

FERROMAGNETISM AND FERRIMAGNETISM OF OXYGEN SPINELS CONTAINING TETRAVALENT MANGANESE

G. BLASSE

Philips Research Laboratories,
N. V. Philips' Gloeilampenfabrieken, Eindhoven, Netherlands

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Abstract—The magnetic properties of a number of oxygen spinels containing Mn^{4+} are reported. Some of these compounds appear to be ferromagnetic (e.g. $CuMg_{0.5}Mn_{1.5}O_4$ and $LiZn_{0.5}Mn_{1.5}O_4$), whereas others show a ferrimagnetic behaviour due to crystallographic order of paramagnetic ions on octahedral sites (e.g. $LiNi_{0.5}Mn_{1.5}O_4$ and $ZnNiMnO_4$).

The combination of tetrahedral Cu^{2+} and octahedral Mn^{4+} is shown to be more stable than tetrahedral Cu^{2+} and octahedral Mn^{3+} .

It is concluded that the $90^\circ Mn^{4+}-O^{2-}-Mn^{4+}$ interaction is ferromagnetic and the $90^\circ Ni^{2+}-O^{2-}-Mn^{4+}$ interaction antiferromagnetic.

INTRODUCTION

A NUMBER of oxygen spinels containing Mn^{4+} ions have been reported earlier by us.⁽¹⁾ Their magnetic properties were dealt with in two preliminary short papers.^(2,3) It was found that some of these compounds are ferromagnetic, whereas others are ferrimagnetic, although the tetrahedral sites in these compounds are occupied by diamagnetic ions. It is the aim of the present paper to give a more extensive discussion of these results.

Simultaneously the problem of the charge distribution of Cu and Mn ions in oxygen spinels was solved. The charge distribution of $CuMn_2O_4$ for example, was written by Sinha *et al.* as $Cu^{+}[Mn^{3+}Mn^{4+}]O_4$,⁽⁴⁾ whereas Baltzer *et al.* proposed $Cu^{2+}[Mn_2^{3+}]O_4$.⁽⁵⁾

EXPERIMENTAL

The experimental procedures were the same as those described earlier.⁽¹⁾

RESULTS

Table 1 presents the cell edge, cation distribution, chemical analysis and the magnetic properties of the compounds studied. Figures 1–5 show some of the experimental results obtained (σ - T , σ - H and χ^{-1} - T curves).

Attempts to prepare the following compounds were not successful: $CuAlMnO_4$ (X-ray diagram shows two spinel phases), $CuMn_2O_4$, $CuCo_{0.5}Mn_{1.5}O_4$ and $CuFe_{0.5}Mn_{1.5}O_4$ (X-ray diagrams show mainly spinel phase) and $CuRhTiO_4$, $CuMg_{0.5}Ti_{1.5}O_4$ and $CuNi_{0.5}Ti_{1.5}O_4$.

Table 2 shows the influence of heat treatment on the magnetic properties of $CuMg_{0.5}Mn_{1.5}O_4$. The X-ray patterns of these samples showed weak superstructure reflections of the lithium ferrite type. On sample 3 the following resistivities were

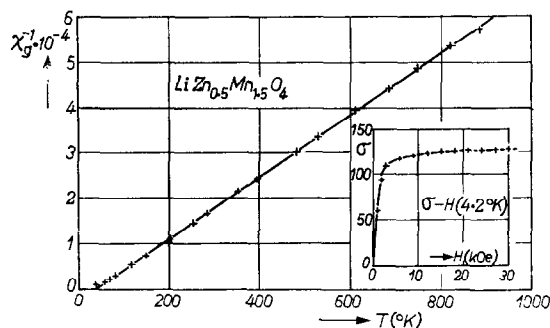


FIG. 1. Reciprocal susceptibility vs. temperature and magnetization vs. applied field at $4.2^\circ K$ for $LiZn_{0.5}Mn_{1.5}O_4$.

Table 1. Oxygen contents, crystallographic and magnetic properties of some oxygen spinels containing manganese

Compound	Cation distribution	Cell edge (Å)	Oxygen contents		$n_B(4.2^\circ\text{K})$		T_C ($^\circ\text{K}$)	θ_A ($^\circ\text{K}$)	Shape $\chi^{-1}-T$ curve and Curie constant*
			exp.	theor.	exp.	theor.			
$\text{LiZn}_{0.5}\text{Mn}_{1.5}\text{O}_4$	$\text{Li}_{1.0}\text{Zn}_{0.5}[\text{Li}_{1.0}\text{Mn}_{1.5}^{4+}]$	8.19	12.7	12.9	4.24	4.50	22	+35	{ <650° straight, 2.74 (2.80) >650° convex }
$\text{CuMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$	$\sim \text{Cu}^+[\text{Mg}_{0.5}\text{Mn}_{1.5}^{4+}]$	8.31	7.18	7.20	3.82	4.50	57	+75	
CuRhMnO_4	$\sim \text{Cu}^+[\text{RhMn}^{4+}]$	8.38	2.85	2.81	2.35	3.00	35	+45	
$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$	$\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}^{4+}]$	8.17	13.0	13.1	3.28	3.40**	130	-60	{ <450° hyperbolic >450° straight, 3.26 (3.30) }
$\text{CuNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$	$\sim \text{Cu}^+[\text{Ni}_{0.5}\text{Mn}_{1.5}^{4+}]$	8.31	6.48	6.69	3.15	3.40**	150	-20	
$\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$	$\sim \text{Cu}^+[\text{Cu}_{0.5}^{2+}\text{Mn}_{1.5}^{4+}]$	8.28	—	—	3.35	4.00	80	—	{ <250° hyperbolic >250° straight, 3.35 (2.87) >50° convex }
ZnNiMnO_4	$\text{Zn}[\text{Ni}^{2+}\text{Mn}^{4+}]$	8.30	6.38	6.59	0.87	0.80**	90	-190	
					—***	—	—	—	
LiMn_2O_4	$\text{Li}[\text{Mn}^{3+}\text{Mn}^{4+}]$	8.25	—	—	—	—	—	-260	{ <350° hyperbolic >350° straight, 4.14 (3.73) }
CuCrMnO_4	$\sim \text{Cu}^+[\text{Cr}^{3+}\text{Mn}^{4+}]$	8.31	—	—	1.47†	—	45	—	
$\text{LiMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$	$\text{Li}[\text{MgMn}_{1.5}]$	8.18	13.9	14.5	2.97†	—	38	+45	
$\text{LiCo}_{0.5}\text{Mn}_{1.5}\text{O}_4$	$\text{Li}[\text{Co}_{0.5}^{2+}\text{Mn}_{1.5}^{4+}]$	8.16	12.8	13.1	0.33†	—	50	-240	

* Spin-only values between brackets; for shape of $\chi^{-1}-T$ curves see also Figs. 1-5.

** Assuming for Ni^{2+} $n_B = 2.2 \mu_B$.

*** Paramagnetic down to 4.2°K^2 .

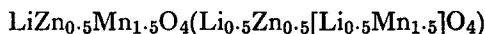
† Value for $H = 30 \text{ kOe}$, in which field the sample is far from saturated.

measured: $> 10^7 \Omega\text{cm}$ at 4.2°K and 77°K and $10^4 \Omega\text{cm}$ at room temperature.

DISCUSSION

1. Ferromagnetic compounds

The compound



is a very peculiar spinel. Not only its crystallographic order is remarkable (1:1 order on *A*-sites and simultaneously 1:3 order on *B*-sites,⁽¹⁾ but also its magnetic order is uncommon for a spinel, viz. ferromagnetic. This follows unambiguously from the shape of the χ^{-1} -*T* curve (Fig. 1) and the value of the saturation moment at 4.2°K and has been proved in the meantime by neutron diffraction.⁽⁶⁾

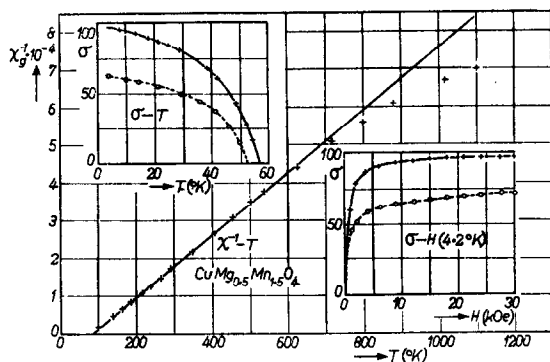


FIG. 2. Reciprocal susceptibility and magnetization vs. temperature and magnetization vs. applied field at 4.2°K for $\text{CuMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Solid curves with crosses relate to sample 3, broken curves with circles to sample 1 (compare Table 2).

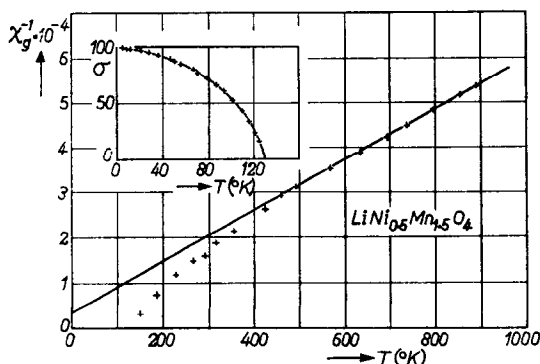


FIG. 3. Reciprocal susceptibility and magnetization vs. temperature for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

The compound $\text{CuMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$ presents a more complicated case. It was already mentioned in the introduction that in the literature two possible charge distributions have been proposed

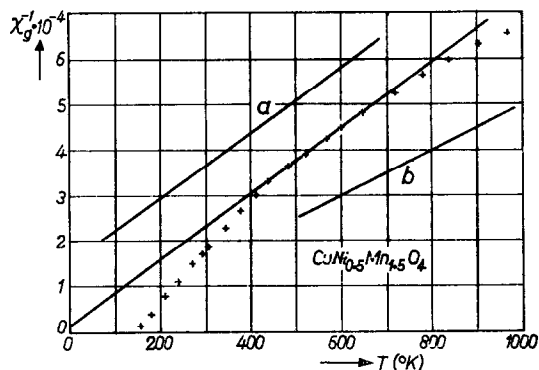


FIG. 4. Reciprocal susceptibility vs. temperature for $\text{CuNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Slope (a) has the spin-only value for the configuration $\text{Cu}^+\text{Ni}^{2+}_0.5\text{Mn}^{4+}_{1.5}\text{O}_4$, slope (b) for

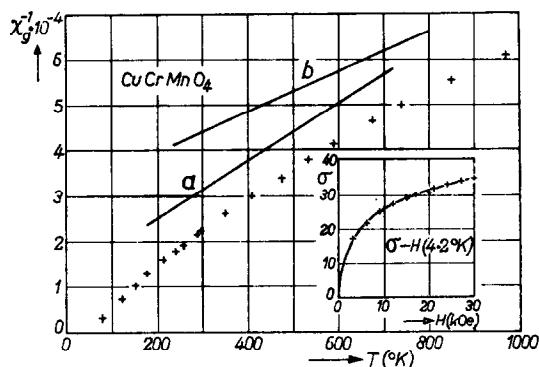
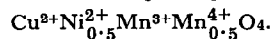
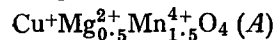
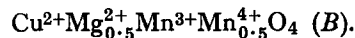


FIG. 5. Reciprocal susceptibility vs. temperature and magnetization vs. applied field at 4.2°K for CuCrMnO_4 . Slope (a) has the spin-only value for the configuration $\text{Cu}^+\text{Cr}^{3+}\text{Mn}^{4+}\text{O}_4$, slope (b) for $\text{Cu}^{2+}\text{Cr}^{3+}\text{Mn}^{3+}\text{O}_4$.

for the spinel CuMn_2O_4 , viz. $\text{Cu}^+\text{Mn}^{3+}\text{Mn}^{4+}\text{O}_4$ and $\text{Cu}^{2+}\text{Mn}^{3+}_2\text{O}_4$. By analogy two distributions are possible for $\text{CuMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$, viz.



and



Our experimental results present strong evidence for the following model: distribution (A) has the lower

Table 2. Influence of heat treatment on the magnetic properties of $\text{CuMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$

Nr.	Preparation	Heat treatment	$\theta_A(^{\circ}\text{K})$	Curie constant	$n_B(4.2^{\circ}\text{K})$	$\frac{d\sigma^*}{dH}$
1	Heating oxides at 900°C	Cooled in the furnace	+45	3.2	2.79	4×10^{-4}
2	Heating oxides at 900°C	Extremely slowly cooled**	+60	2.92	3.43	2×10^{-4}
3	Heating nitrates at 700°C	Extremely slowly cooled**	+75	2.85	3.82	0.3×10^{-4}
Theoretical values			—	2.80	4.50	—

* In the region 20–30 kOe.

** About $5^{\circ}/\text{hr}$.

energy, but the energy difference between (*A*) and (*B*) is small. Let us summarize the arguments. A compound with distribution (*A*) is expected to be ferromagnetic due to the presence of Mn^{4+} ions as the only kind of paramagnetic ions on *B*-sites (compare $\text{LiZn}_{0.5}\text{Mn}_{1.5}\text{O}_4$). A compound with distribution (*B*) is expected to be ferrimagnetic. Up to about 650°K $\text{CuMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$ behaves as is to be expected for the distribution $\text{Cu}^+[\text{Mg}_{0.5}\text{Mn}_{1.5}^{4+}]\text{O}_4$: the value of the saturation moment at 4.2°K and the shape and slope of the $\chi^{-1}-T$ curve present ample evidence for this statement. At higher temperatures the $\chi^{-1}-T$ curve becomes convex, which points to the formation of Cu^{2+} and Mn^{3+} .

In this way it is also possible to explain the dependence of the magnetic properties on heat treatment and the somewhat too low value of the magnetic moment (Table 2). If the energy difference between distributions (*A*) and (*B*) is small, copper is present as Cu^+ and Cu^{2+} and manganese as Mn^{3+} and Mn^{4+} at the reaction temperature ($900\text{--}1000^{\circ}\text{K}$). For such a complicated system of ions we can hardly expect to reach the ideal cation distribution with Cu exclusively on *A*-sites at the reaction temperature. The deviation from the distribution $\text{Cu}[\text{Mg}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ will be larger if the reaction temperature is higher and the cooling rate more rapid. If the distribution is not exactly $\text{Cu}^+[\text{Mg}_{0.5}\text{Mn}_{1.5}^{4+}]\text{O}_4$, Cu and Mn ions may partly change sites.† The result of this is that locally the

ferromagnetic order of Mn^{4+} ions on *B*-sites is disturbed by Mn^{3+} ions on *A*-sites and Cu^{2+} on *B*-sites. It seems highly improbable that the combination Mn^{4+} on *A*-sites and Cu^+ on *B*-sites would be more stable than Mn^{3+} and Cu^{2+} because of the electron configurations ($\text{Mn}^{4+} : d^3$ and $\text{Cu}^+ : d^{10}$) and the large radius of the Cu^+ ion (about 1 Å). Consequently $\text{Mn}^{3+}\text{--Mn}^{4+}$ *AB*-interactions and $\text{Cu}^{2+}\text{--Mn}^{4+}$ *BB*-interactions are present. The former is probably negative, the latter is negative (see below). All this is deduced from the following experimental results. The more rapid the cooling rate, the higher the Curie constant (more Cu^{2+} and Mn^{3+}), the lower the asymptotic Curie constant (less positive $\text{Mn}^{4+}\text{--Mn}^{4+}$ *BB*-interactions and more negative interactions), the lower the Curie temperature (compare Fig. 2) and the lower the magnetic moment (antiferromagnetic arrangements). Probably the value of $d\sigma/dH$ at 4.2°K at high fields points also into this direction.

The arguments given above are also valid in the case of the third ferromagnetic compound CuRhMnO_4 , which, therefore, is not discussed any further.

From these results it is concluded that the 90° $\text{Mn}^{4+}\text{--Mn}^{4+}$ interaction in these spinels is positive. The sign of this interaction must be due to the orthogonality of e.g. the d_{xy} orbitals of neighbouring Mn^{4+} ions (compare⁽⁸⁾). The direct overlap of these orbitals is obviously not large enough to overcome this effect. This is the case for the 90° $\text{Cr}^{3+}\text{--Cr}^{3+}$ interaction in oxides, which is strongly negative. This direct overlap is strongly dependent on distance, as has been argued by

† In this connection it is interesting to note that careful X-ray examinations of CuMn_2O_4 have shown that a considerable amount of the Mn ions occupy *A*-sites.⁽⁷⁾

GOODENOUGH.⁽⁹⁾ One should expect therefore, that the $90^\circ \text{Mn}^{4+}\text{--Mn}^{4+}$ interaction also depends on distance. Increasing distance means decreasing direct overlap and consequently a stronger positive exchange. This agrees with the experimental results. In $\text{LiZr}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{CuMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$ the only paramagnetic ions present (Mn^{4+}) occupy the same crystallographic sites. The cell edge of the latter compound is larger and its Curie temperature higher (Table 1). The effect may even be strengthened by the large size of the Cu^+ ion. A large cation on A -sites implies a large u -parameter, so that the $\text{Mn}^{4+}\text{--O}^{2-}\text{--Mn}^{4+}$ angle becomes larger than 90° . This implies a smaller direct overlap.

In one of our earlier papers⁽²⁾ this interaction was concluded to be very weakly negative as had also been found, by Bongers in Li_2MnO_3 .⁽¹⁰⁾ This was inferred from susceptibility measurements at high temperatures and may be due to the Mn^{3+} -contents of these samples, which was somewhat larger than that of the present samples. At the moment the possibility of negative $90^\circ \text{Mn}^{4+}\text{--Mn}^{4+}$ interaction in oxides cannot be excluded due to the distance- and angle-dependence of this interaction. However, up till now it has not been found in stoichiometric samples.

2. Ferrimagnetic compounds

The compound $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ shows a new type of magnetic order in the spinel structure. The ferrimagnetic behaviour of spinels (for example the well-known ferrites) has been explained by Néel by assuming an antiparallel and collinear arrangement of the A - and B -sublattice magnetizations: $\vec{A}[\vec{B}_2]\text{O}_4$.⁽¹¹⁾ In $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ the A -sites are occupied exclusively by diamagnetic Li^+ ions. The B -sites are occupied by Ni^{2+} and Mn^{4+} ions in an ordered arrangement as in lithium ferrite, $\text{Fe}[\text{Li}_{0.5}\text{Fe}_{1.5}]\text{O}_4$. The magnetic behaviour (Table 1, Fig. 3) of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ can easily be explained by assuming an antiparallel and collinear arrangement of Ni^{2+} and Mn^{4+} ions: $\text{Li}[\vec{\text{Ni}}_{0.5}^{2+}\vec{\text{Mn}}_{1.5}^{4+}]\text{O}_4$. Its $\chi^{-1}\text{--}T$ curve is hyperbolic as is to be expected for a ferrimagnetic compound and its saturation moment equal to the difference of the postulated sublattices.

This phenomenon has been observed earlier by SWOBODA *et al.*⁽¹²⁾ in the corundum structure.

CoMnO_3 and NiMnO_3 have ilmenite structure (i.e. ordered corundum) and are ferrimagnetic: $\vec{\text{Co}}^{2+}\vec{\text{Mn}}^{4+}\text{O}_3$ and $\vec{\text{Ni}}^{2+}\vec{\text{Mn}}^{4+}\text{O}_3$.

From our results on $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ it is clear that the $90^\circ \text{Ni}^{2+}\text{--Mn}^{4+}$ interaction is negative. An important contribution to this interaction will be due to the non-orthogonality of e.g. the $d_{x^2-y^2}$ orbital of the Ni^{2+} ion and the d_{xy} orbital of the Mn^{4+} ion.

It is interesting to note that the $\text{Ni}^{2+}\text{--Mn}^{4+}$ interaction in oxides is one of the few interactions, for which something is known about the dependence on the angle $\text{Ni}^{2+}\text{--O}^{2-}\text{--Mn}^{4+}$. In the perovskite $\text{La}_2\text{Ni}^{2+}\text{Mn}^{4+}\text{O}_6$ (angle $\text{Ni}^{2+}\text{--O}^{2-}\text{--Mn}^{4+}$ about 180°) the $\text{Ni}^{2+}\text{--Mn}^{4+}$ interaction is (relatively) strongly positive,⁽¹³⁾ in the ilmenite $\text{Ni}^{2+}\text{Mn}^{4+}\text{O}_3$ (angle $\text{Ni}^{2+}\text{--O}^{2-}\text{--Mn}^{4+}$ about 135°) it is negative⁽¹²⁾ as it is in the spinel $\text{LiNi}_{0.5}^{2+}\text{Mn}_{1.5}^{4+}\text{O}_4$ (angle $\text{Ni}^{2+}\text{--O}^{2-}\text{--Mn}^{4+}$ 90°).

Returning to $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ it is noted that the sublattice interaction within the Mn^{4+} -sublattice is positive (compare $\text{LiZn}_{0.5}\text{Mn}_{1.5}\text{O}_4$), whereas the interaction between Ni^{2+} ions mutually will be very weak, since in this ordered structure no Ni^{2+} pairs occur (every Ni^{2+} ion is surrounded by six Mn^{4+} ions). The antiferromagnetic alignment of the Ni^{2+} and Mn^{4+} sublattice is therefore not disturbed by interactions within the sublattice.

The other ferrimagnetic compounds can now be mentioned briefly. $\text{CuNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is analogous to $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, viz. $\text{Cu}^+[\vec{\text{Ni}}_{0.5}^{2+}\vec{\text{Mn}}_{1.5}^{4+}]\text{O}_4$. The $\chi^{-1}\text{--}T$ curve (Fig. 4) becomes convex at higher temperatures, which can be ascribed to the same phenomenon as in the case of $\text{CuMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (formation of Cu^{2+} and Mn^{3+}). The cell edge of the Cu compound is larger than that of the Li compound, so that the $\text{Mn}^{4+}\text{--Mn}^{4+}$ interaction is expected to be stronger positive as is reflected by the less negative asymptotic Curie temperature (-20 vs. -60°K). For $\text{CuNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ we observed a similar dependence of heat treatment on the magnetic properties as in the case of $\text{CuMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$, which is ascribed to the same fact.

$\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$ is analogous to $\text{CuNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$: $\text{Cu}^+[\vec{\text{Cu}}_{0.5}^{2+}\vec{\text{Mn}}_{1.5}^{4+}]\text{O}_4$, so that the $90^\circ \text{Cu}^{2+}\text{--Mn}^{4+}$ interaction proves to be also negative.

Finally ZnNiMnO_4 is mentioned. This compound was prepared for the first time by

BONGERS,⁽¹⁰⁾ who deduced from paramagnetic susceptibility measurements the charge and cation distribution $\text{Zn}[\text{Ni}^{2+}\text{Mn}^{4+}]\text{O}_4$. He found a hyperbolic $\chi^{-1}-T$ curve and a saturation moment at 77°K. Recently French investigators have reported 1:1 order between divalent and tetravalent ions on the octahedral spinel sublattice, viz. in the case of $\text{Zn}[\text{ZnTi}]\text{O}_4$ ⁽¹⁴⁾ and $\text{Mn}[\text{MnTi}]\text{O}_4$.⁽¹⁵⁾ In view of these results it seems probable that the spinel ZnNiMnO_4 shows at least short-range or even long-range 1:1 order between Ni^{2+} and Mn^{4+} ions. Due to the small difference between the scattering power of these ions the absence of superstructure reflections in the X-ray diagram does not necessarily mean that there is no order. If there is order, then ZnNiMnO_4 is expected to be a ferrimagnet of the type $\text{Zn}[\text{Ni}^{2+}\text{Mn}^{4+}]\text{O}_4$, especially because the $\text{Mn}^{4+}-\text{Mn}^{4+}$ interaction will be positive and the $\text{Ni}^{2+}-\text{Ni}^{2+}$ interaction is very weak.

The experimental results can be explained in this way. The $\chi^{-1}-T$ curve has a hyperbolic shape characteristic of a ferrimagnetic compound. The saturation moment at 4.2°K amounts to $0.87 \mu_B$, which is about equal to the difference between the magnetic moments of the Ni^{2+} and Mn^{4+} ion.

3. Other compounds

The results of the measurements on the other compounds cannot be explained so easily.

LiMn_2O_4 remains paramagnetic down to 4.2°K with a large asymptotic Curie temperature ($\theta_A = -260^\circ\text{K}$). One would expect a crystallographic order between the Mn^{3+} and Mn^{4+} ions on *B*-sites (distribution $\text{Li}[\text{Mn}^{3+}\text{Mn}^{4+}]\text{O}_4$) like in magnetite, $\text{Fe}^{3+}[\text{Fe}^{2+}\text{Fe}^{3+}]\text{O}_4$ ⁽¹⁷⁾, which should be reflected in the magnetic properties, but there is no indication of such a transition. This is perhaps due to clustering of Mn^{3+} ions.^(18,19)

The situation in CuCrMnO_4 is a little more clear (Fig. 5). The $\chi^{-1}-T$ curve is convex. In the region 300–500°K it approaches a straight line with a slope calculated for $\text{Cu}^+\text{Cr}^{3+}\text{Mn}^{4+}\text{O}_4$ (see Fig. 5); above 500°K it becomes more convex, due to the formation of Cu^{2+} and Mn^{3+} and below 300°K it is more or less hyperbolic. Below 45°K the compound shows a saturation moment, but saturation is not obtained in fields up to 30 kOe (Fig. 5), which probably indicates non-

collinear spin arrangements.⁽²⁰⁾ At low temperatures the cation distribution will be approximately $\text{Cu}^+[\text{Cr}^{3+}\text{Mn}^{4+}]\text{O}_4$, but long-range magnetic order on *B*-sites is not easy to achieve, because there is no crystallographic order. Moreover, the $\text{Cr}^{3+}-\text{Cr}^{3+}$ interaction is known to be strongly negative.⁽⁹⁾

In this connection something may be said about CuMn_2O_4 . We could not obtain pure samples of this compound. The same was reported by BONGERS⁽¹⁰⁾ and RIENÄCKER and WERNER.⁽²¹⁾ From the foregoing results there seems to be no doubt that the original idea of SINHA *et al.*⁽⁴⁾ is correct and that the charge distribution is $\text{Cu}^+[\text{Mn}^{3+}\text{Mn}^{4+}]\text{O}_4$. However, if the samples are cooled too rapidly, part of the Mn ions remain on *A*-sites, so that the distribution is then $\text{Cu}_{1-x}^+\text{Mn}_x^{3+}[\text{Cu}_x^{2+}\text{Mn}^{3+}\text{Mn}_{1-x}^{4+}]\text{O}_4$ (compare the discussion of $\text{CuMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$).

We could not prepare $\text{LiMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{LiCo}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with the correct oxygen contents (Table 1). The experimental values are somewhat too low. This implies that there is a certain amount of Mn^{3+} ions present. From Table 1 it is seen that $\text{LiMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$ does not behave like $\text{LiZn}_{0.5}\text{Mn}_{1.5}\text{O}_4$, nor $\text{LiCo}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Especially the fact that the samples could not be saturated in fields up to 30 kOe is noteworthy. This may be due to the presence of trivalent manganese. We expect that stoichiometric $\text{LiMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is ferromagnetic and stoichiometric $\text{LiCo}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ferrimagnetic.

Finally it is noted that the Cu^+ ion seems only to be stable in oxygen spinels, if Mn^{4+} is simultaneously present. Compare for example the compositions CuRhMnO_4 and CuRhTiO_4 . The first is a spinel, the second is not.

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REFERENCES

1. BLASSE G., *Philips Res. Rep.*, Supplements, No. 3 (1964), *J. Inorg. Nucl. Chem.* **25**, 230, 743 (1963) and **26**, 1473 (1964).
2. BLASSE G., *Philips Res. Rept.* **18**, 400 (1963).
3. BLASSE G., *Solid St. Comm.* **3**, 67 (1965).

4. SINHA A. P. B., SANJANA N. R. and BISWAS A. B., *J. Phys. Chem.* **62**, 191 (1958).
5. BALTZER P. K. and LOPATIN E., *Proc. Int. Conf. on Magnetism*, Nottingham, p. 564 (1964).
6. PLUMIER R., C.E.N., Saclay (personal communication).
7. DELORME C., Thèse, Grenoble (1956); SHEFTEL I. T., ZASLAVSKII A. I. and KURVLINA E. V., *Sov. Phys. Solid St.* **3**, 1979 (1962); AOKI I., *J. Phys. Soc. Japan* **20**, 871 (1964).
8. ANDERSON P. W., *Magnetism I* (editors RADO and SUHL) p. 25. Academic Press (1963).
9. GOODENOUGH J. B., *Phys. Rev.* **117**, 1442 (1960).
10. BONGERS P. F., Thesis, Leiden (1957).
11. NÉEL L., *Annls. Phys.* **3**, 137 (1948).
12. SWOBODA T. J., TOOLE R. C. and VAUGHAN J. D., *J. Phys. Chem. Solids* **5**, 293 (1958).
13. BLASSE G., *J. Phys. Chem. Solids* **26**, 1969 (1965).
14. BILLIET Y. and POIX P., *Bull. Soc. Chim. Fr.* 477 (1963).
15. HARDY A., LECERF A., RAULT M. and VILLIERS G., *C. R. Acad. Sci. Paris* **259**, 3462 (1964).
16. BLASSE G. and FAST J. F., *Philips Res. Rept.* **18**, 393 (1963).
17. VERWEY E. J. W. and HAAIJMAN P. W., *Physica Amsterdam* **8**, 979 (1941).
18. GOODENOUGH J. B., *J. Appl. Phys.* **36**, 2342 (1965).
19. BLASSE G., *Philips Res. Rept.* **20**, 528 (1965).
20. JACOBS I. S., *J. Phys. Chem. Solids* **15**, 54 (1960).
21. RIENÄCKER G. and WERNER K., *Z. anorg. Chem.* **327**, 275 (1964).