed by the Goldschmidt tolerance factor t in the relation:

$$R_K + R_F = t\sqrt{2}(R_{Mn} + R_F),$$

where R_K, R_{Mn}, and R_F are the ionic radii. The low value of $t=0.94$ for KMnF₃ implies that the Mn⁺² and F⁻ ions are touching, while the K⁺ ions are more free to vibrate. The low tolerance factor also implies crystallographic instability, which might be associated with the phase change that occurs at 184°K.

The low-temperature phases show superlattice lines halfway between the cubic layer lines. The reflections can be indexed with a unit cell of four molecules. The determination of systematic absences is complicated by the twinning of the crystal, since several different crystallographic reflections add together in each spot. However, reflections of the type ($h0l$) with ($h+l$) odd

[8] A. J. Freeman, Acta Cryst. 12, 929 (1959).
[9] L. H. Thomas and K. Umeda, J. Chem. Phys. 26, 293 (1957).

TABLE II. Coordinates of the ions in KMnF$_3$, D_{2h}^{16}—$Pbnm$.

Ion	Position[a]	Scatturin et al. 4°K			65°K			84°K			95°K		
K⁺	4(c)	0	0	¼	−0.005	0.02	¼	−0.01	0.02	¼	−0.01	0.02	¼
Mn⁺²	4(b)	½	0	0	½	0	0	½	0	0	½	0	0
F$_I$⁻	4(c)	0.01	0.5	¼	0.035	0.50	¼	0.038	0.49	¼	0.023	0.49	¼
F$_{II}$⁻	8(d)	−0.270	0.040	0.260	−0.280	0.28	0.030	−0.268	0.268	0.018	−0.25	0.25	0.034

[a] Positions: 4(c): ±(x, y, ¼; ½−x, ½+y, ¼); 4(b): (½,0,0; ½,0,½; 0,½,0; 0,½,½); 8(d): ±(x, y, z; ½−x, ½+y, ½−z; x̄, ȳ, ½+z; ½+x, ½−y, z̄).

are missing as well as reflections (0kl) with k odd. A possible space group is D_{2h}^{16}—$Pbnm$. In extensive studies of perovskite like compounds involving rare-earth ions, Geller and co-workers[10] have found that this space group is common. An analysis shows that for KMnF₃ the observed intensities fit well to the same type of distortion. The orthorhombic cell is shown in Fig. 4, where for simplicity the ions are shown in their undistorted positions. Figure 4 also shows the pseudocell with the fluorine octahedron as it appears in Fig. 1. Table II gives the general coordinates of the ions according to the space group $Pbnm$. There are two kinds of fluorine ion positions. The ions at the top and bottom of the octahedron, F$_I$⁻ are in 4(c), while the side ions, F$_{II}$⁻, are in 8(d).

Because of the twinning of the crystal, the standard methods for solving the structure with least-squares refinements could not be applied. The seven unknown parameters had to be evaluated instead on a trial and error basis. The observed reflections divide into four groups, of which the group, (h+k) even, l even, represent the strong reflections that are only slightly changed from the room-temperature phase. The weak superstructure lines, (h+k) odd, l odd, are sensitive to the x coordinates of K⁺ and F$_I$⁻ and the z coordinate of F$_{II}$⁻. A change in these fluorine coordinates means a tilting of the fluorine octahedron. Reflections, (h+k) odd, l even, depend mainly on the x and y coordinates of F$_{II}$⁻, thus representing a twisting of the octahedron. The twinning of the crystal causes reflections (hkl) always to be accompanied by (khl). It is therefore impossible to distinguish between the x and y coordinates of F$_{II}$⁻. The data give only the magnitude of x+y, and as the most probable solution with regard to the fact that the a and b axes are alike, x is put equal to y.

The temperature factors were in the first approximation estimated from the room-temperature data assuming a linear temperature dependence. It turned out, however, that this gave too large a factor for K⁺. A good fit was obtained with an over-all B=0.2 A².

The linear absorption coefficient of KMnF₃ for Mo K radiation is 58 cm⁻¹. With a crystal of 0.1-mm size the absorption is small and practically independent of the Bragg angle. The absorption coefficient for Cu K is 490 cm⁻¹, giving a high absorption in the crystal. As a check, films taken with Cu radiation were corrected for absorp-

tion assuming a cylindrical sample. The intensities then turned out to be consistent with the Mo intensities.

By the trial and error procedure the sum $\sum p|F_c|^2$ for the different reflections contributing to a spot was fitted to the observed $\sum p|F_0|^2$. The multiplicity factor p here also includes a weighing factor, determined under the assumption that the different crystallites formed with the same probability. The ionic coordinates for the temperatures 65, 84, and 95°K are shown in Table II. The 95-degree picture was taken under conditions of lowering the temperature and shows the regular phase.

DISCUSSION

The distortions in KMnF₃ are mainly those of the fluorine octahedron surrounding the center manganese ions. Accordingly there are only small differences between the room-temperature picture and the low-temperature pictures. The main feature is the appearance of the superstructure lines indicating the unit cell of four molecules, shown in Fig. 4. The fluorine distortions result in both a tilting and a twisting of the fluorine octahedron in the antiferromagnetic state. Figure 5 shows the distortions of the fluorines surrounding two adjacent manganese ions of opposite spin directions. As is evident from the figure the tilting takes place along a
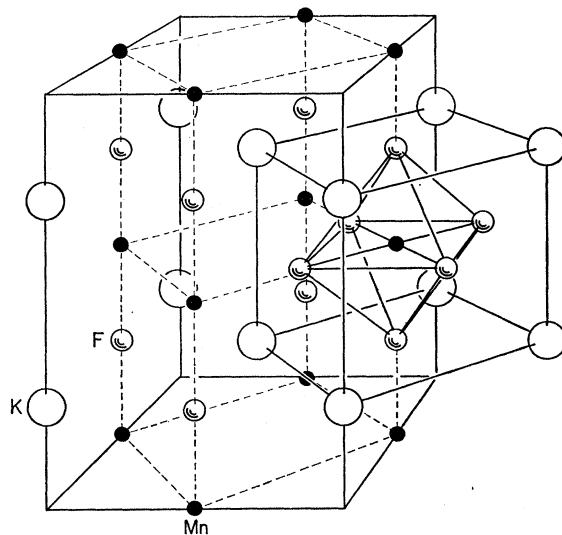

FIG. 4. The unit cell of KMnF₃ in the orthorhombic phase. The distortions from the regular positions are not indicated. The relation to the cubic unit cell of Fig. 1 is shown.

[10] S. Geller et al., Acta Cryst. 9, 563, 1019 (1956); 10, 243 (1957). M. A. Gilleo, Acta Cryst. 10, 161 (1957).

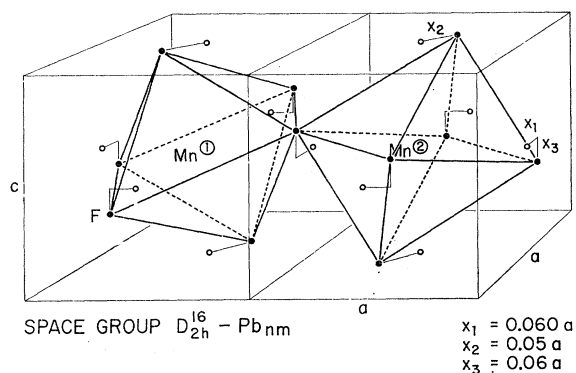SPACE GROUP D_{2h}^{16} – Pbnm

$x_1 = 0.060\,a$
$x_2 = 0.05\,a$
$x_3 = 0.06\,a$

FIG. 5. The fluorine octahedron distortions for two adjacent manganese ions. Crystal Structure of KMnF$_3$ at 65°K.

⟨110⟩ direction of the pseudocell, i.e., the fluorine F_I are moved in the x direction of the orthorhombic cell. The tilting occurs in opposite directions for the octahedra belonging to the two kinds of magnetic ions. The twisting also occurs in opposite directions. Looking along the c axis, however, all the octahedra in the same row are twisted in the same direction, regardless of the spin direction of the manganese ions.

In the temperature range studied here the 65°K picture shows the largest distortion, one that is even larger than that found by Scatturin *et al.* at 4°K. The neutron diffraction data have not indicated any distortion of the potassium ions, probably because the lines especially sensitive to potassium distortions are too weak to be observed by the neutron powder method.

In the pure antiferromagnetic state at 84°K the distortions are less pronounced than at 65°K. The paramagnetic phase at 95°K is characterized by a tilting only of the fluorine octahedran. The c/a ratio is greater than unity and the F_{II} ions have therefore some freedom

to move in the z direction. The potential energy of the lattice resulting from the Coulomb attraction was calculated by the method of Bertaut.[11] These calculations in general confirmed the x-ray data and showed that the crystal will not gain any energy by twisting the fluorine octahedra in the paramagnetic state.

The interionic distances for the fluorine octahedra are given in Table III. It is evident that the octahedron is

TABLE III. Interionic distances (A) in the fluorine octahedron of KMnF$_3$.

	65°K	84°K	95°K
Mn^{+2}–F_I^-	2.09	2.10	2.10
Mn^{+2}–F_{II}^-	2.12	2.10	2.10
F_I^-–F_{II}^-	2.89	2.93	2.80
	2.91	2.95	2.86
	3.04	2.98	3.07
	3.06	2.99	3.13
F_{II}^-–F_{II}^-	2.97	2.96	2.94
	3.01	2.97	3.00

greatly distorted in the 65°K phase, while the 84°K phase is characterized by a mere tilting and rotating of an almost regular octahedron.

[11] F. Bertaut, J. phys. radium 13, 499 (1952).