281. *The Preparation and Magnetic Properties of some Complex Fluorides having the Perovskite Structure.*

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The magnetic properties of compounds of the type $KM^{II}F_3$ (M^{II} = Mn, Fe, Co, Ni, Cu, and Zn) have been studied in the temperature range 80—300°K. With the exception of $KCuF_3$, all have the perovskite structure. The compounds were prepared from aqueous solution; published methods of preparation lead to contamination of the product with the transition metal hydroxide, which seriously affects the magnetic properties of the bulk material, and a method is described by which products of maximum purity can be obtained. The iron, cobalt, and nickel compounds have been shown to be antiferromagnetic, with Neel points at 112°, 135°, and 280°K, respectively. The manganese compound shows evidence of antiferromagnetism, with a Neel point below 80°K. These values of the Neel points are in the order expected from the ionic radii of the M^{II} ions. Our measurements on $KCuF_3$ are consistent with an antiferromagnetic interaction with a Neel point at 215°K; this finding is discussed in the light of others to the contrary. The structure of the copper compound is distorted from the cubic perovskite to one with tetragonal symmetry. Such a distortion is expected in a d^9-compound, and is repeated in $KCrF_3$ where the d^4-configuration leads one to expect distortions from octahedral symmetry.

We also report magnetic measurements on solid solutions of $KZnF_3$ and $KNiF_3$, prepared in the same way as the single compounds. The observed changes in the magnetic properties of $KNiF_3$ as increasing numbers of nickel ions are replaced by diamagnetic zinc ions are discussed, and an explanation is offered.

Paramagnetic materials may be divided into two main classes, the first of these being the so-called magnetically dilute compounds, in which each paramagnetic atom is well shielded from its neighbours by diamagnetic ligands. It is here that studies of the temperature-dependence of susceptibility yield most information on stereochemistry, oxidation state, etc. Secondly, there are the magnetically concentrated compounds in which interactions between neighbouring paramagnetic atoms determine the temperature-dependence of susceptibility. Compounds of the second class do not obey the Curie–Weiss law below a characteristic temperature, and the measured magnetic moments may be much below expected values; they exhibit ferromagnetism or antiferromagnetism. We discuss here a number of fluorides of the type $KM^{II}F_3$ (M^{II} = Mn, Fe, Co, Ni, Cu, or Zn), which have the perovskite structure and show evidence of antiferromagnetism. The susceptibility of an antiferromagnetic compound rises to a maximum at a temperature (the Neel point) that is characteristic of the material being studied. This behaviour arises from an exchange interaction in the lattice which tends to align the magnetic moments of neighbouring atoms antiparallel. This interaction can arise from direct orbital overlap of neighbouring paramagnetic atoms; but a common alternative mechanism is super-exchange in which an intervening diamagnetic ion (*e.g.*, O^{2-} or F^-) takes an active part; super-exchange interaction is often very strong, an example of an oxygen-containing system being $LaMnO_3$. The perovskite structure is particularly suitable for super-exchange since it contains an infinite, linear, three-dimensional M–F–M–F array, which leads to interesting magnetic properties. Further, since potassium trifluorozincate, $KZnF_3$, is isomorphous with the paramagnetic members of the series, we have been able to study the effects of random substitution of nickel ions by zinc ions on the antiferromagnetic interaction in potassium trifluoronickelate, $KNiF_3$. The magnetic properties of solid solutions of the type $KNi_{\alpha}Zn_{1-\alpha}F_3$ for $0{\cdot}1 < \alpha = 1$ are described here.

There has been considerable interest in these compounds since their antiferromagnetism was first reported,[1] particularly among physicists, and the reported results are conflicting, as may be seen in Table 1. We have carefully studied the preparation and composition of these compounds as prepared from aqueous solution and have found that small amounts of impurity can affect their magnetic properties profoundly. It is thus convenient first to discuss the preparative procedures employed.

TABLE 1.

Summary of previous studies of the system KMF_3.

Compound	Neel point (K)	Prepn.*	Crystal structure §¶** at 300°K	at 80°K
$KMnF_3$ ...	95 †	S	Cubic, $a = 4{\cdot}191$ Å	Monoclinic, $a, b, c = 4{\cdot}188, 4{\cdot}171, 4{\cdot}185$ Å, $\alpha = 89° 51'$
	89 †	M		
	88·5 ‡	M		
	88 §	S		
$KFeF_3$	121 §	S	Cubic, $a = 4{\cdot}122$ Å	Rhombic, $a = 4{\cdot}109$ Å, $\alpha = 89° 51'$
	115 ¶	S		
$KCoF_3$	136 §	S	Cubic, $a = 4{\cdot}069$ Å	Tetragonal, $a = 4{\cdot}057$, $c = 4{\cdot}049$ Å
	135 ¶	S		
$KNiF_3$	280 §	S	Cubic, $a = 4{\cdot}015$ Å	Cubic, $a = 4{\cdot}002$ Å
	275 ¶	S		
$KCuF_3$ ...	243 §	S	Tetragonal, $a = 4{\cdot}140$, $c = 3{\cdot}926$ Å	Tetragonal, $a = 4{\cdot}121$, $c = 3{\cdot}913$ Å
	<100 ¶			
$KZnF_3$ ...	—	S	Cubic, $a = 4{\cdot}05$ Å	

* Preparation is from aqueous solution (S) or from a melt (M). † Ogawa, *J. Phys. Soc. Japan*, 1959, **14**, 1115. ‡ Schulman, Knox, and Wyluda, *Bull. Amer. Phys. Soc.*, 1959, **4** (NA 11); Beckman and Knox, *Phys. Rev.*, 1961, **121**, 376. § Okazaki, Suemone, and Fuchikama, *J. Phys. Soc. Japan*, 1959, **14**, 1823; 1961, **16**, 671. ¶ Martin, Nyholm, and Stephenson, *Chem. and Ind.*, 1956, 83. ** See also Beckman *et al.*, *Acta Cryst.*, 1960, **13**, 506; Knox, *Acta Cryst.*, 1961, **14**, 583.

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[1] Martin, Nyholm, and Stephenson, *Chem. and Ind.*, 1956, 83.

EXPERIMENTAL

(*a*) *Preparation of Compounds.*—Two basic preparative methods are available. The first uses a melt as the reaction medium; *e.g.*, Ogawa [2] prepared potassium trifluoromanganate(II), from a melt of potassium chloride, manganous chloride, and potassium fluoride. This method would be expected to provide a material of high purity, but the absence of published analytical data makes this hard to assess. The fact that Ogawa's product was brown implies the presence of some manganese dioxide, which will seriously affect the magnetic properties of the product. The second method was described by Nuka [3] for the above complex salt and was repeated by Palmer [4] for the nickel and the zinc compound; it involves addition of a solution of the transition-metal chloride (1 mol.) to a boiling solution of potassium fluoride (3 mol.) in water, and boiling until precipitation is complete. We have modified this method as described below, and found the optimum conditions for obtaining a material as near to pure KMF_3 as possible, having reproducible composition and magnetic properties. We shall consider the nickel analogue in the discussion since it is most readily analysed, and has the highest Neel point.

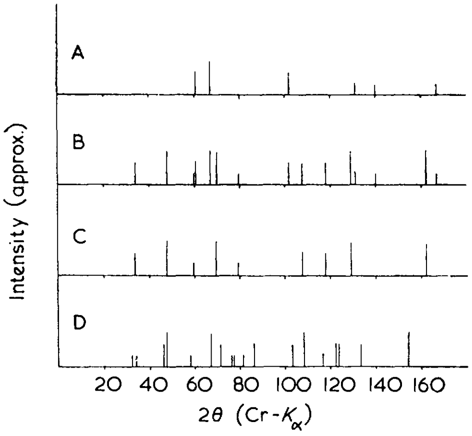

FIG. 1. X-Ray powder diffraction patterns for (A) NiO, (B) $KNiF_3$ prepared by Palmer's method, and dried *in vacuo* at 300°, (C) $KNiF_3$ prepared by the modified method and dried *in vacuo* at 300° and (D) $KCuF_3$ (Cr-K_α radiation).

X-Ray powder photographs of potassium trifluoronickelate prepared by Palmer's method show the presence of some nickel hydroxide in the product, and, if the material is heated to 300°C *in vacuo*, lines due to nickel oxide appear in the powder pattern (see Fig. 1). Thus attempts to improve the preparative method were aimed at preventing hydrolysis. The ideal way of achieving this, the use of non-aqueous solvents, failed because none could be found in which potassium fluoride and nickelous chloride or fluoride were sufficiently soluble; mixed acetone– and alcohol–water were also unsuitable as solvents.

The following procedure has proved the most satisfactory: A saturated solution of nickel fluoride was prepared by dissolving freshly precipitated nickel carbonate (1 mol.) in the calculated amount of dilute hydrofluoric acid. This solution, and a separate saturated solution of potassium fluoride (3 mol.) were heated almost to the b. p. and then mixed in a platinum basin and rapidly heated just to the b. p. After continued boiling for not more than 10 sec., the precipitate was immediately filtered off, washed with cold water, then acetone, and dried at 120° in air. This method is valuable in all cases, but for metals other than nickel the amount obtainable from a single preparation is small because of the low solubility of the metal fluoride and the low yields that follow the brief boiling of the reaction mixture. The essential precautions are (i) to keep the quantity of free acid to a minimum, (ii) to use saturated solutions, and (iii) not to prolong boiling of the solution (the product is not formed below 100°). In the case of the manganese compound, the precipitate must be washed with dilute hydrofluoric acid to prevent hydrolysis. It proved impossible to prepare potassium trifluorocuprate(II) of similar purity by this method. Analytical data are listed in Table 2. The compounds $KNi_\alpha Zn_{1-\alpha}F_3$ were prepared by co-precipitation from a solution of nickel and zinc fluoride in suitable

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[2] Ogawa, *J. Phys. Soc. Japan*, 1959, **14**, 1115.
[3] Nuka, *Z. anorg. Chem.*, 1929, **180**, 235.
[4] Palmer, " Experimental Inorganic Chemistry," Cambridge Univ. Press, 1954.

TABLE 2.

Analytical data for compounds KMF_3.

Compound	K (%)		M (%)		F (%)		Compound	K (%)		M (%)		F (%)	
	Found	Calc.	Found	Calc.	Found	Calc.		Found	Calc.	Found	Calc.	Found	Calc.
$KMnF_3$	25·5	25·9	37·4	36·4	37·6	37·8	$KNiF_3$	25·0	25·3	37·9	37·9	35·8	36·8
$KFeF_3$	25·6	25·7	36·6	36·8	37·4	37·5	$KCuF_3$	23·9	24·5	39·6	39·8	35·1	35·7
$KCoF_3$	25·7	25·2	37·9	38·0	36·6	36·8	$KZnF_3$	24·1	24·2	40·5	40·5	35·0	35·3

TABLE 3.

Analytical data for compounds $KNi_{\alpha}Zn_{1-\alpha}F_3$.

Ni (%)	α *	K (%)		Zn (%)		F (%)	
Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
35·7	0·943	24·7	25·2	2·32	2·36	36·5	36·7
32·9	0·874	24·5	25·1	5·36	5·32	36·5	36·6
31·9	0·845	24·5	25·1	6·41	6·50	36·4	36·6
30·3	0·804	24·7	25·1	8·13	8·21	36·4	36·5
29·2	0·778	24·6	25·0	9·25	9·29	36·4	36·5
27·6	0·736	24·6	25·0	10·2	10·3	36·3	36·4
25·5	0·682	23·9	25·0	13·1	13·3	36·1	36·3
22·5	0·604	24·1	24·8	16·3	16·4	36·1	36·2
19·4	0·521	24·6	24·7	19·8	19·8	36·0	36·0
18·0	0·484	23·7	24·7	21·2	21·3	35·6	36·0
12·6	0·341	24·4	24·6	27·0	27·1	35·7	35·8
8·29	0·226	23·1	24·4	31·6	31·6	35·4	35·6
3·98	0·109	23·4	24·3	36·3	36·6	35·3	35·5

* The value of α is calculated from the observed nickel analysis, this being the most accurate estimation. All other figures for the calculated composition were computed from this value of α.

proportions. The zinc compound is evidently formed more readily since a much greater proportion of nickel is present in the reaction mixture than is found in the product. Table 3 contains analytical data for this series of compounds.

Magnetic measurements between 80° and 300°K were made on the Gouy apparatus described by Figgis and Nyholm.[5] Values of $\mu_{\text{eff.}}$ have been calculated from the relation $\mu_{\text{eff.}} = 2{\cdot}84(\chi_A \times T)^{\frac{1}{2}}$, where T = temperature (K) and the convention used in the Curie–Weiss law was $\chi \propto 1/(T + \theta)$.

RESULTS AND DISCUSSION

Known magnetic and crystallographic data on these compounds, together with the methods of preparation, are summarised in Table 1. Some of the compounds change their symmetry slightly at low temperatures and data on this aspect are also included in Table 1.

In addition, Scatturin, Corliss, Elliott, and Hastings[6] have described neutron-diffraction studies of this series of compounds. Neutrons are scattered by interaction with the nuclei of a material through which they pass, but in addition they interact with the magnetic moment vectors of the atoms. If these magnetic vectors are randomly arranged, the magnetic scattering will be coherent, but in an antiferromagnetic material the magnetic vectors are aligned at temperatures below the Neel point; then, if the resulting magnetic unit cell is different in size from the chemical unit cell, extra diffraction angles will be observed, and the exact pattern of the ordering can be deduced. Scatturin *et al.* have shown that in compounds KMF_3 (M = Mn, Fe, Co, and Ni) the magnetic moment vector of an ion is antiparallel to those of its six nearest neighbours. This confirms the view that a super-exchange interaction is in operation. When M is copper, no magnetic scattering of neutrons was observed, but when M is chromium (not studied in this work) the ordering is ferromagnetic within a layer and antiferromagnetic between layers. Failure to observe

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[5] Figgis and Nyholm, *J.*, 1959, 331.

[6] Scatturin, Corliss, Elliott, and Hastings, *Acta Cryst.*, 1961, **14**, 19.

magnetic scattering with the copper compound is surprising, since we have detected a maximum in its susceptibility.

The effect of the presence of small amounts of nickel hydroxide on the magnetic properties of potassium trifluoronickelate(II) is shown in Fig. 2. Curve A shows the temperature dependence of susceptibility of an almost pure sample; precise analysis for elements other than nickel is very difficult, but the nickel analysis in this case indicates that contamination is small. Curve B is the temperature-dependence of susceptibility of the same sample deliberately contaminated with 2% of nickel hydroxide; it may be seen that the Neel point apparently falls, and there is an increase in the susceptibility at low temperatures. This apparent change in the Neel temperature may account for the disagreements in reported values. Curve C illustrates the effect of boiling the pure sample in water for five minutes; the failure of Palmer's method to yield pure samples is thus emphasised. It is of interest to note that if a sample which contains some nickel hydroxide is heated to 300° *in vacuo*, in order to convert the hydroxide into oxide, the resulting material shows increasing ferromagnetic characteristics as temperature and/or time of heating are increased; after 2 hours at 300° the susceptibility at room temperature had increased from 1900×10^{-6} to 5500×10^{-6} c.g.s.u. per g.-atom, and the field-dependence of susceptibility had increased from a negligible value to a factor of 2 between 6300 and 3000 oersteds.

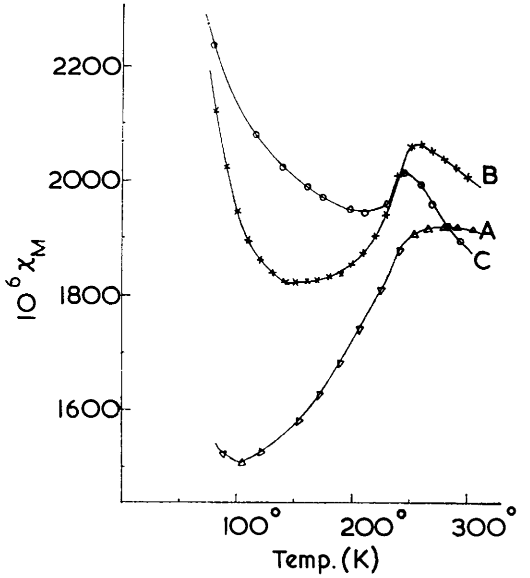

FIG. 2. Plot of magnetic susceptibility per mole against temperature for (A) $KNiF_3$, (B) $KNiF_3$ contaminated with 2% of $Ni(OH)_2$, and (C) $KNiF_3$ boiled for 5 min. in water.

Figs. 3—5 show the temperature dependence of susceptibility of the manganese, iron, cobalt, nickel, and copper compounds, and the results are listed in Tables 4 and 5. The iron, cobalt, and nickel compounds are antiferromagnetic, the Neel points being 112°, 135°, and 280°K, respectively. The increase in the Neel points in the sequence Fe $<$ Co $<$ Ni is related to the ionic radii of the transition-metal ions, which decrease in the same order (the unit-cell sizes also decrease in this order). The plot of susceptibility against temperature for potassium trifluoromanganate(II) appears to approach a maximum not far below 80°K, which also fits the above sequence of ionic radii. The results for the copper compound are ambiguous; Fig. 5 shows that we have detected a maximum in the susceptibility at 215°K. This value is lower than that reported by Okazaki, Suemone, and Fuchikama;[7] however, this is not unreasonable since the increase which we observe in

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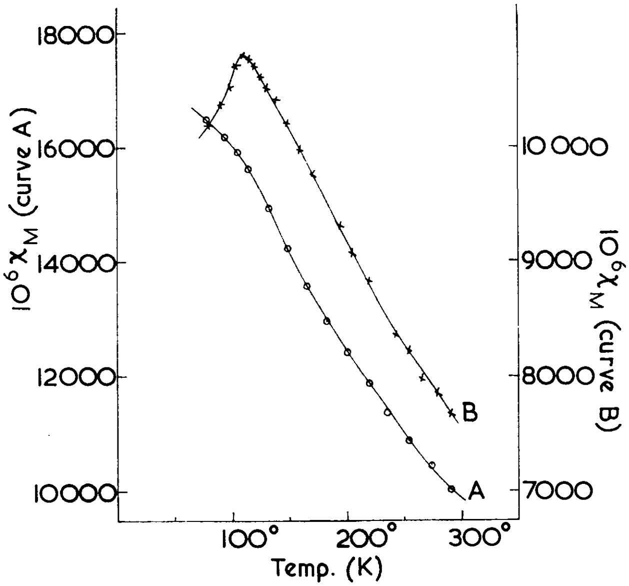
[7] Okazaki, Suemone, and Fuchikama, *J. Phys. Soc. Japan*, 1959, **14**, 1823.

the susceptibility at lower temperatures, and the blue colour of our sample imply that it is contaminated with hydrolysis products, and these would tend to lower the observed Neel point; there is no doubt that, of the compounds studied, this was the most contaminated as a result of hydrolysis. Thus on the magnetic evidence we would conclude that potassium trifluorocuprate is an antiferromagnetic compound. The ambiguity arises in this case from the fact that Scatturin *et al.* did not observe magnetic scattering of neutrons in this salt. The structure would be expected to show tetragonal distortion as a result of a Jahn–Teller effect observed in d^9-systems. Such distortion has been reported by Edwards and Peacock[8] and confirmed by Scatturin *et al.*, the figures given by

FIG. 3. Plot of magnetic susceptibility per mole against temperature for (A) $KMnF_3$ and (B) $KFeF_3$.



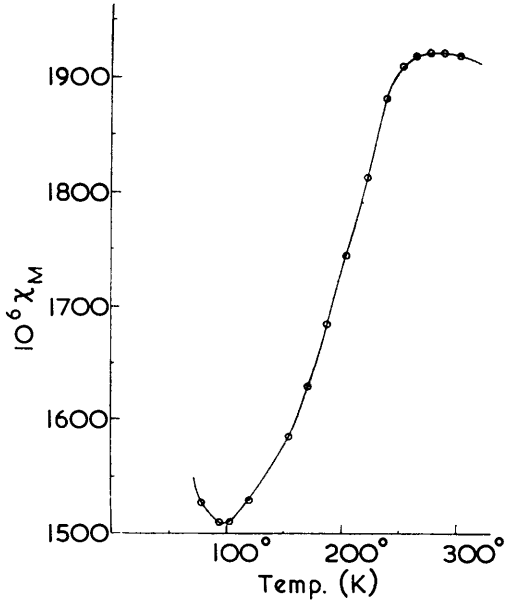


FIG. 4. Plot of magnetic susceptibility per mole against temperature for $KNiF_3$.

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[8] Edwards and Peacock, *J.*, 1959, 4126.

TABLE 4.

Present measurements on the system KMF_3.

Compound	Neel point (K)	$\mu_{eff.}$ at 300°K	$\mu_{s.o.}$ *	Ionic radius of M^{2+}	Colour
$KMnF_3$	<80°	4·86	5·92	0·89	Off-white
$KFeF_3$	112	4·27	4·90	0·83	Pale brown
$KCoF_3$	135	3·92	3·87	0·82	Pink
$KNiF_3$	280	2·19	2·83	0·79	Greenish-yellow
$KCuF_3$	215	1·38	1·73	0·75	Pale blue
$KZnF_3$	—	—	—	0·74	White

* This is the " spin only " value of the magnetic moment; $\mu_{s.o.} = [4s(s + 1)]^{\frac{1}{2}}$.

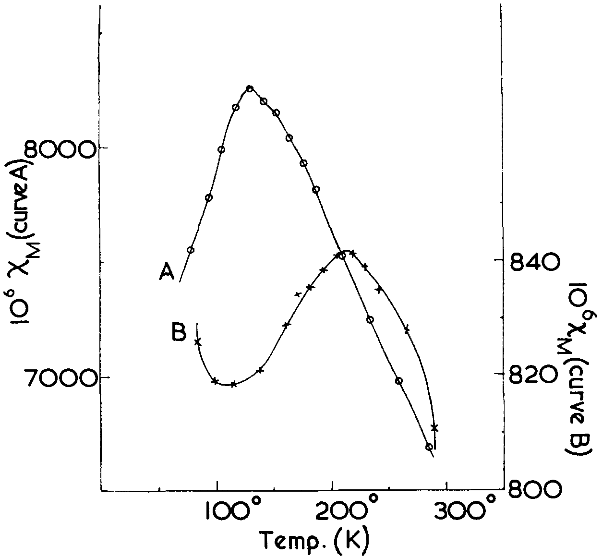

FIG. 5. Plot of magnetic susceptibility per mole against temperature for (A) $KCoF_3$ and (B) $KCuF_3$.

the former authors being $a = 4{\cdot}13$ Å, $c = 3{\cdot}92$ Å. Powder patterns of our preparations of potassium trifluoro-nickelate(II) and -cuprate and compared in Fig. 1; they are clearly different. Chromium(II) compounds are also subject to Jahn–Teller distortion arising from their d^4-configuration, and for potassium trifluorochromate(II) Scatturin *et al.* report a different kind of magnetic ordering in which ferromagnetic alignment occurs in layers, with antiferromagnetic coupling between layers. Neutron diffraction indicates that neither type of ordering is present in the copper compound; thus, since if there is any magnetic ordering in this case the magnetic unit cell must be at least twice the size of the chemical unit cell, the diffraction evidence becomes hard to reconcile with our findings. It should perhaps be pointed out that for all except the nickel and zinc compounds the structure becomes distorted at low temperatures. Calculations by Fyffe and Verhoogen [9] of " the number of electrons participating in covalent bonding " as a guide to the nature of these interactions are of little help, since for potassium trifluorocuprate the number is presumably nine, *i.e.*, a ferromagnetic coupling is predicted. It might be wise to carry out magnetic and neutron-diffraction experiments on a single sample.

Preparation of the compounds $KNi_{\alpha}Zn_{1-\alpha}F_3$ has already been described. The magnetic properties of several preparations with the same value of α have been shown to be identical, suggesting that substitution by zinc ions in the $KNiF_3$ lattice is a random process; however, the possibility of micelle formation with varying concentrations of nickel ions cannot be excluded. The results of our measurements on this system are shown in Figs. 6—8;

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[9] Fyffe and Verhoogen, *Nature*, 1960, **187**, 1108.

TABLE 5.

Magnetic measurements on the compounds KMF_3.

Temp. (K)	$10^6\chi_M$	Temp. (K)	$10^6\chi_M$	Temp. (K)	$10^6\chi_M$	Temp. (K)	$10^6\chi_M$	Temp. (K)	$10^6\chi_M$	Temp. (K)	$10^6\chi_M$
$KMnF_3$		$KMnF_3$		$KFeF_3$		$KFeF_3$		$KCoF_3$		$KCoF_3$	
291·2°	10,020	165·6°	13,580	292·2°	7670	149·4°	10,210	283·2°	6689	152·2°	8151
273·4	10,450	148·1	14,260	292·0	7612	138·0	10,420	257·4	6976	141·0	8233
254·1	10,870	132·6	14,950	279·6	7850	132·2	10,530	233·7	7247	130·0	8258
236·2	11,360	115·5	15,640	267·0	7956	126·9	10,630	209·9	7526	118·5	8177
218·2	11,880	105·2	15,960	253·9	8231	121·4	10,720	186·7	7817	106·4	7984
200·4	12,420	93·6	16,200	242·5	8352	115·4	10,780	175·2	7936	95·2	7778
182·8	12,970	78·1	16,550	218·7	8839	109·6	10,830	163·6	8041	78·0	7453
				206·7	9072	103·6	10,730				
				195·0	9313	97·8	10,540				
				171·7	9754	91·5	10,390				
				160·0	9988	80·4	10,200				

Temp. (K)	$10^6\chi_M$	Temp. (K)	$10^6\chi_M$	Temp. (K)	$10^6\chi_M$	Temp. (K)	$10^6\chi_M$	Temp. (K)	$10^6\chi_M$
$KNiF_3$		$KNiF_3 + 2\%\ Ni(OH)_2$				$KNiF_3$ boiled in water		$KCuF_3$	
303·9°	1919	300°	2011	180°	1831	294·6°	1898	291·7°	810·8
292·0	1921	290	2026	170	1828	283·0	1923	266·9	828·3
279·3	1921	280	2041	160	1828	269·6	1960	241·6	834·9
266·8	1919	270	2055	150	1826	257·8	1998	229·0	838·9
254·0	1910	260	2065	140	1828	245·0	2018	217·9	841·2
241·8	1882	250	2064	130	1843	233·1	1962	205·8	841·2
224·0	1812	240	2010	120	1865	211·2	1947	193·9	838·5
205·9	1744	230	1940	110	1899	198·9	1952	182·2	835·6
189·0	1684	220	1904	100	1948	174·5	1971	171·6	834·1
171·8	1629	210	1875	90	2025	163·4	1991	160·0	829·2
154·8	1584	200	1854	80	2122	139·6	2024	137·6	821·0
137·8	1584	190	1839			116·5	2081	115·5	818·5
121·2	1529					78·0	2237	98·4	819·6
104·6	1508							84·1	826·0
93·6	1509								
78·8	1526								

and are listed in summary, and in detail in Tables 6 and 7. It is convenient to divide the results into three groups for discussion: (i) the range $1 = \alpha > 0\cdot7$, (ii) a transition region $\sim 0\cdot7 > \alpha > 0\cdot5$, and (iii) the remaining compounds $0\cdot5 > \alpha > 0\cdot1$. If one plots $\mu_{\text{eff.}}$ against α at single temperatures, the resulting curves show three regions with differing $\mu_{\text{eff.}}/\alpha$ slopes, corresponding to these ranges of α.

TABLE 6.

Summary of the magnetic properties of the system $KNi_{\alpha}Zn_{1-\alpha}F_3$.

α	1·00	0·943	0·874	0·845	0·804	0·778	0·736	0·683
Neel point (K) ...	280°	267°	260°	254°	232°	230°	220°	200°
$\mu_{\text{eff.}}$ * at 300°K ...	2·17	2·17	2·20	2·23	2·25	2·28	2·32	2·38

α	0·604	0·521	0·484	0·341	0·226	0·109
Neel point (K) ...	—	—	—	—	—	—
$\mu_{\text{eff.}}$ * at 300°K ...	2·43	2·48	2·53	2·71	2·91	3·08

* Calc. from the relation $\mu_{\text{eff.}} = 2\cdot84(\chi_{\text{Ni}} \times T)^{\frac{1}{2}}$.

We have seen that the antiferromagnetism of potassium trifluoronickelate(II) is due to super-exchange interaction which operates throughout the three-dimensional Ni–F–Ni–F array in the lattice. Random replacement of nickel by zinc in this system may thus be expected to weaken the interaction by decreasing the length of an interacting chain, and thus leading to progressive lowering of the Neel point as more zinc ions are added. This trend is observed in the region (i), the Neel point steadily decreasing as α decreases, from 280°K when $\alpha = 1$ to about 220°K when α has fallen to 0·7 (see Table 6 for a summary of

TABLE 7.

Magnetic measurements on the system $KNi_{\alpha}Zn_{1-\alpha}F_3$.

Temp. (K)	$10^6\chi_{Ni}$	Temp. (K)	$10^6\chi_{Ni}$	Temp. (K)	$10^6\chi_{Ni}$	Temp. (K)	$10^6\chi_{Ni}$	Temp. (K)	$10^6\chi_{Ni}$
α = 0·943		α = 0·874		α = 0·845		α = 0·804		α = 0·778	
291·6°	1992	291·8°	2050	291·5°	2094	290·0°	2166	291·4°	2216
279·6	2003	279·5	2055	279·2	2107	279·0	2185	279·0	2239
266·9	2005	266·6	2061	266·4	2113	266·6	2203	266·6	2253
254·3	2000	254·4	2061	254·0	2120	253·7	2210	255·9	2254
242·0	1992	241·6	2049	241·6	2116	241·5	2215	241·5	2266
230·5	1975	230·2	2026	230·0	2104	230·0	2220	230·0	2274
212·6	1920	218·3	1996	218·3	2086	218·1	2214	218·5	2269
195·2	1857	206·6	1970	206·2	2065	206·2	2204	207·7	2263
177·8	1795	189·7	1933	194·6	2048	188·8	2190	188·7	2254
160·7	1733	172·2	1892	177·2	2022	171·4	2162	170·6	2235
143·8	1688	153·4	1859	160·6	1998	148·9	2131	153·4	2218
126·9	1662	138·0	1830	143·6	1979	126·5	2113	132·1	2201
110·3	1625	121·2	1807	125·5	1955	108·2	2093	109·6	2176
95·7	1616	105·1	1799	109·6	1946	94·0	2086	96·8	2157
79·6	1617	93·9	1798	95·7	1952	84·5	2086	79·2	2159
		79·4	1799	84·8	1958				
α = 736		α = 0·682		α = 0·604		α = 0·521			
291·3°	2295	291·5°	2399	290·6°	2529	291·6°	2612		
279·2	2313	272·9	2439	272·6	2581	273·1	2674		
266·4	2334	253·9	2478	253·6	2629	253·1	2737		
253·8	2347	235·9	2519	236·0	2685	236·2	2818		
241·8	2351	223·9	2537	218·2	2737	218·4	2853		
230·4	2363	212·1	2557	200·4	2782	200·6	2912		
218·6	2368	200·6	2569	183·1	2824	182·7	2961		
206·6	2368	188·5	2584	168·0	2869	165·6	3052		
195·1	2363	171·8	2607	149·3	2917	148·4	3156		
183·4	2358	154·5	2629	132·3	2988	131·2	3278		
171·9	2356	137·8	2666	115·6	3075	115·3	3437		
154·8	2347	120·8	2713	104·9	3145	104·5	3567		
133·8	2337	104·5	2781	93·1	3256	93·0	3726		
121·6	2347	93·4	2844	84·7	3332	84·0	3906		
105·5	2358	84·2	2906						
93·6	2362								
79·9	2373								
α = 0·484		α = 0·341		α = 0·226		α = 0·109			
	$1/\chi_{Ni}$		$1/\chi_{Ni}$		$1/\chi_{Ni}$		$1/\chi_{Ni}$		
291·5°	368·1	291·6°	320·7	291·0°	278·1	303·7°	258·6		
272·6	359·0	266·6	305·0	273·4	267·0	285·5	248·0		
247·6	347·9	241·7	297·2	254·2	257·0	266·5	235·1		
223·7	339·3	218·3	276·0	236·2	246·4	247·7	222·0		
200·2	329·3	194·5	261·9	218·6	235·4	230·2	210·7		
177·2	318·8	171·4	245·8	208·8	225·3	212·4	198·5		
154·5	305·3	148·4	229·5	183·0	214·2	195·0	187·4		
138·0	293·7	126·4	210·2	166·4	201·6	177·5	176·5		
120·9	279·7	115·6	202·3	149·7	192·0	160·4	163·1		
106·2	266·6	104·6	192·3	132·5	175·6	143·6	152·0		
92·5	253·3	92·0	181·2	115·8	166·6	126·2	138·7		
84·1	241·6	86·3	173·9	104·6	157·7	115·6	128·2		
				93·6	147·1	104·1	121·1		
				85·3	138·9	98·9	110·6		
						85·0	104·0		

these measurements). As α decreases in region (i), the maximum in the susceptibility becomes rapidly shallower, degenerating to an inflexion before disappearing completely in region (ii). As the interaction becomes progressively weaker, the magnetic moment increases steadily towards the expected value for an octahedral nickel(II) compound, 3·1—3·3 B.M. However, by the time that the Neel point has disappeared, $\mu_{eff.}$ has increased only to 2·3 B.M., indicating that a considerable magnetic interaction is still in operation. One might expect a steady fall in the Neel point to continue as α was further decreased, but in region (ii) this is not so and no maximum in the susceptibility is observed. In this second region, however, if replacement of nickel ions has been random, there will no longer be even pairs of nickel ions separated by a single fluoride ion, and the smallest

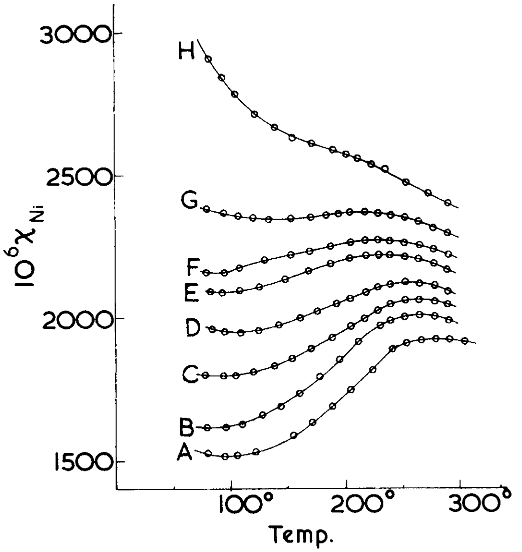


FIG. 6. Plot of magnetic susceptibility per g.-atom against temperature of compounds $KNi_{\alpha}Zn_{1-\alpha}F_3$: (A) $\alpha = 1·00$; (B) $\alpha = 0·943$; (C) $\alpha = 0·874$; (D) $\alpha = 0·845$; (E) $\alpha = 0·804$; (F) $\alpha = 0·778$; (G) $\alpha = 0·736$; (H) $\alpha = 0·682$.

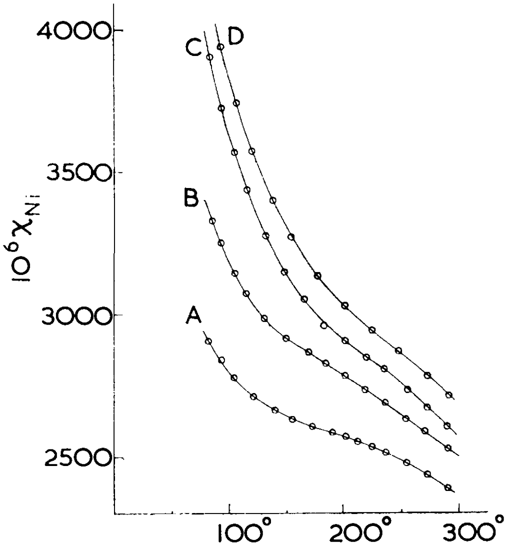


FIG. 7. Plot of magnetic susceptibility per g.-atom against temperature for compounds $KNi_{\alpha}Zn_{1-\alpha}F_3$: (A) $\alpha = 0·682$, (B) $\alpha = 0·604$; (C) $\alpha = 0·521$; (D) $\alpha = 0·484$.

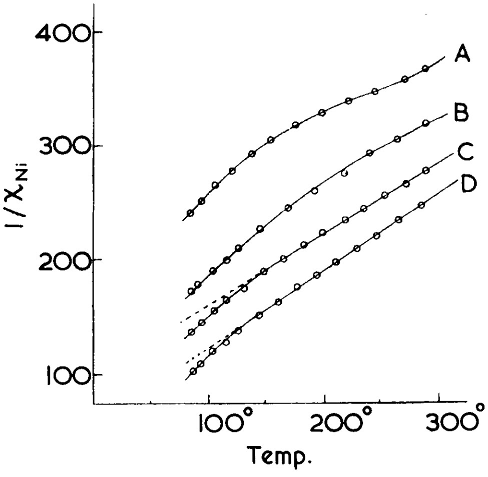
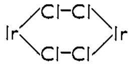


FIG. 8. Plot of inverse magnetic susceptibility per g.-atom against temperature for compounds $KNi_{\alpha}Zn_{1-\alpha}F_3$: (A) $\alpha = 0·484$; (B) $\alpha = 0·341$; (C) $\alpha = 0·226$; (D) $\alpha = 0·109$.

repeating unit in the structure will be of the type Ni–F–Zn–F–Ni–F, and the original type of interaction cannot occur. There is evidence, however, for long-range interactions, since, *e.g.*, an antiferromagnetic material often does not obey the Curie–Weiss law until several hundred degrees above its Neel temperature, where in principle the system is completely randomised. Further, Owen and his colleagues[10] have described an antiferromagnetic interaction which occurs in the system (A), the Neel point in this case being about 3°K, *i.e.*, a rather weak interaction. We thus regard region (ii) as a transition region between region (i) where the strong nearest-neighbour interactions give rise to high Neel points and region (iii) in which only comparatively weak, long-range interactions occur, sufficient to reduce $\mu_{\text{eff.}}$ considerably but giving rise to Neel points below 80°K, the limit of our observations (and probably well below this temperature). In region (iii) the steady rise in $\mu_{\text{eff.}}$ as α is decreased reflects the progressive weakening of these interactions in the same way as in region (i), until, for $\alpha = 0{\cdot}226$, the high-temperature susceptibility obeys the Curie–Weiss law, the Weiss constant, θ, being 168°K in this case. θ falls to only 84°K when $\alpha = 0{\cdot}109$, and $\mu_{\text{eff.}}$ has risen to 3·08 B.M., indicating that any residual interaction is very weak. The steady increase in $\mu_{\text{eff.}}$ over the whole composition range studied makes it unlikely that the disappearance of the Neel point is due to the existence of a solubility limit in the system since, if this were the case, $\mu_{\text{eff.}}$ should remain constant at its value at the solubility limit. We have observed a similar trend in properties in the system $KCo_{\alpha}Zn_{1-\alpha}F_3$.



(A)

We have also prepared some solid solutions of the type $KNi_{\alpha}Co_{1-\alpha}F_3$, *i.e.*, containing two different paramagnetic atoms. The temperature-dependence of susceptibility of two samples of this material ($\alpha = 0{\cdot}43$ and $0{\cdot}62$) proved to be similar to that obtained by summation of the appropriate values for the separate components, indicating that the exchange energies of the two systems are too different to permit a single interaction embracing both cobalt and nickel ions.

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[10] Griffiths, Owen, Park, and Partridge, *Proc. Roy. Soc.*, 1959, *A*, **250**, 84; Cooke, Lazenby, McKim, Owen, and Wolf, *ibid.*, p. 97; Judd, *ibid.*, p. 110.