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The Crystal Structure of Manganese Trifluoride, MnF_3

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MnF_3 is monoclinic with $a=8{\cdot}904\pm0{\cdot}003$, $b=5{\cdot}037\pm0{\cdot}002$, $c=13{\cdot}448\pm0{\cdot}005$ Å; $\beta=92{\cdot}74\pm0{\cdot}04°$. The structure is pseudo-rhombohedral and has atoms in the following positions of space group $C2/c$–C_{2h}^6:

4 Mn at (*a*): 8 Mn at (f_1), with $x_1=\frac{1}{6}$, $y_1=\frac{1}{2}$, $z_1=\frac{1}{3}$; 4 F at (*e*), with $y_e=0{\cdot}617$; 8 F at (f_2), with $x_2=0{\cdot}310$, $y_2=0{\cdot}714$, $z_2=0{\cdot}244$; 8 F at (f_3), with $x_3=0{\cdot}167$, $y_3=0{\cdot}117$, $z_3=0{\cdot}583$; 8 F at (f_4), with $x_4=0{\cdot}477$, $y_4=0{\cdot}214$, $z_4=0{\cdot}577$; 8 F at (f_5), with $x_5=0{\cdot}143$, $y_5=0{\cdot}214$, $z_5=0{\cdot}911$.

Since its fluorine-atom packing is mid-way between close-packed hexagonal and an ReO_3-type cubic close-packing, MnF_3 is classified as a VF_3-type transition-element trifluoride. The lower symmetry of the structure, in comparison with other trifluorides, results from three different Mn–F bond lengths (2·09, 1·91 and 1·79 Å) in each MnF_6 octahedron. Reasons for this unsymmetrical bonding and for its unique occurrence in MnF_3 are offered in terms of crystal-field theory.

Introduction

The classification of transition-element trifluorides into three types according to their fluorine-atom arrangements (Hepworth, Jack, Peacock & Westland, 1957) is correlated with the position of the metal in the Periodic Table. The structure of MnF_3 was therefore expected to be of the VF_3-type. Although this expectation is realized in the present work, it is shown that the distortion of the MnF_6 octahedra, which are joined by sharing corners, gives rise to a structure of much lower symmetry than that of the other trifluorides in the first long period. The distortion of each MnF_6 octahedron is due to the occurrence of unequal Mn–F bond lengths, for which an explanation is offered.

Experimental

MnF_3 was prepared by a modification of the method described by Sharpe & Woolf (1951). Manganous iodate was dissolved in bromine trifluoride and excess of the solvent was evaporated at room temperature under reduced pressure. After heating the solid product in a vacuum at 140° C., it was transferred to an alumina boat contained in an alumina tube. Fluorine was passed over it at 20 litres/hour for about 1 hr. at 500° C. to remove traces of BrF_3, to complete the fluorination, and to allow crystal growth. The pale-pink MnF_3 was transferred to a dry-box and filled into 0·5 mm. diameter X-ray specimen capillaries (found: F 51·3%; calculated for MnF_3: F 50·9%).

X-ray photographs were taken at 18±2° C. in a 19 cm. Unicam powder camera with crystal-reflected Fe $K\alpha$ radiation (α_1, 1·93597; α_2, 1·93991 Å) from a lithium fluoride monochromator. The relative intensity of each reflexion was measured on at least two films with a Dobson-type microphotometer constructed from a design by Taylor (1951). Since the powder method relies upon the accurate measurement of a limited number of X-ray intensities, special care was taken with the photometry. Exposure times were such that the density of blackening against intensity was kept within the linear portion of the characteristic curve for the emulsion, and, where necessary, differently exposed films, suitably scaled with respect to each other, were used for the measurements of different reflexions. Density readings were taken along the film at 0·01 cm. intervals and the areas under the plotted photometer curves were measured with a planimeter.

Results

A comparison of the powder photographs of FeF_3 and MnF_3 (see Fig. 1) indicated that the structure of the latter was a lower-symmetry distortion of the FeF_3 rhombohedral structure. By applying various distortions to the FeF_3 reciprocal lattice, it was concluded that the observed MnF_3 X-ray reflexions were consistent only with a monoclinic unit cell derived from the orthohexagonal pseudo-cell containing six bimolecular rhombohedral units of a VF_3-type structure (see Jack & Gutmann, 1951; Hepworth *et al.*, 1957). Excellent agreement between observed and calculated $\sin^2\theta$ values was finally obtained by indexing the MnF_3 reflexions on the basis of a monoclinic cell with dimensions

$$a = 8{\cdot}904\pm0{\cdot}003,\quad b = 5{\cdot}037\pm0{\cdot}002\,,$$
$$c = 13{\cdot}448\pm0{\cdot}005\text{ Å};$$
$$\beta = 92{\cdot}74\pm0{\cdot}04°\,.$$

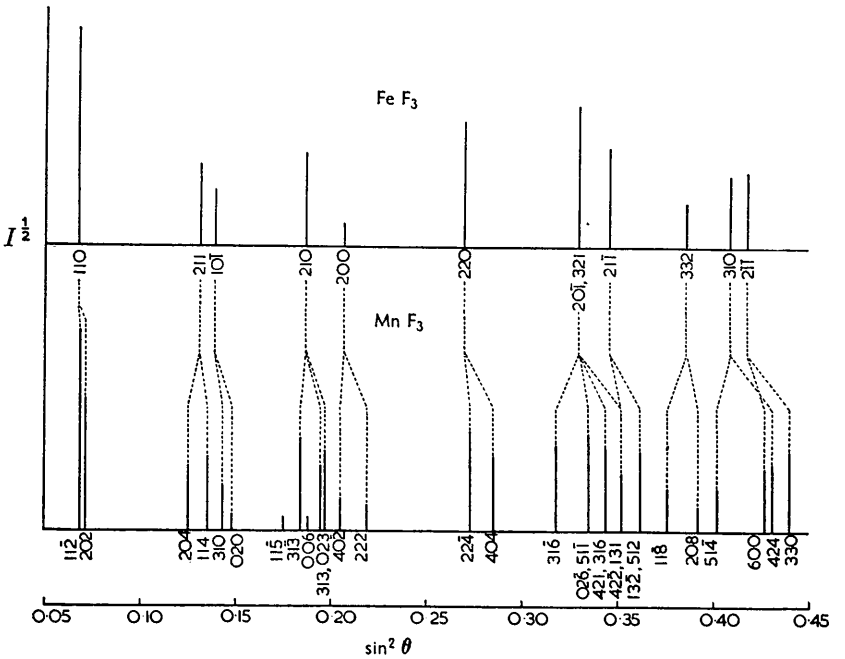


Fig. 1. Comparison of the powder diffraction data of FeF_3 and MnF_3.

For comparison, the orthohexagonal pseudo-cell of iron trifluoride, containing 12 FeF_3, has dimensions

$$a = \sqrt{3}.b = 9{\cdot}004,\ b = 5{\cdot}198,\ c = 13{\cdot}331\ \text{Å}.$$

The density calculated for 12 MnF_3 per unit cell (3·701 g.cm.$^{-3}$) may be compared with the value (3·54 g.cm.$^{-3}$) found by Moissan (1900).

The observed absences (see Table 1; hkl with $h+k$ odd, $h0l$ with l odd, $0k0$ with k odd) require space group Cc–C_s^4 or $C2/c$–C_{2h}^6; the structure was provisionally assigned to the centrosymmetrical group $C2/c$. In addition, however, there are other systematic absences. The only MnF_3 reflexions observed have $2h+l = 3n$. A simple matrix transformation shows that this condition requires a pseudo-rhombohedral symmetry of the structure by which any atom at x, y, z is related to two identical atoms at $x+\frac{1}{6}$, $y+\frac{1}{2}, z+\frac{1}{3}$ and $x-\frac{1}{6}, y-\frac{1}{2}, z-\frac{1}{3}$. To satisfy this condition and to preserve correspondence with the metal-atom arrangement in FeF_3, twelve manganese atoms were placed in the following positions:

4 Mn at (a): $(0, 0, 0;\ \frac{1}{2}, \frac{1}{2}, 0)+\quad (0, 0, 0;\ 0, 0, \frac{1}{2})$.

8 Mn at (f_1): $(0, 0, 0;\ \frac{1}{2}, \frac{1}{2}, 0)+ \pm(x, y, z;\ \bar{x}, y, \frac{1}{2}-z)$,
with $x_1 = 0{\cdot}167(\frac{1}{6})$, $y_1 = 0{\cdot}500(\frac{1}{2})$, $z_1 = 0{\cdot}333(\frac{1}{3})$.

It should be noted that the co-ordinates of the Mn atoms at (f_1) are related to those at (a) by $\pm(\frac{1}{6}, \frac{1}{2}, \frac{1}{3})$.

The calculated intensity of a powder reflexion (hkl) obtained with monochromatic X-radiation and without any temperature correction is given by

$$I_c = \text{constant} \times F_{hkl}^2 \frac{1+\cos^2 2\alpha \cos^2 2\theta}{\sin^2\theta \cos\theta} pA\ , \qquad (1)$$

where α is the angle of reflexion for the monochromator and where the remaining symbols have their usual meanings.

For a structure in which all the atoms vibrate isotropically about their mean lattice positions with equal amplitudes

$$I_o/I_c = \exp\{-2B\ (\sin\theta/\lambda)^2\} \qquad (2)$$

(see Lipson & Cochran, 1953), and, from equations (1) and (2), if

$$\log_{10} I_o - \log_{10}\left\{F_{hkl}^2 \frac{1+\cos^2 2\alpha \cos^2 2\theta}{\sin^2\theta \cos\theta} pA\right\} = \log_{10} Q\ , \qquad (3)$$

then

$$\log_{10} Q = \text{constant} - \frac{2B}{2{\cdot}303\lambda^2} \sin^2\theta\ . \qquad (4)$$

Thus, for such a structure, a plot of $\log_{10} Q$ against $\sin^2\theta$ for various reflexions will give a straight line (Bradley & Lu, 1937), from the slope of which the exponential constant (B) of the temperature factor may be calculated. It was assumed that the temperature factor for MnF_3 would be similar to that for FeF_3 ($B = 2{\cdot}24$ Å^2 (Hepworth *et al.*, 1957)). Values of $\log_{10} Q'$ were first calculated from equation (3) by neglecting any contribution of the fluorine atoms to the structure amplitude, i.e.

$$F' = \Sigma f_{Mn} \cos 2\pi(hx+ky+lz) \qquad (5)$$
$$= 12 f_{Mn} \text{ for } l \text{ even};\ = 0 \text{ for } l \text{ odd}\ .$$

$\text{Log}_{10} Q'$ was plotted against $\sin^2\theta$ and the deviation of each point (for reflexions with l even) from a straight line of slope corresponding to $B = 2{\cdot}24$ Å^2

then enabled the sign and the approximate magnitude of the fluorine-atom contribution to the structure amplitude to be calculated. Since the contribution of the fluorine atoms is of the same order as that of the manganese atoms for certain reflexions (e.g. 006, 600, $60\bar{6}$, and 0,0,12), the scatter of points representing $\log_{10} Q'$ was wide. However, by taking into account the maximum possible contribution of the fluorine atoms ($\pm 36 f_F$), by adjusting the value of the temperature factor, and by assuming that the fluorine-atom arrangement was not widely different from that of FeF_3, it was possible to obtain parameters for the fluorine atoms. The procedure was similar to that used in locating the positions of the interstitial atoms in austenite (Petch, 1942; Jack, 1951).

Finally, after trial-and-error refinement, excellent agreement between the observed and calculated X-ray

Table 1. *Calculated and observed X-ray data for* MnF_3

(Fe $K\alpha$ radiation)

$a = 8{\cdot}904 \pm 0{\cdot}003$, $b = 5{\cdot}037 \pm 0{\cdot}002$, $c = 13{\cdot}448 \pm 0{\cdot}005$ Å; $\beta = 92{\cdot}74 \pm 0{\cdot}04°$

	$\sin^2\theta$		Relative intensities			
hkl	Calc.	Obs.	Calc.			Obs.
111	0·0548	—	< 1			—
$11\bar{2}$	0·0681	0·0678	1708			1792
202	0·0712	0·0713	807			800
$20\bar{4}$	0·1246	0·1246	218			215
114	0·1350	0·1350	260			246
310	0·1437	0·1434	114			108
020	0·1479	0·1481	15			14
$11\bar{5}$	0·1750	0·1750	8			9
$31\bar{3}$	0·1837	0·1837	383	395		406
006	0·1872	0·1881	12			
023	0·1947	0·1945	193			
313	0·1973	0·1974	296	496		543
$22\bar{1}$	0·1990		7			
$40\bar{2}$	0·2044	0·2046	45			47
222	0·2191	0·2191	32			31
$22\bar{4}$	0·2725	0·2725	432			443
404	0·2848	0·2850	223			231
117	0·3089	0·309	5			*vvw*
$31\bar{6}$	0·3174	0·3176	337			337
225	0·3328	—	1			—
$51\bar{1}$	0·3348	0·3351	33	432		411
$02\bar{6}$	0·3351		399			
316	0·3444	0·3445	287	315		322
421	0·3457		27			
131	0·3506	0·3519	39	160		157
$42\bar{2}$	0·3523		121			
512	0·3617	0·3624	161	283		294
$13\bar{2}$	0·3639		122			
$11\bar{8}$	0·3756	0·3760	80			79
208	0·3922	0·3921	27			27
$51\bar{4}$	0·4016	0·4021	83			86
600	0·4268	0·4268	183			
134	0·4308	0·4314	125			
424	0·4327		79	669		680
330	0·4395	0·4396	278			
$22\bar{7}$	0·4396		4			
$42\bar{5}$	0·4525	0·4526	12			10
$13\bar{5}$	0·4708	0·4710	37			34
$33\bar{3}$	0·4795	0·4821	6	27		26
515	0·4822		21			
333	0·4931	—	3	65		65
$40\bar{8}$	0·4984	0·4992	62			

Table 1 (*cont.*)

	$\sin^2\theta$		Relative intensities			
hkl	Calc.	Obs.	Calc.			Obs.
228	0·5401	0·5398	209	286		271
$31\bar{9}$	0·5446	0·5448	77			
2,0,$\bar{1}\bar{0}$	0·5526	0·5526	34			32
517	0·5619	0·5620	11			9
029	0·5691	0·5694	36			35
620	0·5747	0·5763	25	139		148
1,1,10	0·5763		114			
319	0·5852	0·5854	45	86		83
$60\bar{6}$	0·5870	—	< 1			
040	0·5916	0·5917	41			
137	0·6047	0·6049	10			
$62\bar{3}$	0·6080	0·6074	26	58		61
$33\bar{6}$	0·6132	0·6130	6			
427	0·6133		16			
$71\bar{2}$	0·6282	0·6294	117	192		201
711	0·6284		27			
$53\bar{1}$	0·6306		48			
623	0·6350	0·6397	20			
043	0·6384		17			
336	0·6402		9			
$60\bar{6}$	0·6410	—	2			
$24\bar{1}$	0·6427	0·6465	16	484		495
$42\bar{8}$	0·6463		86			
532	0·6575	0·6578	94			
$24\bar{2}$	0·6628	0·6628	184			
1,1,$\bar{1}\bar{1}$	0·6697	0·6715	4			
$13\bar{8}$	0·6714		52			
518	0·6962	0·6968	47	109		110
$53\bar{4}$	0·6974		37			
2,2,$\bar{1}\bar{0}$	0·7003		25			
$24\bar{4}$	0·7160	—	6	43		41
$71\bar{5}$	0·7216	0·7225	15			
$71\bar{4}$	0·7221		22			
$62\bar{6}$	0·7349	0·7352	128	131		130
4,0,10	0·7396	—	3			
0,0,12	0·7488	0·7488	123			125
245	0·7765	0·7778	19	112		117
535	0·7780		45			
046	0·7788		48			
626	0·7889	0·7885	92			*ms*
441	0·7894	—	< 1			—
802	0·7912	0·7912	53			*m*
$44\bar{2}$	0·7960	0·7961	108			*ms*
5,1,$\bar{1}\bar{0}$	0·8159	0·8166	78	89		*ms*
$80\bar{4}$	0·8176		11			
$33\bar{9}$	0·8404	—	4			—
2,2,11	0·8410	—	< 1			—
$53\bar{7}$	0·8577	0·8571	39			*mw*
3,1,$\bar{1}\bar{2}$	0·8655	0·865	19			*vw*
1,3,10	0·8721	0·8725	40			*mw*
444	0·8764	0·8765	34			*mw*
339	0·8810	—	1			—
4,2,10	0·8875	0·8877	102			*ms*
445	0·8962	—	1			—
0,2,12	0·8967	—	12			—
$82\bar{1}$	0·9055	—	< 1			—
$71\bar{8}$	0·9087	0·9097	33	73		*m*
717	0·9095		40			
3,1,12	0·9195	0·9193	28			*w*
$73\bar{2}$	0·9240	0·9232	25			*w*
731	0·9242	—	< 1			—
4,2,$\bar{1}\bar{1}$	0·9337	—	6			—
1,1,13	0·9374	—	8			—
822	0·9391	—	8			—
151	0·9422	—	7			—
$62\bar{9}$	0·9554	0·9561	40	54		*w*
$15\bar{2}$	0·9555		14			
1,3,$\bar{1}\bar{1}$	0·9655	0·9668	54	369		*s*
$82\bar{4}$	0·9655		315			

data (see Table 1) was obtained by taking $B=2{\cdot}43$ Å^2 and by placing 12 Mn and 36 F atoms in the following positions of space group $C2/c$:

4 Mn at (a): $(0,0,0;\ \frac{1}{2},\frac{1}{2},0)+\quad(0,0,0;\ 0,0,\frac{1}{2})$.
8 Mn at (f_1): $(0,0,0;\ \frac{1}{2},\frac{1}{2},0)+\ \pm(x,y,z;\ \bar{x},y,\frac{1}{2}-z)$,
with $x_1=0{\cdot}167(\frac{1}{6})$, $y_1=0{\cdot}500(\frac{1}{2})$, $z_1=0{\cdot}333(\frac{1}{3})$.
4 F at (e): $(0,0,0;\ \frac{1}{2},\frac{1}{2},0)+\ \pm(0,y,\frac{1}{4})$, with $y_e=0{\cdot}617$.
8 F at (f_2), with $x_2=0{\cdot}310$, $y_2=0{\cdot}714$, $z_2=0{\cdot}244$.
8 F at (f_3), with $x_3=0{\cdot}167$, $y_3=0{\cdot}117$, $z_3=0{\cdot}583$.
8 F at (f_4), with $x_4=0{\cdot}477$, $y_4=0{\cdot}214$, $z_4=0{\cdot}577$.
8 F at (f_5), with $x_5=0{\cdot}143$, $y_5=0{\cdot}214$, $z_5=0{\cdot}911$.

Just as the co-ordinates of the Mn atoms at (f_1) are related to those at (a) by $\pm(\frac{1}{6},\frac{1}{2},\frac{1}{3})$, the F atoms at (f_3) are similarly related to those at (e) and the positions (f_4) and (f_5) are likewise related to (f_2).

The estimated error of these atomic co-ordinates is probably not greater than $\pm0{\cdot}003$. The scattering factors used are those given for the unionized atoms (*International Tables*, 1935) after correction in the case of manganese for dispersion by the K electrons (see James, 1948; for Fe $K\alpha$ radiation $\Delta f_{Mn}=-4{\cdot}04$). Less satisfactory agreement between the observed and calculated X-ray data was obtained by using scattering-factor values for the fluoride anion; those for the trivalent manganese cation are not available. No evidence was obtained to suggest that the temperature factors of the different atoms in MnF_3 are unequal or that they are anisotropic.

Discussion of the MnF_3 structure

Except for the monoclinic distortion of the unit cell, the metal atoms in MnF_3 are in exactly corresponding positions to those of the FeF_3 structure. For a similar correspondence between the F-atom arrangements, the values required for the co-ordinates in MnF_3 would be $y_e=0{\cdot}586$; $x_2=0{\cdot}293$, $y_2=0{\cdot}707$, $z_2=0{\cdot}250$, with the positions (f_3), (f_4) and (f_5) dependent as before on (e) and (f_2). Since the observed co-ordinates are

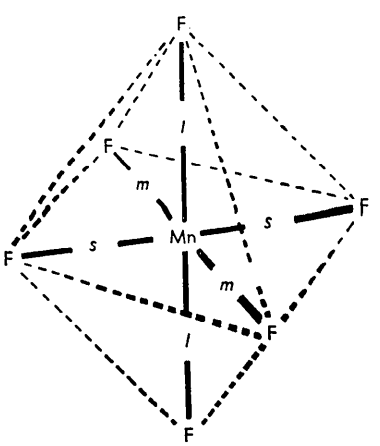


Fig. 2. Dimensions of the MnF_6 octahedron.
$l=2{\cdot}1$ Å, $m=1{\cdot}9$ Å, $s=1{\cdot}8$ Å.

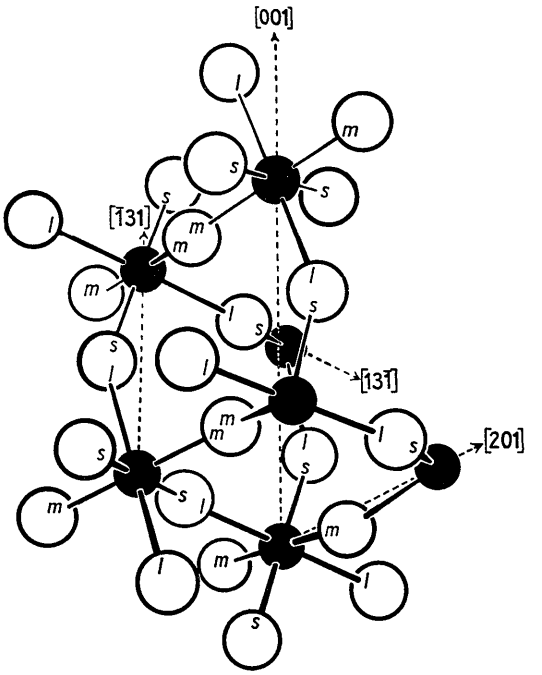


Fig. 3. Spatial relationships between adjacent MnF_6 octahedra.

appreciably different from these values, it is clear that the fluorine-atom arrangement in MnF_3 is not merely a small monoclinic distortion of the arrangement in FeF_3. The fluorine packing in both trifluorides is approximately mid-way between close-packed hexagonal and a ReO_3-type cubic close packing, so that MnF_3 must be classed like FeF_3 as a VF_3-type transition-element trifluoride. The MnF_3 structure is, however, much less regular than that of any trifluoride so far reported. It consists of MnF_6 octahedra joined by sharing all corners. The dimensions of each octahedron are given in Fig. 2, and Fig. 3 shows the relative orientations of neighbouring octahedra. Each Mn is co-ordinated by 6 F: 2 at 2·09, 2 at 1·91 and 2 at 1·79 Å. This wide variation in the Mn–F distances within the same octahedral group is unusual. In MnF_2, which has the rutile-type structure (Griffel & Stout, 1950), each Mn has 2 F at 2·14 and 4 F at 2·11 Å.

Like VF_3, the MnF_3 structure consists of alternate and regularly spaced planes of metal atoms and planes of fluorine atoms. A projection of the unit cell on (001) along the direction [001] (see Fig. 4) shows twelve such successive planes. Each fluorine-atom plane 1, 3, 5 etc. is puckered and has one-third of its atoms 0·08 Å above (+) and one-third 0·08 Å below (−) the remaining third. The principal interatomic distances F–F (p and q), M–F (r) and M–M (s), and the M–F–M bond angles (φ), are compared with the corresponding distances and angles of VF_3, FeF_3 and CoF_3 in Table 2. The mean values for MnF_3 agree quite closely with those of the related trifluorides, and the individual abnormalities appear to be due to the marked distortion of the MnF_6 octahedron which results from the

Table 2. *Structural data for* MnF_3 *compared with those for* VF_3, FeF_3 *and* CoF_3

(Co-ordination numbers are given in parentheses.)

	Interatomic distances (Å)				Bond angle (°)
	F–F		*M*–F	*M*–*M*	*M*–F–*M*
	p	*q*	*r*	*s*	φ
VF_3	(4) 2·75	(4) 2·74	(6) 1·94	(6) 3·73	147
MnF_3 (i)	(2) 2·64 (2) 2·81	(2) 2·60 (2) 2·85	(i) (2) 2·09		(i) 144
MnF_3 (ii)	(2) 2·64 (2) 2·74	(2) 2·60 (2) 2·76	(ii) (2) 1·91	(i) (2) 3·63 (ii) (4) 3·73	(ii) 148
MnF_3 (iii)	(2) 2·74 (2) 2·81	(2) 2·76 (2) 2·85	(iii) (2) 1·79		(iii) 148
MnF_3	2·73	2·74	1·93	3·70	146
FeF_3	(4) 2·72	(4) 2·72	(6) 1·92	(6) 3·73	153
CoF_3	(4) 2·66	(4) 2·69	(6) 1·89	(6) 3·65	149

three different Mn–F bond lengths. The octahedra are joined by sharing corners in such a way that three sets of linkages

$$\cdots\text{–F–Mn–F–Mn–F–Mn–}\cdots$$

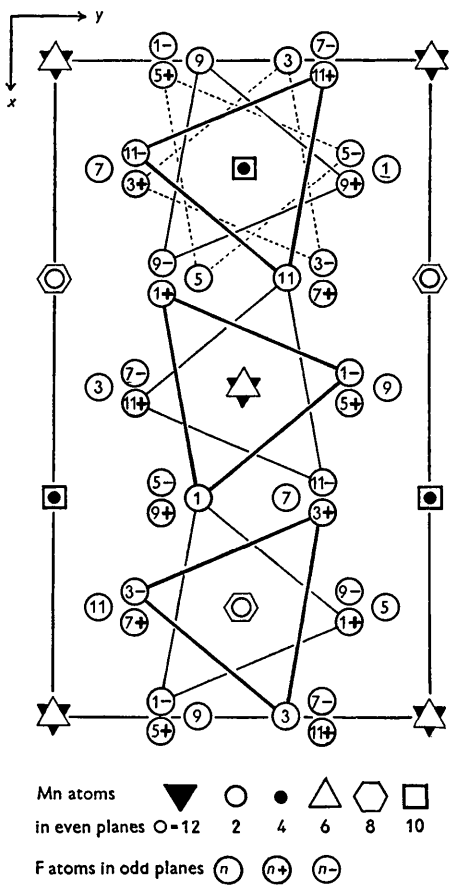


Fig. 4. Projection along [001] on (001) of the MnF_3 unit cell.

run continuously throughout the structure. Since the structure may be regarded as a considerably distorted pseudo-cubic ReO_3 type (Hepworth *et al.*, 1957), the three sets of linkages run in general directions which are approximately at right-angles to one another. The Mn–F distances of the F–Mn–F links in two of these directions are alternately long and short (2·09 and 1·79 Å respectively), and in the third direction the Mn–F distances are all equal (see Fig. 5).

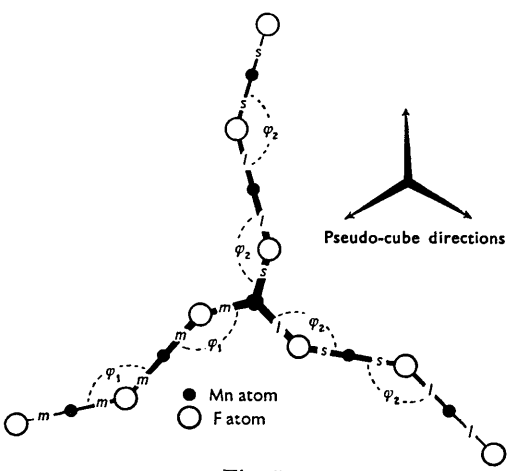


Fig. 5.
Mn–F bond distances along three pseudo-cubic directions.
$l=2{\cdot}1$ Å, $m=1{\cdot}9$ Å, $s=1{\cdot}8$ Å; $\varphi_1=144°$, $\varphi_2=148°$.

Simple compounds of trivalent manganese are rare, and since no structural data other than those given in the present work are available, values of the Mn–F distance calculated for ionic and for covalent bonding are unreliable. The ionic and covalent radii for fluorine are respectively 1·36 and 0·67 Å, and those for manganese are assessed (see Pauling, 1940; and Sidgwick 1950) as 0·64 and 1·22 Å. Thus, the Mn–F distance is

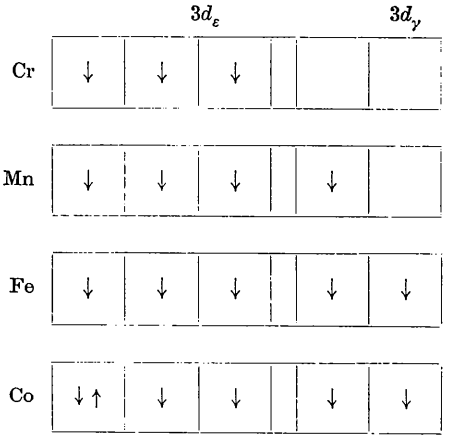
probably about 2·00 Å for ionic bonding and about 1·89 Å for covalent bonding. The mean of the two shorter observed distances in MnF_3 (1·91 and 1·79 Å) is slightly less than the estimated covalent value, but the remaining Mn–F bond (2·09 Å) is even longer than the calculated ionic value.

Interatomic bonding in MnF_3

The crystal-field (or ligand-field) theory (see Orgel, 1952) interprets the stereochemistry of complex compounds of the transition metals by considering the effect of the electric field due to ligand lone-pairs of electrons upon the arrangements of the *d*-orbitals of the co-ordinated atom. In the field-free atom (e.g. manganese) the five 3*d* orbitals are degenerate, but on bringing up six octahedrally co-ordinated charges along the *x*, *y* and *z* axes a stage is reached when the cubic field is strong enough to split the *d*-levels into two groups—a set of three degenerate d_ε orbitals and a set of two d_γ orbitals of higher energy. The d_ε orbitals are of lower energy because their lobes of electron density point in between the *x*, *y* and *z* axes, i.e. away from the incoming six ligand charges. The d_γ orbitals, however, point along the bond directions, and if they are occupied they will interact repulsively with the incoming charges. As an example of its application, Harris, Nyholm & Stephenson (1956) have recently used the theory to account for the observed bond lengths in $Pd(diarsine)_2I_2$. The structure of the latter consists of discrete molecules in which the central metal atom is surrounded by 4 As atoms in a square plane at 2·38 Å. The 2 I atoms complete a distorted octahedron with elongated Pd–I bonds (3·52 Å). The normal Pd–I bond distance in square complexes is only 2·65 Å. Prof. R. S. Nyholm (private communication) has suggested that the abnormally long bonds in the MnF_6 octahedra of the MnF_3 structure might be explained in a similar way.

The magnetic moment of MnF_3 is 4·9 B.M. (Nyholm & Sharpe, 1952), from which it is inferred that there are four unpaired electrons in the 3*d* shell of the Mn(III) atom. Three of these occupy the d_ε orbitals and the remaining electron is most probably in a $3d_{z^2}$ orbital. The empty $3d_{(x^2-y^2)}$ orbital points in the directions of four fluorine ions and, together with the 4*s* and two 4*p* orbitals, forms four hybrid dsp^2 bonds directed towards the corners of a square. The three singly-occupied d_ε orbitals offer no repulsion since they point between the fluorine atoms. The singly-occupied $3d_{z^2}$ orbital points along the axis of the remaining two Mn–F bonds and must exert a repulsion. These two F atoms are held either by ionic bonds or by linear hybrid $4p4d$ bonds—an interpretation which is in accordance with the abnormally long bond length of 2·09 Å. The four hybrid $3d_{(x^2-y^2)}4s4p^2$ orbitals are not all exactly equivalent since the bonds in the plane (1·91 and 1·79 Å) are not of equal lengths. Neighbouring MnF_6 octahedra are oriented in such a way that a fluorine atom common to both is either equidistant at 1·91 Å from each metal atom or is abnormally distant (2·09 Å) from one manganese atom and at the same time abnormally close (1·79 Å) to the other manganese atom. In this way, the close-packing of distorted octahedra with shared corners is maintained. In terms of classical valency theory, the three different Mn–F bonds might be described as having different covalent and ionic contributions, the ionic contribution increasing with increasing bond length.

Ligand-field theory also offers an explanation for the unique difference between manganese and its neighbouring metals in their trifluoride structures. Chromium, manganese, iron and cobalt each in the trivalent state, have electronic configurations represented by:



It is only for manganese, where the electron occupation of the d_γ orbitals is unsymmetric, that the d_γ interaction with the ligands might be expected to be anisotropic.

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A Simple Adapter for Rotation Cameras to Improve the Accuracy of Measurement of Identity Periods

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A simple adapter is described which makes it possible to measure identity periods from rotating-crystal photographs with an accuracy of the order of 0·1%.

Introduction

Identity periods in crystals are related to the separation of layer lines in rotating-crystal photographs by the expression

$$a = n\lambda/\sin \nu_n , \qquad (1)$$

where a is the identity period and ν_n the semi-opening cone angle of the nth layer (Fig. 1). Differentiation of (1) leads to

$$\Delta a/a = -\cot \nu . \Delta \nu , \qquad (2)$$

which relates the error in a to the error in the measurement of ν.

For the conventional film mounting in a rotation camera (Fig. 1 (position A) and Fig. 2(a)) two factors limit the accuracy. First, ν is limited to angles $< 55°$, so that $\cot \nu$ is always $> 0{\cdot}7$. Secondly, in the terminology of Buerger (1942, p. 95), $\Delta \nu = \cos^2 \nu / r . \Delta y$, where r is the radius of the camera and Δy is the error in the measurement of the separation of the layer lines. At the upper limit of ν, $\cos^2 \nu = 0{\cdot}3$, but, owing to beam divergence and oblique incidence of the diffracted beams on the double-coated film, Δy increases about 4–5 times (a value determined from Fig. 2(a), but representative of typical rotation photographs) and hence $\Delta \nu$ for upper layer lines is slightly greater than for lower layer lines. The expected increase in accuracy for upper layer lines due to the $\cot \nu$ term in (2) is therefore partly reduced by the increase in $\Delta \nu$.

Principle of the adapter

A film mounting which would permit normal incidence of reflexions in the range $0° < \nu < 90°$, would overcome these disadvantages (Fig. 1 (position B)) since the size of reflexions would not vary with ν for a small crystal of the usual dimensions. $\Delta \nu$ would remain constant and full advantage could be taken of the

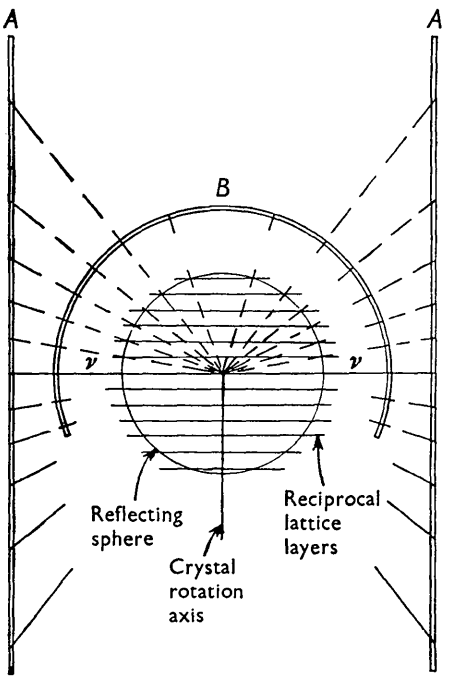

Fig. 1. Rotating-crystal technique with film in the standard position A and in the modified position B permitting normal incidence of reflexions. The direct X-ray beam is normal to the plane of the paper and the diagram illustrates the section at $2\theta = 90°$.