

## NaCdAlF<sub>6</sub>: A New Structure with [AlF<sub>5</sub>]<sub>n</sub><sup>2n-</sup> Chains and "Independent F<sup>-</sup>"

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Crystals of NaCdAlF<sub>6</sub> are orthorhombic (space group *Pnma*) with  $a = 12.506(1) \text{ \AA}$ ,  $b = 3.6406(6) \text{ \AA}$ ,  $c = 9.902(1) \text{ \AA}$ , and  $Z = 4$ . The structure was solved from single crystal data using 982 independent reflections ( $R = 0.019$ ,  $R_w = 0.019$ ). Aluminum octahedra form a new arrangement of linear *trans*-connected [AlF<sub>5</sub>]<sub>n</sub><sup>2n-</sup> chains, running in the [010] direction, between which sodium and cadmium ions, in six- and seven-fold coordination, respectively, and an independent fluorine ion are located. Cationic tetrahedra (3 Cd<sup>2+</sup> + 1 Na<sup>+</sup>) around independent fluorine ions form chains of formula [FNaCd]<sub>n</sub><sup>2n+</sup>, running in the [010] direction. © 1990 Academic Press, Inc.

### Introduction

The fluorinated compounds NaMnM<sup>III</sup>F<sub>6</sub> are derived from the Na<sub>2</sub>SiF<sub>6</sub>-type (*I-3*) by the substitution Na<sup>+</sup> + Si<sup>4+</sup> → Mn<sup>2+</sup> + M<sup>III</sup> (M<sup>III</sup> = Al, Cr, Ga, Fe). In these compounds the cations fill half of the available octahedral sites. With divalent cations having an ionic radius larger than 0.83 Å (Mn<sup>2+</sup>), such as Ca<sup>2+</sup> or Cd<sup>2+</sup>, the sixfold coordination is not the only stable coordination and new phases can be obtained. Nevertheless, the compounds NaM<sup>II</sup>CrF<sub>6</sub> (M<sup>II</sup> = Ca<sup>2+</sup> and Cd<sup>2+</sup>) (2) and β-NaCaAlF<sub>6</sub> (4) crystallize with the Na<sub>2</sub>SiF<sub>6</sub>-type structure but with a cationic distribution different from that in NaMnMF<sub>6</sub>.

For Cd<sup>2+</sup> ( $r_{\text{Cd}^{2+}[6]} = 0.95 \text{ \AA}$ ) and Al<sup>3+</sup> ions, a new phase NaCdAlF<sub>6</sub> has been obtained. The present paper describes the crystal structure of this compound.

### Preparation

In the solid state, by heating of the mixture NaF + CdF<sub>2</sub> + AlF<sub>3</sub> in a sealed gold tube under argon atmosphere at 660°C (40 hr) single crystals were obtained beside powder. Below 600°C, only a powder mixture of CdF<sub>2</sub>, Na<sub>5</sub>Al<sub>3</sub>F<sub>14</sub>, and AlF<sub>3</sub> is obtained.

The thermal study (DTA Netsch 404S) shows an incongruent melting point at 695(3)°C (heating rate of 300°C/hr).

### Structure Resolution

A needle-shaped crystal with an approximate volume of  $5.4 \cdot 10^{-4} \text{ mm}^3$  was selected for X-ray data collection on a Siemens AED2 four-circle diffractometer. The conditions of the diffraction experiment are summarized in Table I. The unit cell is

TABLE I  
CRYSTAL DATA AND CONDITIONS OF DATA COLLECTION AND REFINEMENT FOR NaCdAlF<sub>6</sub>

Symmetry	Orthorhombic
Space group	<i>Pnma</i> (No. 62)
Cell parameters	$a = 12.506(1) \text{ \AA}$ , $b = 3.6406(6) \text{ \AA}$ , $c = 9.902(1) \text{ \AA}$ ; $V = 450.83 \text{ \AA}^3$ ; $Z = 4$
Crystal volume ( $10^{-3} \text{ mm}^3$ )	0.54
Radiation	MoK $\alpha$ (graphite monochromatized)
Detector aperture (mm)	$3.5 \times 3.5$
Scanning mode	$\omega/2\theta$ step-scan mode in $N$ steps of $\Delta\omega^\circ$ , $38 \leq N \leq 48$ , $0.025 \leq \Delta\omega^\circ \leq 0.027$
	Time per step: 1–4 sec
Profile fitting data analysis (4)	Isotropic linewidth, $\omega = (0.92 + 0.025 \tan \theta)^\circ$
Range registered	$2\theta_{\min} - 2\theta_{\max}$ : $4 - 75^\circ$ , $hkl_{\max}$ 22 6 17
Absorption correction	Gauss method, $\mu = 51.56 \text{ cm}^{-1}$
	$t_{\min} = 0.65$ , $t_{\max} = 0.79$
Reflections measured:	
Total	2821
Independent	1453 ( $R_{\text{average}} = 0.018$ )
Used in refinement	982 ( $I/\sigma(I) > 3$ )
Number of refined parameters	56
Weighting scheme	$\omega = 2.11/(\sigma^2(F))$
Secondary extinction	$\epsilon = 7.3 \times 10^{-8}$
Maximum height in final Fourier difference map	$0.19 \text{ e}^-/\text{\AA}^3$

orthorhombic and the lattice parameters— $a = 12.506(1) \text{ \AA}$ ,  $b = 3.6406(6) \text{ \AA}$ ,  $c = 9.902(1) \text{ \AA}$ —were refined from the positions of 30 reflections in the vicinity of  $30^\circ$  ( $2\theta$ ) centered by the double scan technique. The limiting conditions for the reflections observed— $0kl$ ,  $k + l = 2n$  and  $hk0$ ,  $h = 2n$ —are in agreement with the centric space group *Pnma* and with the noncentric one *Pn2<sub>1</sub>a*.

Intensities were corrected for Lorentz polarization effects as well as for absorption. All calculations were performed with SHELX-76 (6). Ionic scattering factors and anomalous dispersion parameters were taken from "International Tables for X-ray Crystallography" (7). In the space group *Pnma*, application of the direct methods TANG option allowed us to locate the cadmium atom in a  $4c$  site. After least-squares refinement ( $R = 0.29$ ), successive Fourier difference maps and refinements led to the positions of the other atoms, located in a  $4c$  site as well. With these positions and iso-

tropic thermal motion for all atoms, the  $R$  factor was 0.05. The introduction of anisotropic thermal motion led to 0.019 and 0.019 for  $R$  and  $R_w$ , respectively. The calculations performed in the noncentrosymmetric group did not improve significantly the results of the preceding refinement. Table II lists the atomic coordinates and the thermal motion parameters whereas Table III gives the main interatomic distances and angles. A table specifying the calculated and observed structure factors can be obtained on request to the authors.

### Structure Description and Discussion

The main feature of this structure pertains to the existence of an independent fluorine  $F_5$ , besides those which are bonded to  $Al^{3+}$ . There are therefore two ways for describing NaCdAlF<sub>6</sub>. The first, more conventional, starts from the anionic coordination of  $Al^{3+}$ ,  $Na^+$ , and  $Cd^{2+}$ , respectively, 6, 6, and 7, and the second description is

TABLE II  
ATOMIC PARAMETERS, ANISOTROPIC TEMPERATURE FACTORS ( $U_{ij} \times 10^4$ ), AND  $B_{\text{eq}}$  ( $\text{\AA}^2$ ) FOR NaCdAlF<sub>6</sub>

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$	$B_{\text{eq}}$ ( $\text{\AA}^2$ )
Cd <sup>2+</sup>	4c	0.1197(0)	1/4	0.4998(0)	95(1)	79(1)	113(1)	0	-16(1)	0	0.75(1)
Al <sup>3+</sup>	4c	0.3354(1)	1/4	0.6802(1)	80(3)	56(3)	82(4)	0	-12(3)	0	0.57(3)
Na <sup>+</sup>	4c	0.4142(1)	1/4	0.3255(1)	144(5)	126(5)	111(6)	0	50(5)	0	1.00(4)
F1	4c	0.3000(1)	1/4	0.5046(2)	139(8)	187(9)	72(8)	0	-8(7)	0	1.05(6)
F2	4c	0.4728(1)	1/4	0.6443(2)	106(8)	165(9)	226(11)	0	9(7)	0	1.31(7)
F3	4c	0.1663(2)	1/4	0.1868(2)	251(10)	62(7)	208(11)	0	17(8)	0	1.37(7)
F4	4c	0.3567(1)	1/4	0.8611(2)	192(8)	113(8)	94(9)	0	-37(7)	0	1.05(6)
F5 <sup>a</sup>	4c	0.4574(1)	1/4	0.0977(2)	104(7)	107(8)	104(8)	0	9(6)	0	0.83(6)
F6	4c	0.1925(1)	1/4	0.7138(2)	95(7)	189(9)	116(9)	0	-3(6)	0	1.05(6)

<sup>a</sup> Independent fluorine ion.

TABLE III  
MAIN INTERATOMIC DISTANCES ( $\text{\AA}$ ) AND ANGLES ( $^\circ$ )  
IN NaCdAlF<sub>6</sub>

Na <sup>+</sup> octahedron (symmetry <i>m</i> )			
Na-F <sub>1</sub> =	2.276(1)	F <sub>1</sub> -Na-F <sub>5</sub> =	154.7(1)
Na-F <sub>3</sub> <sup>a</sup> =	2.319(2)	F <sub>1</sub> -Na-F <sub>2</sub> = 2 ×	106.3(1)
Na-F <sub>2</sub> = 2 ×	2.324(1)	F <sub>1</sub> -Na-F <sub>6</sub> = 2 ×	90.6(1)
Na-F <sub>4</sub> = 2 ×	2.513(1)	F <sub>5</sub> -Na-F <sub>3</sub> = 2 ×	89.0(1)
(Na-F) =	2.378	F <sub>5</sub> -Na-F <sub>6</sub> = 2 ×	72.3(1)
F-F <sub>min</sub> =	2.855(2)	F <sub>2</sub> -Na-F <sub>2</sub> =	103.1(1)
F-F <sub>max</sub> =	3.683(1)	F <sub>2</sub> -Na-F <sub>6</sub> = 2 ×	79.2(1)
		F <sub>6</sub> -Na-F <sub>6</sub> =	92.8(1)
		F <sub>2</sub> -Na-F <sub>6</sub> = 2 ×	161.2(1)
Cd <sup>2+</sup> polyhedron (symmetry <i>m</i> )			
Cd-F <sub>5</sub> <sup>a</sup> =	2.248(1)		
Cd-F <sub>1</sub> =	2.255(1)		
Cd-F <sub>3</sub> <sup>a</sup> = 2 ×	2.277(1)		
Cd-F <sub>4</sub> = 2 ×	2.299(1)		
Cd-F <sub>6</sub> =	2.307(2)		
(Cd-F) =	2.280		
Al <sup>3+</sup> octahedron (symmetry <i>m</i> )			
Al-F <sub>2</sub> =	1.755(2)	F-Al-F <sub>min</sub> =	87.9(1)
Al-F <sub>1</sub> =	1.794(2)	F-Al-F <sub>max</sub> =	93.2(1)
Al-F <sub>6</sub> =	1.811(2)	F <sub>3</sub> -Al-F <sub>3</sub> =	175.7(1)
Al-F <sub>4</sub> =	1.817(2)	Al-F <sub>3</sub> -Al =	175.7(1)
Al-F <sub>3</sub> = 2 ×	1.822(0)	F-F <sub>min</sub> =	2.469(2)
(Al-F) =	1.8035	F-F <sub>max</sub> =	2.592(3)
F <sub>5</sub> <sup>a</sup> tetrahedron (symmetry <i>m</i> )			
F <sub>5</sub> -Cd =	2.248(1)	Cd-F <sub>5</sub> -Cd = 2 ×	101.5(1)
F <sub>5</sub> -Cd = 2 ×	2.277(1)	Cd-F <sub>5</sub> -Na = 2 ×	108.4(1)
F <sub>5</sub> -Na =	2.319(2)	Cd-F <sub>5</sub> -Cd =	106.1(0)
(F <sub>5</sub> -Na, Cd) =	2.281	Cd-F <sub>5</sub> -Na =	129.0(1)
		Cd-Cd <sub>min</sub> =	3.504(0)
		Cd-Na =	4.122(1)

<sup>a</sup> Independent fluorine F<sub>5</sub> ion.

based on the cationic coordination of the independent fluorine in association with the octahedral network coming from Al<sup>3+</sup> ions.

From Fig. 1 it is clear that NaCdAlF<sub>6</sub> can be described from connected sodium and aluminum octahedra and cadmium polyhedra which build up a three-dimensional network. This network can be broken up into three chains running in the [010] direction for each cationic polyhedra.

The first type of chain with formula [AlF<sub>5</sub>]<sub>*n*</sub><sup>2*n*-</sup> is made by AlF<sub>6</sub> octahedra connected by opposite corners. The AlF<sub>6</sub> octahedra are slightly distorted and the longer

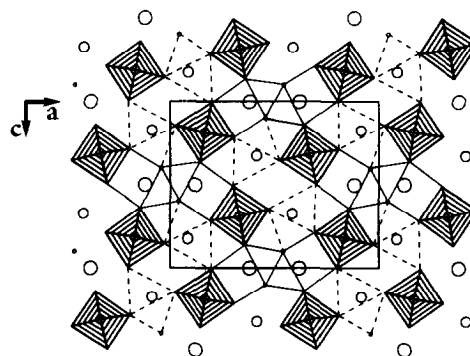


FIG. 1. NaCdAlF<sub>6</sub> structure: (001) projection (Cd, Na, F: large, medium, and small circles, respectively; AlF<sub>6</sub> octahedra: shaded; NaF<sub>6</sub> octahedra: dotted lines; and CdF<sub>7</sub> polyhedra: heavy lines).

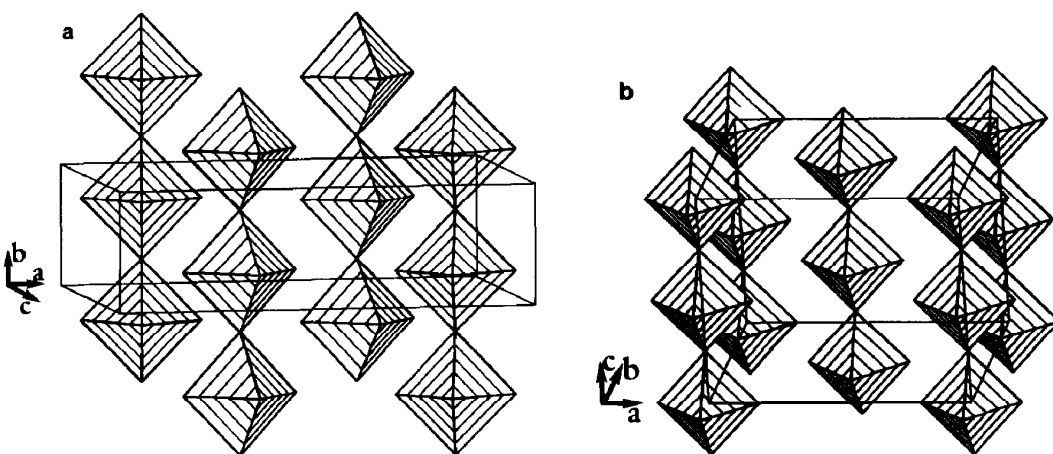


FIG. 2. (a) Perspective view of chains of *trans*-linked  $\text{AlF}_6$  octahedra in  $\text{NaCdAlF}_6$ . (b) Perspective view of  $[\text{AlF}_5]_n^{2n-}$  chains in  $\text{K}_2\text{AlF}_5 \cdot \text{H}_2\text{O}$ .

Al–F distances are related to the shared  $\text{F}_3$  fluorine; the mean Al–F distance (1.804 Å) being very close to the sum of the ionic radii (8) and to the Al–F distances observed in the compounds with *trans* octahedra connection (Table IV). Within these chains, both Al– $\text{F}_3$ –Al and  $\text{F}_3$ –Al– $\text{F}_3$  angles are bent down to  $175.7^\circ$ . In  $\text{NaCdAlF}_6$  along *b*, two consecutive chains are shifted by  $b/2$  (1.8203 Å) and we observe a short *b* axis— $b = 3.6906$  Å—in the direction of the chains. It represents the height of one  $\text{AlF}_6$  octahedron whereas, in the other compounds with *trans*-connected  $[\text{MF}_5]_n^{2n-}$  chains ( $\text{CaCrF}_5$  (12),  $\text{CaFeF}_5$  (13),  $(\text{NH}_4)_2\text{MnF}_5$  (14),  $\text{Li}_2\text{MnF}_5$  (15), and  $\text{K}_2\text{AlF}_5 \cdot \text{H}_2\text{O}$  (9)), the parameter corresponds to two  $\text{AlF}_6$  octahedra (Fig. 2).

TABLE IV

Compounds	$\langle \text{Al-F} \rangle$	Refs.
$\text{NaCdAlF}_6$	1.8035 Å	This work
$\text{K}_2\text{AlF}_5 \cdot \text{H}_2\text{O}$	1.805 Å	(9)
$\text{Rb}_2\text{AlF}_5 \cdot \text{H}_2\text{O}$	1.817 Å	(10)
$\alpha\text{-CaAlF}_5$	1.809 Å	(11)

The second type of infinite chains running in the [010] direction is formed by  $\text{NaF}_6$ -distorted octahedra (Fig. 3) which share opposite edges. Along *b*, two consecutive chains formulated  $[\text{NaF}_2\text{F}_{4/2}]_n^{3n-}$  are also shifted from  $b/2$  (Fig. 4). Such a condensed chain is observed in the  $\text{Na}_2\text{CuF}_4$  compound (16) but without any shift. Nevertheless, for the latter compound it also exists a short axis—3.26 Å—in the chain direction corresponding to a fundamental unit of one  $\text{CuF}_6$  octahedron.

The third type of chain is developed by

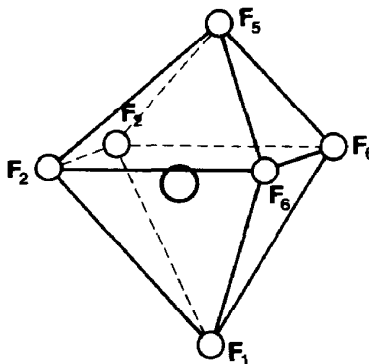


FIG. 3. Na-distorted octahedra.

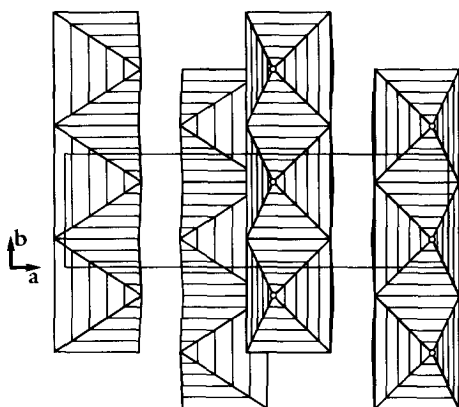


FIG. 4. NaF<sub>6</sub> octahedra: (001) projection (small circles: independent F<sub>5</sub>).

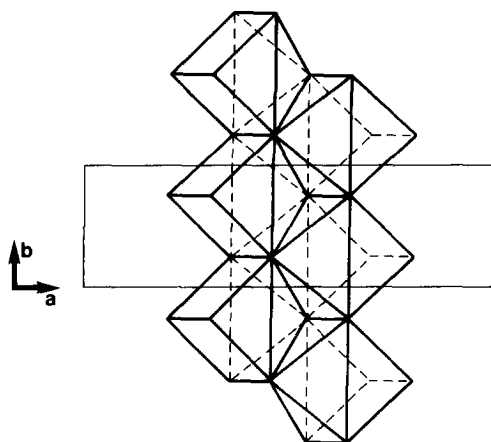


FIG. 6. Double chain of CdF<sub>7</sub> polyhedra: (001) projection.

the particular connection of CdF<sub>7</sub> polyhedra which look like monocapped trigonal prisms (Fig. 5). In this case, two chains of CdF<sub>7</sub> polyhedra, sharing opposite edges and shifted one to the other by  $b/2$ , are connected by two neighboring edges to form a condensed double chain of composition  $[\text{CdF}_2\text{F}_{2/2}\text{F}_{3/3}] = [\text{CdF}_4]_n^{2n+}$  as shown in Fig. 6. A structural correlation can be made with the Ba<sub>2</sub>PdO<sub>3</sub> compound (17) where a three-dimensional network of Ba<sup>2+</sup>-monocapped trigonal prisms exhibits the same type of double chain.

These three types of chains, with all the cations at levels  $y = 1/4$  or  $y = 3/4$ , build up

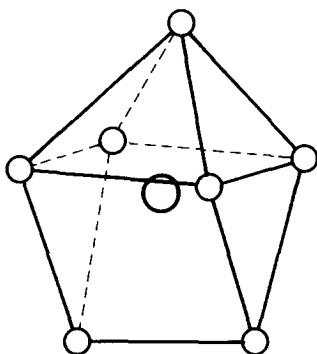


FIG. 5. Cd monocapped trigonal prism.

the three-dimensional network already shown in Fig. 1.

According to the formulation NaCdAlF<sub>6</sub> and the existence of  $[\text{AlF}_5]_n^{2n-}$  chains, there exists an "independent F<sup>-</sup>" ion, labeled F<sub>5</sub>, surrounded by three Cd<sup>2+</sup> and one Na<sup>+</sup> ions with a tetrahedral coordination. These tetrahedra build up chains of formula  $[\text{FNaCd}_{3/3}]_n^{2n+}$  by sharing two Cd–Cd edges and are inserted between  $[\text{AlF}_5]_n^{2n-}$  chains (Fig. 7). In these chains of tetrahedra, Na<sup>+</sup> ions are terminal, as in the Na<sub>2</sub>Ca<sub>3</sub>Al<sub>2</sub>F<sub>14</sub> structure (18) where the  $[\text{FNaCa}_{3/2}]$  tetrahedra are connected only by the Ca vertices. Such  $[\text{FM}_4]$  tetrahedra have been already encountered in the Ca<sub>2</sub>F<sub>2</sub>CO<sub>3</sub> structure (19) but with a more complicated connection mode (corners and/or edges sharing). Finally it can be noticed that the "anti-tetrahedra"  $[\text{MX}_2]_n$  chains belong to class II(c) according to Wells (20) (two shared edges have a common vertex). They have not been encountered in other compounds to our knowledge, whereas the only possible other type of single chain (class I(c), sharing two opposite edges) exists in sulfide compounds like KFeS<sub>2</sub> (21) and in fibrous silica (22).

In conclusion, it seems that NaCdAlF<sub>6</sub>

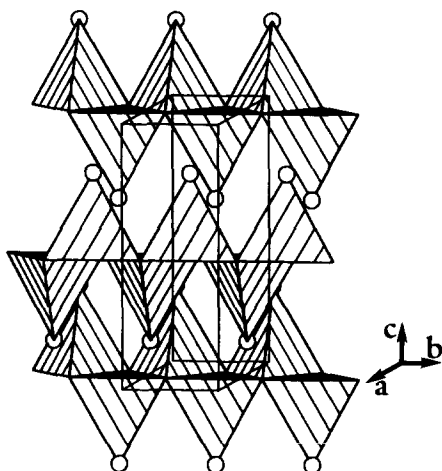


FIG. 7. "Anti-tetrahedra" chains of formula  $[\text{FCdNa}]_n^{2n+}$ : perspective view (circles: terminal sodium atoms).

can be viewed as a new  $[\text{AlF}_5]_n^{2n-}$  monodimensional network in which a  $[\text{FA}_2]_n^{2n+}$  subnetwork has been inserted. This last  $\text{FA}_2$  subnetwork is related to the existence of an independent "F<sup>-</sup>." From this point of view, this structure can be compared to the  $\text{SrPbF}_6$  one (23) in which the octahedra chains  $[\text{PbF}_5]_n^{n-}$ , running in the [001] direction, are separated by infinite linear entities  $[\text{SrF}]_n^{n+}$  (along the [100] and [010] directions) corresponding to an alternance of independent fluorine and strontium atoms.

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### References

1. G. COURBION, C. JACOBONI, AND R. DE PAPE, *Acta Crystallogr. Sect. B* **33**, 1405 (1977).
2. G. COURBION, Thesis, Le Mans (1979).
3. G. COURBION AND M. LEBLANC, *J. Magn. Magn. Mater.* **74**, 158 (1988).
4. A. HEMON AND G. COURBION, *J. Solid State Chem.* **84**, 153 (1990).
5. W. CLEGG, *Acta Crystallogr. Sect. A* **37**, 22 (1981).
6. G. SHELDRIK, "SHELX76: A Program for Crystal Structure Determination," University of Cambridge (1976).
7. "International Tables for X-ray Crystallography," Vol. IV, Kynoch Press, Birmingham (1968).
8. R. D. SHANNON, *Acta Crystallogr. Sect. A* **32**, 751 (1976).
9. J. L. FOURQUET, B. BOULARD, AND F. PLET, *J. Solid State Chem.* **81**, 35 (1989).
10. J. L. FOURQUET, F. PLET, AND R. DE PAPE, *Rev. Chim. Minér.* **18**, 19 (1981).
11. A. HEMON, "DEA Sciences des Matériaux," Le Mans (1988).
12. K. K. WU AND I. D. BROWN, *Mater. Res. Bull.* **8**, 593 (1973).
13. R. VON DER MUHLL AND J. RAVEZ, *Rev. Chim. Minér.* **11**, 652 (1974).
14. D. R. SEARS AND J. L. HOARD, *J. Chem. Phys.* **50**, 1066 (1969).
15. J. PEBLER, W. MASSA, H. LASS AND B. ZIEGLER, *J. Solid State Chem.* **71**, 87 (1987).
16. D. BABEL, *Z. Anorg. Allg. Chem.* **336**, 201 (1965).
17. Y. LALIGANT, A. LE BAIL, G. FERREY, M. HERVIEU, B. RAVEAU, A. WILKINSON AND A. K. CHEETHAM, *Eur. J. Solid State Inorg. Chem.* **25**, 237 (1988).
18. G. COURBION AND G. FERREY, *J. Solid State Chem.* **76**, 426 (1988).
19. U. LEUFER AND E. TILLMANN, *Tschermaks Mineral. Petrogr. Mitt.* **27**, 261 (1980).
20. A. F. WELLS, *Acta Crystallogr. Sect. B* **39**, 39 (1983).
21. W. BRONGER, A. KYAS, AND P. MULLER, *J. Solid State Chem.* **70**, 262 (1987).
22. F. LIEBAU, "Structural Chemistry of Silicates," p. 93, Springer-Verlag, Berlin (1985).
23. R. HOPPE AND K. BLINNE, *Z. Anorg. Allg. Chem.* **293**, 251 (1958).