

Contribution from the Departments of Chemistry, Brooklyn Polytechnic Institute of New York, Brooklyn, New York 11201, The Chung Cheng Institute of Technology, Taiwan, Republic of China, and The University of Mississippi, University, Mississippi 38677, and Airtron Inc., Morris Plains, New Jersey 07950

## Ferromagnetic Behavior in $\text{KMnCrF}_6$

E. BANKS,<sup>1a</sup> M. SHONE,<sup>1b</sup> Y. S. HONG,<sup>1c</sup> R. F. WILLIAMSON,<sup>1d</sup> and W. O. J. BOO\*<sup>1d</sup>

Received September 24, 1981

The tetragonal tungsten bronze-like system  $\text{K}_x\text{Mn}^{\text{II}}_x\text{Cr}^{\text{III}}_{1-x}\text{F}_3$  was studied at compositions  $x = 0.42, 0.45, 0.50, 0.55,$  and  $0.57$ . Magnetic properties at  $x = 0.50$  are consistent with a  $\text{Mn}^{2+}\text{-Cr}^{3+}$  ionically ordered structure, space group  $P4_2bc$ . Magnetic susceptibilities from 4.2 to 300 K displayed no maxima. Observed  $C_M$  values were identical with calculated values within experimental error. Magnetic ordering temperatures,  $T_N$ , ranged from 25 K ( $x = 0.42$ ) to 34 K ( $x = 0.57$ ), but  $\Theta$  and  $\sigma_0$  are maximum at  $x = 0.50$ . The magnitude of the magnetic moment at  $x = 0.50$  is  $\sigma_0 = 1.9 \mu_B$  (powder sample) and  $2.1 \mu_B$  (single crystal). The single crystal showed no anisotropy at 4.2 K. A proposed model explaining the magnetic behavior at  $x = 0.50$  has magnetic ions located on two sets of 8c sites (8  $\text{Mn}^{2+}$  and 8  $\text{Cr}^{3+}$ ) antiparallel to those on 4b sites (2  $\text{Mn}^{2+}$  and 2  $\text{Cr}^{3+}$ ), generating a calculated moment of  $2.4 \mu_B/\text{formula unit}$   $\text{K}_{0.50}\text{Mn}^{\text{II}}_{0.50}\text{Cr}^{\text{III}}_{0.50}\text{F}_3$  ( $4.8 \mu_B$  for  $\text{KMnCrF}_6$ ).

### Introduction

Compounds of first-row transition metals with fluorine ( $\text{MF}_2$  and  $\text{MF}_3$ ) have received widespread attention primarily because of their interesting magnetic properties. The  $\text{AMF}_3$  compounds (where A, is K, Rb, Cs, or Tl) have been equally interesting. These materials share the common tendency to order antiferromagnetically between 4.2 and 300 K. Although they have served well as models for magnetic behavior, their limitation is that all M-F-M interactions are between identical metal ions. According to Goodenough<sup>2a</sup> and Kanamori,<sup>2b</sup> 90 and 180° M-X-M' interactions (where M and M' are two different transition-metal ions and X is a closed-shell anion) can be predicted to be antiferromagnetic or ferromagnetic depending upon electronic configurations and crystal fields. The Goodenough-Kanamori rules have not gained universal acceptance, however, for lack of experimental evidence. Studies of ordered structures in which different mixed-metal ions have been systematically substituted are needed so that the nature of M-F-M' interactions and related effects can be understood.

Recently, a class of ternary fluorides  $\text{K}_x\text{M}^{\text{II}}_x\text{M}^{\text{III}}_{1-x}\text{F}_3$  (where  $x$  varies from 0.4 to 0.6) having tetragonal tungsten bronze-like structures have been reported.<sup>3-12</sup> These structures can accommodate  $\text{M}^{2+}$  and  $\text{M}^{3+}$  ions that either are homonuclear or are of two different metals, and they are often described as perovskite-like since all  $\text{MF}_6$  octahedra are corner sharing and all M-F-M bond angles are close to 180°. For experimental reasons, it is also significant that they order magnetically above 4.2 K.

Table I. Chemical Analysis of  $\text{K}_x\text{Mn}_x\text{Cr}_{1-x}\text{F}_3$  Compounds

element	% found	% calcd	formula	
			exptl	theor
K	13.66	13.76	$\text{K}_{0.45}\text{Mn}_{0.45}\text{Cr}_{0.55}\text{F}_{2.99}$	$\text{K}_{0.45}\text{Mn}_{0.45}\text{Cr}_{0.55}\text{F}_3$
Mn	19.47	19.33		
Cr	22.34	22.36		
F	44.53	44.56		
K	14.96	15.04	$\text{K}_{0.50}\text{Mn}_{0.50}\text{Cr}_{0.50}\text{F}_{3.00}$	$\text{K}_{0.50}\text{Mn}_{0.50}\text{Cr}_{0.50}\text{F}_3$
Mn	21.24	21.13		
Cr	19.89	20.00		
F	43.91	43.84		
K	16.19	16.28	$\text{K}_{0.55}\text{Mn}_{0.55}\text{Cr}_{0.45}\text{F}_{3.04}$	$\text{K}_{0.55}\text{Mn}_{0.55}\text{Cr}_{0.45}\text{F}_3$
Mn	22.69	22.87		
Cr	17.68	17.71		
F	43.44	43.14		

Magnéli<sup>13</sup> reported the structure of tetragonal tungsten bronze  $\text{K}_x\text{WO}_3$ , space group  $P4/mbm$ , in which tungsten ions occupy both 8j and 2c sites. Banks, Nakajima, and Williams<sup>10</sup> reported that  $\text{K}_{0.54}\text{Mn}^{\text{II}}_{0.54}\text{Fe}^{\text{III}}_{0.46}\text{F}_3$  belongs to space group  $P4_2bc$ . In this fluoride analogue of tungsten bronze, the  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$  ions occupy three octahedral sites. The  $\text{Mn}^{2+}$  ions were found on one set of 8c sites designated M(1) and on 4b sites designated M(3). The  $\text{Fe}^{3+}$  ions were found on a second set of 8c sites designated M(2), as well as on 4b sites, M(3). This ionically ordered structure is illustrated in Figure 1 for the ideal composition  $\text{K}_{0.50}\text{M}^{\text{II}}_{0.50}\text{M}^{\text{III}}_{0.50}\text{F}_3$ . It is significant that ionic ordering within 8c sites is such that all nearest neighbors of  $\text{Mn}^{2+}$  ions are  $\text{Fe}^{3+}$  ions and vice versa. Hong, Williamson, and Boo<sup>9</sup> suggested that this ionic ordering explains very nicely the magnetic properties of  $\text{K}_x\text{V}^{\text{II}}_x\text{V}^{\text{III}}_{1-x}\text{F}_3$  ( $x = 0.45\text{-}0.56$ ). In  $\text{K}_x\text{VF}_3$  all M-F-M magnetic exchange interactions appear to be antiferromagnetic, consistent with the Goodenough-Kanamori rules.

This paper reports structural and magnetic properties of the mixed-ion system  $\text{K}_x\text{Mn}^{\text{II}}_x\text{Cr}^{\text{III}}_{1-x}\text{F}_3$ . Conclusions regarding ionic and magnetic ordering are based on X-ray and magnetic data.

### Experimental Section

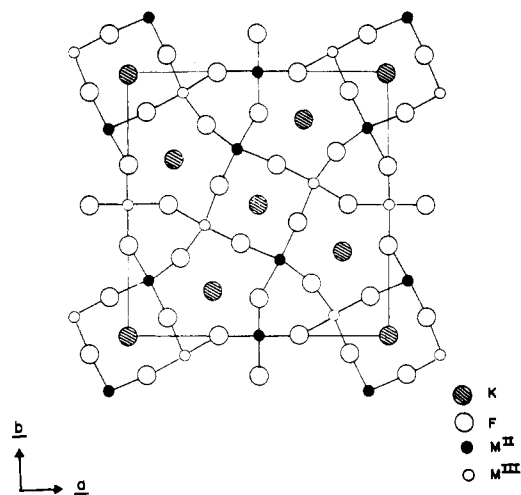
Samples of composition  $x = 0.40, 0.45, 0.50, 0.55,$  and  $0.60$  were studied. Preliminary investigations were made on materials made at Brooklyn Polytechnic Institute of New York (A series); their preparation has been described previously.<sup>5</sup> The sizes of samples from the A series, however, were not sufficient to do a complete characterization, in particular, the chemical analyses. A second set of samples was prepared at The University of Mississippi (B series) by vacuum encapsulating starting materials ( $\text{KF}, \text{MnF}_2,$  and  $\text{CrF}_3$ ) inside molybdenum containers using electron beam welding techniques. The

- (1) (a) Brooklyn Polytechnic Institute of New York. (b) Airtron, Inc. (c) The Chung Cheng Institute of Technology. (d) The University of Mississippi.
- (2) (a) J. B. Goodenough, "Magnetism and the Chemical Bond", Interscience, New York, 1963, pp 165-185; (b) J. Kanamori, *Phys. Chem. Solids*, **10**, 87 (1959).
- (3) R. de Pape, C. R. *Hebd. Seances Acad. Sci.*, **260**, 4527 (1965).
- (4) D. N. E. Buchanan, M. Robbins, H. J. Guggenheim, G. K. Wertheim, and V. G. Lambrecht, Jr., *Solid State Commun.*, **9**, 583 (1971).
- (5) E. Banks, O. Berkooz, and J. A. DeLuca, *Mater. Res. Bull.*, **6**, 659 (1971).
- (6) C. Cross, R. Feurer, M. Pouchard, and P. Hagenmuller, *Rev. Chim. Miner.*, **11**, 585 (1974).
- (7) B. J. Garrard, B. M. Wanklyn, and S. H. Smith, *J. Cryst. Growth*, **22**, 169 (1974).
- (8) R. F. Williamson and W. O. J. Boo, *Inorg. Chem.*, **16**, 649 (1977).
- (9) Y. S. Hong, R. F. Williamson, and W. O. J. Boo, *Inorg. Chem.*, **19**, 2229 (1980).
- (10) E. Banks, S. Nakajima, and G. J. B. Williams, *Acta Crystallogr., Sect. B*, **B35**, 46 (1979).
- (11) E. Banks, G. Torre, and J. A. DeLuca, *J. Solid State Chem.*, **22**, 95 (1977).
- (12) A. Hardy, A. M. Hardy, and G. Ferey, *Acta Crystallogr., Sect. B*, **B29**, 1654 (1973).

(13) A. Magnéli, *Ark. Kemi*, **1**, 213 (1949).

Table II. Lattice and Magnetic Constants for Tetragonal  $\text{K}_x\text{Mn}_x\text{Cr}_{1-x}\text{F}_3$ 

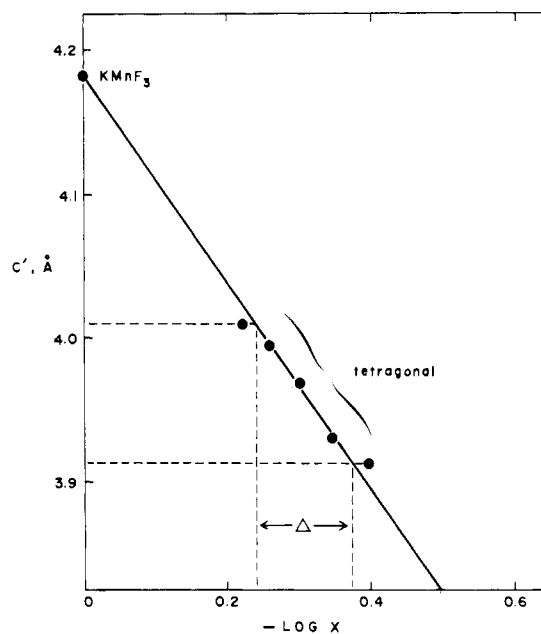
compd	lattice constants ( $\pm 0.05\%$ ), Å		$T_N$ , K	$\Theta$ , K	$C_M$ , $\text{cm}^3 \text{deg mol}^{-1}$		$\sigma_0$ , $\mu_B$
	Cu $K\alpha_1$ radiation	Cr $K\alpha_1$ radiation			obsd	calcd	
$\text{K}_{0.42}\text{Mn}_{0.42}\text{Cr}_{0.58}\text{F}_3$	$a = 12.563$ $c = 7.826$	$a = 12.567$ $c = 7.826$	25	-11	2.92	2.89	1.30
$\text{K}_{0.45}\text{Mn}_{0.45}\text{Cr}_{0.55}\text{F}_3$	$a = 12.588$ $c = 7.863$	$a = 12.587$ $c = 7.861$	26	-2	3.04	2.97	1.75
$\text{K}_{0.50}\text{Mn}_{0.50}\text{Cr}_{0.50}\text{F}_3$	$a = 12.649$ $c = 7.935$	$a = 12.652$ $c = 7.937$	31	0	3.13	3.10	1.90
$\text{K}_{0.55}\text{Mn}_{0.55}\text{Cr}_{0.45}\text{F}_3$	$a = 12.720$ $c = 7.988$	$a = 12.717$ $c = 7.987$	33	-9	3.28	3.23	1.63
$\text{K}_{0.57}\text{Mn}_{0.57}\text{Cr}_{0.43}\text{F}_3$	$a = 12.761$ $c = 8.019$	$a = 12.758$ $c = 8.016$	34	-10	3.26	3.28	1.29


 Figure 1. Proposed ionic ordering for  $\text{K}_{0.50}\text{Mn}^{\text{II}}_{0.50}\text{Mn}^{\text{III}}_{0.50}\text{F}_3$ .

sealed Mo containers were fired at  $850^\circ\text{C}$  for 16 days. All samples were examined by polarized microscopy for homogeneity and impurities. A crystal of composition  $\text{K}_{0.50}\text{Mn}_{0.50}\text{Cr}_{0.50}\text{F}_3$  ( $\text{KMnCrF}_6$ ) from the A series, weighing 26 mg, was established to be single. Precision lattice constants were obtained by Guinier-Hägg techniques using both Cu  $K\alpha_1$  and Cr  $K\alpha_1$  X radiations. Samples were analyzed chemically by Galbraith Laboratories. Elemental analyses were by atomic absorption for potassium and volumetric methods for manganese and chromium, and fluorine was obtained by difference. Experimental formulas were calculated by setting the relative compositions of Mn + Cr = 1. Magnetic measurements were made from 4.2 to 300 K and between 0 and 10 kG with a Foner type PAR vibrating-sample magnetometer equipped with a Janis liquid-helium Dewar and gallium arsenide temperature controller. Magnetic fields were measured with an F. W. Bell Hall-probe gauss meter, Model 8860. All samples were corrected for core diamagnetism from ionic susceptibility tables of Mulay.<sup>14</sup>

## Results

Optical and X-ray analyses indicated the presence of impurity phases of hexagonal  $\text{K}_x\text{Mn}_x\text{Cr}_{1-x}\text{F}_3$  ( $x = 0.40$ ) and  $\text{KMnF}_3$  ( $x = 0.60$ ). The impurities were too finely divided to be removed mechanically, therefore, these two samples were not analyzed chemically. Chemical analyses of samples with  $x = 0.45, 0.50$ , and  $0.55$  (B series) are given in Table I. In each case, chemical analyses are identical with theoretical values within experimental error. Guinier-Hägg results are shown in Table II. Although no superlattice reflections were observed by X-ray diffraction which would double the  $c$  axis, the magnetic data indicates  $\text{K}_x\text{Mn}^{\text{II}}_x\text{Cr}^{\text{III}}_{1-x}\text{F}_3$  has the same structure as  $\text{K}_x\text{Mn}^{\text{II}}_x\text{Fe}^{\text{III}}_{1-x}\text{F}_3$ . Therefore,  $c$  should be two layers deep in the fluoride analogues as opposed to one layer deep in the tungsten bronze structure. The chemical compositions of the tetragonal phases in samples with theoretical


 Figure 2. Linear plot of interlayer distance  $c'$  vs.  $-\log x$  for  $\text{K}_x\text{Mn}_x\text{Cr}_{1-x}\text{F}_3$  compounds.

values  $x = 0.40$  and  $x = 0.60$  were obtained from a linear plot of the interlayer distances ( $c'$ ) vs.  $(-\log x)$  (Figure 2). The straight line on this plot includes  $c'$  values from samples  $x = 0.45, 0.50$ , and  $0.55$  plus the limiting values,  $x = 1.00$ , from  $\text{KMnF}_3$  ( $c' = a = 4.182 \text{ \AA}$ ).<sup>15</sup> The linear equation is

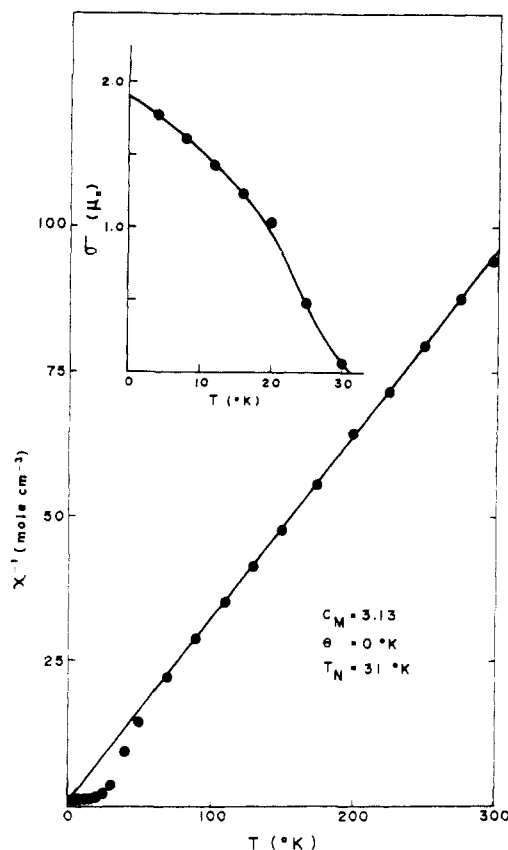
$$c' = 0.720 \log x + 4.182$$

The values of  $c'$  for samples with theoretical  $x$  values  $0.40$  and  $0.60$  give corrected compositions  $x = 0.42$  and  $0.57$ , respectively.

Magnetic susceptibilities of the five powdered samples and the single crystal were similar in appearance, and none displayed a maximum over the temperature range  $4.2\text{--}300 \text{ K}$ . All samples displayed large magnetic moments at low temperatures. The inverse susceptibility vs.  $T$  and the magnetic moments extrapolated to zero field ( $\sigma$ ) vs.  $T$  of a powdered sample of  $\text{K}_{0.50}\text{Mn}^{\text{II}}_{0.50}\text{Cr}^{\text{III}}_{0.50}\text{F}_3$  are shown in Figure 3. The temperature at which the extrapolated value goes to zero is defined as  $T_N$ . This is based on the assumption that the crystal field involved is several orders of magnitude greater than the externally applied field ( $\sim 10 \text{ kG}$ ), and the temperature at which the thermal energy overcomes that of the crystal field should be defined as the magnetic ordering temperature. From Figure 3,  $T_N$  is seen to be  $31 \text{ K}$ . The true magnitude of the moment is the value of the moment extrapolated to zero field and  $0 \text{ K}$  ( $\sigma_0$ ). From Figure 3, the value of  $\sigma_0$  for  $\text{K}_{0.50}\text{Mn}^{\text{II}}_{0.50}\text{Cr}^{\text{III}}_{0.50}\text{F}_3$  (B series) is  $1.9 \mu_B$ . A summary of magnetic

(14) L. N. Mulay, "Magnetic Susceptibility", Interscience, New York, 1963, p 1782.

(15) K. Knox, *Acta Crystallogr.*, **14**, 583 (1961).

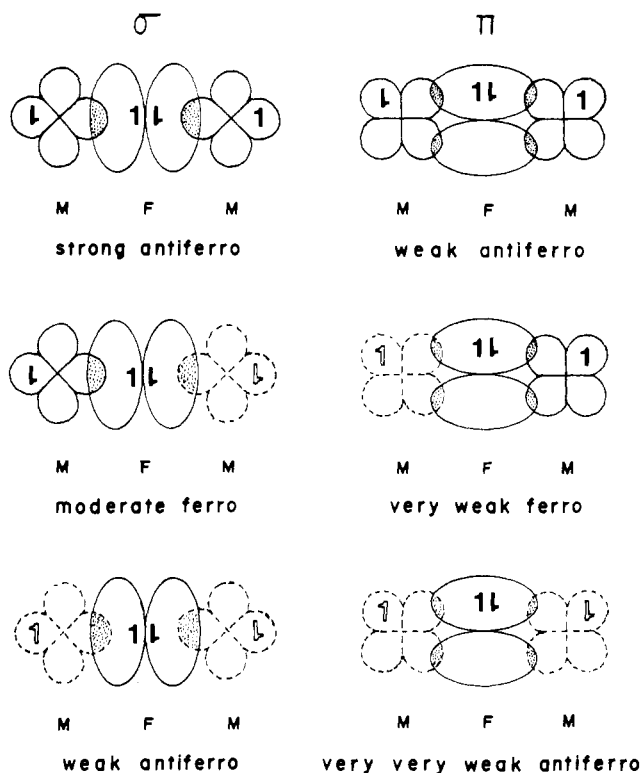


**Figure 3.** Inverse susceptibility vs. temperature and magnetic moments extrapolated to zero field vs. temperature of  $K_{0.50}Mn_{0.50}Cr_{0.50}F_3$ .

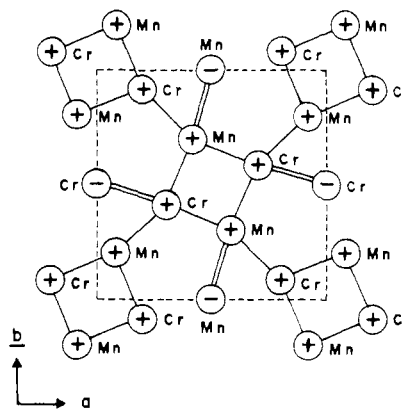
constants is given in Table II. No corrections were made on magnetic data of samples containing small amounts of impurity phases. Since neither of these impurities display spontaneous magnetic moments, values of  $\sigma_0$  for  $K_{0.42}Mn_{0.42}Cr_{0.58}F_3$  and  $K_{0.57}Mn_{0.57}Cr_{0.43}F_3$  shown in Table II and Figure 6 would be slightly larger but not significantly different. The susceptibility of the single crystal (A series,  $x = 0.50$ ) appeared almost identical with that of the powder (B series,  $x = 0.50$ ), but its magnetic moment extrapolated to zero field and 0 K was slightly larger than that of the powder. At 4.2 K, the crystal showed no anisotropy as it was rotated from a position in which its crystallographic  $c$  axis was parallel to the field to one in which it was perpendicular to the field. At temperatures below their respective  $T_N$  values, magnetic moments returned to zero upon removal of the external field.

### Discussion

The dominating superexchange mechanism in the  $K_xMn^{II}_xCr^{III}_{1-x}F_3$  system is believed to be correlation and is, therefore, ideal for testing the Goodenough-Kanmori rules. The possible  $\pi$  and  $\sigma$   $180^\circ$  contributions to  $M-F-M'$  correlation interactions are shown in Figure 4. From this figure, one sees three contributions to  $Mn^{II}-F-Mn^{II}$  ( $d^5-d^5$ ) interactions: one  $\sigma$  ( $1/2$  filled  $e_g$  with  $1/2$  filled  $e_g$ ) and two  $\pi$  ( $1/2$  filled  $t_{2g}$  with  $1/2$  filled  $t_{2g}$ ), which are strongly and weakly antiferromagnetic, respectively. Therefore, the  $Mn^{II}-F-Mn^{II}$  interactions resulting from the sum of these three contributions should be very strongly antiferromagnetic. Likewise, there are three contributions to a  $Cr^{III}-F-Cr^{III}$  ( $d^3-d^3$ ) interaction: one  $\sigma$  (empty  $e_g$  with an empty  $e_g$ ) and two  $\pi$  ( $1/2$  filled  $t_{2g}$  with  $1/2$  filled  $t_{2g}$ ), all of which are weakly antiferromagnetic. The resultant  $Cr^{III}-F-Cr^{III}$  interactions should be moderately antiferromagnetic. The  $Mn^{II}-F-Cr^{III}$  ( $d^5-d^3$ ) interactions have one  $\sigma$  ( $1/2$  filled  $e_g$  with an empty  $e_g$ , moderately ferromagnetic) and two  $\pi$  ( $1/2$  filled  $t_{2g}$  with  $1/2$  filled  $t_{2g}$ , weakly antiferromagnetic). Consequently, the resultant  $Mn^{II}-F-Cr^{III}$



**Figure 4.** Correlation superexchange mechanisms for  $180^\circ$   $\sigma$  [ $d(e_g)-p-d(e_g)$ ] and  $\pi$  [ $d(t_{2g})-p-d(t_{2g})$ ] interactions. Empty orbitals are shown as broken lines and the absent electrons as open arrows.



**Figure 5.** Proposed magnetic structure of  $K_{0.50}Mn_{0.50}Cr_{0.50}F_3$ . The direction of the spin is indicated as (+) or (-).

interactions should be weakly to very weakly ferromagnetic.

The results of magnetic measurements made on  $K_{0.50}Mn_{0.50}Cr_{0.50}F_3$  are illustrated in Figure 3. Plots of data for the other four powder samples and the single crystal were qualitatively similar. Magnetic constants, like the lattice constants, are composition dependent. Table II shows that  $T_N$  and  $C_M$  increase with  $x$ , which is accounted for by the increased concentration of  $Mn^{2+}$ . The table also shows maximum  $\theta$  and  $\sigma_0$  values for composition  $x = 0.50$ . If we assume the ionic structure of  $K_{0.50}Mn_{0.50}Cr_{0.50}F_3$  to be that shown in Figure 1, then the number of  $Mn^{II}-F-Mn^{II}$ ,  $Cr^{III}-F-Cr^{III}$ , and  $Mn^{II}-F-Cr^{III}$  bonds per unit cell are 4:4:52, respectively, since the unit cell is two layers deep. If all nearest-neighboring  $Mn^{II}-Mn^{II}$  pairs are arranged antiparallel, all nearest-neighboring  $Cr^{III}-Cr^{III}$  pairs antiparallel, and the maximum number of  $Mn^{II}-Cr^{III}$  pairs parallel, the resulting structure is that shown in Figure 5. It should be emphasized that this is a proposed model and the correct magnetic structure can only be determined by neutron diffraction. In

this structure, all of the 60 bond conditions per unit cell, including those between layers, are satisfied except for eight  $\text{Mn}^{\text{II}}\text{-F-Cr}^{\text{III}}$  bonds in which the  $\text{Mn}^{2+}$  and  $\text{Cr}^{3+}$  spin moments are forced to be antiparallel. This condition provides a very weak constraint to magnetic ordering and probably lowers the temperature at which long-range ordering occurs by only a few degrees. It is noteworthy that magnetic ordering in the  $\text{K}_x\text{Mn}_x\text{Cr}_{1-x}\text{F}_3$  compounds involves three types of magnetic interactions (two antiferromagnetic and one ferromagnetic). As was pointed out earlier, one would predict the strengths of these interactions to be different in energy by about an order of magnitude. Specifically,  $\text{Mn-Mn} > \text{Cr-Cr} > \text{Mn-Cr}$ . Kanamori<sup>2b</sup> warns, however, that in addition to any particular mechanism such as correlation, symmetry and orthogonality relationships of cations and intervening anions must be considered. The truth of this statement becomes apparent if one compares  $T_N$  values of the  $\text{KMF}_3$  perovskites of the first-row transition-metal series. In this structure, all metal ions are surrounded octahedrally by six  $\text{F}^-$  ions and all  $\text{M-F-M}$  interactions (which are antiferromagnetic) are  $180^\circ$ . The values are as follows:  $\text{KVF}_3$ ,<sup>16</sup>  $t_{2g}^3$  ( $T_N = 130$  K);  $\text{KCrF}_3$ ,<sup>17</sup>  $t_{2g}^3e_g$  ( $T_N = 40$  K);  $\text{KMnF}_3$ ,<sup>18</sup>  $t_{2g}^3e_g^2$  ( $T_N = 88$  K);  $\text{KFeF}_3$ ,<sup>18</sup>  $(t_{2g}^2)t_{2g}^2e_g^2$  ( $T_N = 113$  K);  $\text{KCoF}_3$ ,<sup>18</sup>  $(t_{2g}^4)t_{2g}e_g^2$  ( $T_N = 114$  K);  $\text{KNiF}_3$ ,<sup>18</sup>  $(t_{2g}^6)e_g^2$  ( $T_N = 275$  K);  $\text{KCuF}_3$ ,<sup>18</sup>  $(t_{2g}^6)(e_g^2)e_g$  ( $T_N = 243$  K). [The paired electrons are shown in parentheses, i.e.,  $(t_{2g}^6)e_g^2$  for  $\text{KNiF}_3$ .] In each case where there is mixing of unpaired  $t_{2g}$  and  $e_g$  electrons, the magnetic interaction is weakened, as reflected by a lower value of  $T_N$ . We should expect nearest-neighbor  $\text{Mn}^{\text{II}}\text{-Mn}^{\text{II}}$  ions in the  $\text{K}_x\text{Mn}_x\text{Cr}_{1-x}\text{F}_3$  compounds (on the basis of the  $T_N$  of  $\text{KMnF}_3$ ) to couple near 100 K. One would expect  $d^3\text{-}d^3$  interactions of  $\text{Cr}^{\text{III}}\text{-Cr}^{\text{III}}$  to not differ significantly from  $\text{V}^{\text{II}}\text{-V}^{\text{II}}$  interactions in  $\text{KVF}_3$ . Therefore, one would expect  $\text{Cr}^{\text{III}}\text{-Cr}^{\text{III}}$  coupling in  $\text{K}_x\text{Mn}_x\text{Cr}_{1-x}\text{F}_3$  to also occur near 100 K. There are, unfortunately, no previous examples of  $d^5\text{-}d^3$  interactions in the literature to support qualitative conclusions regarding  $\text{Mn}^{\text{II}}\text{-Cr}^{\text{III}}$  interactions. Our conclusions are that in  $\text{K}_x\text{Mn}_x\text{Cr}_{1-x}\text{F}_3$ ,  $\text{Mn}^{\text{II}}\text{-Mn}^{\text{II}}$  and  $\text{Cr}^{\text{III}}\text{-Cr}^{\text{III}}$  short-range antiferromagnetic order first commences near 100 K. Ferromagnetic coupling ( $\text{Mn}^{\text{II}}\text{-Cr}^{\text{III}}$ ) occurs at a lower temperature, resulting in three-dimensional long-range order. This combination of ordering steps eliminates the possibility of observing a maximum in  $\chi$  at  $T_N$ . The defined  $T_N$  for these compounds is that temperature where three-dimensional long-range ordering, which is accompanied by a spontaneous moment, occurs. There is some question that the long-range ordering temperature should be called  $T_C$  rather than  $T_N$  since it is believed to occur as a consequence of ferromagnetic interactions. However, since the  $\Theta$  values are negative (except for  $x = 0.50$ , in which  $\Theta = 0$ ), the combined strengths of the antiferromagnetic interactions exceed the ferromagnetic ones, and on that basis alone, we have used  $T_N$ .

A theoretical magnetic moment of the ordered structure can be calculated from the relationship

$$\sigma_0 = \sum_i S_i g_i (\text{parallel}) - \sum_j S_j g_j (\text{antiparallel})$$

where  $S_i$  are the spins of  $\text{Mn}^{2+}$  ( $d^5$ ) and  $\text{Cr}^{3+}$  ( $d^3$ ) aligned parallel,  $S_j$  are those aligned antiparallel, and  $g_i$  and  $g_j$  are assumed to be 2.0. If  $\sigma_0$  is the net sum of spin moments per unit cell of the structure illustrated in Figure 5, its magnitude is  $48 \mu_B$ . For the formula  $\text{K}_{0.50}\text{Mn}_{0.50}\text{Cr}_{0.50}\text{F}_3$ , the moments is  $2.4 \mu_B$ . Figure 6 is a plot of the experimental  $\sigma_0$ 's. The

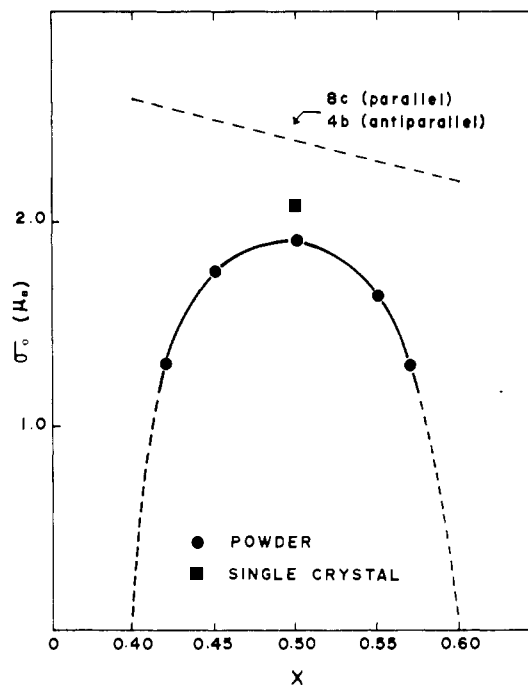


Figure 6. Magnetic moments extrapolated to zero field and 0 K vs.  $x$  of  $\text{K}_x\text{Mn}_x\text{Cr}_{1-x}\text{F}_3$  compounds.

dashed line represents the ideal situation where perfect ordering exists on 8c sites with all of its  $\text{Mn}^{2+}$  and  $\text{Cr}^{3+}$  spins parallel but antiparallel to all spins located on 4b sites. The data clearly indicate this model is incorrect for compositions other than for  $x = 0.50$ . As seen in the plot, the values  $1.9$  (powder) and  $2.1 \mu_B$  (single crystal) approach the calculated value  $2.4 \mu_B$ . These results are qualitatively consistent with the Goodenough-Kanamori rules as illustrated in Figure 5. The data in Figure 6 clearly show that  $\sigma_0$  tends toward 0 at the theoretical limiting compositions  $x = 0.40$  and  $0.60$ . If the ionic structure were known at these compositions, one could further speculate what the magnetic structures might be by an analysis similar to that illustrated in Figure 5.

Although the magnetic structure proposed for the composition  $x = 0.50$  is speculative, the  $\text{K}_x\text{Mn}_x\text{Cr}_{1-x}\text{F}_3$  materials do demonstrate typical ferromagnetic behavior. In addition to large  $\sigma_0$  values and  $\Theta$  values close to 0, these compounds demonstrate an absence of magnetic anisotropy (the magnetic moments always align themselves with the field). Furthermore, when the external field is removed at temperatures below  $T_N$ , the magnetic moment completely disappears, which indicates ferromagnetic domains are formed.

Neutron diffraction measurements to determine the magnetic structure of  $\text{KMnCrF}_6$  are in progress.

**Acknowledgment.** The authors gratefully acknowledge the National Science Foundation (Grants DMR 79-00313, DMR 76-83360, and DMR 74-11970) for financial support, including the purchase of major equipment, and The University of Mississippi for cost sharing. The work done at Polytechnic Institute of New York was partially supported by Army Grant No. DAAG 29-75-G-0096. They also thank the NASA Langley Research Center for the loan of an electromagnet and power supply. Appreciation is expressed to The University of Mississippi Computer Center for providing data reduction time.

**Supplementary Material Available:** Magnetic susceptibilities vs. temperature of  $\text{K}_x\text{Mn}_x\text{Cr}_{1-x}\text{F}_3$  at 10 kG (Table III) and spontaneous moments vs. temperature of  $\text{K}_x\text{Mn}_x\text{Cr}_{1-x}\text{F}_3$  extrapolated to zero field (Table IV) (2 pages). Ordering information is given on any current masthead page.

- (16) R. F. Williamson and W. O. J. Boo, *Inorg. Chem.*, **16**, 646 (1977).  
 (17) S. Yoneyama and K. Hirakawa, *J. Phys. Soc. Jpn.*, **21**, 183 (1966).  
 (18) Kinshiro Hirakawa, Kazuyoshi Hirakawa, and T. Hashimoto, *J. Phys. Soc. Jpn.*, **15**, 2063 (1960).