

A New Refinement of the Crystal Structure of MnAlF_5 : New Structural Correlations with MnCrF_5 and Cr_2F_5 Using Orthogonal Subcell Twinning

GÉRARD FERREY,* MARC LEBLANC, AND ANNE-MARIE MERCIER

*Laboratoire des Fluorures, U.A. CNRS 449, Faculté des Sciences
Université du Maine, Route de Laval, 72017 Le Mans Cedex, France*

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A new refinement of the crystal structure of MnAlF_5 , needed for further powder neutron diffraction studies, shows that it is centric (S.G. $Cmcm$, $a = 3.5837(4) \text{ \AA}$, $b = 9.854(1) \text{ \AA}$, $c = 9.537(1) \text{ \AA}$, $Z = 4$). The structure was refined from 720 independent reflections ($R = 0.023$, $R_w = 0.022$). Its crystal chemistry is basically the same as previously described, but a new comparison with MnCrF_5 and Cr_2F_5 is proposed. It first shows that the latter two structures represent two different monoclinic distortions of the same structural type, despite large differences in their lattice parameters. This leads to a description of MnAlF_5 as a twinning of two subcells of this structural type and to an introduction of the concept of subcell orthogonal twinning. © 1993 Academic Press, Inc.

1. Introduction

MnAlF_5 (1) was one of the first ABF_5 pentafluorides to be synthesized. Its orthorhombic structure ($a = 9.54 \text{ \AA}$, $b = 9.85 \text{ \AA}$, $c = 3.58 \text{ \AA}$, $Z = 4$) was solved from single-crystal data (2) using space group $Ama2$, but the reliability factor was very high ($R = 0.156$) and cast some doubts on the veracity of the determination. The choice of the noncentric group was based only on the test of Howell *et al.* (3), and the refinement led to atomic coordinates which were very close to special positions of the corresponding nonstandard centrosymmetric space group $Amam$; this hypothesis was not tested by the authors. An accurate redetermination of the structure of MnAlF_5 was then neces-

sary, not only to obtain more accurate data but also to allow further neutron diffraction studies of the magnetic state.

Indeed, MnAlF_5 is very important from the magnetic point of view since it provides a unique example of isolated chains of edge-sharing Mn^{2+} octahedra, which sheds some light on the nature of the superexchange coupling between Mn^{2+} ions, when it is not influenced by topological frustration (4, 7, and references therein). Its antiferromagnetism below 2.35 K, previously characterized by powder neutron diffraction (5), but using a wrong space group, provides information on the magnetic frustration which could occur in BaMnFeF_7 (6, 7); this last structure is built up from rutile blocks involving edge-sharing Mn^{2+} octahedra.

Finally, attention is paid to the ABF_5 family ($A^{II}, B^{III} = 3d$ transition metals and Al) since the literature claims the existence of

* To whom correspondence should be addressed.

TABLE I
 DETAILS OF THE X-RAY DATA COLLECTION OF MnAlF_5

Determination of cell parameters	22 reflections ($24^\circ \leq 2\theta \leq 30^\circ$)
Space group	$Cmcm$ ($n^\circ 63$) $hkl: h + k = 2n$ $h0l: l \times 2n$
Cell dimensions	$a = 3.5837(4) \text{ \AA}$ $b = 9.854(1) \text{ \AA}$ $c = 9.537(1) \text{ \AA}$
Volume/Z	$V = 336.8 \text{ \AA}^3$ $Z = 2$
Density	3.52(5) calc.: 3.49
Wavelength	0.71069 \AA (Mo $K\alpha$)
Scan mode	$\omega - 2\theta$
Step scan	$37 \leq N \leq 46$, $\Delta\omega = 0.035^\circ$, and $t = 2 \text{ sec.}$
Aperture	$D = 4.0 \text{ mm}$
Absorption correction	Gaussian method
Transmission factors	$A_{\max} = 0.841$; $A_{\min} = 0.546$
Absorption coefficient	$\mu = 25.4 \text{ cm}^{-1}$
Angular range of data collection	$2\theta \leq 90^\circ$
Range of measured h, k, l	$0 \leq h \leq 7$; $-19 \leq k \leq 19$; $-18 \leq l \leq 18$
Standard reflections (3)	(111); (040); (200)
Measured every	120 min
Maximum intensity variation	1.5%
Measured reflections	4218
independent ref. ($ F > 3\sigma F $)	720
R (from averaging)	0.039
Number of refined parameters	27
Secondary extinction factor	$1.1(2) \times 10^{-7}$
Weighting scheme	$w = 1.0[\sigma(F)^2 + 0.0003 F^2]$
Shift/e.s.d.	
mean	0.013
max	0.057
Final Fourier residuals	-0.79 to $0.80 e^- \cdot \text{ \AA}^{-3}$
R/R_w	0.023/0.022

three different structural types for this composition. Study of the structural correlations between the Cr_2F_5 (8), MnCrF_5 (9), and MnAlF_5 families shows that the first two correspond to two different distortions of the same aristotype which is described below. Their relations with MnAlF_5 can be understood by introducing the concept of orthorhombic subcell twinning which implies breathing modes for MF_6 octahedra in order to imagine a transition between the two structures.

Experimental

Single crystals of MnAlF_5 were obtained by heating a 1 : 1 mixture of MnF_2 and AlF_3

at 850° C during 20 days in sealed gold tubes. A rhomboid-based prismatic crystal ($0.080 \times 0.080 \times 0.019 \text{ mm}^3$), limited by (100), (012), and (02-1) faces, was selected for the X-ray study.

Laue and precession photographs confirm the orthorhombic symmetry. After an interchange between the parameters given by Rimsky *et al.* (2), the reflection conditions are in agreement with the space group $Cmcm$ or its subgroup $Cmc2$. Diffraction data were collected on an automatic four-circle diffractometer Siemens AED2 and were corrected for Lorentz polarization and absorption. Table I shows the details of the data collection.

TABLE II
ATOMIC COORDINATES AND ISOTROPIC THERMAL
PARAMETERS OF MnAlF_5

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	$B(\text{\AA}^2)^*$
Mn(4b)	1/2	0	0	72(1)	84(1)	106(1)	41(1)	0.69(1)
Al(4c)	0	2059	1/4	40(2)	49(2)	60(2)	0	0.39(2)
F1(8f)	0	3296	1176	254(6)	134(5)	191(5)	107(4)	1.52(4)
F2(8f)	0	731	1156	144(4)	121(4)	94(3)	-49(3)	0.94(3)
F3(4c)	0	6923	1/4	39(5)	230(8)	315(8)	0	1.54(6)

Note. Atomic thermal parameters are multiplied by 10^4 ; $U_{13} = U_{12} = 0$. Standard deviations of atomic coordinates are all 1 or less in the last digit.)

All calculations were performed with the program SHELX (10); using the scattering factors provided by (11). The $Cmcm$ transposed coordinates of Rimsky (2) were taken as starting values for the calculations which rapidly converted to $R = 0.052$ ($R_w = 0.053$) by refining all atomic coordinates and isotropic thermal parameters. Further refinement of anisotropic thermal parameters leads to $R = 0.023$ ($R_w = 0.022$) for 720 independent reflections (four rejects). For sake of comparison, the corresponding refinement in the noncentric group leads to higher values of R ($R = 0.028$; $R_w = 0.028$) from 1292 remaining reflections (1413 selected; 121 rejected). Whatever the chosen space group, anisotropic thermal parameters are strictly the same. Moreover, MnAlF_5 does not present nonlinear optical properties (12). For these reasons, MnAlF_5 will be described as centric in the following. The final values of x , y , z , and U_{ij} are listed in Table II.

Description of the Structure

The structure of MnAlF_5 remains basically the same as that previously described (Fig. 1). By sharing their two opposite F3 ions, AlF_6 octahedra form trans chains along the a axis, whereas MnF_6 is linked by four F2 ions to build up edge-sharing rutile-like chains, also running along a . Four AlF_6

chains are connected to a rutile chain in two ways (Fig. 2), via either F1 or F2 ions. In the former case, Al and Mn chains share corners and lead to an Al-F1-Mn angle close to 180° (Table III). In the latter case, F2 has three metallic neighbors (2 Mn + Al); this corresponds to Al-F2-Mn angles of 125.3° . The other characteristic angles and distances are listed in Table III and lead to several remarks omitted up to now.

It is worth noting the large discrepancy among distances within the Mn^{2+} octahedron, both for Mn-F and F-F lengths. From

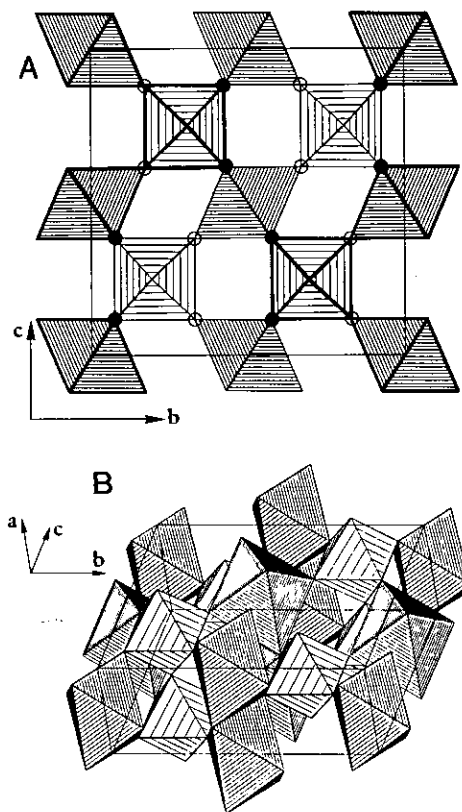


FIG. 1. (100) projection (A) and perspective view (B) of MnAlF_5 . Mn and Al octahedra are strongly and lightly hatched, respectively. F1 and F2 ions are represented as full and empty circles, respectively. F3 projects at the center of the Al octahedra. On this projection, heavily outlined octahedra correspond to metals at the $x = 1/2$ level.

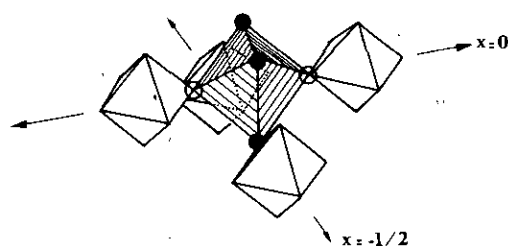


FIG. 2. Detailed perspective view showing the corner sharing of AlF_6 octahedra with the rutile-like chains (same symbols as in Fig. 1).

the geometrical point of view, the sixfold coordination of Mn^{2+} is better described by two short Mn-F1 (2.020 Å) and four long Mn-F2 (2.224 Å) distances. Moreover, among all the F-F distances within the octahedron, two of the four F2-F2 distances are particularly large, since they correspond to the a parameter of the cell (3.583 Å). Obviously, they induce the large Mn-F distances noted above. However, this apparent anomaly may be easily explained from valence bond analysis. F2 ions are shared between three octahedra: one of Al and two of Mn. So, the bond strengths donated to F2 by

Al^{3+} and Mn^{2+} in octahedral coordination are about $3/6$ and $2 \times 2/6$, respectively. F2 would then receive more than 1 valence unit (v.u) if AlF_6 and MnF_6 octahedra were regular. As 1 v.u. saturates the bonding possibilities of F, a weakening of the Mn-F2 strength can be expected, and correlatively, Mn-F1 is reinforced. A quantitative valence bond analysis (Table IV) confirms this hypothesis.

Considering the AlF_5 chains within the diagonal planes (011) and (0 - 11), two types of interchain distances appear: 6.261 and 7.505 Å (Fig. 3). This discrepancy is due to the different orientations of the MnF_6 octahedra which link the two AlF_5 chains. The shortest distance (6.261 Å) corresponds to a linkage between Al and Mn chains via F2 ions which already form the common edge between two MnF_6 octahedra of a rutile chain. The longer connection between the two AlF_5 chains involves the "terminal" F1 ions of the rutile chain. In other words, it can be said that, for 6.261 Å, two fluoride ions in cis position within the MnF_6 octahedron ensure the linkage; for 7.505 Å, the bridging fluoride ions are in trans position in

TABLE III
BOND LENGTHS (Å) AND ANGLES (°) IN MnAlF_5

Al octahedron		
Al-F1: $2 \times 1.755(1)$	F1-F1: $1 \times 2.525(2)$	F1-Al-F1: $1 \times 92.0(1)$
Al-F2: $2 \times 1.832(1)$	F2-F2: $1 \times 2.564(2)$	F2-Al-F2: $1 \times 88.8(1)$
Al-F1: $2 \times 1.797(1)$	F1-F2: $2 \times 2.528(2)$	F1-Al-F2: $2 \times 89.6(1)$
	F1-F3: $4 \times 2.576(2)$	F1-Al-F3: $4 \times 86.9(1)$
$\langle \text{Al-F} \rangle$: 1.795(1)	F2-F3: $4 \times 2.497(2)$	F2-Al-F3: $4 \times 92.9(1)$
	$\langle \text{F-F} \rangle$: 2.536(2)	
Mn octahedron		
Mn-F1: $2 \times 2.019(1)$	F1-F2: $4 \times 2.942(2)$	F2-Mn-F2: $2 \times 72.6(1)$
Mn-F2: $4 \times 2.224(1)$	F1-F2: $4 \times 3.012(2)$	F2-Mn-F2: $2 \times 107.4(1)$
	F2-F2: $2 \times 2.634(2)$	F1-Mn-F2: $4 \times 90.3(1)$
$\langle \text{Mn-F} \rangle$: 2.156(1)	F2-F2: $2 \times 3.583(2)$	F1-Mn-F2: $4 \times 89.6(1)$
	$\langle \text{F-F} \rangle$: 3.020(2)	
Al-F-Mn angles		
Mn-F2-Mn: 107.4(1)	Al-Fe-Al: 171.4(1)	
Al-F2-Mn: 125.3(1)	Al-F1-Mn: 167.7(1)	

TABLE IV
VALENCE BOND ANALYSIS OF $MnAlF_5$

	Mn	Al	Σ	Σ_{expected}
F1	0.366	0.566	0.932	1
	0.366	0.566		
F2	0.307×2	0.460	1.075	1
	0.307×2	0.460		
F3		0.506×2	1.012	1
Σ	1.96	3.06		
Σ_{expected}	2.00	3.00		

Note. The Zachariasen law $s = 1/K * (\exp((d_0 - d)/B))$ ($B = 0.37$) was taken for the calculations, with $K = 1/3$ and $d_0 = 2.109$ for Mn^{2+} and $K = 1/2$ and $d_0 \times 1.801$ for Al^{3+} (19)

the Mn polyhedron. In the following, we shall call these fluoride ions only cis and trans, according to the above definitions. These two types of arrangements within the same plane are the specific characteristics of $MnAlF_5$ with respect to the other pentafluorides, as we see in further detail below. This fact was not taken into account by previous authors (2, 13–15).

The two interchain distances found here are closely related to the values of some of the cell parameters of Cr_2F_5 (8), $b = 7.540$ Å, and of $MnCrF_5$ (9), $b = 6.291$ Å. This

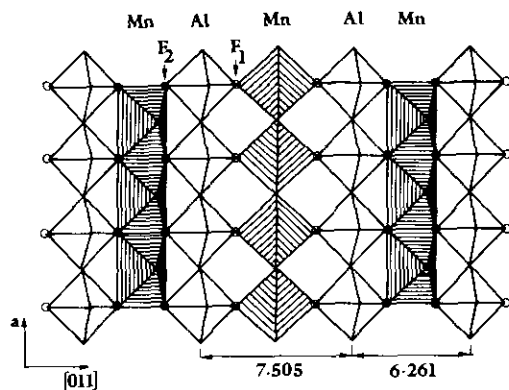


FIG. 3. View of (011) plane, showing the two modes of connection between AlF_6 and MnF_6 octahedra (same symbols as in Fig. 1).

TABLE V
CELL PARAMETERS ($Z = 2$) AND ATOMIC COORDINATES OF THE THEORETICAL ARISTOTYPE OF $M^{2+}AlF_5$ (S.G. *Immm*)

Atom	Site	x	y	z
M^{2+}	$2c$	$1/2$	$1/2$	0
Al^{3+}	$2a$	0	0	0
F1	$2b$	$1/2$	0	0
F2	$4g$	0	y	0
F3	$4i$	0	0	z

$V = 173.2 \text{ \AA}^3$
 $V = 177.3 \text{ \AA}^3$

$y = 0.29$
 $z = 0.237$

led us to reexamine carefully the crystal chemistry of these two compounds in order to establish new structural correlations between the three compounds.

Structural Correlations

1. Comparison of Cr_2F_5 and $MnCrF_5$ Structures.

Cr_2F_5 and $MnCrF_5$ are monoclinic (S.G. $C2/c$), but with rather different cell parameters (Table VI). They both exhibit an important distortion of M^{2+} octahedra due, respectively, to the Jahn-Teller effect and the strong tilting of the M^{3+} chains. This leads to coordinations of $4 + 2$ for Cr^{2+} and $4 + 2 + 1$ for Mn^{2+} . However, if we consider the six nearest fluorine ions around Mn^{2+} ,

TABLE VI
CELL PARAMETERS OF Cr_2F_5 AND $MnCrF_5$ AND THEIR RELATION WITH THOSE OF THE ARISTOTYPE

Cr_2F_5	$MnCrF_5$
$a_c = 7.773(5)$ Å	$a_M = 8.586(5)$ Å
$b_c = 7.540(5)$ Å	$b_M = 6.291(3)$ Å
$c_c = 7.440(5)$ Å	$c_M = 7.381(4)$ Å
$\beta_c = 124.25(9)^\circ$	$\beta_M = 115.46(7)^\circ$
$Z = 4$	$Z = 4$
$7.280 \text{ \AA} = 2a_0 \approx c_c \approx c_M$	(axis of M^{3+} trans chains)
$6.270 \text{ \AA} = b_0 \approx a_c. \sin \beta_c \approx b_M$	(short interchain distance)
	(with cis F^- of $M^{II}F_6$)
$7.590 \text{ \AA} = c_0 \approx b_c \approx a_M. \sin \beta_M$	(long interchain distance)
	(with trans F^- of $M^{II}F_6$)

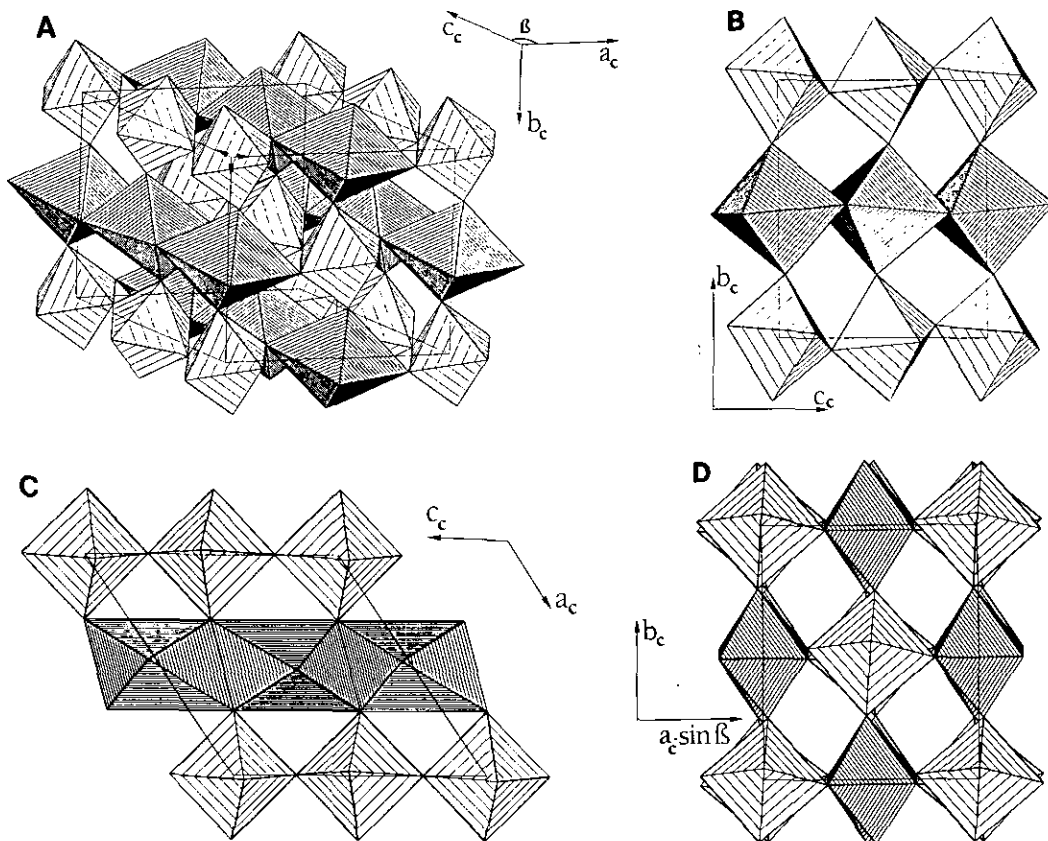


FIG. 4. Perspective view and projections on the three faces of the cell of Cr_2F_5 (A, B, C, D) and of MnCrF_5 (E, F, G, H).

it is clear (Fig. 4) that Cr_2F_5 and MnCrF_5 correspond to the same structural type with corner-sharing trans chains of $M^{3+}\text{F}_6$ octahedra linked to the rutile-type chains of $M^{2+}\text{F}_6$ octahedra via cis F^- in one plane and via trans F^- in the orthogonal plane. Cr_2F_5 and MnCrF_5 are then two different monoclinic distortions of the same theoretical orthorhombic aristotype (see note at the end of this paper). The simplest description of the latter (Table V) uses space group $I mmm$. Cell parameters are defined from Shannon's ionic radii (16) by the relations

$$a_0 = 2R_{M^{3+}} + 2R_{\text{F}^-}$$

(F in twofold coordination: 1.285 Å),

$$b_0 = 2R_{M^{3+}} + 4R_{\text{F}^-}$$

(F in threefold coordination: 1.30 Å),

$$c_0 = 2R_{M^{3+}} + 2R_{M^{2+}} + 4R_{\text{F}^-}$$

(F in twofold coordination).

In this cell (Fig. 5), M^{2+} and M^{3+} are located on a center of symmetry and on three twofold axes. The chains of M^{3+} octahedra are not tilted, but the distortion of the M^{2+} octahedra, noted above for MnAlF_5 , already exists with F2–F2 distances along the a_0 axis as long as those encountered for MnAlF_5 . This implies that, if the aristotype exists, it would involve the smallest M^{3+} ions (i.e., Al^{3+}). Larger M^{3+} cations give rise to a tilting of the $M^{3+}\text{F}_6$ chains. This

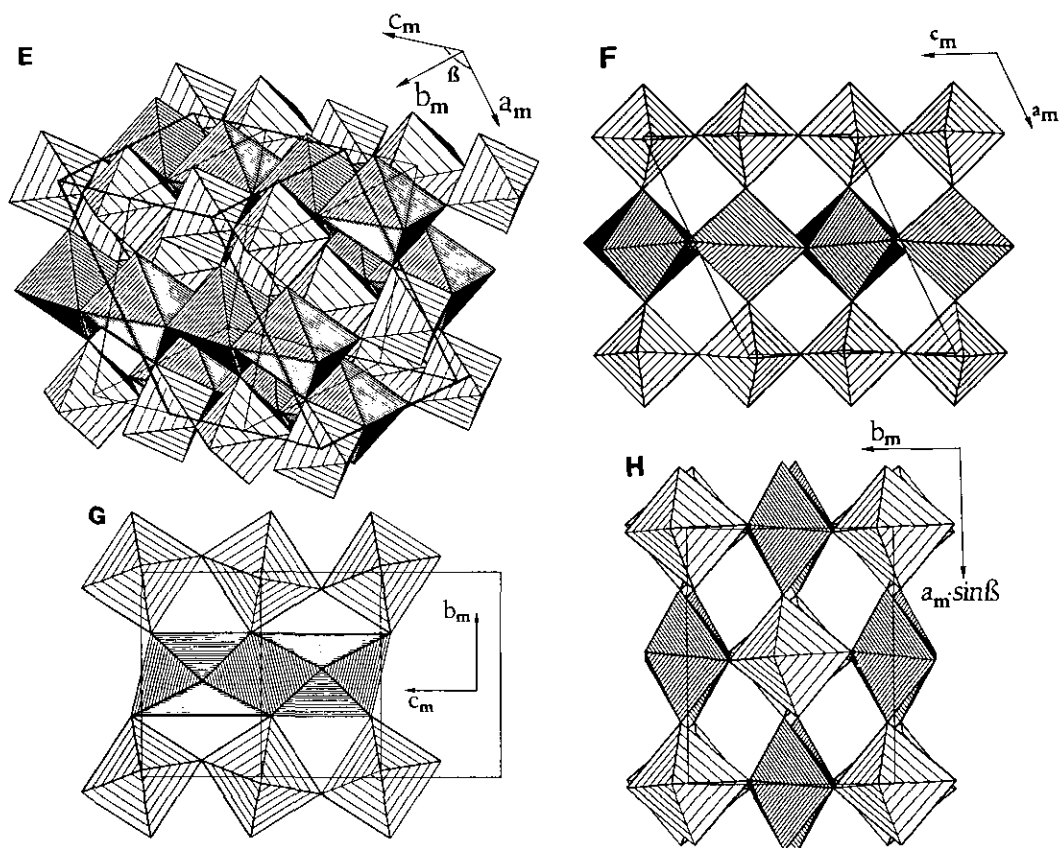


FIG. 4—Continued

tilting requires the doubling of the a_0 parameter and leads to the c axis of the monoclinic cells of both Cr_2F_5 and $MnCrF_5$. It is worth noting that, in both structures, M^{3+} are located exclusively on centers of symmetry. Moreover, valence bond considerations show that the anisotropic character, and therefore the chemical nature, of the divalent ions inserted between the M^{3+} chains governs the type of monoclinic distortion of the aristotype and the tilting mode of the trans chains of $M^{3+}F_6$ octahedra.

Indeed, along the c_0 axis of the aristotype, $M^{3+}F_6$ and $M^{2+}F_6$ octahedra share only corners via F3 ions which receive theoretically $3/6$ and $2/6$ valence units from M^{3+} and M^{2+} , respectively. This does not saturate the bonding possibilities of F3. Therefore, the satu-

ration will be reached only if $M^{3+}-F3$ and $M^{2+}-F3$ distances are shorter than their usual values; consequently, the main distortion of M^{2+} octahedra will occur within the (a_0b_0) plane, inside of which two ways of distortion are possible due to the nature of the M^{2+} ions.

A Jahn-Teller ion like Cr^{2+} leads to two long (in trans position) and four short bonds. Two of the latter are along c_0 (see above). Thus the two long and the remaining two short bonds are within the (a_0b_0) plane. This has two consequences: the first concerns Cr^{2+} itself which is required to settle on a center of symmetry in order to respect the opposite long bonds; the second is related to the disposition of the two M^{3+} chains in the (a_0b_0) plane. The distortion of Cr^{2+}

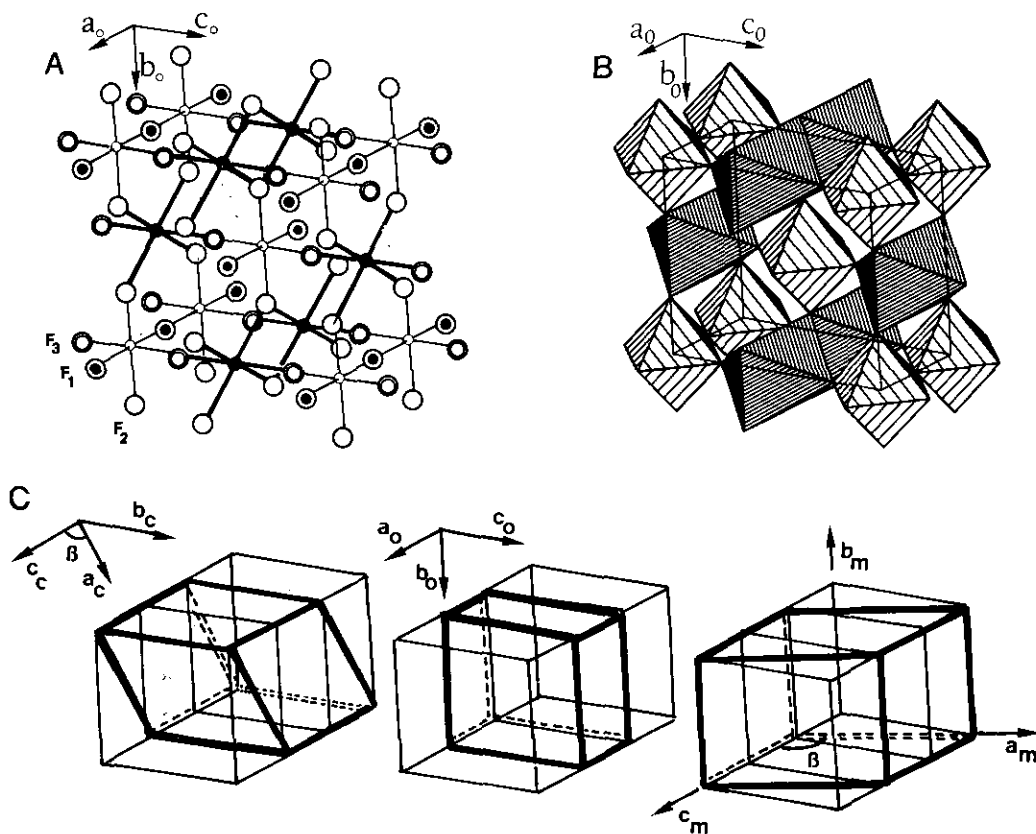


FIG. 5. Perspective view of the orthorhombic aristotype (A, B) and its cell relations (C) with Cr_2F_5 (left) and $MnCrF_5$ (right).

octahedra in this plane forbids that one of the two chains be exactly above the other. Therefore, the monoclinic distortion of the cell of Cr_2F_5 occurs in the (a_0b_0) plane, and the γ_0 angle becomes larger than 90° . This implies that F1 atoms ($\frac{1}{2}00$) of the aristotype orthorhombic cell must remain on the twofold axis parallel to c_0 . This excludes any tilting of the $M^{3+}F_6$ chains within the (a_0b_0) plane; it could however occur in the (a_0c_0) and, to a lower extent, in the (b_0c_0) planes.

When $M^{2+} = Mn$, which is not a Jahn-Teller ion, the existence of the short distances along c_0 noticed above requires two long and two medium bonds in the (a_0b_0) plane also, but this time the Jahn-Teller

condition (two opposite long bonds) is not required. Therefore, the distortion can respect a twofold symmetry with Mn^{2+} on this symmetry element (whereas Cr^{2+} was obliged to be on a center of symmetry). In this case, the twofold axis must be parallel to the b_0 axis of the orthorhombic cell, and therefore prohibits any tilting of the $M^{3+}F_6$ chains in the (b_0c_0) plane. The tilting occurs in the (a_0c_0) and in the (a_0b_0) planes. First, this allows two chains of the latter plane to be perfectly aligned, one over the other, and keeps γ_0 strictly equal to 90° . Moreover, the tilting modes of the two chains belonging to the (a_0c_0) plane are opposite each other. This explains why the monoclinic distortion

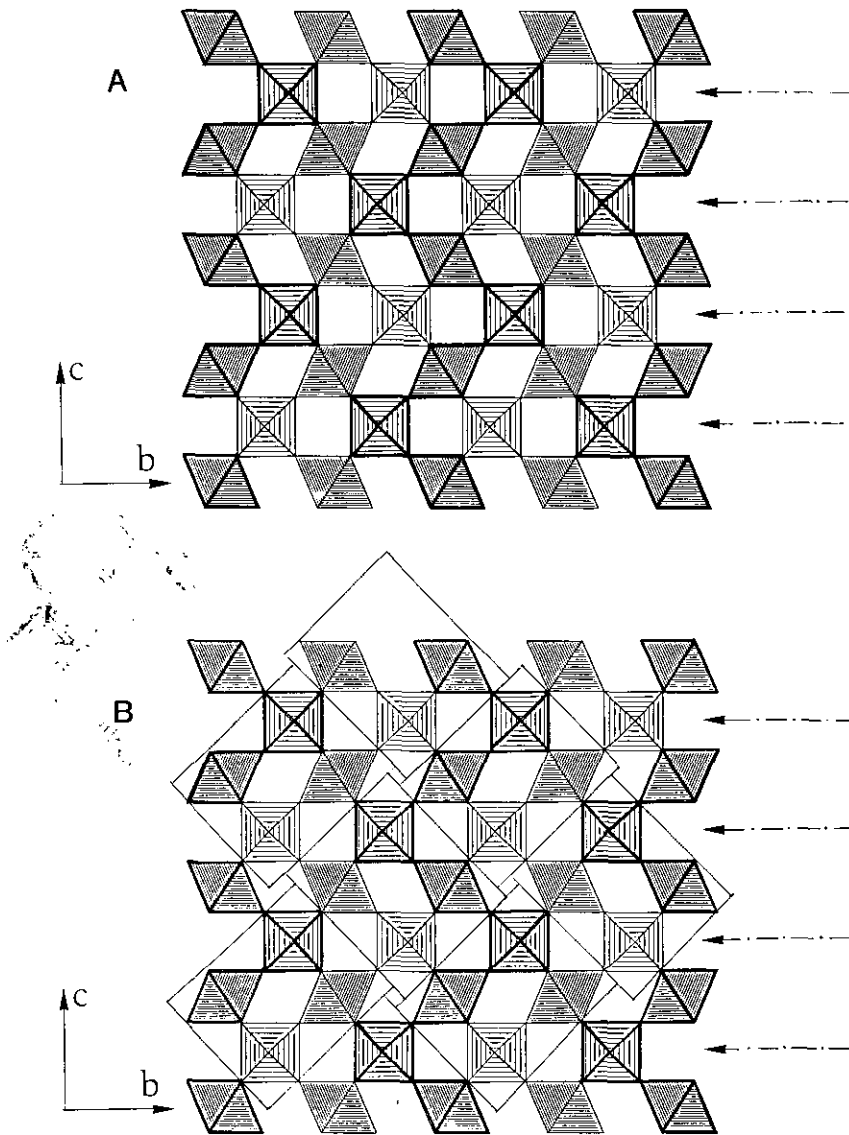


FIG. 6. $MnAlF_5$ described in terms of twinning using the Andersson concept (upper part) and of the orthogonal subcell twinning (lower part). Dotted lines correspond to the swinging planes.

of the cell of $MnCrF_5$ occurs in the (a_0c_0) plane instead of in the (a_0b_0) plane as it does for Cr_2F_5 . This careful examination of the latter two structures proves that it was not necessary to introduce, as previously noted by (13), a translation of $c/4$ for M^{2+} to correlate Cr_2F_5 and $MnCrF_5$ when the true correlated axes are properly chosen.

One can regret, however, that we have not found the true space group of the orthorhombic aristotype. If its crystal chemistry is well described with $Immm$; this space group does not lead to $C2/c$ subgroups. $Immm$ must then be considered as a first approximation in the description of the aristotype. On the contrary, monoclinic Cu

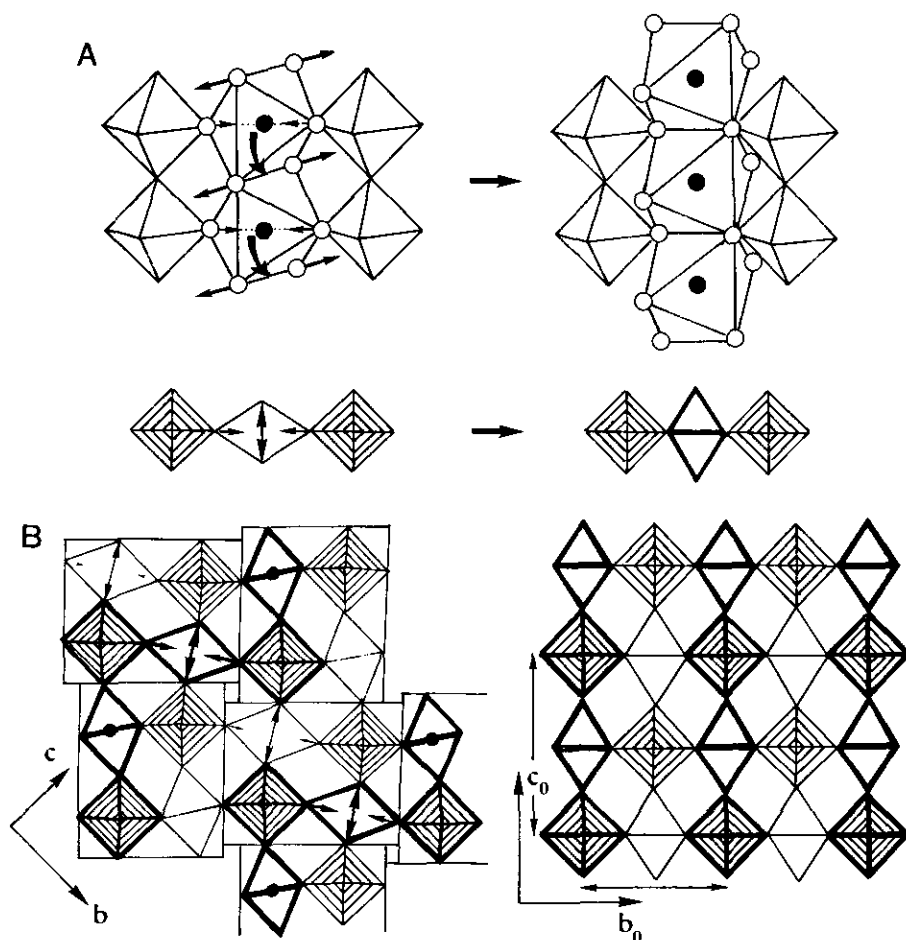


FIG. 7. $M^{2+}F_6$ breathing mode allowing the transition between $MnAlF_5$ and aristotype.

WO_3F_2 (S.G. $P 2_1/m$) (17) is derived from orthorhombic $MnAlF_5$ (S.G. $C mcm$) by a direct group-subgroup relation. We shall now examine the relationship between $MnAlF_5$ and the two structures of Cr_2F_5 and $MnCrF_5$.

2. Comparison with $MnAlF_5$

In the latter two compounds, the two different modes of linkage of $M^{3+}F_6$ chains by $M^{2+}F_6$ ones, illustrated in the "description of the structure" section, occurred in two orthogonal directions, whereas they appear in the same plane for $MnAlF_5$. Conse-

quently the surroundings of the $M^{3+}F_6$ chains are different in $MnAlF_5$ than in Cr_2F_5 and $MnCrF_5$. In contrast, the surroundings of the $M^{2+}F_6$ chains are always identical, whatever the structure.

This remark leads to an analysis of $MnAlF_5$ in terms of chemical twinning with two alternative approaches: the first concerns the well-known chemical twinning concept of Andersson and Hyde (18) for which $MnAlF_5$ provides a good illustration (Fig. 6), with swinging planes at $z = \frac{1}{4}$ and $\frac{3}{4}$; the second, which we shall call "orthogonal subcell twinning," requires a definition. It

was seen above that the b_0 and c_0 parameters of the orthorhombic aristotype were different. Nevertheless, they can be fit in order to give, after some tilting of octahedra, a long range order. Indeed, if a noncentric subcell (indicated as a rectangle in Fig. 6B) is defined, MnAlF_5 can be described (Fig. 6) as an orthogonal twinning of the two enantiomorphs of this subcell. Its "detwinning" corresponds to the aristotype and might give rise to an eventual phase transition between MnAlF_5 and either Cr_2F_5 or MnCrF_5 types according to the nature of the divalent cation. The transformation can be imagined (Fig. 7) from a breathing mode of M^{2+} octahedra at the $x = 0$ level, corresponding to an enlargement of the distances between F2, followed by a shift of $a/2$ of M^{2+} , and finally by a decrease of the F1-F1 distance; this recreates the octahedron with a different orientation, destroys the "twinning," and generates the aristotype. However, the close values of the volumes of 1 formula unit of MnAlF_5 (84.2 \AA^3) and of the aristotype (at least 86.6 \AA^3 from the values of the ionic radii) prevents us from predicting what might be the high pressure form.

Note added in proof. At the end of the writing of this paper, we were informed (20) of the synthesis of FeAlF_5 which exhibits the structure of the aristotype proposed in this paper.

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