JOURNAL OF SOLID STATE CHEMISTRY **98**, 358–365 (1992)

New Pentamers of Octahedra: Structural and Magnetic Characterization of $Na_3Sr_4Cr_5F_{26}$

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Received July 19, 1991; in revised form December 9, 1991

$Na_3Sr_4Cr_5F_{26}$ is monoclinic (S.G.: $C2/c$): a = 19.959(2) Å, b = 7.450(1) Å, c = 29.291(6) Å, β = 111.244(9)°, and Z = 8. The structure was solved from single crystal data using 5180 independent reflections (R = 0.034, R_W = 0.031). Isolated $[M_5F_{26}]^{11-}$ octahedra pentamers are present as in $Na_3Sr_4Al_5F_{26}$, but here the four CrF_6 octahedra form a tetrahedron around the central octahedron, instead of a plane. Magnetic study reveals any magnetic order in the temperature range 300–4.2 K.

Introduction

After the study of fluorinated compounds in the ternary systems AF–MnF_2–MF_3 (A = Li^+ or Na^+, M = first row transition cations) (*1–9*) 10 years in scope to look at the magnetic behavior of crystal structures, now we are searching for new original structures based on anionic octahedra in the ternary systems NaF–MF_2–$M'F_3$ (M = Ca^{2+}, Sr^{2+}; M' = Al^{3+}, Cr^{3+}, Ga^{3+}, Fe^{3+}, V^{3+}, Ti^{3+}). So with the aluminum cation, in the system NaF–CaF_2–AlF_3, we have evidenced two new crystal structures ($Na_2Ca_3Al_2F_{14}$ (*10*) and $Na_4Ca_4Al_7F_{33}$ (*11*)) and a low temperature form of Na_2SiF_6 type: β-$NaCaAlF_6$ (*11*). By substitution of Ca^{2+} for Sr^{2+}, we have synthesized two phases of new structural type: $NaSrAlF_6$ (*12*) and $Na_3Sr_4Al_5F_{26}$ (*13*); for the latter, isolated plane $[Al_5F_{26}]^{11-}$ pentamers are evidenced. The synthesis of these new compounds, with particular octahedra arrangements, interesting from a magnetic point of view, led us to substitute the Al^{3+} cation by magnetic trivalent 3d cations. With the Cr^{3+} ion, we have performed the synthesis of three new compounds: (i) β-$NaSrCrF_6$ (*14*), which presents a distortion with regard to $NaSrAlF_6$ (*12*); (ii) $NaSr_2CrF_8$ (*15*), which exhibits two independent fluorines; and (iii) $Na_3Sr_4Cr_5F_{26}$, of which both structure and magnetic behavior are presented here.

Experimental

Single crystals were grown, in a chloride flux (*2, 16*), by slow cooling (6°C/hr from 775°C) of the mixture NaF + SrF_2 + $2CrF_3$ + 4.5NaCl + $2.75ZnCl_2$ in a platinum crucible under argon atmosphere. Two kinds of green crystals were isolated: $NaCrF_4$ (needle-shaped) and the new compound (plate habit), the formulation of which was deter-

0022-4596/92 $5.00

mined as $Na_3Sr_4Cr_5F_{26}$ after structure resolution.

In the solid state (650°C $< T <$ 760°C, 15hr) a stoichiometric mixture of the elementary fluorides, in sealed gold tubes, does not allow us to prepare the compound in the pure state; the impurity observed is in agreement with the JCPDS card 30-1289 corresponding to $Sr_2Cr_3F_{12}$.

The thermal study of crushed crystals (DTA Netsch 404S) shows an endothermic peak at 705(5)°C and a decomposition peak at 782(5)°C.

Structure Determination

A plate habit crystal, limited by faces ±{100, 010, 001}, was selected for X-ray data collection on a Siemens AED2 four-circle diffractometer. The experimental conditions are listed in Table 1. The cell automatic search led to a monoclinic cell whose lattice parameters—a = 19.959(2) Å, b = 7.450(1) Å, c = 29.291 (6) Å, β = 111.244(9)°—were refined from the positions of 28 reflections in the vicinity of 30° (2θ) centered by the double scan technique. The systematic extinctions (hkl $h + k = 2n$ and $h0l$ $h,l = 2n$) observed are consistent with the centric space group $C2/c$ and with the noncentric one Cc. Corrections for Lorentz and polarization effects were applied. Atomic scattering factors and anomalous dispersion corrections were taken from "International Tables for Crystallography" (*18*). The structure was solved, in the space group $C2/c$, using the direct methods (option TANG) and all refinement calculations were performed using the SHELX-program (*19*). Those provided the position of heavy atoms: Sr atoms in four sites 8f and chromium atoms in four sites of the same type (after refinement, R = 0.38). Then successive differences Fourier synthesis and refinements allowed to complete the structure. The refinement of all atomic coordinates and isotropic thermal parameters led to R = 0.046 and R_W = 0.043, then R = 0.034 and R_W = 0.031 when applying anisotropic thermal motion. The final parameters are listed in Table II and the main interatomic distances and angles are given in Table III. A table specifying the calculated and observed structure factors can be obtained upon request to the authors.

TABLE I

CONDITIONS OF DATA COLLECTION AND CRYSTALLOGRAPHIC CHARACTERISTICS FOR $Na_3Sr_4Cr_5F_{26}$

Symmetry	Monoclinic
Space group	$C2/c$ (No. 15)
Cell parameters	a = 19.959(2) Å
	b = 7.450(1) Å
	c = 29.291(6) Å
	β = 111.244(9)°
	V = 4059.57 Å^3
	Z = 8
Density	d_{cal} = 3.84
Crystal size (10^{-3} mm^3)	1.7
Radiation	Mo$K\alpha$ (graphite monochromatized)
Aperture (mm)	3.5 × 3.5
Scanning mode	$\omega/2\theta$ step scan mode in N steps of $\Delta\omega$°
	$38 \leq N \leq 46$, $0.025 \leq \Delta\omega° \leq 0.030$
	Time per step: 1–4 sec
Profile fitting data analysis (*17*)	Isotropic linewidth, ω = (0.78 + 0.29tgθ)°
Step scan range: θ_{min}, θ_{max} (°)	1.5–35
Range of measurement	$-32 \leq h \leq 32$
	$0 \leq k \leq 12$
	$0 \leq l \leq 47$
Absorption coefficient	μ = 129.09 cm^{-1}
Absorption correction	No
Reflections measured	9498 (one independent set)
independent	7645
used in refinement	5180 ($F_o > 6\,\sigma(F_o)$)
Number of refined parameters	345
Weighting scheme	$w = 2.07/[\sigma^2(F)]$
Secondary extinction factor	6×10^{-9}
Maximum electron density in final Fourier synthesis	0.22e^- · Å^3 (close to Sr_4)

Structure Description

As in the $Na_3Sr_4Al_5F_{26}$ structure (*13*), the most striking feature of the $Na_3Sr_4Cr_5F_{26}$ structure is the existence of isolated pentamers $[Cr_5F_{26}]^{11-}$ built up from five chromium octahedra. However, the arrangement of the four chromium octahedra

TABLE II

ATOMIC PARAMETERS, ANISOTROPIC TEMPERATURE FACTORS $U_{ij} \times 10^4$ AND B_{eq} (Å^2) FOR $Na_3Sr_4Cr_5F_{26}$

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	B_{eq}
Sr_1	8*f*	0.30813(2)	0.0412(1)	0.25372(1)	135(2)	109(2)	121(2)	6(1)	67(1)	−5(2)	0.84(2)
Sr_2	8*f*	0.18742(2)	−0.0408(1)	0.34955(1)	115(2)	113(2)	89(2)	6(1)	24(1)	7(1)	0.79(2)
Sr_3	8*f*	0.17752(2)	−0.0038(1)	0.09344(1)	127(2)	105(2)	95(2)	−6(1)	43(1)	−13(2)	0.78(2)
Sr_4	8*f*	0.32007(2)	−0.0015(1)	0.00634(1)	111(2)	109(2)	84(2)	−1(1)	30(1)	−3(2)	0.74(2)
Cr_1	8*f*	0.36549(3)	0.0376(1)	0.39923(2)	86(3)	95(3)	76(3)	−4(2)	28(2)	−6(2)	0.62(3)
Cr_2	8*f*	0.12635(3)	−0.0023(1)	0.22038(2)	76(3)	94(3)	77(3)	11(2)	22(2)	1(2)	0.61(3)
Cr_3	8*f*	0.37239(3)	−0.0055(1)	0.15738(2)	87(3)	91(3)	78(3)	−9(2)	31(2)	3(2)	0.61(3)
Cr_4	8*f*	0.13385(3)	0.0393(1)	−0.03438(2)	76(3)	96(3)	77(3)	1(2)	23(2)	−1(2)	0.61(3)
Cr_5	8*f*	0.00002(3)	0.2488(1)	0.11290(2)	77(3)	86(3)	76(3)	5(2)	22(2)	7(2)	0.59(3)
Na_1	4*e*	0	0.7469(4)	$\frac{1}{4}$	166(13)	240(15)	225(14)	0	60(11)	0	1.55(13)
Na_2	4*e*	0	0.2519(4)	$\frac{1}{4}$	166(14)	170(15)	590(23)	0	57(15)	0	2.33(16)
Na_3	8*f*	−0.0004(1)	0.2575(4)	0.6260(1)	145(10)	553(16)	139(9)	−18(10)	41(7)	−22(10)	2.12(11)
Na_4	8*f*	0.0005(1)	0.2504(3)	−0.0026(1)	139(8)	197(10)	173(9)	−19(8)	51(7)	−47(8)	1.24(9)
F_1	8*f*	0.1887(2)	0.1687(4)	0.4869(1)	185(14)	115(14)	313(16)	−49(12)	38(12)	−35(11)	1.54(15)
F_2	8*f*	0.4147(1)	0.2273(4)	0.1600(1)	165(13)	123(13)	215(14)	0(11)	96(11)	−12(11)	1,14(14)
F_3	8*f*	0.2990(1)	0.1544(4)	0.4216(1)	130(12)	172(14)	143(12)	9(10)	86(10)	31(10)	1.01(13)
F_4	8*f*	0.0821(1)	0.2314(4)	0.7027(1)	159(12)	137(14)	138(12)	10(10)	32(10)	45(10)	1.08(13)
F_5	8*f*	0.0466(1)	0.1208(4)	0.1739(1)	138(12)	265(16)	141(13)	82(12)	8(10)	52(12)	1.42(14)
F_6	8*f*	0.0806(1)	0.0139(4)	0.2676(1)	125(12)	202(15)	117(11)	20(11)	54(9)	42(11)	1.06(13)
F_7	8*f*	0.1990(1)	0.1556(4)	0.0212(1)	163(12)	165(14)	94(11)	−20(10)	12(10)	−67(11)	1.09(13)
F_8	8*f*	0.3030(1)	0.4039(4)	0.0672(1)	159(13)	198(15)	140(13)	−6(11)	78(10)	−51(11)	1.16(14)
F_9	8*f*	0.0820(1)	0.4870(4)	0.2723(1)	160(13)	174(14)	110(11)	−4(10)	32(10)	−18(11)	1.11(13)
F_{10}	8*f*	0.0695(1)	0.4394(4)	0.1304(1)	160(13)	151(14)	176(13)	−20(11)	97(11)	−65(10)	1.10(14)
F_{11}	8*f*	0.3198(2)	−0.0003(4)	0.0897(1)	252(14)	248(16)	70(11)	3(11)	18(10)	16(13)	1.46(14)
F_{12}	8*f*	0.3032(1)	0.0926(4)	0.3348(1)	151(12)	191(14)	96(11)	28(10)	17(10)	−7(11)	1.12(13)
F_{13}	8*f*	0.1775(2)	0.2137(4)	0.2419(1)	223(14)	164(15)	188(14)	−6(11)	62(11)	−57(12)	1.39(15)
F_{14}	8*f*	0.2945(1)	0.1135(4)	0.1661(1)	98(11)	189(14)	152(12)	14(11)	58(10)	47(10)	1.04(13)
F_{15}	8*f*	−0.0541(1)	0.1302(4)	0.4169(1)	193(14)	191(15)	170(13)	49(11)	81(11)	−38(11)	1.30(14)
F_{16}	8*f*	0.1890(1)	0.3245(4)	0.1080(1)	136(12)	115(13)	226(14)	13(11)	61(11)	23(10)	1.14(14)
F_{17}	8*f*	0.0837(1)	0.2437(4)	0.5914(1)	147(12)	100(12)	193(13)	−26(10)	79(10)	−40(10)	1.01(13)
F_{18}	8*f*	0.1703(2)	0.2740(4)	0.3412(1)	360(18)	143(15)	247(16)	−2(12)	87(14)	117(13)	1.81(17)
F_{19}	8*f*	0.0452(2)	0.3806(4)	0.3490(1)	159(13)	279(17)	199(14)	50(12)	80(11)	−58(12)	1.52(15)
F_{20}	8*f*	0.0538(1)	0.3668(4)	0.4441(1)	202(14)	162(14)	124(12)	−71(10)	28(11)	−54(11)	1.23(14)
F_{21}	8*f*	0.4184(1)	0.0240(4)	−0.0351(1)	165(12)	227(15)	84(11)	−4(11)	12(9)	−12(11)	1.23(13)
F_{22}	8*f*	−0.0694(1)	−0.0597(4)	0.5971(1)	158(13)	192(15)	99(12)	14(10)	−6(10)	67(11)	1.19(13)
F_{23}	8*f*	0.2967(1)	0.3747(3)	0.2315(1)	100(11)	107(12)	119(12)	−23(10)	16(9)	−25(9)	0.83(12)
F_{24}	8*f*	0.1781(2)	0.0243(4)	0.6786(1)	212(13)	222(15)	158(12)	7(11)	117(11)	−2(12)	1.33(14)
F_{25}	8*f*	0.0794(1)	0.0220(4)	0.5045(1)	171(12)	249(16)	142(12)	19(12)	84(10)	61(12)	1.32(14)
F_{26}	8*f*	−0.0836(1)	0.2600(4)	0.5505(1)	152(13)	146(14)	148(12)	9(11)	19(10)	−32(11)	1.14(13)

around the central octahedron by sharing corners build up a tetrahedra, whereas in $Na_3Sr_4Al_5F_{26}$ the same entity forms a plane (Fig. 1). From Fig. 2, it is clear that all the sodium atoms and the pentamers build up together (*b*,*c*)-planes ($x \approx 0$ and $x \approx \frac{1}{2}$) which are connected by strontium atoms. In a (*b*,*c*)-plane two pentamers, with the same *y* level for the central chromium atom, are connected through a Na_2 polyhedron in eightfold coordination (Fig. 3). Along the *b*-axis, Na_1 polyhedron (slightly distorted cube) share four edges with four Cr octahedra of four pentamers, whereas Na_3 polyhedron (very distorted octahedra; 65.6° < F–Na–F < 113.9°) establishes the connection between two pentamers via edges

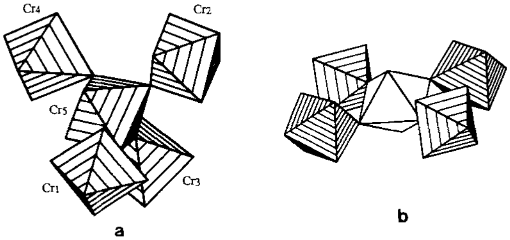

FIG. 1. $[M_5F_{26}]^{11-}$ pentamer in (a) $Na_3Sr_4Cr_5F_{26}$ and (b) $Na_3Sr_4Al_5F_{26}$.

TABLE III

MAIN INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN $Na_3Sr_4Cr_5F_{26}$

Sr_1^{2+} Polyhedron [*9*]

Sr_1	F_{12}	F_{13}	F_{14}	F_{23}	F_{23}	F_9	F_4	F_{24}	F_{13}
F_{12}	**2.444(2)**	3.713(3)	4.883(5)	3.648(3)	2.753(4)	4.575(2)	3.162(3)	4.434(3)	3.093(4)
F_{13}	98.6(2)	**2.454(2)**	3.918(3)	4.983(4)	2.777(3)	3.132(3)	4.522(3)	3.561(3)	4.634(4)
F_{14}	157.3(2)	103.4(2)	**2.537(2)**	2.720(5)	4.406(1)	2.645(4)	3.912(2)	2.682(3)	3.831(2)
F_{23}	93.6(2)	167.7(2)	64.5(3)	**2.558(2)**	4.471(3)	3.796(3)	2.609(4)	3.767(3)	2.777(3)
F_{23}	66.1(2)	66.6(2)	118.1(1)	120.2(1)	**2.600(2)**	4.920(3)	5.006(4)	2.607(5)	2.638(5)
F_9	130.2(1)	76.5(2)	62.0(2)	94.8(2)	142.2(1)	**2.600(3)**	2.925(5)	4.473(3)	5.244(4)
F_4	75.7(2)	122.7(2)	96.7(2)	59.5(2)	141.8(1)	67.0(2)	**2.697(2)**	5.264(2)	4.492(3)
F_{24}	116.3(2)	85.7(2)	60.5(2)	89.9(2)	58.0(2)	112.7(1)	148.5(1)	**2.772(2)**	2.569(6)
F_{13}	71.7(2)	123.1(2)	91.3(2)	62.1(2)	58.2(2)	151.3(2)	109.2(2)	54.8(3)	**2.813(3)**

$\langle Sr_1{-}F\rangle = 2.608$ $d_{\text{Shannon}} = 2.615$ (Ref. (*20*))

Sr_2^{2+} Polyhedron [*9*]

Sr_2	F_{18}	F_8	F_{16}	F_{23}	F_6	F_2	F_{14}	F_{12}	F_3
F_{18}	**2.370(3)**	3.748(3)	4.277(3)	3.851(2)	2.968(4)	4.408(5)	4.987(5)	3.042(4)	2.926(4)
F_8	103.2(2)	**2.411(2)**	2.989(2)	4.865(4)	4.619(3)	3.114(4)	3.670(3)	4.372(1)	2.867(3)
F_{16}	121.4(2)	74.3(2)	**2.533(2)**	3.496(3)	4.927(2)	4.263(3)	2.685(4)	2.575(6)	2.646(5)
F_{23}	101.9(2)	153.7(2)	86.2(2)	**2.585(3)**	2.650(3)	3.837(2)	2.720(5)	2.753(4)	4.681(2)
F_6	73.1(2)	134.3(2)	147.4(1)	61.5(2)	**2.601(2)**	2.988(5)	3.922(3)	4.197(3)	5.119(3)
F_2	124.5(2)	76.6(2)	112.0(2)	95.2(1)	70.0(2)	**2.609(2)**	2.613(3)	5.179(4)	5.162(2)
F_{14}	164.3(2)	92.5(2)	62.2(2)	62.4(3)	96.3(2)	59.4(2)	**2.664(3)**	4.062(4)	4.781(2)
F_{12}	73.6(2)	117.9(1)	59.0(3)	62.9(2)	105.0(1)	155.6(2)	98.7(2)	**2.690(2)**	2.615(5)
F_3	67.5(2)	65.4(2)	58.5(3)	118.8(1)	139.7(1)	142.0(1)	120.2(1)	56.2(2)	**2.851(3)**

$\langle Sr_2{-}F\rangle = 2.590$

Sr_3^{2+} Polyhedron [*9*]

Sr_3	F_{16}	F_{24}	F_{15}	F_{17}	F_7	F_{25}	F_3	F_{14}	F_{11}
F_{16}	**2.479(3)**	3.376(4)	2.907(4)	4.672(4)	2.909(4)	3.979(2)	5.088(4)	2.685(4)	3.737(3)
F_{24}	85.5(2)	**2.494(3)**	3.202(4)	3.042(4)	4.962(3)	4.754(4)	3.940(3)	2.682(3)	4.486(2)
F_{15}	70.2(2)	78.4(2)	**2.572(3)**	2.840(4)	3.935(2)	2.773(4)	4.634(4)	4.527(3)	5.324(4)
F_{17}	135.3(2)	73.8(2)	67.0(2)	**2.573(2)**	4.669(1)	3.010(5)	2.617(3)	4.784(2)	5.065(4)
F_7	69.9(2)	154.4(2)	99.2(1)	129.2(1)	**2.595(2)**	2.615(4)	4.087(3)	3.988(3)	2.773(4)
F_{25}	102.1(1)	135.9(2)	64.3(2)	70.6(2)	60.0(2)	**2.636(2)**	3.546(3)	5.209(3)	4.538(3)
F_3	164.6(2)	99.8(2)	124.9(2)	60.0(2)	102.2(1)	84.2(2)	**2.655(3)**	4.279(2)	3.432(4)
F_{14}	62.7(2)	62.4(2)	119.3(1)	131.6(1)	98.4(1)	157.8(2)	106.9(1)	**2.673(3)**	2.608(4)
F_{11}	88.1(2)	113.0(2)	155.1(2)	136.4(2)	60.6(2)	110.6(2)	76.5(2)	55.9(2)	**2.880(3)**

$\langle Sr_3{-}F\rangle = 2.617$

Sr_4^{2+} Polyhedron [*10*]

Sr_4	F_{11}	F_1	F_{20}	F_{26}	F_3	F_{21}	F_7	F_8	F_1	F_7
F_{11}	**2.445(3)**	3.298(4)	3.185(3)	3.138(3)	4.925(4)	4.743(3)	4.050(3)	4.415(3)	3.432(3)	2.773(4)
F_1	84.2(2)	**2.476(3)**	2.925(4)	4.696(4)	2.914(5)	3.969(2)	5.122(4)	4.121(3)	2.585(4)	4.316(4)
F_{20}	78.2(2)	70.3(2)	**2.600(2)**	2.835(4)	3.969(3)	2.778(5)	4.627(2)	5.260(3)	4.800(3)	5.136(4)
F_{26}	76.7(2)	134.9(2)	66.0(2)	**2.609(3)**	4.687(1)	2.993(5)	2.610(4)	4.613(2)	5.221(3)	4.155(3)
F_3	152.8(2)	69.7(3)	98.9(1)	127.3(1)	**2.622(4)**	2.619(4)	4.071(3)	2.867(3)	3.401(2)	4.694(1)
F_{21}	136.4(2)	101.1(1)	63.7(2)	69.2(2)	59.4(2)	**2.662(3)**	3.470(3)	4.206(3)	5.063(3)	5.299(2)
F_7	104.2(2)	165.8(2)	122.2(1)	59.1(3)	100.2(2)	80.9(2)	**2.685(2)**	2.743(4)	4.481(4)	3.081(3)
F_8	117.6(2)	105.0(2)	163.5(1)	120.1(1)	65.0(2)	102.9(1)	61.1(2)	**2.715(2)**	2.573(6)	2.612(5)
F_1	82.1(2)	58.7(2)	126.7(2)	152.2(2)	78.2(2)	137.5(1)	110.5(2)	56.0(3)	**2.769(3)**	2.596(5)
F_7	62.5(2)	107.8(2)	140.5(1)	98.9(2)	117.9(1)	147.6(1)	67.5(2)	55.8(2)	54.9(3)	**2.857(3)**

$\langle Sr_4{-}F\rangle = 2.644$ $d_{\text{Shannon}} = 2.666$

Cr_1^{3+} Octahedron

Cr_1	F_{21}	F_{17}	F_{12}	F_{16}	F_3	F_{10}
F_{21}	**1.884(2)**	2.651(3)	3.769(3)	2.665(3)	2.619(3)	2.900(3)
F_{17}	89.4(2)	**1.886(3)**	2.778(2)	3.775(4)	2.617(3)	2.683(3)
F_{12}	173.6(2)	94.7(2)	**1.890(2)**	2.575(4)	2.615(3)	2.631(3)
F_{16}	89.8(2)	176.3(3)	85.8(3)	**1.892(3)**	2.646(3)	2.825(3)
F_3	87.8(2)	87.7(2)	87.5(2)	88.7(2)	**1.892(3)**	3.831(2)
F_{10}	98.4(2)	88.8(2)	86.6(2)	94.8(2)	172.8(1)	**1.946(4)**

$\langle Cr_1{-}F\rangle = 1.898$ $d_{\text{Shannon}} = 1.915$

TABLE III—*Continued*

Cr_2^{3+} Octahedron

Cr_2	F_{24}	F_{13}	F_{23}	F_4	F_5	F_6
F_{24}	**1.874(3)**	2.569(4)	2.607(4)	2.745(3)	2.795(4)	3.787(3)
F_{13}	86.1(2)	**1.888(2)**	2.638(3)	3.789(4)	2.739(3)	2.754(3)
F_{23}	87.4(2)	88.3(2)	**1.901(4)**	2.609(3)	3.813(2)	2.650(3)
F_4	93.2(2)	174.8(2)	86.6(2)	**1.905(2)**	2.769(3)	2.644(4)
F_5	95.1(2)	92.2(2)	177.5(1)	93.0(2)	**1.913(4)**	2.699(3)
F_6	175.2(2)	92.7(2)	87.9(2)	87.5(2)	89.6(2)	**1.917(3)**

$\langle Cr_2\text{–}F\rangle = 1.900$

Cr_3^{3+} Octahedron

Cr_3	F_{18}	F_{11}	F_{14}	F_2	F_{19}	F_9
F_{18}	**1.858(3)**	2.583(4)	2.654(4)	3.773(6)	2.707(4)	2.667(3)
F_{11}	87.5(3)	**1.877(2)**	2.608(3)	2.806(3)	2.787(3)	3.800(5)
F_{14}	90.3(3)	87.7(2)	**1.887(2)**	2.613(3)	3.805(4)	2.645(3)
F_2	175.8(4)	95.3(2)	86.7(2)	**1.918(2)**	2.744(4)	2.655(4)
F_{19}	91.5(3)	94.5(2)	177.2(3)	91.3(3)	**1.919(3)**	2.722(3)
F_9	89.6(3)	174.6(3)	87.8(2)	87.3(3)	90.1(2)	**1.927(2)**

$\langle Cr_3\text{–}F\rangle = 1.898$

Cr_4^{3+} Octahedron

Cr_4	F_1	F_7	F_8	F_{25}	F_{26}	F_{22}
F_1	**1.869(2)**	2.596(4)	2.573(4)	2.651(3)	3.760(4)	2.853(3)
F_7	87.5(3)	**1.885(2)**	2.612(4)	2.615(3)	2.610(3)	3.842(2)
F_8	86.4(2)	87.6(2)	**1.889(3)**	3.775(2)	2.766(3)	2.642(3)
F_{25}	89.6(2)	87.6(2)	173.9(1)	**1.891(3)**	2.667(4)	2.920(3)
F_{26}	174.8(3)	87.3(2)	93.9(2)	89.6(2)	**1.895(2)**	2.707(4)
F_{22}	96.1(2)	172.9(1)	86.6(2)	98.5(2)	89.1(2)	**1.964(2)**

$\langle Cr_4\text{–}F\rangle = 1.899$

Cr_5^{3+} Octahedron

Cr_5	F_{15}	F_{20}	F_{22}	F_{10}	F_{19}	F_5
F_{15}	**1.842(3)**	2.672(3)	2.693(3)	2.649(4)	3.772(1)	2.718(4)
F_{20}	92.8(2)	**1.848(2)**	2.657(3)	2.687(3)	2.730(4)	3.781(2)
F_{22}	91.7(2)	89.9(2)	**1.912(2)**	3.832(4)	2.809(3)	2.618(3)
F_{10}	89.5(2)	91.0(2)	178.5(3)	**1.920(2)**	2.608(3)	2.808(3)
F_{19}	172.6(1)	92.3(2)	93.7(2)	85.1(2)	**1.938(3)**	2.581(4)
F_5	91.9(2)	173.7(1)	85.7(2)	93.4(2)	83.5(3)	**1.939(2)**

$\langle Cr_5\text{–}F\rangle = 1.900$

Na_1^+ Polyhedron [*8*]

Na_1	F_9	F_9	F_6	F_6	F_4	F_4	F_2	F_2
F_9	**2.466(3)**	3.054(3)	3.927(4)	4.956(4)	4.172(3)	2.925(5)	2.655(5)	4.150(2)
F_9	76.5(3)	**2.466(3)**	4.956(4)	3.927(4)	2.925(5)	4.172(3)	4.150(2)	2.655(5)
F_6	104.8(2)	176.8(2)	**2.492(3)**	3.003(3)	4.085(3)	2.644(5)	2.988(5)	4.231(2)
F_6	176.8(2)	104.8(2)	74.1(2)	**2.492(3)**	2.644(5)	4.085(3)	4.231(2)	2.988(5)
F_4	114.1(2)	72.1(2)	109.7(2)	63.9(3)	**2.505(3)**	4.999(3)	3.129(3)	4.011(4)
F_4	72.1(2)	114.1(2)	63.9(3)	109.7(2)	172.6(1)	**2.505(3)**	4.011(4)	3.129(3)
F_2	63.5(3)	110.9(2)	72.3(3)	113.3(2)	76.1(2)	104.4(2)	**2.573(2)**	5.137(5)
F_2	110.9(2)	63.5(3)	113.3(2)	72.3(3)	104.4(2)	76.1(2)	173.5(3)	**2.573(2)**

$\langle Na_1\text{–}F\rangle = 2.509$ $d_{\text{Shannon}} = 2.49$

Na_2^+ Polyhedron [*8*]

Na_2	F_6	F_6	F_9	F_9	F_{19}	F_{19}	F_5	F_5
F_6	**2.323(3)**	3.003(3)	3.527(4)	4.645(4)	3.856(3)	4.384(2)	3.631(2)	2.699(5)
F_6	80.5(3)	**2.323(4)**	4.645(4)	3.527(4)	4.384(2)	3.856(3)	2.699(5)	3.631(2)
F_9	98.7(2)	176.7(2)	**2.324(5)**	3.054(3)	2.722(4)	3.628(3)	4.411(2)	3.845(3)
F_9	176.7(2)	98.7(2)	82.2(3)	**2.324(3)**	3.628(3)	2.722(4)	3.845(3)	4.411(2)
F_{19}	95.3(2)	114.7(2)	62.1(3)	87.9(2)	**2.871(7)**	5.413(5)	2.581(5)	5.492(3)
F_{19}	114.7(2)	95.3(2)	87.9(2)	62.1(3)	141.0(2)	**2.871(3)**	5.492(3)	2.581(5)

TABLE III—*Continued*

F_5	87.8(2)	61.4(3)	115.5(1)	94.6(2)	53.3(3)	145.4(1)	**2.880(3)**	5.420(3)
F_5	61.4(3)	87.8(2)	94.6(2)	115.5(1)	145.4(1)	53.3(3)	140.4(1)	**2.880(6)**

$\langle Na_2–F\rangle = 2.600$

Na_3^+ Polyhedron [*6*]

Na_3	F_{26}	F_{17}	F_2	F_4	F_{10}	F_{22}
F_{26}	**2.234(4)**	3.115(3)	3.219(4)	4.491(4)	3.827(2)	2.707(5)
F_{17}	87.9(2)	**2.257(4)**	4.514(2)	3.275(3)	2.683(5)	3.853(3)
F_2	91.6(2)	179.4(2)	**2.257(4)**	3.129(3)	4.103(3)	3.171(4)
F_4	175.5(3)	92.9(2)	87.7(2)	**2.261(4)**	3.191(4)	4.079(2)
F_{10}	103.4(2)	66.0(3)	113.9(2)	81.0(2)	**2.633(4)**	5.294(4)
F_{22}	65.6(3)	101.3(2)	78.7(2)	109.9(2)	164.3(2)	**2.712(3)**

$\langle Na_4–F\rangle = 2.392$ $d_{\text{Shannon}} = 2.32$

Na_4^+ Polyhedron [*8*]

Na_4	F_{21}	F_{25}	F_{20}	F_{15}	F_{25}	F_{26}	F_{17}	F_{21}
F_{21}	**2.318(2)**	4.519(4)	3.087(3)	3.077(4)	3.814(3)	2.993(4)	4.331(2)	3.182(3)
F_{25}	154.1(2)	**2.319(4)**	3.055(4)	3.062(3)	3.104(4)	4.329(2)	3.010(4)	3.843(3)
F_{20}	79.8(2)	78.8(2)	**2.490(3)**	2.672(4)	4.543(2)	4.906(2)	4.236(3)	2.778(5)
F_{15}	79.1(3)	78.6(2)	64.6(3)	**2.509(6)**	2.773(4)	4.274(3)	4.920(4)	4.598(1)
F_{25}	103.6(2)	79.4(2)	129.5(2)	66.7(3)	**2.533(4)**	2.667(5)	3.973(2)	5.053(4)
F_{26}	76.0(2)	126.2(2)	155.1(1)	115.9(1)	63.5(3)	**2.534(4)**	3.115(3)	4.004(3)
F_{17}	126.3(2)	76.5(2)	114.9(2)	154.6(2)	103.3(2)	75.8(2)	**2.535(4)**	2.651(5)
F_{21}	81.0(2)	103.4(2)	66.5(3)	129.6(1)	163.6(2)	103.3(2)	62.5(3)	**2.572(5)**

$\langle Na_4–F\rangle = 2.476$

Interatomic angles and distances in the pentamers

$Cr_5–F_{10}–Cr_1 = 133.8(1)$
$Cr_5–F_5–Cr_2 = 152.8(1)$
$Cr_5–F_{19}–Cr_3 = 151.0(1)$
$Cr_5–F_{22}–Cr_4 = 132.5(1)$

$Cr_5–Cr_1 = 3.557(1)$
$Cr_5–Cr_2 = 3.744(1)$
$Cr_5–Cr_3 = 3.734(1)$
$Cr_5–Cr_4 = 3.547(1)$

$Cr_1–Cr_2 = 4.946(1)$
$Cr_1–Cr_3 = 6.042(1)$
$Cr_1–Cr_4 = 5.904(1)$
$Cr_2–Cr_3 = 6.002(1)$
$Cr_2–Cr_4 = 6.019(1)$
$Cr_3–Cr_4 = 4.973(1)$

Main Cr–Cr distances between pentamers

$Cr_1–Cr_2 = 5.375(1)$
$Cr_1–Cr_4 = 5.423(1)$
$Cr_1–Cr_4 = 5.441(1)$
$Cr_1–Cr_3 = 5.584(1)$
$Cr_1–Cr_4 = 5.657(1)$
$Cr_1–Cr_2 = 5.674(1)$
$Cr_1–Cr_3 = 5.996(1)$
$Cr_1–Cr_5 = 6.008(1)$

$Cr_2–Cr_3 = 5.143(1)$
$Cr_2–Cr_3 = 5.178(1)$
$Cr_2–Cr_3 = 5.839(1)$
$Cr_2–Cr_2 = 5.899(1)$
$Cr_2–Cr_2 = 5.920(1)$
$Cr_2–Cr_3 = 6.031(1)$
$Cr_3–Cr_4 = 5.337(1)$
$Cr_3–Cr_4 = 5.912(1)$

(Fig. 3). The Na_1, Na_2, Na_3, and Na_4 polyhedra build up a 2*d* network ($x \approx 0$ and $x \approx \frac{1}{2}$) of $[Na_3F_{14}]^{11-}$ formulation (Fig. 4). Therefore, octahedra pentamers can be seen as inserted inside this bidimensional network.

In spite of observed structural differences between $Na_3Sr_4Al_5F_{26}$ and $Na_3Sr_4Cr_5F_{26}$, at the level of pentamers geometry and at the level of connection modes between polyhedra and octahedra, two common points can be brought out: the cell relations—$a_{Cr} \cos(\beta-\pi/2) \approx c_{Al}$; $b_{Cr} \approx \sqrt{2}/2\ a_{Al}$; $c_{Cr} \approx 2\sqrt{2}\ a_{Al}$ ($V_{(Z=1)Cr} = 507$ Å^3; $V_{(Z=1)Al} = 484$ Å^3)—and the same geometry of some polyhedra of sodium and strontium (Na_1, Na_2: C.N. = 8 and Sr_1, Sr_2, Sr_3: C.N. = 9 (monocapped cube)).

Magnetic Behavior

The magnetic susceptibility of powdered sample was measured using a Faraday-type

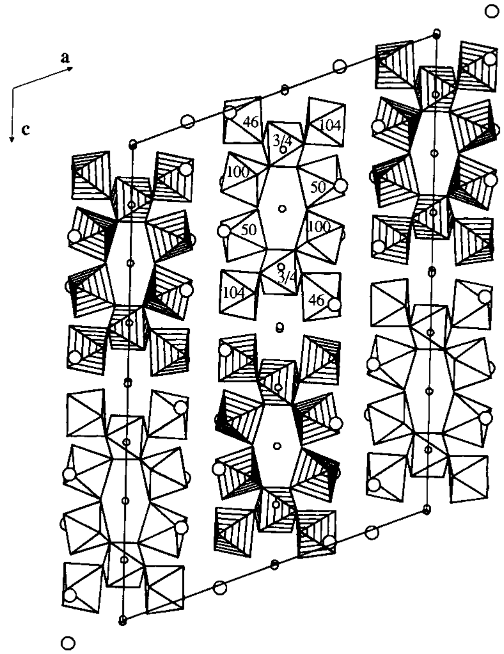

FIG. 2. [010] projection of $Na_3Sr_4Cr_5F_{26}$. Shaded and unshaded pentamers are located at $y \approx \frac{1}{4}$ and $y \approx \frac{3}{4}$, respectively (y atomic coordinate of Cr_5, see Table II). Na and Sr ions are represented by small and large circles, respectively. Numbers indicate the y coordinate of chromium ions.

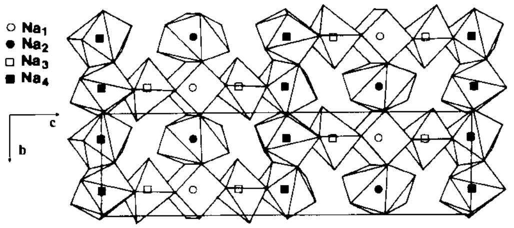

FIG. 4. (100) view of the bidimensional network of sodium polyhedra ($-0.10 < x < 0.10$).

balance in the range 4.2–300 K. The thermal variation of the inverse susceptibility (Fig. 5) follows a Curie–Weiss law with $\theta_P = -8 \pm 3$ K and $C_{\text{Mexp}} = 9.26(5)$ ($C_{\text{Mtheo}} = 9.375$). So, down to 4.2 K, no 3D magnetic order is observed in the $Na_3Sr_4Cr_5F_{26}$ compound. Nevertheless, the negative value of θ_P characterizes predominant antiferromagnetic interactions.

From Table III, it can be seen that the first nearest chromium neighbors are observed within the pentamers ($d_{\text{Cr-Cr}} \approx 3.6$ Å), whereas the second nearest neighbors are found both within and between the pentamers (4.55 Å $< d_{\text{Cr-Cr}} <$ 6 Å). Considering only the nearest neighbors magnetic interactions, a possible explanation of the paramagnetic like behavior is to consider a cluster model with a spin $S' = \frac{3}{2}$ (Fig. 6). This

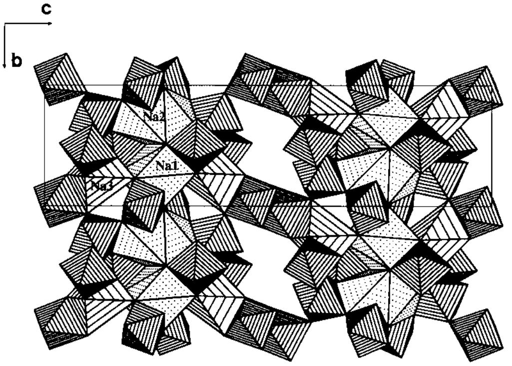

FIG. 3. (100) projection of $Na_3Sr_4Cr_5F_{26}$ ($-0.25 < x < 0.25$). View of the connection mode between pentamers and $Na_{1,2,3}$ polyhedra.

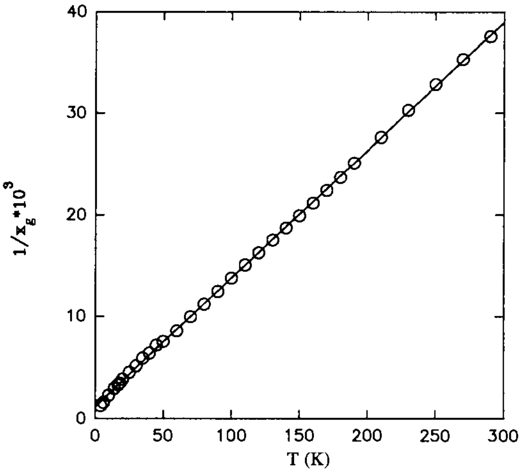

FIG. 5. Thermal evolution of the inverse magnetic susceptibility of $Na_3Sr_4Cr_5F_{26}$.

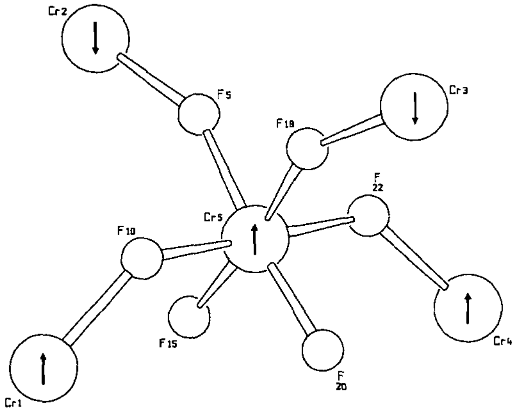

FIG. 6. Possible magnetic cluster with $S' = \frac{3}{2}$.

implies two antiferromagnetic interactions for superexchange angles > 150° (Cr_2–F_5–Cr_5 and Cr_3–F_{19}–Cr_5) and two ferromagnetic interactions for angles close to 133° (Cr_1–F_{10}–Cr_5 and Cr_4–F_{22}–Cr_5). Such a model is in agreement with the Kanamori–Goodenough's rules (*21, 22*) which state that the d^3–d^3 superexchange mechanism is antiferromagnetic when angles are in the range 150°–180° and ferromagnetic when the angles are between 125° and 90°.

In order to confirm the previous explanation, theoritical calculations are projected and attempts to prepare an isotypic compound with Fe^{3+} ion are in progress.

Acknowledgement

The authors are very indebted to Professor M. Leblanc (Université du Maine) for help in X-ray data collection.

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