

## Crystal Structures of NaBaCr<sub>2</sub>F<sub>9</sub> and NaBaFe<sub>2</sub>F<sub>9</sub>: Structural Correlations with Other Ennefluorides, Particularly with KPbCr<sub>2</sub>F<sub>9</sub>

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NaBaCr<sub>2</sub>F<sub>9</sub> and NaBaFe<sub>2</sub>F<sub>9</sub> are monoclinic (SG *P*2<sub>1</sub>/*n*, No. 14). Lattice constants are found to be  $a = 7.318(2) \text{ \AA}$ ,  $b = 17.311(4) \text{ \AA}$ ,  $c = 5.398(1) \text{ \AA}$ ,  $\beta = 91.14^\circ(3)$  for chromium, and  $a = 7.363(2) \text{ \AA}$ ,  $b = 17.527(4) \text{ \AA}$ ,  $c = 5.484(1) \text{ \AA}$ ,  $\beta = 91.50^\circ(5)$  for iron. The structures were solved from 507 and 1113 X-ray reflections, respectively, for the Cr and Fe compounds; the corresponding  $R_w$  values are 0.025 and 0.037. The network is built from tilted double *cis* chains of octahedra  $(M_2F_9)_n^{3n-}$  [ $M = \text{Cr, Fe}$ ], linked by Na<sup>+</sup> and Ba<sup>2+</sup> ions. The structures are compared to the previously described structures, particularly KPbCr<sub>2</sub>F<sub>9</sub>, whose symmetry and parameters are different. The difference is analyzed first in terms of tilted octahedra, but principally in terms of bond strengths and steric activity of the Pb<sup>2+</sup> lone pair. A mechanism is proposed for the transformation between the structures of NaBaCr<sub>2</sub>F<sub>9</sub> and KPbCr<sub>2</sub>F<sub>9</sub>. © 1985 Academic Press, Inc.

### Introduction

During the investigation of the ternary systems BaF<sub>2</sub>–M<sup>II</sup>F<sub>2</sub>–M<sup>III</sup>F<sub>3</sub> ( $M^{\text{II}} = \text{Fe, Co, Ni, Zn}$  and  $M^{\text{III}} = \text{V, Cr, Fe}$ ) we recently found a new structural family of fluorides with formula Ba<sub>2</sub>M<sup>II</sup>M<sup>III</sup>F<sub>9</sub> (1). Its monoclinic structure (2) is built from isolated double *cis* chains of octahedra linked by Ba<sup>2+</sup> cations. The ordering between divalent and trivalent cations leads to ferrimagnetic properties under strong magnetic fields (3). In the compounds that we stud-

ied, the degree of order between the two cationic sites was characterized by Mössbauer spectroscopy (4). It varies between 100% (Fe<sup>2+</sup>–Fe<sup>3+</sup>) and 90% (Fe<sup>2+</sup>–Cr<sup>3+</sup>), depending on the nature of the 3d metallic species; on the contrary, Ba<sub>2</sub>ZnAlF<sub>9</sub>, studied by Fleischer and Hoppe (5), is described in the derived orthorhombic cell with a random distribution of Zn<sup>2+</sup> and Al<sup>3+</sup>; this leads to a wide range of M–F distances (1.842–2.172 Å) in the octahedra.

We further showed that our monoclinic structure can exist with only M<sup>3+</sup> cations in

the octahedra (6), half of the Ba<sup>2+</sup> being replaced by Na<sup>+</sup> or K<sup>+</sup>. This substitution leads to the A<sup>I</sup>BaM<sub>2</sub><sup>III</sup>F<sub>9</sub> composition (A<sup>I</sup> = Na, K and M<sup>III</sup> = V, Fe, Ga, Cr), often associated with antiferromagnetic properties.

The synthesis and structure of a similar material KPbCr<sub>2</sub>F<sub>9</sub> has recently been reported (7); however, its symmetry is orthorhombic with cell parameters very different from those we gave for the A<sup>I</sup>BaM<sub>2</sub><sup>III</sup>F<sub>9</sub> compounds, in spite of the existence of similar double cis chains in both structures. We carried out a crystallographic study of NaBaCr<sub>2</sub>F<sub>9</sub> and NaBaFe<sub>2</sub>F<sub>9</sub> (hereafter noted NB) in order to compare with KPbCr<sub>2</sub>F<sub>9</sub> (hereafter KP) and determine the reasons for their different arrangement.

### Experimental

Green (Cr) and beige (Fe) powder samples were obtained by heating at 700°C for 10 hr a stoichiometric mixture of NaF, BaF<sub>2</sub>, and MF<sub>3</sub> in sealed gold tubes. Single crystals were easily grown using the previously described (6) congruent melting of these compounds (*T*<sub>m</sub> = 990°C for Cr and 725°C for Fe). The liquid was slowly cooled (5°C/hr)

TABLE I  
STRUCTURAL DATA

Symmetry: monoclinic			
Space group: <i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)			
Reflection conditions: <i>h</i> 0 <i>l</i> : <i>h</i> + <i>l</i> = 2 <i>n</i>			
0 <i>k</i> 0: <i>k</i> = 2 <i>n</i>			
		Cr	Fe
Cell parameters:	<i>a</i> (Å)	7.318(2)	7.363(2)
	<i>b</i> (Å)	17.311(4)	17.527(4)
	<i>c</i> (Å)	5.398(1)	5.484(1)
	β (°)	91.14(3)	91.50(5)
Density ( <i>Z</i> = 4):	ρ <sub>exp</sub> (g/cm <sup>3</sup> )	4.20(3)	4.18(3)
	ρ <sub>calc</sub> (g/cm <sup>3</sup> )	4.23	4.16
Absorption: μ(MoKα) (cm <sup>-1</sup> )		89.4	97.4

TABLE II  
DETAILS OF DATA COLLECTION AND REDUCTION

Wavelength: 0.71069 Å (MoKα)			
Monochromator: Graphite			
Maximum θ: 20° (Cr); 25° (Fe)			
Scan mode: ω - 2θ			
<i>hkl</i> limits:	-7 ≤ <i>h</i> ≤ +7	0 ≤ <i>k</i> ≤ 16	0 ≤ <i>l</i> ≤ 5 (Cr)
	-8 ≤ <i>h</i> ≤ +8	0 ≤ <i>k</i> ≤ 20	0 ≤ <i>l</i> ≤ 6 (Fe)
Number of steps/reflection: 100			
Scan speed: 0.66 s/step			
Number of unique reflections: 620 (Cr); 1231 (Fe)			
Significant reflections [ F  > 6σ( F )]: 517 (Cr); 1113 (Fe)			

from 1100 to 800°C (Cr) and from 800 to 500°C (Fe) in sealed platinum tubes. Small crystals with triangular shape (0.1 × 0.1 × 0.1 mm<sup>3</sup>) were selected for the X-ray studies.

Laue and precession photographs are consistent with monoclinic symmetry. The crystallographic data are given in Table I and confirm the similarity with the cell of Ba<sub>2</sub>CoFeF<sub>9</sub>. The diffraction data were collected on an automatic four-circle diffractometer (Philips PW1130); Table II shows the details of the data collection. No absorption corrections were applied.

Both structures were solved in the pseudoorthorhombic nonstandard space group *P*2<sub>1</sub>/*n* (No. 14). All calculations were performed with the program SHELX (8). Beginning with the chromium compound, Ba<sup>2+</sup> and Cr<sup>3+</sup> were localized by using the direct method (option TANG of SHELX) and a Fourier synthesis. Scattering factors for Ba<sup>2+</sup>, Cr<sup>3+</sup>, Na<sup>+</sup>, and F<sup>-</sup> were taken from the International Tables of Crystallography (9). Refinement of Cr<sup>3+</sup> and Ba<sup>2+</sup> coordinates led to an agreement factor *R* = 0.23. Fluorine and isoelectronic Na<sup>+</sup> were then localized indistinctly on a difference Fourier map. The *R* factor dropped to 0.045 after refinement of all atomic coordinates and isotropic thermal parameters; further refinements of anisotropic thermal parameters lead to *R* = 0.024 (*R*<sub>w</sub> = 0.025). Na<sup>+</sup> ions were further distinguished from crystallochemical considerations.

TABLE III

FINAL ATOMIC COORDINATES ( $\times 10^4$ ) AND THERMAL PARAMETERS OF  $\text{NaBaCr}_2\text{F}_9$  (FIRST LINE) AND  $\text{NaBaFe}_2\text{F}_9$  (SECOND LINE)

Atoms	x	y	z	$B_{\text{eq}}$ ( $\text{\AA}^2$ )
Na	3163(6)	420(3)	7449(10)	2.19(25)
	3102(4)	408(2)	7490(5)	1.16(11)
Ba	697(1)	2844(1)	7314(2)	0.96(5)
	679(1)	2851(1)	7260(2)	0.73(4)
$M(1)$	4078(3)	6218(1)	2220(4)	0.68(10)
	4080(2)	6238(1)	2238(2)	0.45(5)
$M(2)$	2725(2)	4200(1)	2672(4)	0.67(10)
	2702(2)	4185(1)	2629(3)	0.51(7)
F(1)	1314(8)	4181(4)	-225(11)	1.22(35)
	1339(5)	4181(2)	-303(7)	1.39(17)
F(2)	42(8)	9229(3)	4188(12)	1.07(32)
	22(5)	9223(2)	4173(7)	0.87(15)
F(3)	2823(8)	3135(4)	2885(13)	1.54(33)
	2843(6)	3115(2)	2928(7)	1.48(16)
F(4)	4352(9)	9179(4)	420(12)	1.54(33)
	4390(5)	9176(2)	470(7)	1.22(16)
F(5)	2721(8)	1645(3)	4837(12)	1.07(32)
	2754(5)	1643(2)	4867(7)	1.07(16)
F(6)	2016(8)	1624(4)	17(12)	1.25(33)
	2040(5)	1640(2)	23(6)	1.09(16)
F(7)	2412(8)	308(3)	2492(13)	1.40(40)
	2376(5)	307(2)	2449(6)	0.84(13)
F(8)	4422(8)	2917(3)	8096(13)	1.36(33)
	4352(5)	2912(2)	8169(8)	1.23(18)
F(9)	4085(8)	4299(3)	5768(12)	1.06(30)
	4063(5)	4303(2)	5796(6)	0.91(15)

Note. Standard deviations are given in parentheses and refer to the last digit.

TABLE IV

BOND DISTANCES ( $\text{\AA}$ ) IN  $\text{NaBaCr}_2\text{F}_9$  AND  $\text{NaBaFe}_2\text{F}_9$

	$M(1)$ octahedron		Cr	Fe
	Cr	Fe		
$M(1)-F_6^c$	1.845	1.872	F2-F5	2.591 2.609
$M(1)-F_5^c$	1.860	1.893	F6-F5	2.644 2.696
$M(1)-F_8^c$	1.868	1.902	F7-F5	2.647 2.703
$M(1)-F_7^b$	1.924	1.962	F6-F7	2.654 2.697
$M(1)-F_9^b$	1.932	1.963	F6-F8	2.669 2.773
$M(1)-F_2^b$	1.955	2.002	F7-F9	2.677 2.669
$\langle M(1)-F \rangle$	1.897	1.932	F5-F8	2.684 2.763
$\langle M(1)-F_c \rangle$	1.857	1.889	F2-F7	2.685 2.758
$\langle M(1)-F_b \rangle$	1.937	1.976	F6-F9	2.711 2.786
			F8-F9	2.714 2.769
			F8-F2	2.729 2.753
			F9-F2	2.788 2.828
			$\langle F-F \rangle$	2.683 2.734

TABLE IV—Continued

	$M(2)$ octahedron		Cr	Fe
	Cr	Fe		
$M(2)-F_3^c$	1.847	1.887	F3-F4	2.588 2.649
$M(2)-F_4^c$	1.853	1.884	F4-F9	2.590 2.626
$M(2)-F_1^c$	1.857	1.874	F1-F7	2.608 2.676
$M(2)-F_7^b$	1.923	1.968	F1-F4	2.649 2.724
$M(2)-F_9^b$	1.935	1.992	F4-F7	2.673 2.720
$M(2)-F_2^b$	1.935	1.972	F1-F3	2.691 2.786
$\langle M(2)-F \rangle$	1.891	1.929	F3-F9	2.696 2.748
$\langle M(2)-F_c \rangle$	1.852	1.882	F7-F9	2.696 2.669
$\langle M(2)-F_b \rangle$	1.931	1.977	F3-F2	2.709 2.770
			F1-F2	2.714 2.736
			F7-F2	2.719 2.720
			F9-F2	2.765 2.807
			$\langle F-F \rangle$	2.675 2.719
Standard deviations: $M-F \leq 0.007 \text{\AA}$ (Cr), $\leq 0.004 \text{\AA}$ (Fe)				
F-F $\leq 0.01 \text{\AA}$ (Cr), $\leq 0.007 \text{\AA}$ (Fe)				
	$\text{Na}^+$ environment		Cr	Fe
	Cr	Fe		
Na-F4	2.241	2.259		
Na-F1	2.491	2.497		
Na-F5	2.565	2.611		
Na-F2	2.565	2.535		
Na-F6	2.651	2.697		
Na-F7	2.728	2.733		
Na-F9	2.733	2.691		
Na-F7	2.796	2.790		
Na-F4	2.807	2.850		
Na-F1	2.828	2.959		
$\langle \text{Na}-F \rangle$	2.640	2.662		
Standard deviations: $\leq 0.01 \text{\AA}$ (Cr), $\leq 0.004 \text{\AA}$ (Fe)				
	$\text{Ba}^{2+}$ environment		Cr	Fe
	Cr	Fe		
Ba-F1	2.702	2.725		
Ba-F3	2.724	2.720		
Ba-F6	2.732	2.779		
Ba-F5	2.737	2.761		
Ba-F4	2.743	2.761		
Ba-F8	2.752	2.739		
Ba-F8	2.775	2.768		
Ba-F5	2.893	2.941		
Ba-F3	2.923	2.931		
Ba-F6	2.085	3.052		
Ba-F3	3.397	3.408		
$\langle \text{Ba}-F \rangle$	2.860	2.871		
Standard deviations: $\leq 0.003 \text{\AA}$ (Cr), $\leq 0.006 \text{\AA}$ (Fe)				

The final positional and isotropic thermal parameters are given in Table III. They were used as starting values for the refinement of isotypic  $\text{NaBaFe}_2\text{F}_9$ . The agreement factor rapidly converges to 0.0320 ( $R_w = 0.0374$ ) for 1123 reflections (anisotropic thermal parameters). Bond distances are given in Table IV. A list of observed and calculated structure factors as well as  $U_{ij}$

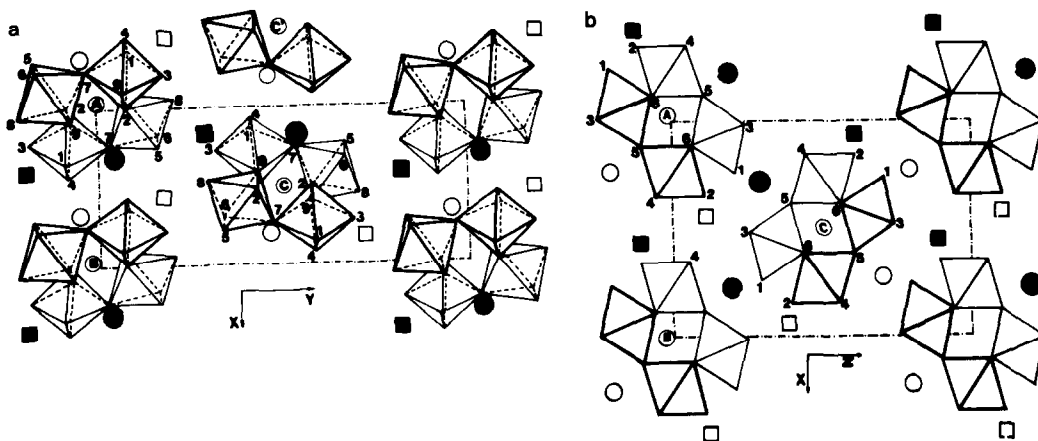


FIG. 1. (a) The (001) projection of the structure of NaBaCr<sub>2</sub>F<sub>9</sub>. (b) The (010) projection of the structure of KPbCr<sub>2</sub>F<sub>9</sub>. Monovalent cations are represented as circles and divalent cations by squares (open and full symbols refer to  $z = \frac{1}{2}$  and  $z = \frac{3}{2}$ , respectively). Letters A, B, C, and C' are used to identify the chains (see text and Tables VI and VII).

values may be obtained from one of the authors (G.F.).

### Description of the Structure and Discussion

A (001) projection of the structure of NaBaCr<sub>2</sub>F<sub>9</sub> is given in Fig. 1. It clearly shows the existence of isolated double *cis* chains of octahedra ( $M_2F_9$ )<sup>3n-</sup> as in Ba<sub>2</sub>CoFeF<sub>9</sub> and KPbCr<sub>2</sub>F<sub>9</sub>. However, compared to the latter structure, NB presents three main differences:

(i) The tilting of the octahedra in the chains.

(ii) The position of the interchain cations.

(iii) The orientation of a chain with respect to neighboring chains.

(i) The tilting of the CrF<sub>6</sub> octahedra in the chains may conveniently be described by comparison with an ideal chain derived from the perovskite structure, for which we define a system of coordinates  $x_{CH}$ ,  $y_{CH}$ ,  $z_{CH}$  (Fig. 2a). The tilting of the octahedra in Ba<sub>2</sub>CoFeF<sub>9</sub> and KP can be described by an alternate rotation of the octahedra around  $z_{CH}$  alone (Fig. 2b); it occurs around the three

axes in NB (Fig. 2c). The increase of the tilting in this structure is probably due to the small radius of Na<sup>+</sup> ions ( $r_{Na^+}^{CN 10} = 1.32$  Å), compared to K<sup>+</sup> ( $r_{K^+}^{CN 9} = 1.55$  Å), and Ba<sup>2+</sup> ( $r_{Ba^{2+}}^{CN 11} = 1.57$  Å) (10). As a consequence, the Cr–F–Cr angles decrease,

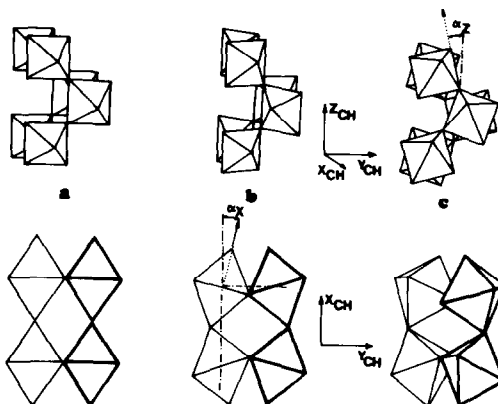


FIG. 2. Description of the tilting mode (TM) of the octahedra in the chains of  $ABM_2F_9$  structures: perspective view (top) and projection in the plane  $x_{ch}$ ,  $y_{ch}$  (bottom). (a) Ideal chain derived from the perovskite. (b) Two-dimensional TM in Ba<sub>2</sub>CoFeF<sub>9</sub> ( $\alpha_x = 19.1^\circ$ ,  $\alpha_y = 21.3^\circ$ ) and in KPbCr<sub>2</sub>F<sub>9</sub> ( $\alpha_x = 13.6^\circ$ ,  $\alpha_y = 15^\circ$ ). (c) Three-dimensional TM in NaBaCr<sub>2</sub>F<sub>9</sub> ( $\alpha_x = 18.9^\circ$ ,  $\alpha_y = 16.5^\circ$ ,  $\alpha_z = 13.6^\circ$ ). (Heavy lines correspond to octahedra at  $z = \frac{1}{2}$ .)

TABLE V  
EVOLUTION OF  $T_N$  AND  $\theta_p$  WITH SUPEREXCHANGE  
ANGLE

Compound	$\widehat{\text{Cr-F-Cr}}$	Ref.	$T_N$ (K)	$\theta_p$ (K)
$\text{NH}_4\text{CrF}_4$	$166^\circ$	(23)	34	-67
$\text{KPbCr}_2\text{F}_9$	$156.8^\circ$	(7)	17	-95
$\text{CaCrF}_5$	$152.2^\circ$	(24, 25)	<4.2	-28
$\text{NaCrF}_4$	$149^\circ$	(26)	8	-64
$\text{NaBaCr}_2\text{F}_9$	$140.8^\circ$	This work	<6	-21
$\text{BaCrF}_5$	$137.4^\circ$	(11)	3.4	-21

which explains (11) the lowering of the Néel temperature of NB with regard to KP;  $T_N$  and Cr-F-Cr angles given in Table V for a few compounds clearly show this trend.

(ii) The major structural difference between KP and NB is, however, the arrangement of the mono- and divalent cations between the chains (Fig. 3). First, their coordination number is different: 9 for  $\text{K}^+$  and  $\text{Pb}^{2+}$  (however,  $\text{K}^+$  has two further  $\text{F}^-$  neighbors at 3.24 Å) but 10 and 11, respectively, for  $\text{Na}^+$  and  $\text{Ba}^{2+}$  (Table IV). Moreover, in KP the biggest cation ( $\text{K}^+$ :  $r = 1.55$  Å) forms two zigzag chains which run along the  $a$  axis at  $y = \frac{1}{4}$  and  $\frac{3}{4}$  (Fig. 3a), respectively, whereas in NB, the largest cation ( $\text{Ba}^{2+}$ :  $r = 1.58$  Å) forms somewhat similar chains (Fig. 3b) but with  $\text{Ba}^{2+}$  alternatively at  $z = \frac{1}{4}$  and  $\frac{3}{4}$  in the same chain.

Most of the differences between KP and NB can be understood from valence bond theory and geometrical arguments. Indeed a characteristic feature of all the structures with  $(M_2F_9)_n^{3n-}$  chains of octahedra is the occurrence of two kinds of anions:

—terminal fluorine ions  $\text{F}_t^-$ , bonded to a single trivalent cation with a short distance  $\text{Cr-F}_t \sim 1.86\text{--}1.89$  Å;

—bridging fluorine ions  $\text{F}_b^-$  shared by two trivalent cations with a slightly longer distance  $\text{Cr-F}_b \sim 1.92\text{--}1.94$  Å.

The bond strength (17, 18) donated by a trivalent ion in sixfold coordination is about  $\frac{3}{8} = 0.5$  valence units (v.u.); then a  $\text{F}^-$  bonded to two  $\text{Cr}^{3+}$  receives about 1 v.u. which, according to the valence sum rule, "saturates" its bonding possibilities. In other words, a  $\text{F}_b^-$  bonded to two trivalent cations can only form very weak bonds (if any) with other cations. A terminal  $\text{F}_t^-$  receives only  $\sim 0.5$  v.u. and must therefore bond to other cations. To make this discussion more quantitative, we made a valence bond analysis of NB and KP; a list of valence bond parameters for fluorine-cation bonds is given in the review by Brown (18), but some of them are not very accurate, and the  $\text{Pb}^{2+}\text{-F}^-$  parameters are not known. To overcome this difficulty we redetermined all these parameters using the most recent structural results available (see Appendix).

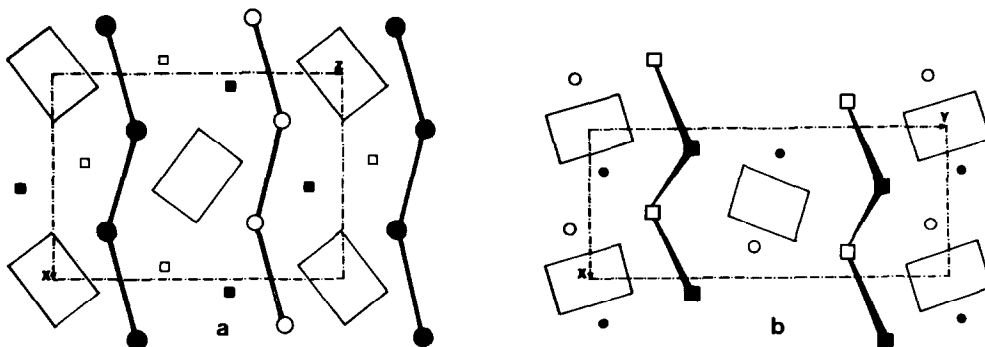


FIG. 3. Arrangement of inserted cations in the lattice of KP (a) and NB (b). The chains are represented by small rectangles and the cations  $A^+$  and  $B^{2+}$  by circles and squares as in Fig. 1.

TABLE VI  
VALENCE BOND ANALYSIS OF NaBaCr<sub>2</sub>F<sub>9</sub>

Anion	Cations							Σ
	Cr1	Cr2	Na bonded to		Ba bonded to			
			Chain A	Chain B	Chain A	Chain C	Chain C'	
F1 t	—	.571	.115	.057	—	.239	—	0.98(2)
F2 b	.439	.463	.099	—	—	—	—	1.00(2)
F3 t	—	.586	—	—	.226	{.136 .041	—	0.99(2)
F4 t	—	.577	.060	.194	—	.215	—	1.05(2)
F5 t	.566	—	.099	—	.147	—	.219	1.03(2)
F6 t	.589	—	.083	—	.222	—	.090	0.98(2)
F7 b	.477	.478	.071/.061	—	—	—	—	1.09(2)
F8 t	.554	—	—	—	.199	.211	—	0.96(2)
F9 b	.467	.463	.070	—	—	—	—	1.00(2)
Σ	3.09(5)	3.14(5)	.66(1)	.25(1)	.79(1)	.84(2)	.31(1)	
Σ Expected	3	3		1		2		1

Note. Parameters used to calculate bond valences are given in Table A-I. The four different chains (A, B, C, and C') are defined in Fig. 1.

The results of the valence bond analysis of NB and KP are presented in Tables VI and VII. Detailed examination of these two tables shows that the valence sum rule is well obeyed in both structures. In addition, one can notice that more than 90% of the total valence of a bridging fluorine comes from Cr<sup>3+</sup>, the rest being provided by one or two Na<sup>+</sup> (NB) or by one K<sup>+</sup> (KP). (In the latter

structure, all the valence of F6 is provided by the two Cr<sup>3+</sup>, and this fluorine is not bonded to any other cation.)

A common feature of these two structures is then that the bridging fluorines are only bonded to the univalent cation A<sup>+</sup> and not to the divalent cation B<sup>2+</sup>, irrespective of the ionic radii of A<sup>+</sup> and B<sup>2+</sup>. However, they differ in the distribution of bond

TABLE VII  
VALENCE BOND ANALYSIS OF KPbCr<sub>2</sub>F<sub>9</sub>

Anions	Cations							Σ
	Cr1	Cr2	K bonded to		Pb bonded to			
			Chain A	Chain C	Chain A	Chain B	Chain C	
F1 t	.527	—	2 × .059	—	.363	—	—	1.01(1)
F2 t	—	.563	.155	—	2 × .130	—	—	0.98(2)
F3 t	2 × .548	—	2 × .061	2 × .091	—	—	2 × .319	1.02(2)
F4 t	—	2 × .532	—	2 × .122	2 × .140	2 × .233	—	1.02(2)
F5 b	.473	.480	—	2 × .025	—	—	—	1.00(1)
F6 b	2 × .486	2 × .493	—	—	—	—	—	0.98(1)
Σ	3.07(5)	3.07(5)	.39(1)	.48(1)	.90(1)	.47(1)	.64(1)	
Σ Expected	3	3		1		2		1

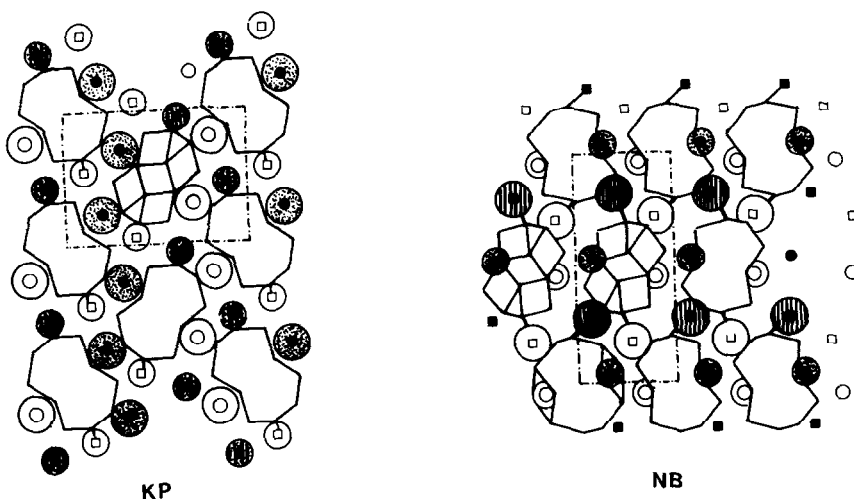


FIG. 4. Comparison of the packing of  $A^+$ ,  $B^{2+}$  and chains in NB and KP.

strength between the univalent cation  $A^+$  and the chains; indeed in both structures  $A^+$  is bonded to two chains and  $B^{2+}$  to three chains, but examination of Tables VI and VII shows that bond strength around  $K^+$  is almost equally distributed between the two nearest chains (noted chain A and chain C) whereas about 73% of the bond strength for  $Na^+$  in NB comes from chain A. This simple calculation shows that  $Na^+$  and  $K^+$  do not play the same role in the cohesion of the two different structures.  $Na^+$  is preferentially attached to one chain and must be considered as belonging to the motif  $(ACr_2F_9)^{2-}$ , while  $K^+$  is equally bonded to two chains and displays the same "cement" behavior as  $Ba^{2+}$  and  $Pb^{2+}$  for the cohesion of the chains. In other words, the formulation of the basic unit differs in NB and KP: it is, respectively,  $(Ba^{2+})[NaCr_2F_9]^{2-}$  and  $(K^+ Pb^{2+})[Cr_2F_9]^{3-}$ ; in this notation the elements inside the parentheses represent the "cement" ions while the chain is inside the brackets. The observed structures will then correspond to the optimum packing of chains and "cement" ions. A comparison of the packing of NB and KP is given in Fig. 4. Moreover, it seems that the cement behavior of the ions between the chains in-

creases with the ionic radius ( $10$ ) of the element.

(iii) A question arises now: is the analysis sufficient to explain the different orientation of a chain with respect to the neighbouring chains in both structures? It must be kept in mind that in KP,  $Pb^{2+}$  ions may have an active lone pair and, consequently, a specific influence on the adopted structure. So we analyzed KP and NB using the formalisms of Andersson ( $12$ ) and Galy ( $13$ ).

According to the Andersson rule ( $12$ ), the volume per formula unit is  $170.9 \text{ \AA}^3$  for NB and  $184.9 \text{ \AA}^3$  for KP. The mean "anionic" volume ( $12$ ) which includes the large cations (here  $Na^+$ ,  $K^+$ ,  $Pb^{2+}$ ,  $Ba^{2+}$ ) as well as anions to the close packing, is  $15.93 \text{ \AA}^3$  for NB (as in  $TiO_2$ ) and  $16.81 \text{ \AA}^3$  for KP. When the lone pair on  $Pb^{2+}$  is taken into account, the last value is lowered to  $15.41 \text{ \AA}^3$ , very close to the result for NB; this indicates some influence of the lone pair of  $Pb^{2+}$ .

In order to determine the exact position of the lone pair, calculations were carried out using the method described by Galy *et al.* ( $13-15$ ). The reexamination of the Pb-F distances in KP shows (Fig. 5) that three of

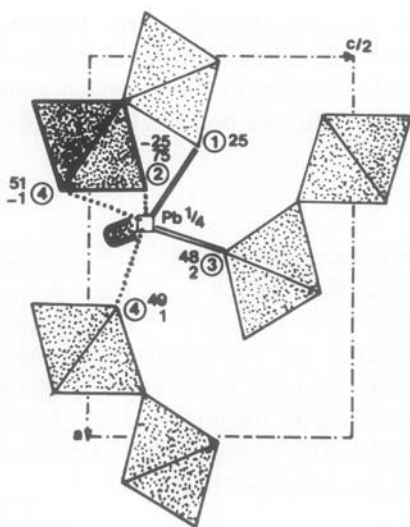


FIG. 5. Environment of Pb<sup>2+</sup> in KP: the three short distances (Pb–F<sub>1</sub> = 2.398 Å, 2 × Pb–F<sub>3</sub> = 2.451 Å) are represented by double lines. The long distances appear as dotted lines. Fluorine ions are identified by a circled number (same numbering as in Ref. (7)) and by the value of their coordinate *y*. The heavy-lined octahedron has its Cr<sup>3+</sup> ion at *y* =  $\frac{1}{2}$ , the others at *y* =  $\frac{1}{4}$ .

them are very short. The tetrahedral model of Galy was then applied. It leads to the lone pair *E* coordinates 0.44,  $\frac{1}{4}$ , 0.10. The Pb–*E* distance of 0.14 Å characterizes a very low activity compared to the values in PbWO<sub>4</sub> (0.55 Å) and yellow PbO (1.26 Å). The doublet points toward the barycenter of the four F<sub>4</sub> atoms and explains the large distance (3.40 Å) between these ions in the (*a*, *c*) plane. The corresponding cavity allows us to place a sphere with a radius of 0.9 Å between the four F<sub>4</sub> ions. The result is to increase the distance separating the chains along *a*, and to induce a rotation of the chains around *b*.

This rotation is the relation between the two structures. The relative disposition of the basic structural units A<sub>2</sub>B<sub>2</sub>Cr<sub>4</sub>F<sub>18</sub>—inside the circle in Fig. 6—is different in KP and NB. If their orientation is defined by the polar angle  $\gamma$  between the OA vector and (–*a*) axis (Fig. 6),  $\gamma$  values of 52° and 16.8° are found, respectively, in the KP and

NB structures. So, if the basic units are considered as independent, a rotation of  $\theta_1 = 35.2^\circ$  for units centered on the corners, and of  $\theta_2 = 144.8^\circ$  for the unit in the middle of the cell would allow to pass from KP to NB. A smaller value of  $\theta_2$  (35.2°) may give the same result if the chains undergo simultaneously a translation of *b*/2. Consequently the *a* parameter decreases from 9.81 to 7.318 Å and the longest parameter increases from 13.93 to 17.31 Å. It must be noted that this rotation also restores the correct disposition of Na<sup>+</sup> and Ba<sup>2+</sup> in NB, starting from K<sup>+</sup> and Pb<sup>2+</sup> positions in KP.

#### Appendix: Determination of Bond-Valence Parameters

Since its introduction by Pauling (16) the electrostatic valence rule has been frequently used in discussing inorganic structures. The usefulness of the concept was later extended when it was found that the bond valence correlates well with bond length. (For a complete description of the

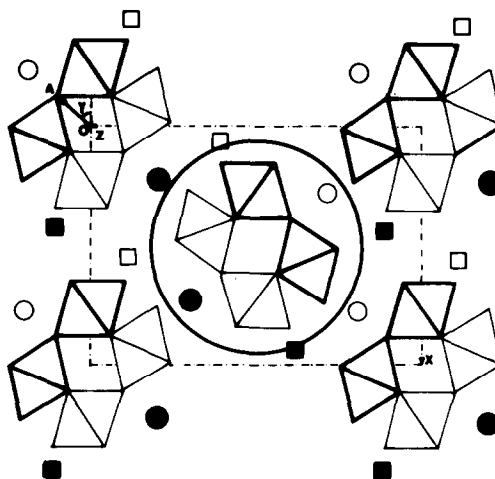


FIG. 6. Transformation from KP structure to NB structure by rotation of the chains. For the sake of comparison, all the atoms of KP have been translated by *b*/2 with respect to the original data and *z* coordinates have been inverted in order to present the chains like in NB structure.



bond–valence method see the review papers by Brown (17, 18).) Several expressions have been proposed for obtaining the correlation between the bond valence ( $s$ ) of a bond and its length ( $d$ ). The most commonly used are the Zachariasen's logarithmic relationship (19)

$$s = \exp\left(\frac{d_0 - d}{B}\right) \quad (1)$$

and the Brown–Shannon inverse power law (20, 21)

$$s = (d/d_0)^{-N}, \quad (2)$$

where  $d_0$  is the length of a bond of unit valence;  $B$  and  $N$  are fitted constants. Both expressions usually give similar results in their range of interest. We have chosen to use the Zachariasen function; however we modified expression (1) to the relation

$$s = \frac{z}{CN_0} \exp\left(\frac{d_0 - d}{B}\right), \quad (3)$$

where  $z$  is the valence (or formal charge) of a cation and  $CN_0$  its usual (or reference) coordination number. With this formal modification  $d_0$  will represent the length of a bond in a regular polyhedron.

The parameters given in Table A-I have been obtained by a statistical procedure

TABLE A-I  
VALENCE BOND PARAMETERS (EQ. A-3)

Bond	$CN_0$	$D_0$ (Å)	$B$ (Å)	$n$	RMSD (%)
Na <sup>+</sup> -F	6	2.313	.483	46	6.8
K <sup>+</sup> -F	6	2.671	.301	53	11.0
Ba <sup>2+</sup> -F	8	2.685	.391	21	4.9
Pb <sup>2+</sup> -F	8	2.568	.455	6	2.8
Cr <sup>3+</sup> -F	6	1.906	(.374)	19	2.2
Fe <sup>3+</sup> -F	6	1.926	(.374)	32	3.6

Note.  $CN_0$  = reference coordination number;  $n$  = number of cation environments used to determine  $D_0$  and  $B$ ; RMSD = root-mean squared relative deviation

$$= \left[ \frac{1}{n} \sum_1^n \frac{(z - \sum s)^2}{z^2} \right]^{1/2}.$$

similar to that described by Brown and Shannon (20). For all cations except Cr<sup>3+</sup> and Fe<sup>3+</sup> the parameters  $d_0$  and  $B$  were refined by fitting the bond valence sums

$$\sum_1^{CN} s_i$$

to the valence  $z$  of the cation. In the case of Cr<sup>3+</sup> and Fe<sup>3+</sup> which exist only in sixfold coordination,  $B$  could not be obtained directly from the least-squares fit since almost any value of  $B$  gives an equally good fit; therefore we fixed the values of  $B(\text{Cr}^{3+}-\text{F})$  and  $B(\text{Fe}^{3+}-\text{F})$  to 0.374 Å, the value obtained for  $B(\text{Fe}^{3+}-\text{O})$  (22).

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### References

1. A. DE KOZAK AND M. SAMOUËL, *Rev. Chim. Miner.* **15**, 406 (1978) and references therein.
2. A. DE KOZAK, M. LEBLANC, M. SAMOUËL, G. FEREY, AND R. DE PAPE, *Rev. Chim. Miner.* **18**, 659 (1981).
3. A. DE KOZAK, M. LEBLANC, M. SAMOUËL, G. FEREY, AND R. DE PAPE, "Proceedings of the 2nd European Meeting of Solid State Chemistry, Veldhoven," p. 607 Elsevier, Amsterdam (1983).
4. P. LIU, F. VARRET, A. DE KOZAK, M. SAMOUËL, M. LEBLANC, AND G. FEREY, *Solid State Commun.* **48**(10), 875 (1983).
5. T. FLEISCHER AND R. HOPPE, *Z. Anorg. Allg. Chem.* **492**, 83 (1982).
6. A. DE KOZAK, M. LEBLANC, M. SAMOUËL, AND G. FEREY, *Rev. Chim. Miner.* **19**, 668 (1982).
7. M. VLASSE, J. P. CHAMINADE, J. M. DANCE, M. SAUX, AND P. HAGENMULLER, *J. Solid State Chem.* **41**, 272 (1982).
8. G. M. SHELDRIK, "SHELX: Program for Crystal Structure Determination," University of Cambridge, U.K. (1976).
9. "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham (1968).
10. R. SHANNON, *Acta Crystallogr. Sect. A* **32**, 751 (1976).
11. H. HOLLER, W. KURTZ, D. BABEL, AND W. KNOP, *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **37**, 54 (1982).

12. S. ANDERSSON AND A. ÅSTROM, "Solid State Chemistry," Proceedings of the 5th Material Research Symposium, NBS Special Publication 364, p. 3 (1972).
13. J. GALY AND S. ANDERSSON, "Solid State Chemistry," Proceedings of the 5th Material Research Symposium, NBS Special Publication 364, p. 29 (1972).
14. J. GALY, G. MEUNIER, S. ANDERSSON, AND A. ÅSTROM, *J. Solid State Chem.* **13**, 142 (1975).
15. J. GALY AND R. ENJALBERT, *J. Solid State Chem.* **44**, 1 (1982).
16. L. PAULING, *J. Amer. Chem. Soc.* **51**, 1010 (1929).
17. I. D. BROWN, *Chem. Soc. Rev.* **7**, 353 (1978).
18. I. D. BROWN, in "Structure and Bonding" (M. O'Keeffe and A. Navrotsky, Eds.), Vol. II, pp. 1-29, Academic Press, New York (1981).
19. W. H. ZACHARIASEN, *J. Less-Common Met.* **62**, 1 (1978).
20. I. D. BROWN AND R. D. SHANNON, *Acta Crystallogr. Sect. A* **29**, 266 (1973).
21. I. D. BROWN AND K. K. WU, *Acta Crystallogr. Sect. B* **32**, 1957 (1976).
22. J. PANNETIER, unpublished results.
23. G. KNOKE, D. BABEL, AND T. HINRICHSEN, *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **34**, 934 (1979).
24. D. DUMORA, R. VON DER MÜHLL, AND J. RAVEZ, *Mater. Res. Bull.* **6**, 561 (1971).
25. K. K. WU AND I. D. BROWN, *Mater. Res. Bull.* **8**, 593 (1973).
26. G. KNOKE, W. VERSCHAEREN, AND D. BABEL, *J. Chem. Res. (S)* 213, (M) 2579 (1979).