282. *The Magnetic Properties of Some Complex Fluorides related to the Perovskites* $KM^{II}F_3$.

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The properties of compounds $NaM^{II}F_3$, (M^{II} = Mn, Fe, Co, Ni, or Zn), which are not isomorphous with the corresponding potassium compounds, are described. The nickel compound at least is ferromagnetic. Dilution with $NaZnF_3$ gives unexpected results. We have been unable to prepare similar compounds with other univalent cations. We report also the hydrated compounds, KMF_3,H_2O (M = Co or Ni), $NaNiF_3,H_2O$, and NH_4NiF_3,H_2O, all of which have properties similar to those of anhydrous analogues; the ammonium compound shows no evidence of strong magnetic interactions.

THE radius-ratio rules which must be obeyed if a compound is to crystallise with the perovskite structure are very strict. The compounds KMF_3 (M = Mn, Fe, Co, Ni, Cu, or Zn) have this structure,[1] and we have tried to prepare analogues with univalent ions other than potassium. Efforts were made to prepare compounds XMF_3 by using aqueous

[1] Machin, Martin, and Nyholm, preceding paper.

solutions of XF and the transition metal fluoride MF_2, where X = Li, Na, Rb, Cs, Ag, NH_4, or NEt_4. Only when X = Na was such a product obtained, and we have shown that even this material does not have the perovskite structure. Failure to obtain products in other cases was surprising since Nuka [2] claims to have prepared NH_4MnF_3, although his analyses do not agree very well with this formula. Allamagny [3] describes the preparation of compounds for X = Na, K, and Rb by treating the corresponding chloride with gaseous

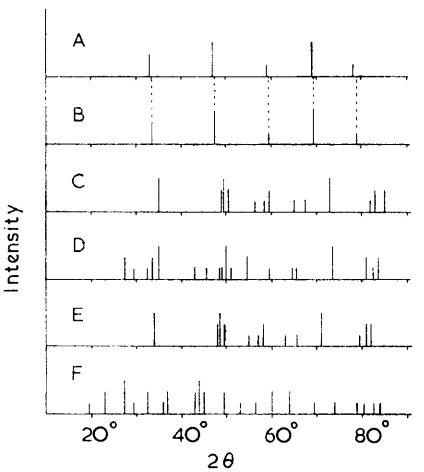

FIG. 1. *X*-Ray powder photographs (Cr-K_α radiation). (A) $KNiF_3,H_2O$. (B) $KNiF_3$. (C) $NaNiF_3$. (D) $NaNiF_3,H_2O$. (E) $NaFeF_3$. (F) NH_4NiF_3,H_2O.

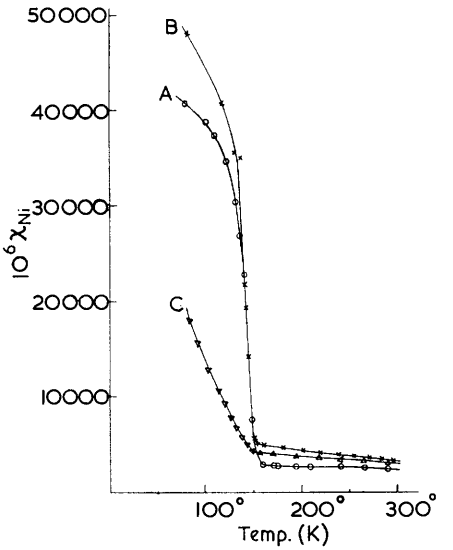

FIG. 2. Plot of magnetic susceptibility per g.-atom against temperature for (A) $NaNiF_3$, (B) $NaNiF_3,H_2O$, and (C) $NaNi_{0.553}Zn_{0.447}F_3$. Measurements made at a field strength of 6300 oersteds.

hydrogen fluoride. Simonov, Batsanova, and Kovba [4] describe the preparation of compounds with X = Na, K, Rb, Cs, and NH_4 from aqueous solution, and claim that all except the cæsium compound have the perovskite structure, a finding which is at variance with our observations. We have prepared compounds $NaMF_3$ for M = Mn, Fe, Co, Ni, and Zn, and report their magnetic properties over the temperature range 80—300°K. We were unable to prepare sodium trifluorocuprate, $NaCuF_3$, from aqueous solution, but this is not surprising since we were unable to obtain pure samples of the potassium analogue by this method and the sodium compounds in this series are each more difficult to prepare than their potassium analogues. The *X*-ray powder patterns of potassium and sodium trifluoronickelate(II) are compared in Fig. 1. These compounds are clearly not isomorphous, and so the sodium compound cannot have the perovskite structure. However, the series of sodium compounds are isomorphous, with similar small increases in unit-cell sizes in the sequence Mn < Ni, such as were observed for the potassium compounds (compare the powder patterns for sodium trifluoro-nickelate and -ferrate in Fig. 1).

Our magnetic measurements on the series of sodium compounds are summarised in Table 1. The temperature-dependence of susceptibility of sodium trifluoronickelate(II) is shown in Fig. 2, curve A. The behaviour is typical of a ferromagnetic material, the Curie

[2] Nuka, *Z. anorg. Chem.*, 1929, **180**, 235.
[3] Allamagny, *Bull. Soc. chim. France*, 1960, 1009.
[4] Simonov, Batsanova, and Kovba, *Zhur. neorg. Khim.*, 1957, **2**, 2410.

TABLE 1.

Summary of magnetic data.

Compound	μ_{eff} at 300°K	Neel (T_N) or Curie (T_C) point (K)	θ (K)	Compound	μ_{eff} at 300°K	Neel (T_N) or Curie (T_C) point (K)	θ (K)
$NaNiF_3$	2·40	$T_C = 142°$	540°	$KNiF_3$	2·19	$T_N = 280°$	—
$NaNiF_3,H_2O$	2·88	$T_C = 142$	215	$KNiF_3,H_2O$	2·48	$T_N = 240$	—
$NaNi_{0\cdot553}Zn_{0\cdot447}F_3$	2·72	$T_C = ?$	226	$KCoF_3$	3·92	$T_N = 135$	502°
				$KCoF_3,H_2O$	4·17	$T_N = 95$	300
$NaMnF_3$	5·20	—	117				
$NaFeF_3$	4·53	—	100	NH_4NiF_3,H_2O	3·16	—	35
$NaCoF_3$	4·41	—	207				

temperature being 142°K in this case. We hope to solve the structure of this compound since it would be interesting to know (i) the nickel–nickel distance in the crystal and (ii) whether the nearest-neighbour nickel atoms are separated by fluorine atoms, *i.e.*,

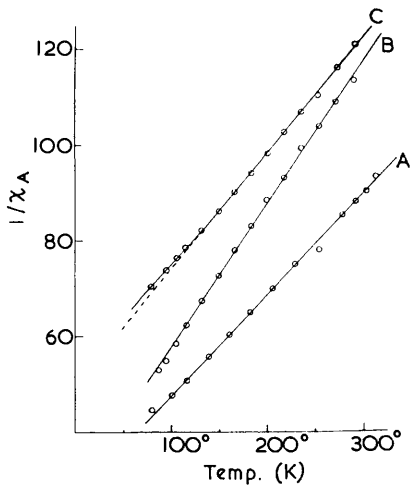

FIG. 3. Plot of inverse magnetic susceptibility per g.-atom against temperature for (A) $NaMnF_3$, (B) $NaFeF_3$, and (C) $NaCoF_3$.

whether ferromagnetism can arise from a super-exchange mechanism. The first point is of particular interest when considering the effects of metal–metal separation on the nature of the magnetic interaction, since in potassium trifluoronickelate(II) the interaction is antiferromagnetic in nature. We have investigated the effect of isomorphous dilution with sodium trifluorozincate on the magnetic properties of the nickel analogue, the temperature-dependence of the susceptibility of a material of composition $NaNi_\alpha Zn_{1-\alpha}F_3$, $\alpha = 0\cdot553$, being shown in Fig. 2, curve C. Although the shape of the susceptibility–temperature curve has altered considerably from that of the pure nickel compound, there is little change in the temperature at which the susceptibility starts to increase rapidly in the dilute sample. There is also a small increase in the room-temperature susceptibility despite the fact that the strength of the interaction appears to be unaltered on dilution. It is not completely clear whether the behaviour of the dilute compound is that of a true ferromagnetic material, since there is no very sharp increase in the susceptibility, although below 140°K the susceptibility is strongly field-dependent. These effects contrast with our observations on the dilution of potassium trifluoronickelate(II), where the Neel point decreased steadily as the proportion of zinc present was increased, with a parallel rise in the value of μ_{eff} towards the spin-only value. Thus it may be that the factors which affect

TABLE 2.

Magnetic measurements (at 6300 oersteds).

Temp. (K)	$10^6\chi_{Ni}$	Temp. (K)	$10^6\chi_{Ni}$	Temp. (K)	$10^6\chi_{Ni}$	Temp. (K)	$10^6\chi_{Co}$	Temp. (K)	$10^6\chi_{N}$
$NaNiF_3$		$NaNiF_3,H_2O$		$NaNi_{0.553},Zn_{0.447}F_3$		$KCoF_3,H_2O$		$KNiF_3,H_2O$	
291·7°	2478	296·2°	3498	291·8°	3145	285·9°	7548	302·1°	2521
266·9	2563	284·0	3602	267·0	3305	266·1	7826	289·9	2532
242·0	2637	270·7	3679	242·0	3470	247·4	8113	277·2	2544
218·1	2712	257·6	3788	218·4	3661	227·7	8410	265·2	2551
194·6	2802	238·9	3916	195·0	3857	209·8	8696	252·6	2554
176·8	2847	219·6	4171	172·1	4031	190·5	9010	239·4	2556
171·4	2858	200·9	4408	155·2	4267	171·2	9340	226·0	2550
159·2	2975	180·7	4883	149·6	4472	158·6	9576	215·0	2557
148·0	7828	161·8	5028	144·0	5187	145·9	9786	202·6	2532
142·6	22,970	154·0	5225	138·5	5887	135·9	9963	190·1	2504
136·8	27,010	150·5	5803	132·6	6774	124·0	10,130	176·2	2437
133·2	30,470	144·9	14,290	127·0	7857	103·0	10,350	157·0	2359
121·5	34,820	142·7	19,370	121·2	9461	92·6	10,430	129·6	2275
109·8	37,360	142·1	21,840	115·0	10,740	83·9	10,360	86·6	2125
100·5	38,940	137·2	35,060	103·6	12,990	79·4	10,280		
78·0	40,900	130·3	35,580	91·0	15,880				
		116·6	40,720	84·0	18,110				
		81·9	48,260						

Temp. (K)	$1/\chi_{Ni}$	Temp. (K)	$1/\chi_{Mn}$	Temp. (K)	$1/\chi_{Fe}$	Temp. (K)	$1/\chi_{Co}$
NH_4NiF_3,H_2O		$NaMnF_3$		$NaFeF_3$		$NaCoFe_3$	
298·1°	240·1	313·8°	93·52	291·0°	114·4	293·0°	121·4
285·7	231·8	303·5	90·91	272·8	109·2	273·8	116·6
272·3	222·5	292·8	88·35	254·0	104·1	254·1	110·5
259·6	213·2	279·0	85·68	235·9	99·81	235·5	107·3
247·8	205·1	253·5	78·42	217·8	93·37	218·8	102·8
234·4	194·6	229·6	75·19	199·4	88·35	201·1	98·56
221·4	187·1	205·5	70·09	183·1	83·14	183·6	94·42
208·7	176·7	182·4	65·19	166·0	78·13	166·4	90·30
195·7	167·1	159·4	60·39	149·5	72·88	149·4	86·35
183·2	158·7	138·0	55·50	131·8	67·60	131·8	82·38
179·3	155·8	115·1	50·84	114·9	62·88	114·4	78·74
167·2	146·6	98·9	47·83	104·3	58·72	105·6	76·59
154·0	136·1	78·6	44·70	93·0	54·89	93·9	73·96
140·9	125·3			87·0	52·85	78·0	70·13
123·0	110·7						
81·6	77·52						

the strength of a ferromagnetic interaction are not those which control an antiferromagnetic system, or that the ferromagnetic exchange is of direct, rather than super-exchange, type.

The role of the water molecule in the compound $NaNiF_3,H_2O$ will be discussed in detail below, but here we note that the temperature-dependence curve of the hydrate (B, Fig. 2) resembles that of the anhydrous more closely than that of the diluted material; and again there is an increase in susceptibility at room temperature suggesting a weaker interaction than in the anhydrous material, yet the Curie point is unchanged. This is the more remarkable since the crystal structure of the hydrate is somewhat different to that of the anhydrous compound, the *X*-ray powder patterns being different (see Fig. 1). The relative behaviours of these three compounds are thus very interesting.

The temperature-dependence of susceptibility of the remaining sodium compounds [trifluoro-manganate(II), -ferrate(II) and -cobaltate(II)] is illustrated in Fig. 3. These compounds show considerable deviations from the Curie–Weiss law at low temperatures. In the high-temperature region, where the Curie–Weiss law is obeyed by the susceptibility, Weiss constants, θ, are 117°, 100°, and 207°K for the manganese, iron, and cobalt compounds, respectively; thus there is evidence of considerable magnetic interaction in these compounds. Further, since they are isomorphous with the nickel compound, it is tempting

to attribute the high θ values to ferromagnetic interaction; and also a comparison of values of μ_{eff} at 300°K with those of known antiferromagnetic compounds, *i.e.*, KMF_3, shows that in each case μ_{eff} is lower for the potassium analogue (see Table 2) (though this may be fortuitous). Experience has shown us that the sign of the Weiss constant is not a reliable indication of the nature of an interaction; also the direction of deviation of the susceptibility curve from Curie–Weiss-law behaviour is not diagnostic. The final criterion of strong field-dependence of susceptibility of a ferromagnetic material operates only below the Curie point, so that we have no definite evidence of the nature of the interaction except for the nickel compound.

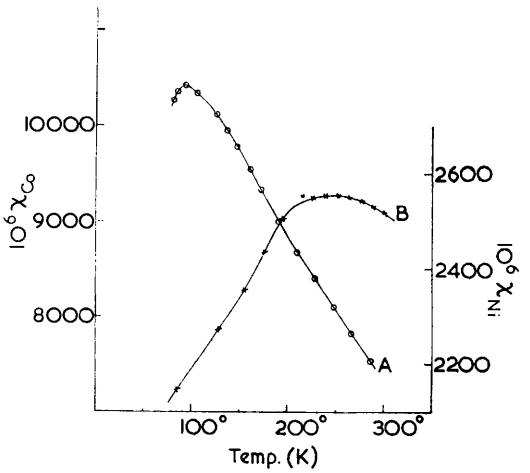

FIG. 4. Plot of magnetic susceptibility per g.-atom against temperature for (A) $KCoF_3,H_2O$ and (B) $KNiF_3,H_2O$.

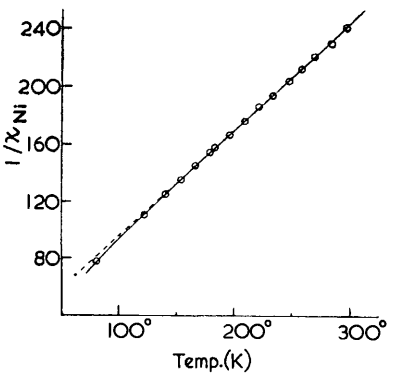

FIG. 5. Plot of inverse magnetic susceptibility per g.-atom against temperature for NH_4NiF_3,H_2O.

The hydrates $KNiF_3,H_2O$ and $KCoF_3,H_2O$ display interesting properties. Analyses for potassium, nickel (or cobalt), and fluorine are consistent with the presence of one mol. of water. The infrared spectra contain sharp absorption bands in the 3 μ and 6·5 μ regions which are characteristic of water molecules (O–H stretching, and H–O–H bending modes, respectively). The presence of sharp bands commonly indicates that the water molecule is co-ordinated, or is so held in a lattice that hydrogen bonding cannot occur, the 3 μ band in particular being broadened by hydrogen bonding. Further, the water is not removed from the nickel hydrate by prolonged heating at 110°; thus it appears that the water molecule in this compound must occupy some definite site in the lattice. The problem arises, however, where to place the water. Comparison of *X*-ray powder photographs of the hydrated and anhydrous nickel compound (Fig. 1) indicates that both compounds have the perovskite structure, with slightly different unit-cell sizes. By relating the observed change in the diffraction angle, 2θ, of a given line to the known unit-cell sizes in the KMF_3 series, we conclude that the unit-cell size of this hydrate is not more than 0·2 Å larger than that of the anhydrous material. The largest " hole " in the perovskite lattice is on the unit-cell edge, between two potassium ions. If the unit-cell edge of the hydrate is taken to be 4·22 Å, then the diameter of this largest hole is 4·22—2·66 = 1·56 Å (unit-cell edge — diameter of K^+), *i.e.*, not large enough to accommodate a water molecule. Since analyses are consistent with the presence of one water molecule per molecule of $KNiF_3$, it is unlikely that such a large number of water molecules will be occupying K^+ or F^- sites. The site of the water molecule is thus uncertain. Now, the unit cell is larger in the hydrate, and thus one would expect a weakening of the antiferromagnetic interaction, an

effect which we have observed. The temperature-dependence of susceptibility of the two hydrates is illustrated in Fig. 4; the behaviour is typical of antiferromagnetic interactions, the Neel points being 240° and 95°K for the nickel and the cobalt compound, respectively. These values may be compared with 280° and 135°K which we have reported previously [1] as the Neel points of the corresponding anhydrous compounds. Thus the increased unit-cell size in the hydrate leads to a weakening of the antiferromagnetic interaction, with a consequent lowering of the Neel point and increase in the value of μ_{eff}.

The temperature-dependence of susceptibility of an ammonium hydrate, NH_4NiF_3,H_2O, is shown in Fig. 5, there being no evidence of a strong magnetic interaction in this case since the susceptibility obeys the Curie–Weiss law with only small deviations at low temperatures. Also the Weiss constant is here only 35°K. The *X*-ray powder pattern of this material (Fig. 1) indicates that its crystal structure is of much lower symmetry than that of the other compounds discussed here. The magnetic moment at room temperature, 3·16 B.M., is of the order expected for an octahedral nickel(II) ion.

Experimental.—Magnetic susceptibilities were measured on the Gouy balance described by Figgis and Nyholm.[5] Values of μ_{eff} quoted in the text were calculated from the relation $\mu_{eff} = 2{\cdot}84(\chi_A T)^{\frac{1}{2}}$ B.M., and Weiss constants were calculated by assuming that the Curie–Weiss law is expressed as $\chi^{-1} = k(T + \theta)$, where T is the temperature (K).

TABLE 3.

Analytical data for compounds XMF_3.

Compound	X (%) Found	X (%) Calc.	M (%) Found	M (%) Calc.	F (%) Found	F (%) Calc.
$NaMnF_3$	16·8	17·1	40·5	40·7	41·8	42·3
$NaFeF_3$	16·7	16·9	41·0	41·1	41·6	42·0
$NaCoF_3$	16·4	16·6	42·6	42·4	42·9	41·0
$NaNiF_3$	16·5	16·6	41·7	42·3	39·8	41·1
$NaNiF_3,H_2O$	14·4	14·7	37·6	37·5	35·9	36·4
$KNiF_3,H_2O$	22·1	22·6	33·8	34·0	32·5	33·0
$KCoF_3,H_2O$	22·5	22·6	34·0	34·1	32·9	32·9
NH_4NiF_3,H_2O	—	—	38·5	38·7	37·0	37·6

The compounds $NaMF_3$ were prepared by precipitation from aqueous solution as described for the potassium compounds.[1] The hydrated compounds were prepared in the laboratories of Messrs. James Wilkinson, in Sheffield; our analyses of these, and the rest of the compounds discussed, are listed in Table 3.

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