

Crystal and Magnetic Structure of the Planar Ferromagnet CsMnF₄

W. MASSA

Fachbereich Chemie und Sonderforschungsbereich 127 (Kristallstruktur und Chemische Bindung), Universität Marburg, Marburg, West Germany

M. STEINER

Hahn-Meitner-Institut für Kernforschung, Berlin, West Germany

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An X-ray single-crystal structure determination ($R = 0.0397$) shows that CsMnF₄ crystallizes in the CsFeF₄-type layer structure (tetragonal, space group $P4/nmm$, $a = 794.40(6)$ pm, $c = 633.76(9)$ pm, $Z = 4$). Anomalous thermal parameters of the bridging F atoms suggest either a planar dynamic Jahn-Teller effect, disorder of opposite oriented (001) layers of antiferrodistortive ordered elongated MnF₆ octahedra, or 1:1 twinning along (110) of an ordered structure of this kind with real space group $P4/n$. Planar superexchange interaction in such cooperatively Jahn-Teller-ordered layers is discussed to explain the ferromagnetism confirmed by powder neutron diffraction measurements. The neutron diffraction patterns were recorded at different temperatures between 2.2 and 25 K and at 300 K. The magnetic Bragg peaks which appeared yield a ferromagnetic structure with the magnetic moments perpendicular to the tetragonal axis. The Curie temperature was found to be $T_c = 18.9$ K, the magnetic moment was $4.04 \mu_B$.

Introduction

CsMnF₄ is of special interest for studies of the influence of a strong Jahn-Teller effect on structural and magnetic properties of a layered structure since the octahedrally coordinated Jahn-Teller ion Mn³⁺ is in the high spin state and has thus an E_g ground state. As reported previously (1, 2), CsMnF₄ was found to show ferromagnetic behavior although it seems to crystallize isotypic to the antiferromagnet CsFeF₄ (3).

Now we present the results of an X-ray single-crystal investigation (at 295 K) and of powder neutron diffraction measurements at low temperatures (down to 2.2 K).

Experimental

Pure powder of CsMnF₄ was prepared by reaction of Cs₂MnF₆ and MnF₂ at 500°C (1). A few crystals grew by slowly cooling the melt from 800 to 650°C in sealed platinum tubes. A clear red-brown plate of about $0.1 \times 0.07 \times 0.04$ mm³ was used for X-ray film exposures on a Precession camera and for intensity measurements on a 4-circle diffractometer (Enraf-Nonius). The space group was found to be $P4/nmm$ as in CsFeF₄, but not $P4/n$ as suggested previously (1, 4). The lattice constants $a = 794.40(6)$ pm, $c = 633.76(9)$ pm were determined by powder methods (1). The 1385 reflections (h and k : 0-14; l : 0-11)

were collected in $\omega/2\theta$ scan mode using monochromatic $\text{MoK}\alpha$ radiation. LP correction was made (5) and a numeric absorption correction applied ($\mu = 115.6 \text{ cm}^{-1}$) (6). After elimination of 314 unobserved and averaging of symmetry equivalent reflections 632 F_0 data remained for refinement of the structure. Calculations were made on a TR440 computer of the Rechenzentrum der Universität Marburg with the SHELX program system (6) using atomic form factors of neutral atoms (7) including dispersion corrections (8).

Neutron scattering experiments have been performed at the BER II at Hahn-Meitner-Institut, Berlin, using the multicounter diffractometer. This setup measures the scattered neutrons in a range of 80° in 2θ simultaneously with an angular resolution of 0.2° (10). It is thus possible to record the whole powder pattern at the same time. The wavelength used was $\lambda = 248.5 \text{ pm}$ and the powder sample had a volume of approximately 0.5 cm^3 . Pattern were recorded at room temperature and 25, 15, 5.1, 4.2, and 2.2 K with a measuring time of about 2 hr. A background measurement was performed with an empty sample holder, which was then subtracted from the powder patterns in order to obtain the pure CsMnF_4 pattern.

Results and Discussion of the X-ray Structure Determination

A least-squares refinement was successful when starting from the atomic parameters of CsFeF_4 (3) in the space group $P4/nmm$ and gave a reliability index for all the 632 reflections of $R = 0.0397$ ($R = \sum \sqrt{w} |F_0| - |F_c| / \sum \sqrt{w} |F_0|$ with weight $w = k/\sigma_{F_0}^2$ where k was refined to 1.49). The resulting parameters are compared with those of CsFeF_4 in Table I. Thus CsMnF_4 has a puckered layer structure (Figs. 1 and 2) which may be derived from the TlAlF_4 type (9). The high space group symmetry $P4/nmm$ should provide compressed

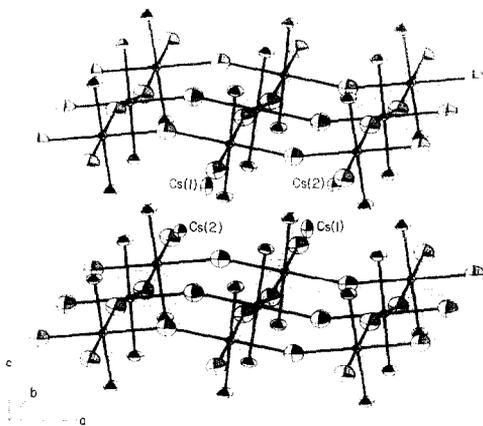


FIG. 1. The CsMnF_4 structure. ORTEP drawing of the unit cell and adjacent atoms with 50% thermal ellipsoids.

$[\text{MnF}_6]$ octahedra, which is very unlikely when looking at other structures of Jahn-Teller unstable ions like Cu^{2+} , Cr^{2+} , and Mn^{3+} in octahedral fluorine coordination.

There are indeed three remarkable differences between the structures of CsFeF_4 and CsMnF_4 :

(i) a decrease of the Mn-F-Mn bridge angle compared with the iron compound despite the lower c/a ratio (see Table II);

(ii) a more distinct compression of the $[\text{MnF}_6]$ group (Fig. 3);

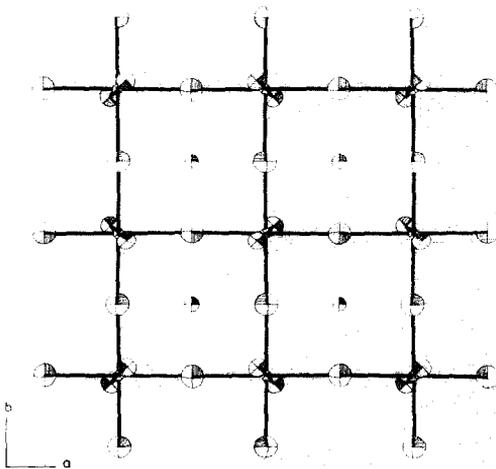


FIG. 2. Projection of a $[\text{MnF}_4]^-$ layer along $[001]$ (50% thermal ellipsoids).

TABLE I
 ATOM COORDINATES AND TEMPERATURE FACTORS^a OF CsMnF₄ COMPARED WITH CsFeF₄ (3)

Atom and Position	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn	0	0	0	0.0087 (2)	0.0087 (2)	0.0084 (3)	0.0002 (2)	0.0002 (2)	0.0005 (4)
Fe	0	0	0	0.0009	0.0009	0.0064	0.0003	0.0003	0.0003
Cs-1 (2b) Mn	0.75	0.25	0.5	0.0149 (2)	0.0149 (2)	0.0337 (4)	0	0	0
Fe	0.75	0.25	0.5	0.0100	0.0100	0.0346	0	0	0
Cs-2 (2c) Mn	0.25	0.25	0.4494 (1)	0.0172 (2)	0.0170 (2)	0.0176 (3)	0	0	0
Fe	0.25	0.25	0.4583 (3)	0.0095	0.0095	0.0215	0	0	0
F-1 (8i) Mn	0.25	-0.0033 (10)	0.0480 (8)	0.038 (2)	0.032 (2)	0.031 (2)	-0.002 (2)	0	0
Fe	0.25	-0.0012 (12)	0.0354 (13)	0.004	0.042	0.033	-0.001	0	0
F-2 (8j) Mn	-0.0276 (4)	-0.0276 (4)	0.02814 (6)	0.025 (1)	0.025 (1)	0.011 (1)	0.002 (1)	0.002 (1)	-0.002 (1)
Fe	-0.0212 (11)	-0.0212 (11)	0.2818 (10)	0.020	0.020	0.013	0.002	0.002	0.001

^a The temperature factors are defined as $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}kb^*c^* + 2U_{13}kla^*c^* + 2U_{12}hka^*b^*)]$.

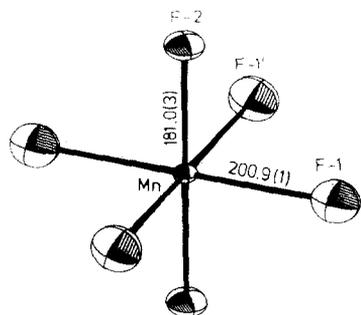


FIG. 3. The $[\text{MnF}_6]^{3-}$ octahedron in CsMnF_4 (50% thermal ellipsoids). Interatomic distances in picometers. The corresponding distances in CsFeF_4 are: Fe-F-1 196.2 pm; Fe-F-2 186.1 pm.

(iii) a significant increase by a factor of about 10 in the temperature factor components of F-1 within the (001) plane (Table I), the other thermal parameters resting nearly unchanged (for better comparison the root mean square displacements have been listed in Table III for the fluorine ions).

In particular these anomalous high-temperature factors of the bridging fluorine atoms clearly suggest that the $[\text{MnF}_6]$ octahedra are not really compressed by Jahn-Teller distortion. Instead of the ferro-distortive order of compressed octahedra as provided by the space group $P4/nmm$ (Fig. 4a) we propose an antiferrodistortive order of elongated octahedra (see (15)) which is possible only by lowering the symmetry (Figs. 4b and c). Superposition of the two

TABLE II
ANGLES IN THE $[\text{MnF}_6]$ OCTAHEDRON OF CsMnF_4
COMPARED WITH CsFeF_4

F-1-Mn-F-1'	89.7°/90.3°
F-1-Fe-F-1'	89.7°/90.3°
F-1-Mn-F-2	88.5°/91.5°
F-1-Fe-F-2	88.3°/91.7°
Bridging angles	
Mn-F-1-Mn	162.5°
Fe-F-1-Fe	166.4°

TABLE III

ROOT MEAN SQUARE DISPLACEMENTS (pm) 1
 CsMnF_4 COMPARED WITH CsFeF_4 (3)^a

Direction	F-1			F-2		
	x	y	z	x	y	z
CsMnF_4	19.5	17.9	17.7	15.8	15.8	10.7
CsFeF_4	6.2	20.4	18.3	17.6	17.6	11.3

^a Italicized components are approximately in bond direction.

equivalent configurations (b) and (c) by averaging in time or in space should generate the apparent higher symmetry and cause the irregular thermal parameters.

This averaging may be effected by three different mechanisms:

(i) a *planar dynamic Jahn-Teller effect*: cooperative oscillation between (b) and (c) in Fig. 4 (A similar mechanism has been discussed previously for some Cu^{2+} compounds (16, 17));

(ii) *disorder* of ordered layers of types (b) and (c) along the [001] direction;

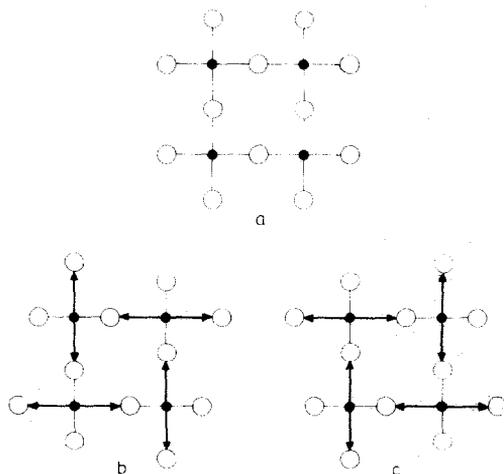


FIG. 4. Schematic projection of high- and low-symmetry (001) layers. (a) Ferrodistortive ordered compressed octahedra agreeing with space group $P4/nmm$, (b and c) Alternative domains of antiferrodistortive ordered elongated octahedra agreeing with space group $P4/n$.

(iii) twinning of an ordered structure like Fig. 4b (space group $P4/n$), e.g., along (110) with a ratio of about 1 : 1 for the two species leading thus to the formation of two types of domains related to each other by a 90° rotation.

By X-ray methods these three cases cannot be distinguished. The only difference worth mentioning between Figs. 4b and c concerns the x parameter of F-1 which represents less than 16% of the electron density in the cell. Therefore a disorder should not be recognizable in X-ray exposures. From a group theoretical point of view, twinning may be expected assuming a Jahn-Teller phase transition from a high-temperature phase with dynamic Jahn-Teller effect (space group $P4/nmm$) to his maximal subgroup $P4/n$ according to a cooperatively ordered antiferrodistortive arrangement of statically Jahn-Teller-distorted elongated octahedra.

The expansion of the (001) planes by Jahn-Teller distortion is partially compensated by a decrease of the bridge angle Mn-F-Mn compared with CsFeF₄. Consequently, the Cs-F distances are somewhat equalized (Table IV, Fig. 5) so that the coordination number of the Cs ions tends to be closer to 12 than in the iron compound.

The Magnetic Structure at Low Temperature

Results

In Fig. 6 the neutron scattering powder diffraction pattern of CsMnF₄ is shown for room temperature and 2.2 K. Both patterns have already been corrected for background. It is obvious that a set of new reflections appears at low temperatures. These peaks can all be indexed in the units of the chemical cell as indicated in Fig. 6. In Fig. 7 we show the temperature dependence of the intensity of the strongest low-temperature peak (001). From these data we deduce a transition temperature of 18.9 ± 0.5 K.

TABLE IV
INTERATOMIC DISTANCES Cs-F (pm)

Cs-1-F-1	4x	347.1
-F-2	8x	314.7
Cs-2-F-1	4x	324.3
-F-2	4x	329.6
-F-2'	4x	302.5

Discussion

CsMnF₄ belongs to the group of the so-called two-dimensional magnets, which have aroused great interest in the last few years due to their special features above and around the magnetic phase transition (see (11)). Previous magnetization measurements have shown (2) that CsMnF₄ exhibits ferromagnetic behavior at low temperatures. This makes CsMnF₄ an especially interesting example of a two-dimensional magnet, since most of the insulating two-dimensional magnets are antiferromagnets. Only few ferromagnetic systems are known in this class like K₂CuF₄ (12), Rb₂CuCl₄ (13), or Cs₂CrCl₄ (14).

The magnetization data clearly show pronounced two-dimensional ferromagnetic correlations far above the Curie temperature, which was given as $T_c = 21 \pm 2$ K. This interesting two-dimensional magnetic effects, however, are not the subject of the study we report here. Our study of a powder

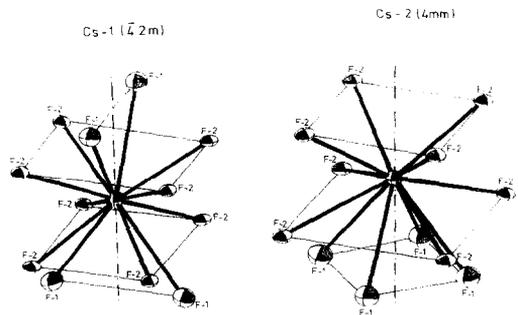


FIG. 5. The coordination sphere of the Cs ions in CsMnF₄.

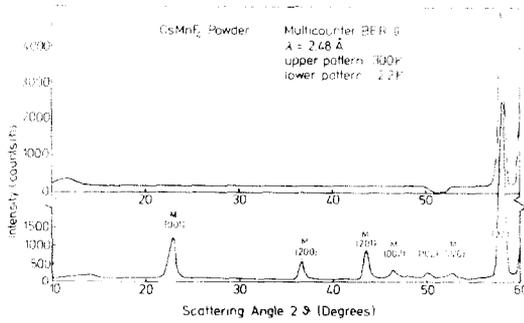


FIG. 6. Neutron diffraction patterns of CsMnF_4 at room temperature (upper) and at 2.2 K (lower). M indicates magnetic reflections. The dip at $2\theta \approx 50^\circ$ is due to an uncertainty in the room temperature background measurement.

sample is restricted to the determination of the three-dimensional magnetic structure of CsMnF_4 .

The following reflections are found below $T_c = 18.9$ K (see Fig. 6): $(0, 0, 1)$; $(2, 0, 0)$; $(2, 0, 1)$; $(0, 0, 2)$; $(2, 2, 0)$. From the above we know that the Mn^{3+} ions occupy the following positions in the unit cell: $(0, 0, 0)$; $(1/2, 0, 0)$; $(0, 1/2, 0)$; $(1/2, 1/2, 0)$.

These two facts already give us a large amount of information about the possible magnetic structure. We start with the assumption that the magnetic structure is a ferromagnetic one, i.e., all magnetic moments are parallel. Then the Mn^{3+} positions above give the following condition for possible reflections (h, k, l) :

$$h, k \text{ even, and } l = 1, 2, 3 \dots$$

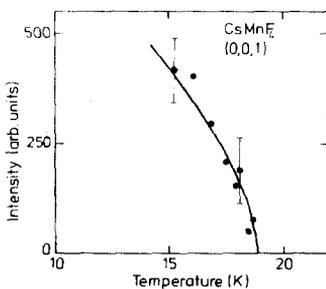


FIG. 7. Intensity versus temperature of the $(0, 0, 1)$ magnetic reflection. Solid line is only a guide for the eye.

As can be seen, this condition is fulfilled by all the magnetic reflections found. Any type of ferromagnetic structure would give other conditions for the possible reflections, and antiferromagnetism is ruled out since a macroscopic moment appears for $T < T_c$. Thus we already know that the magnetic structure of CsMnF_4 is a simple ferromagnetic one.

The only free parameter left of the magnetic structure is the direction of the magnetic moment \mathbf{m} with respect to the crystallographic directions. A first hint to this question gives the appearance of the $(0, 0, 1)$ peak, which would not be there if the moment pointed along c . This is due to the fact that in a neutron scattering process only that moment component contributes which is perpendicular to the scattering vector. Since the $(0, 2, 0)$ and $(2, 0, 0)$ reflections are indistinguishable in a powder experiment no such statement can be made for these directions. We thus calculated the intensities for the reflections found under the assumption that the moment \mathbf{m} is parallel to \mathbf{a} or \mathbf{b} . The results are shown together with the experimental results in Table V. The agreement between calculation and experiment is reasonably good, as can be seen from the column $J_{\text{exp}}/J_{\text{calc}}$. We therefore conclude that the magnetic structure is a simple ferromagnetic one with the moments perpendicular to c . Their direction can be along either \mathbf{a} or \mathbf{b} . Using the nuclear $(2, 2, 1)$ reflection we can put the magnetic intensities on an absolute scale, yielding the value of the magnetic moment of Mn^{3+} at 2.2 K given in the last column of Table V. From these data we find a magnetic moment of $m_{\text{Mn}^{3+}} = 4.04 \pm 0.2 \mu_B$ in good agreement with the expected value for Mn^{3+} with $S = 2$ and with the experimental results from the high-temperature susceptibility data.

In conclusion we state that CsMnF_4 is an insulating ferromagnet with $\mathbf{m} \perp c$, $T_c = 18.9 \pm 0.5$ K. The magnetic moment is found to be $m = 4.04 \pm 0.2 \mu_B$ as expected.

TABLE V

COMPARISON BETWEEN CALCULATED AND MEASURED INTENSITIES OF THE MAGNETIC REFLECTIONS ASSUMING A FERROMAGNETIC STRUCTURE WITH THE MOMENTS ALONG a OR b ^a

(h, k, l)	I_{exp}	F_{calc}	I_{calc}	$I_{\text{exp}}/I_{\text{calc}}$	m (μ_B)
(0, 0, 1)	4744	16	363	13.1	4.27
(2, 0, 0)	1519	16	127	12.0	4.09
(2, 0, 1)	2346	16	207	11.5	4.01
(0, 0, 2)	695	16	70	9.9	3.72
(2, 2, 0)	540	16	47	12.0	4.09

^a The value for the magnetic moment as found by scaling the magnetic intensities through the (221) nuclear reflection is given as well.

However, this magnetic structure no longer has the tetragonal symmetry of the crystallographic structure, since the moment direction in the a - b plane distinguishes one direction. Thus, there must be magnetic domains whose moments presumably make an angle of 90° between each other. In order to study the anisotropy, which determines the moment direction, single-crystal studies are in preparation. Such studies should give also information on the two-dimensional character of the system.

The magnetic structure as found confirms the antiferrodistortive ordering of Jahn-Teller elongated [MnF₆] octahedra as proposed from crystallographic results. Obviously it is such a cooperative effect—restricted to Jahn-Teller unstable ions—which allows asymmetric σ superexchange interactions between empty $d_{x^2-y^2}$ orbitals and half-filled d_{z^2} orbitals of Mn³⁺ (see (2)) and thus makes possible planar ferromagnetic coupling.

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