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THE CRYSTAL STRUCTURE OF CsMnF_3

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The Crystal Structure of CsMnF_3 *

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A single-crystal x-ray diffraction study shows that CsMnF_3 has the hexagonal BaTiO_3 type structure. The space group is $P6_3/mmc$. The unit cell with $a = 6.213 \text{ \AA}$, $c = 15.074 \text{ \AA}$ contains six formula units. Each cesium atom has 12 fluorine neighbors at an average distance of 3.13 \AA . One third of the manganese atoms occupy the centers of fluorine octahedra that share their corners with other octahedra as in the perovskite structure. The remaining two thirds of the manganese atoms are in distorted fluorine octahedra that each share one face and three corners with other octahedra; these manganese atoms are in pairs 3.00 \AA apart. The average Mn-F distance in the octahedra is 2.13 \AA .

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INTRODUCTION

Like many other double fluorides, the compounds XMnF_3 exist in the perovskite type structure when X represents Na, K, NH_4 , or Rb.^{1,2} Simanov, Batsanova, and Kovba² recognized that CsMnF_3 , on the other hand, has the same structure as the hexagonal form of BaTiO_3 ,³ but no atomic coordinates were reported. The compound KMnF_3 has been studied extensively both crystallographically^{4,5} and magnetically⁷⁻¹²; by torsion and magnetic resonance studies it was found to have interesting antiferromagnetic properties at low temperatures. Subsequently interest arose in the properties of CsMnF_3 and the possible effect of the hexagonal structure on its magnetism. Preliminary magnetic resonance and static measurements show that CsMnF_3 has low magnetic anisotropy and antiferromagnetic ordering with the sublattice magnetization directed normal to the c axis.¹³ In the present paper we report an analysis of the structure by means of x-ray diffraction.

EXPERIMENTAL

Single crystals of CsMnF_3 were grown from the melt. Powdered CsF was combined with single crystals of MnF_2 in a modified Stockbarger apparatus.^{14,15} The material was placed in a graphite crucible inside a platinum-10% rhodium tube and heated at 900° for about 24 hours in an atmosphere of anhydrous HF. The system was lowered through a thermal gradient (with the melting point of $750^\circ \pm 20^\circ$ situated at the center of the gradient) at a rate of 2.5 mm/hour. After traversing the thermal gradient, the boule reached a temperature of 680° . It was then annealed

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- ¹⁵D. C. Stockbarger, J. Opt. Soc. Am. 39, 731 (1949).

at the cooling rate of 24° /hour until 200° was reached, and then argon was introduced to cool the system to room temperature. Pink single crystals about 3 mm in size were obtained. With the same apparatus, single crystals could also be made by starting with a precipitate of CsMnF_3 prepared from an aqueous solution.

A triangular crystal fragment plate was selected that measured roughly $0.15 \times 0.15 \times 0.12 \times 0.05$ mm. Weissenberg photographs were taken to establish the symmetry and orientation of the specimen. The crystal was mounted on a General Electric XRD-5 diffractometer equipped with a single crystal orienter, a scintillation counter and a Mo x-ray tube. Intensities were measured of 326 independent reflections of which 31 were recorded as zero. Unit cell dimensions were measured with the diffractometer with $\lambda = 0.70929$ A for Mo $K\alpha_1$ x-rays. The data were corrected for the Lorentz and polarization factors as follows:

$$F_{\text{obs}} = s(I_{\text{obs}} \sin 2\theta)^{1/2} (1 + \cos^2 2\theta)^{-1/2}$$

where F_{obs} is the observed structure factor, I_{obs} is the observed intensity (corrected for background), θ is the diffraction angle, and s is a scaling factor applied uniformly to all the data. The crystal is sufficiently big to require an absorption correction, but due to the complexity of this calculation it was omitted.

STRUCTURE DETERMINATION

The dimensions of the hexagonal unit cell are:

$$a = 6.213 \pm 0.003 \text{ \AA}$$

$$c = 15.074 \pm 0.004 \text{ \AA}$$

$$c/a = 2.426$$

With six formula units per cell, the calculated density is 4.840 g/cc.

The cell dimensions were previously reported as $a = 6.209 \text{ kX}$, $c = 15.16 \text{ kX}$, and $c/a = 2.44$ from x-ray diffraction patterns of the powder.²

From the hexagonal lattice we guessed that the structure was like that of hexagonal BaTiO_3 , for which $c/a = 2.45$.³ A comparison of intensities on our photographs with those published for BaTiO_3 confirmed that the two structures are the same with very similar values of the atomic coordinates. The space group is $P6_3/mmc$, with all atoms in special positions as listed in Table I.¹⁶

Starting with the coordinates reported for BaTiO_3 ,³ the structure was refined by least squares using the full matrix on an IBM-709 computer. The program was modified so that it would properly take account of the symmetry relation between certain x and y coordinates. Each atom was assigned an isotropic temperature factor of the form $\exp(-B_n \lambda^{-2} \sin^2 \theta)$, where B_n is a parameter characteristic of the n th independent atom. Scattering factors for Cs^+ and Mn^{++} of Thomas and Umeda¹⁷ and for F^- of Boys¹⁸ were used. Dispersion corrections, which are small for these

¹⁶The designation of $C6_3/mmc$ (Ref. 3) refers to the same space group in an earlier system of space group symbols.

¹⁷L. H. Thomas and K. J. Umeda, J. Chem. Phys. 26, 293 (1957).

¹⁸S. F. Boys, unpublished work (1958) reported by J. A. Ibers, Tables of Atomic Scattering Factors, to be published.

elements with molybdenum radiation, were neglected. There were 5 positional parameters, 6 temperature parameters, and one scale factor to be refined.

In preliminary refinements with the low-angle data, unreasonably low temperature parameters were obtained because of the heavy absorption effects at low angles. To minimize this error, the final refinement of the 12 parameters was done with 274 independent reflections, omitting the 52 for which $(\sin \theta)/\lambda$ is less than 0.35. For these data, the reliability index $R = \sum |F_{\text{obs}}| - |F_{\text{cal}}| / \sum |F_{\text{obs}}|$ was reduced to 0.092. The resulting coordinates are listed in Table I. The resulting temperature parameters B_n are 0.8, 0.8, 0.8, 0.6, 1.3, and 1.3 Å^2 , in order of the atoms as listed in Table I. These temperature parameters may be systematically smaller than the true values because of remaining effects of absorption.

Convergence in the least squares refinement was rapid because the coordinate changes were small. Four cycles were run in each of several series of calculations, but two would have been sufficient for convergence.

With the final parameters a list of all 326 observed and calculated structure factors was computed, and this is shown in Table II. For these data, $R = 0.121$.

A list of the interatomic distances and their estimated standard deviations is shown in Table III.

DISCUSSION

The coordinates found for cesium and fluorine are the same as those of barium and oxygen in BaTiO_3 within 0.002. Thus these atoms are in the same close-packed arrangement with distances about eight percent larger

in CsMnF_3 according to the larger cell dimensions. Each cesium atom has twelve fluorine neighbors arranged as in hexagonal close packing for Cs_1 and as in cubic close packing for Cs_2 . The point symmetries at these cesium atoms are respectively $\bar{6}m2$ (D_{3h}) and $3m$ (C_{3v}).

Manganese atoms occur in two quite different kinds of environment (Figure 1). Each has six fluorine neighbors at the corners of an octahedron. For Mn_1 , with point symmetry $\bar{3}m$ (D_{3d}), this octahedron shares corners with six other octahedra and the nearest Mn neighbors are arranged as they would be in the perovskite structure. For Mn_2 , with point symmetry $3m$ (C_{3v}), the octahedron shares a face with another octahedron and three corners with three others. Thus the Mn_2 atoms occur in pairs at a distance of 3.004 Å. If the close packing of the Cs and F atoms were perfect and the Mn atoms were at the centers of their octahedra, this distance would be $c/6 = 2.51$ Å. This distance is increased by a distortion of the close packing together with a displacement of each Mn atom from the center of gravity of its octahedron by 0.21 Å. The corresponding displacement of Ti in BaTiO_3 is only 0.11 Å, and the difference of 0.005 in the z parameters of Mn and Ti is the largest discrepancy between the two structures.

The distortion of the structure results in hardly any difference in the various Mn-F distances, which average 2.13 Å. As is to be expected, the F-F distances of 2.69 Å for the edges of the shared faces are significantly shorter than the others (2.94 to 3.52 Å).

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Table I. Atomic positions and parameters for CsMnF_3

2 Cs_1 in 2b: $\pm (0, 0, 1/4)$

4 Cs_2 in 4f: $\pm (1/3, 2/3, z; 2/3, 1/3, 1/2+z)$ with $z = .0986 \pm .0002$

2 Mn_1 in 2a: $0, 0, 0; 0, 0, 1/2$

4 Mn_2 in 4f: $\pm (1/3, 2/3, z; 2/3, 1/3, 1/2+z)$ with $z = .8498 \pm .0004$

6 F_1 in 6h: $\pm (x, 2x, 1/4; 2x, x, 3/4; x, \bar{x}, 1/4)$ with $x = .522 \pm .002$

12 F_2 in 12k: $\pm (x, 2x, z; 2x, x, \bar{z}; x, \bar{x}, z; x, 2x, 1/2-z; 2x, x, 1/2+z; \bar{x}, x, 1/2+z)$ with $x = .835 \pm .002$ and $z = .078 \pm .001$

H	K	L	OBS	CAL	H	K	L	OBS	CAL	H	K	L	OBS	CAL	H	K	L	OBS	CAL	H	K	L	OBS	CAL	H	K	L	OBS	CAL
0	0	2	18	-13	2	0	12	53	46	3	0	16	48	-46	4	0	6	4	0	4	3	9	55	53	5	3	2	28	-29
0	0	4	77	-69	2	0	13	102	101	3	0	17	5	4	4	0	7	121	110	4	3	10	41	-39	5	3	3	49	47
0	0	6	157	-254	2	0	14	39	-31	3	0	18	7	-12	4	0	8	90	75	4	3	11	51	-49	5	3	4	90	88
0	0	8	124	151	2	0	15	0	-4	3	0	19	8	-3	4	0	9	119	109	4	3	12	27	27	5	3	5	25	24
0	0	10	26	25	2	0	16	120	120	3	1	0	8	5	4	0	10	74	-69	4	4	0	161	169	5	3	6	4	-8
0	0	12	155	201	2	0	17	34	-39	3	1	1	18	18	4	0	11	60	-51	4	4	2	0	-0	5	3	7	59	-59
0	0	14	64	-63	2	0	18	27	-24	3	1	2	48	-45	4	0	12	38	34	4	4	4	36	-35	5	3	8	38	33
0	0	16	38	-38	2	0	19	23	-22	3	1	3	96	85	4	0	13	85	-83	4	4	6	69	-70	6	0	0	186	207
0	0	18	50	-44	2	0	20	20	11	3	1	4	151	156	4	0	14	27	-21	4	4	8	61	60	6	0	1	0	-2
0	0	20	114	137	2	1	0	0	-0	3	1	5	52	39	4	0	15	0	6	5	0	0	6	-4	6	0	2	9	-1
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1	0	1	16	-16	2	1	2	49	-45	3	1	7	110	-102	4	0	17	28	33	5	0	2	35	-33	6	0	4	46	-40
1	0	2	56	-48	2	1	3	89	-81	3	1	8	64	52	4	0	18	10	-19	5	0	3	62	55	6	0	5	8	-1
1	0	3	116	-119	2	1	4	156	178	3	1	9	94	-86	4	1	0	198	224	5	0	4	126	119	6	0	6	91	-86
1	0	4	159	214	2	1	5	74	-57	3	1	10	60	-58	4	1	1	13	-7	5	0	5	54	43	6	0	7	0	1
1	0	5	68	-49	2	1	6	7	-6	3	1	11	87	79	4	1	2	15	-14	5	0	6	0	-2	6	0	8	75	71
1	0	6	12	-7	2	1	7	124	127	3	1	12	48	42	4	1	3	10	6	5	0	7	102	-92	6	0	9	0	-1
1	0	7	123	134	2	1	8	67	55	3	1	13	82	82	4	1	4	53	-45	5	0	8	46	39	6	0	10	23	21
1	0	8	76	61	2	1	9	93	86	3	1	14	0	-4	4	1	5	10	-7	5	0	9	66	-61	6	0	11	13	1
1	0	9	111	111	2	1	10	64	-62	3	1	15	24	-22	4	1	6	78	-71	5	0	10	47	-45	6	0	12	104	96
1	0	10	69	-68	2	1	11	86	-82	3	1	16	97	96	4	1	7	8	6	5	0	11	61	57	6	0	13	0	-1
1	0	11	108	-103	2	1	12	49	44	3	1	17	45	-51	4	1	8	111	106	5	0	12	34	30	6	1	0	0	2
1	0	12	60	50	2	1	13	94	-97	3	1	18	22	-22	4	1	9	8	-4	5	0	13	74	75	6	1	1	10	11
1	0	13	98	-101	2	1	14	4	-3	3	2	0	5	-0	4	1	10	29	27	5	0	14	7	-2	6	1	2	29	-28
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1	0	15	32	27	2	1	16	103	104	3	2	2	39	-36	4	1	12	104	94	5	1	0	0	3	6	1	4	99	93
1	0	16	109	114	2	1	17	44	52	3	2	3	95	-84	4	1	13	7	-4	5	1	1	23	-20	6	1	5	26	24
1	0	17	59	62	2	1	18	21	-22	3	2	4	135	133	4	1	14	54	-55	5	1	2	38	-36	6	1	6	5	-6
1	0	18	24	-24	2	1	19	23	25	3	2	5	34	-28	4	1	15	0	3	5	1	3	63	-57	6	1	7	64	-61
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1	0	20	0	-6	2	2	2	6	-4	3	2	7	93	85	4	2	0	10	-8	5	1	5	40	-33	6	1	9	60	-56
1	0	21	0	-6	2	2	4	64	-55	3	2	8	52	43	4	2	1	38	31	5	1	6	8	-8	6	1	10	35	-37
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1	1	4	81	-72	2	2	10	26	25	3	2	11	82	-76	4	2	4	134	130	5	1	9	63	61	6	2	2	32	-32
1	1	6	88	-92	2	2	12	140	149	3	2	12	40	36	4	2	5	60	49	5	1	10	45	-45	6	2	3	66	-59
1	1	8	134	156	2	2	14	49	-50	3	2	13	69	-71	4	2	6	0	2	5	1	11	61	-56	6	2	4	90	86
1	1	10	40	39	2	2	16	34	-35	3	2	14	0	-2	4	2	7	97	-87	5	1	12	34	32	6	2	5	39	-35
1	1	12	116	124	2	2	18	36	-34	3	2	15	16	17	4	2	8	66	56	5	1	13	66	-66	6	2	6	0	2
1	1	14	70	-73	3	0	0	212	287	3	2	16	84	87	4	2	9	95	-88	5	1	14	0	-5	7	0	0	0	-2
1	1	16	47	-49	3	0	1	22	16	3	2	17	45	49	4	2	10	56	-54	5	2	0	158	163	7	0	1	7	-7
1	1	18	11	-13	3	0	2	16	-14	3	3	0	185	205	4	2	11	49	45	5	2	1	11	7	7	0	2	19	-23
1	1	20	108	141	3	0	3	17	-13	3	3	2	19	-16	4	2	12	29	27	5	2	2	5	-8	7	0	3	59	-53
2	0	0	17	-4	3	0	4	74	-63	3	3	4	40	-37	4	2	13	68	68	5	2	3	7	-6	7	0	4	86	82
2	0	1	80	69	3	0	5	19	14	3	3	6	70	-69	4	2	14	15	-16	5	2	4	40	-36	7	0	5	21	-19
2	0	2	121	-126	3	0	6	82	-82	3	3	8	103	99	4	2	15	0	-5	5	2	5	10	7	7	0	6	0	-3
2	0	3	158	189	3	0	7	19	-11	3	3	10	22	21	4	3	0	0	-2	5	2	6	52	-53	7	0	7	57	54
2	0	4	189	257	3	0	8	131	132	3	3	12	91	88	4	3	1	25	-21	5	2	7	11	-6	7	0	8	29	27
2	0	5	113	102	3	0	9	11	8	3	3	14	50	-52	4	3	2	29	-29	5	2	8	79	77	7	1	0	129	131
2	0	6	6	-4	3	0	10	39	36	4	0	0	7	-7	4	3	3	54	-49	5	2	9	7	5	7	1	1	0	-1
2	0	7	140	-147	3	0	11	11	-8	4	0	1	53	-45	4	3	4	106	100	5	2	10	14	22	7	1	2	11	-10
2	0	8	120	112	3	0	12	118	111	4	0	2	83	-74	4	3	5	42	-34	5	2	11	7	-5					
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2	0	10	99	-95	3	0	14	65	-65	4	0	4	163	171	4	3	7	80	75	5	3	0	0	4					
2	0	11	71	61	3	0	15	0	-4	4	0	5	83	-67	4	3	8	39	34	5	3	1	13	13					

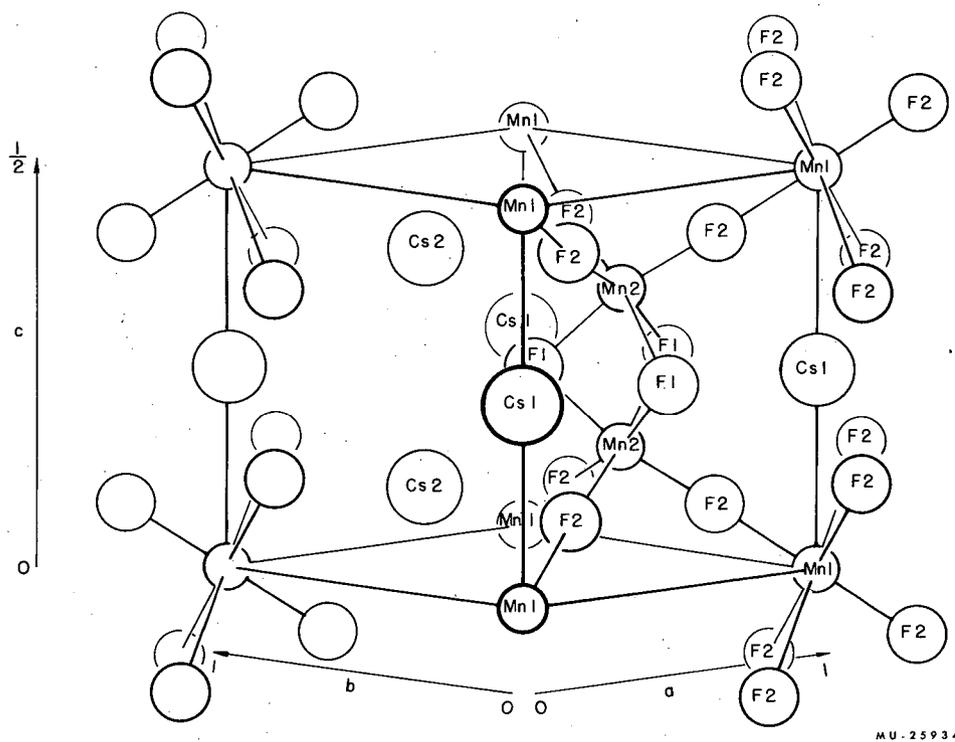
1*** END OF FILE. RECORD 000058. ***

Table II. Observed and calculated structure factors for CsMnF₃.

Table III. Interatomic distances and estimated standard deviations

in CsMnF_3 .

$\text{Cs}_1 - 2 \text{Mn}_1$	$3.769 \pm .001 \text{ \AA}$	$\text{Mn}_2 - 3 \text{Cs}_1$	$3.889 \pm .002 \text{ \AA}$
6 Mn_2	$3.889 \pm .002$	1 Cs_2	$3.753 \pm .006$
6 F_1	$3.12 \pm .02$	3 Cs_2	$3.671 \pm .002$
6 F_2	$3.14 \pm .02$	1 Mn_2	$3.004 \pm .002$
		3 F_1	$2.16 \pm .02$
$\text{Cs}_2 - 1 \text{Mn}_1$	$3.883 \pm .002$	3 F_2	$2.12 \pm .02$
1 Mn_2	$3.753 \pm .006$		
3 Mn_2	$3.671 \pm .002$	$\text{F}_1 - 2 \text{F}_1$	$2.69 \pm .04$
3 F_1	$3.06 \pm .01$	2 F_1	$3.52 \pm .04$
6 F_2	$3.122 \pm .002$	4 F_2	$3.10 \pm .02$
3 F_2	$3.22 \pm .01$		
		$\text{F}_2 - 2 \text{F}_1$	$3.10 \pm .02$
$\text{Mn}_1 - 2 \text{Cs}_2$	$3.769 \pm .001$	2 F_2	$2.94 \pm .02$
6 Cs_2	$3.889 \pm .002$	2 F_2	$3.07 \pm .03$
6 F_2	$2.12 \pm .02$	2 F_2	$3.15 \pm .03$



MU-25934

Fig. 1. A sketch of half of the unit cell of CsMnF_3 shows the two types of Mn atoms and their environs. The cell is outlined from 0 to 1 on the a and b axes, and from 0 to $1/2$ on the c axis.

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