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Magnetic and Crystallographic Transitions in Sc^{3+}, Cr^{3+}, and Ga^{3+} Substituted Mn_2O_3

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X-ray diffraction and magnetic susceptibility measurements have been used to determine the phase diagrams, including magnetic phases, of the systems $(Mn_{1-x}M_x)_2O_3$, where $M \equiv Sc^{3+}, Cr^{3+}, Ga^{3+}$. Maximum values of x are 0.02, 0.13, and 0.27, respectively. Of the substituent ions Cr^{3+}, Fe^{3+}, Sc^{3+} and Ga^{3+}, Cr^{3+} reduces the crystallographic transition temperature least rapidly, Ga^{3+} and Sc^{3+}, most rapidly. Ga^{3+} ion substitution reduces the upper Néel temperature T_{N1} about as rapidly as does Fe^{3+} ion substitution to $x \approx 0.06$, and it appears that if specimens could be made to $x > 0.38$, there would be no more magnetic ordering in the $(Mn_{1-x}Ga_x)_2O_3$ system. Cr^{3+} ion does not decrease T_{N1} as drastically as either Ga^{3+} or Fe^{3+}; at 12-at% Cr^{3+}, T_{N1} is 68 K, while for an equal amount of Ga^{3+}, for example, it is 40 K; for 12-at.% Fe^{3+}, it is 25 K. These results imply that in this structure, empty t_{e_g} orbitals are particularly important to the magnetic interactions, and that Cr^{3+} with two empty t_{e_g} orbitals is more compatible with the Mn^{3+} ion than is any ion with a filled, half-filled, or empty d shell. Sc^{3+} ions reduce the lower Néel temperature T_{N2}; but Cr^{3+} ions raise it, apparently to meet T_{N1} at about 11 or 12% substitution. Ga^{3+}-ion substitution also raises T_{N2} at first; but beyond $x = 0.032$, it is not clear what happens to T_{N2} in this system. Nevertheless, it does seem that substituent ions smaller than Fe^{3+} raise T_{N2}, while Fe^{3+} and Sc^{3+} lower it.

I. INTRODUCTION

Crystals of α-Mn_2O_3 have a unique structure at room temperature[1-3]; it is a distortion of the bixbyite $(Mn_{0.5}Fe_{0.5})_2O_3$ structure. Among trivalent ion sesquioxides of Ti, V, Cr, Fe, and Ga, Mn_2O_3 is the only one that does not give a corundum-type structure. We have proposed elsewhere,[1] that this may be a result of the large Jahn-Teller distortion associated with Mn^{3+}. This has, to an extent, been confirmed by a crystal-structure determination.[2]

It was known from earlier work[4] that Mn_2O_3 undergoes an antiferromagnetic transition at 80 K. In our laboratory, a second magnetic transition was found[1,3,5] at 25 K. This transition was barely observed in a specimen prepared by solid-state reaction,[1,5] but looked like a first-order transition in flux-grown single crystals.[3]

Replacement of various amounts of Mn^{3+} by Fe^{3+} ion resulted in a rather steep drop in both Néel temperatures, the lower one decreasing to 0 K at about 1.5-cation-percent substitution. It appeared that at and beyond 9.0-cation-percent substitution, all $(Mn_{1-x}Fe_x)_2O_3$ remain cubic down to 0 K, and the Néel temperature then increases until 63-cation-percent (maximum) substitution is reached.[3] Using some previously reported neutron diffraction data in addition to that obtained in their investigation, Grant *et al.*[3] hypothesized a magnetic structure for the cubic phase. This structure, and very likely those of the orthorhombic phases, have noncollinear antiferromagnetic sublattices.

The magnetic behavior of the $(Mn_{1-x}Fe_x)_2O_3$ system is unusual in at least two respects: (1) a decrease in Néel temperature upon substitution of Fe^{3+} ion; (2) the nature of the lower magnetic transition. A suggestion was made regarding the latter in a previous paper.[3] We attempt an explanation of the former in the present paper.

To seek an explanation of the effect of Fe^{3+} ion substitution, we use the crystal-chemical approach. That is, we study the effects of substitution of other ions on the magnetic and crystallographic transitions and try to draw relevant inferences from these results. In this paper, we report the results of substitutions of Sc^{3+}, Cr^{3+}, and Ga^{3+} for Mn^{3+} ion. They shed some light on (1) above, but they also raise some additional questions.

II. EXPERIMENTAL

A. Apparatus

X-ray powder photographs were taken as follows: at room temperature with Norelco cameras of 114.59 mm diameter; at low temperatures with a Norelco camera adapted as described by Crandall[6]; at high temperatures with a Bond camera[7] built in our laboratory. Cr $K\alpha$ radiation was used for all photographs.

Magnetization studies were performed by observation of the force on a mass of randomly oriented crystals or powders in a Cu container suspended in an inhomogeneous magnetic field. Data were taken continuously as a function of temperature (see also Ref. 8). The magnetic data reported in the figures of this paper

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[1] S. Geller, J. A. Cape, R. W. Grant, and G. P. Espinosa, Phys. Letters **24A**, 369 (1967); R. W. Grant, J. A. Cape, S. Geller, and G. P. Espinosa, Bull. Am. Phys. Soc. **13**, 462 (1968).

[2] R. Norrestam, Acta Chem. Scand. **21**, 2871 (1967).

[3] R. W. Grant, S. Geller, J. A. Cape, and G. P. Espinosa, Phys. Rev. **175**, 686 (1968).

[4] E. G. King, J. Am. Chem. Soc. **76**, 3289 (1954); R. G. Meisenheimer and D. L. Cook, J. Chem. Phys. **30**, 605 (1959).

[5] S. Geller, R. W. Grant, J. A. Cape, and G. P. Espinosa, J. Appl. Phys. **38**, 1457 (1967).

[6] P. B. Crandall, Rev. Sci. Instr. **40**, 954 (1969).

[7] W. L. Bond, Rev. Sci. Instr. **29**, 654 (1958).

[8] J. A. Cape, Phys. Rev. **132**, 1486 (1963).

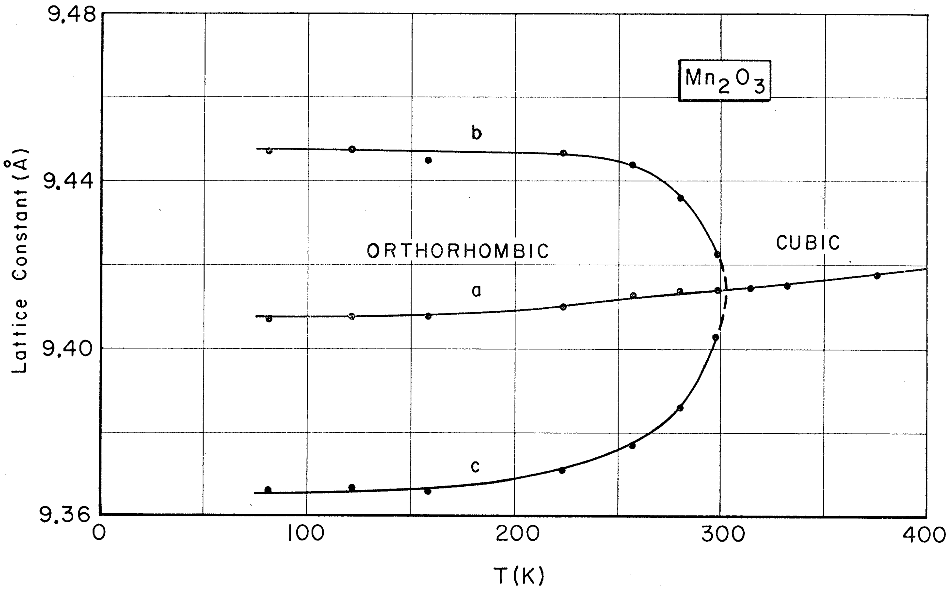

FIG. 1. Lattice constant versus temperature.

were taken at a field of 6 085 Oe with a gradient of 106 Oe/cm.

B. Sample Preparation

Specimens were of two types: single crystals, grown by a flux technique (to be reported separately) and polycrystalline, prepared by solid-state reaction, depending on the ease with which the required specimens could be obtained. In the Sc^{3+} substitutions, one specimen for $x=0.007$ was single crystal; for Cr^{3+}, also, only one, that for $x=0.01$. For Ga^{3+}, only one of the specimens (i.e., for $x=0.02$) on which magnetic measurements were made was prepared by solid state reaction but some specimens made by solid-state reaction were used to determine the x-dependence of the lattice constant. In some cases it was found expedient to fire these mixed with some flux to obtain specimens which gave sharp back-reflection lines in the powder photographs.

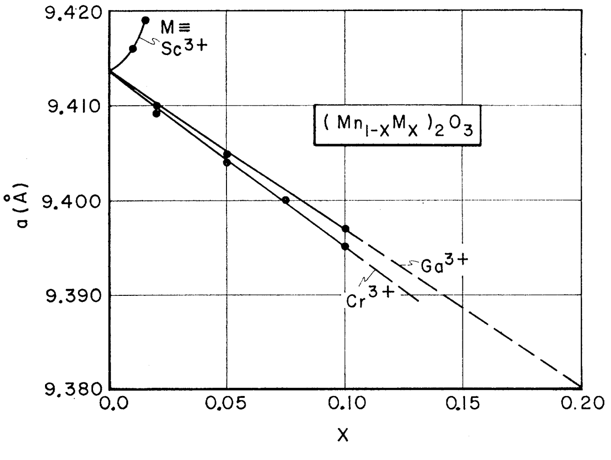

FIG. 2. Lattice constant versus composition.

Firing of specimens made by solid-state reaction was first carried out in the temperature range where the spinel was the stable phase. Final firings were carried out in the temperature region where the bixbyite-type phase was stable and usually in O_2 temperature.

In the case of the $(Mn_{1-x}Fe_x)_2O_3$ system,[3] we found that we were more successful in obtaining homogeneous specimens from flux-grown single crystals than from solid-state reaction of oxides. While the coprecipitation technique also gave homogeneous specimens, it is exceedingly tedious and time consuming. Because of the insignificant variation of lattice constant with composition in the $(Mn_{1-x}Fe_x)_2O_3$ system, the results of powder photography alone could not be used to determine anything about the homogeneity of the specimens. For Sc^{3+}, Ga^{3+}, and Cr^{3+} substitutions, the variation of lattice constant with composition is sufficient for such determination.

TABLE I. Lattice constants versus temperature for Mn_2O_3.

Temp. (K)	a (Å)	b (Å)	c (Å)
81	9.407	9.447	9.366
121	9.408	9.448	9.367
158	9.408	9.445	9.366
223	9.410	9.447	9.371
257	9.413	9.444	9.377
279	9.415	9.436	9.386
298	9.414	9.424	9.405
314[a]	9.414		
332	9.415		
375	9.418		
482	9.426		
702	9.443		

[a] Cubic above 302 K.

TABLE II. Lattice constants, $(Mn_{1-x}Sc_x)_2O_3$ system.

x	Temp. (K)	a (Å)	b (Å)	c (Å)
0.007	81	9.406	9.447	9.366
	233	9.418	9.444	9.383
	248	9.417	9.443	9.387
	268	9.416	9.437	9.390
	288	9.413	9.426	9.402
	298	9.415[a]		
0.01	298	9.416[a]		
0.015	298	9.419[a]		

[a] Cubic.

III. RESULTS

A. X-Ray Diffraction Studies

1. Mn_2O_3

Lattice constants of pure Mn_2O_3 were determined as a function of temperature. The powder specimen was obtained by grinding single crystals of pure Mn_2O_3. The values given (Table I and Fig. 1) for the orthorhombic phase were obtained mainly from the measurements of the 800, 080, and 008 lines. The results given in Ref. 3 indicate that the transition from cubic to orthorhombic symmetry is probably of higher than first order. Extrapolation of b and c to join at a indicates that the transition temperature is 302 K, slightly lower than our earlier estimate of 308 K.

2. $(Mn_{1-x}Sc_x)_2O_3$

Room-temperature lattice constants for this system are given in Table II and Fig. 2. Some lattice constants were also determined (Table II) for the $x=0.007$ specimen in the temperature region in which it is orthorhombic. The extrapolation to equality of these three lattice constants, such as for the pure Mn_2O_3, leads to a crystallographic transition temperature T_t of 294 K.

Low-temperature photographs were not taken of the specimen with $x=0.01$. When $x=0.015$, which appears to be very close to the maximum possible Sc^{3+} ion substitution, the low-temperature photographs indicate a T_t of 273 K.

TABLE III. Lattice constants at room temperature, crystallographic, T_t, and magnetic, T_{N1} and T_{N2}, transition temperatures, $(Mn_{1-x}Cr_x)_2O_3$ system.

x	a (Å)	T_t (K)	T_{N1} (K)	$T_{N2}(L)$
0.01	9.412	293	80	31
0.02	9.409		80	43
0.05	9.404	230	75.5	52
0.075	9.400	150	72	57
0.10	9.395		69.5	
0.12[a]	9.392		68	
0.13(max)[a]	9.390			

[a] Estimated from Fig. 2.

3. $(Mn_{1-x}Cr_x)_2O_3$

Lattice constants at room temperature for this system are given in Table III and Fig. 2. Low-temperature photographs were taken of several specimens. The specimen with $x=0.05$ has $a=9.399$ Å at 233 K; at 183 K it is orthorhombic with $a=9.397$, $b=9.415$, and $c=9.378$ Å. The specimen with $x=0.075$ is still cubic at 173 K with $a=9.391$ Å.

The plot of a, at room temperature, versus x (Fig. 2) is linear for this system. The composition of the single-crystal specimen with $x=0.01$ was determined from this plot. The minimum lattice constant observed in the system is 9.390 Å, implying a maximum Cr^{3+} ion substitution of 0.13. The composition of the specimen written $x=0.12$ was originally intended to be $x=0.13$, but its lattice constant 9.392 Å indicates $x=0.12$; this implies the presence of some unreacted Cr_2O_3, not seen in the x-ray powder photograph.

Crystallographic transition temperatures (see Table III) of some of the specimens were estimated from an examination of the low-temperature powder x-ray diffraction photographs. These are plotted versus composition in Fig. 3; though the extrapolation is long, it appears that beyond $x\cong 0.11$, all compositions are cubic down to 0 K.

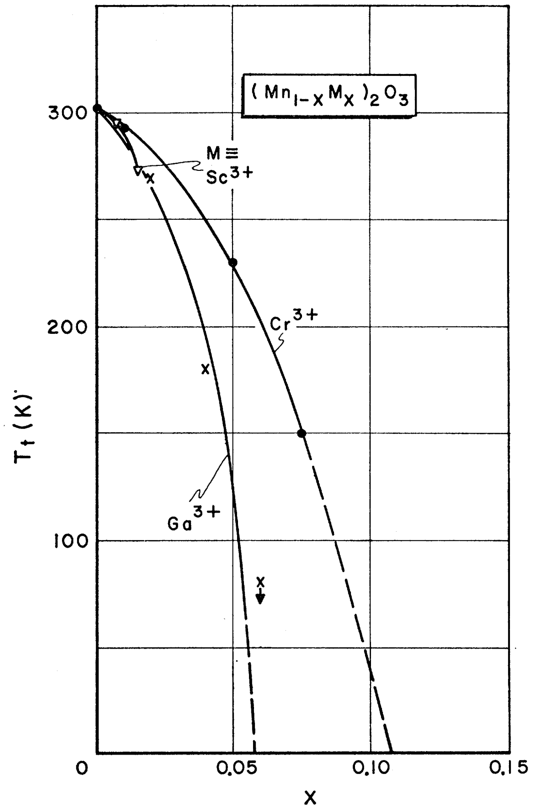

FIG. 3. Crystallographic transition temperature versus composition.

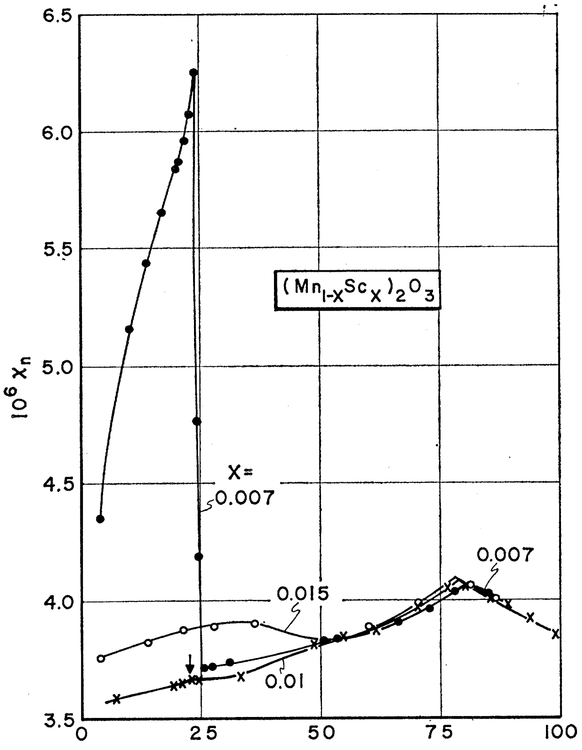

FIG. 4. Susceptibility χ_n (in Bohr magnetons per Oe, per formula unit) versus temperature.

4. $(Mn_{1-x}Ga_x)_2O_3$

Lattice constants at room temperature are given in Table IV and Fig. 2. Compositions listed in Table IV are those from specimens prepared by solid-state reaction, or from chemical analysis of flux-grown crystal specimens, or from Fig. 2. For the specimen with $x=0.02$, examination of low-temperature x-ray powder photographs indicates a T_t of 270 K. A photograph taken at 271 K (not measured) shows broadening of the back-reflection lines ($h^2+k^2+l^2=64$ and 66), which occurs very close to the transition. The specimen with $x=0.04$ appears to transform to the orthorhombic phase at 180 K, and with $x=0.06$ is still cubic at 80 K. A rather long extrapolation (Fig. 3) indicates that for values of $x>0.06$ all the specimens will be cubic down to 0 K.

TABLE IV. Lattice constants and magnetic transition temperatures, T_{N1} and T_{N2}, $(Mn_{1-x}Ga_x)_2O_3$ system.

x	a (Å) at 298 K	T_{N1}	T_{N2}
0.01	9.412	78	26
0.02	9.410	76.5	30
0.032	9.408	71	30
0.04	9.407	67	
0.05	9.405		
0.06	9.403	55	
0.08	9.400	48	
0.10	9.397		
0.13	9.392	39	
0.20	9.381	24	
0.27	9.369	16	

For $x=0.02$

T (K)	a (Å)	b (Å)	c (Å)
278	9.408	(cubic)	
253	9.408	9.426	9.387
223	9.409	9.432	9.378
173	9.405	9.437	9.373
80	9.397	9.435	9.366

B. Magnetic Studies

1. Mn_2O_3

A plot of χ versus T for Mn_2O_3 has been given previously[3] and will not be reproduced here. The important points are: (1) There is a broad peak of very low susceptibility in χ versus T centered at 79 K; and (2) there is anomalous behavior of χ versus T at 25 K, which we have taken to indicate a first-order transformation.

2. $(Mn_{1-x}Sc_x)_2O_3$

Measurements were made on all three specimens listed in Table II. The specimen with $x=0.007$ consisted of small single crystals grown from a flux, while the two others were made by solid-state reaction. The χ_n-versus-T results were dramatically different in the 25-K region (see Fig. 4). A large anomaly occurs for the specimen with $x=0.007$ at 24 K, which is indicative of a first-order transition and reminiscent of this occurrence in pure Mn_2O_3. However, for $x=0.01$ there is only a low peak, at 23 K, and for $x=0.015$, there appears to be a broad high region in the first 50 K, but no discernible peak, which should probably appear at about 21 K. The T_{N1} peaks were all rather sharp, contrasted with those of the $(Mn_{1-x}Fe_x)_2O_3$ system.

3. $(Mn_{1-x}Cr_x)_2O_3$

In this system, again, only one of the specimens (with $x=0.01$) consisted of small single crystals grown from the flux; the others were all polycrystalline, made by solid-state reaction. The specimen with $x=0.01$ gave a large anomalous peak at 31 K and a T_{N1} peak at 80 K, the nature of which is much closer to normal for an antiferromagnetic transition than the peaks observed in the $(Mn_{1-x}Fe_x)_2O_3$ system.

For specimens with $x=0.02$, 0.05, and 0.075, the T_{N2} peaks were easily discernible (see Fig. 5), though much lower relative to that for $x=0.01$. No T_{N2} peak occurred for specimens with $x=0.10$ and 0.12. All the T_{N1} peaks were low in susceptibility, but rather sharp in contrast to those in the $(Mn_{1-x}Fe_x)_2O_3$ system.

In Fig. 6, T_{N1} and T_{N2} are plotted versus x for this system.

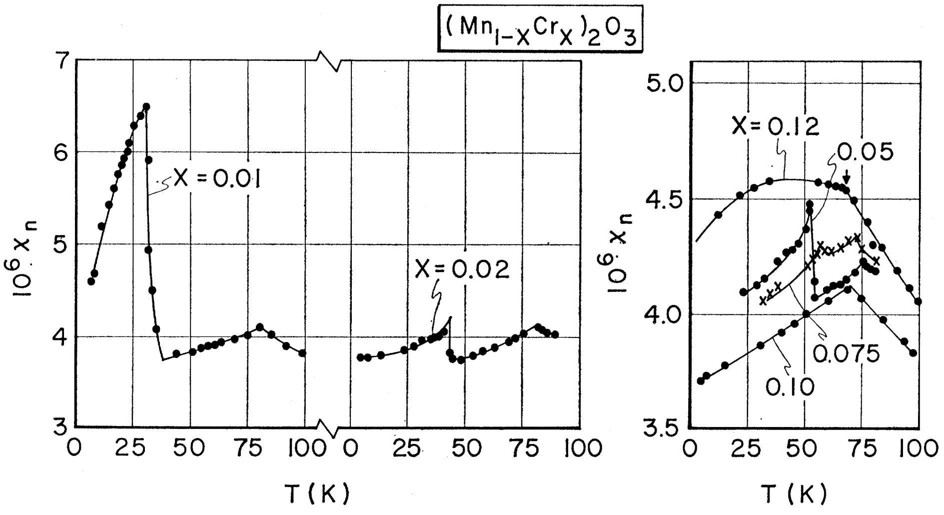

FIG. 5. Susceptibility χ_n (in Bohr magnetons per Oe, per formula unit) versus temperature.

4. $(Mn_{1-x}Ga_x)_2O_3$

Graphs of χ_n versus T in the regions of the transitions are shown in Fig. 7. As in most other cases, susceptibility differences are small over these temperature ranges. For all specimens, except with $x=0.20$ and 0.27, peaks are sharper than for the $(Mn_{1-x}Fe_x)_2O_3$ system. Because of overlap of curves, the one for $x=0.032$ is shown separately in Fig. 7; there is no question that the two magnetic transitions are observed. For $x=0.04$, however, the lower transition was not observed. It was also not observed in this specimen when a run was made at 2.0 kOe instead of at 6.1 kOe or after the specimen was annealed in O_2 for 66 h at 900 C.

C. Discussion

The results of the investigation of the $(Mn_{1-x}Fe_x)_2O_3$ system[3] implied the existence of a relation between the crystallographic transition and the upper Néel tem-

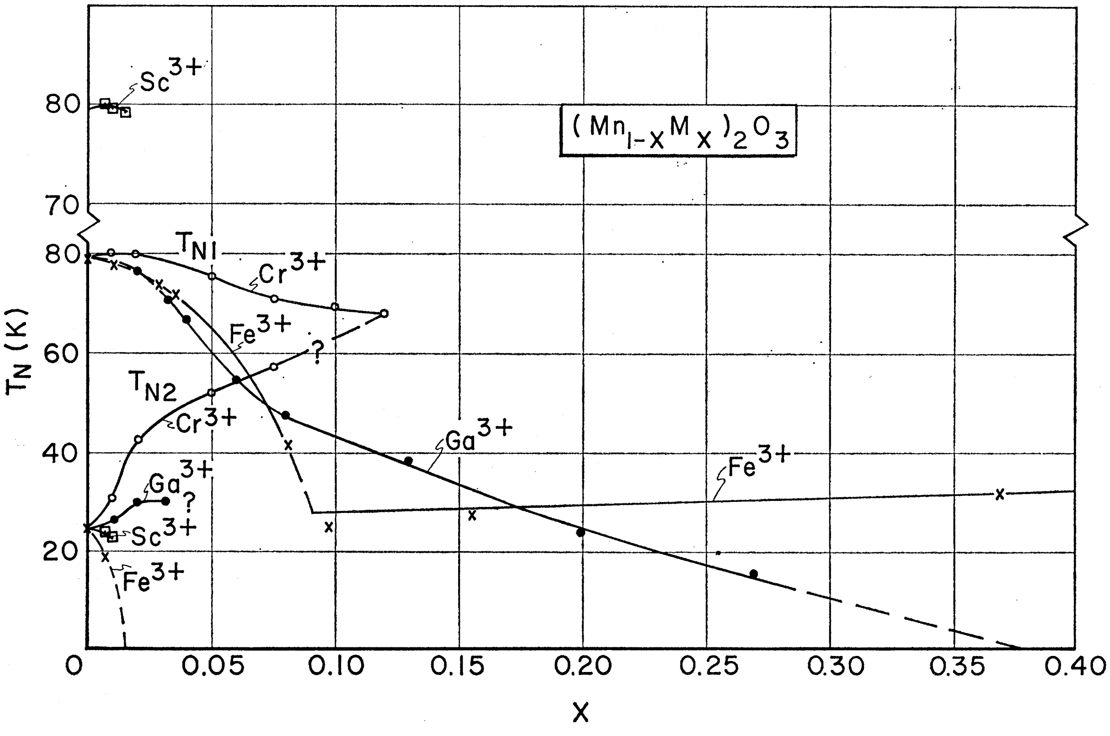

FIG. 6. Néel temperatures (T_{N1} and T_{N2}) versus composition.

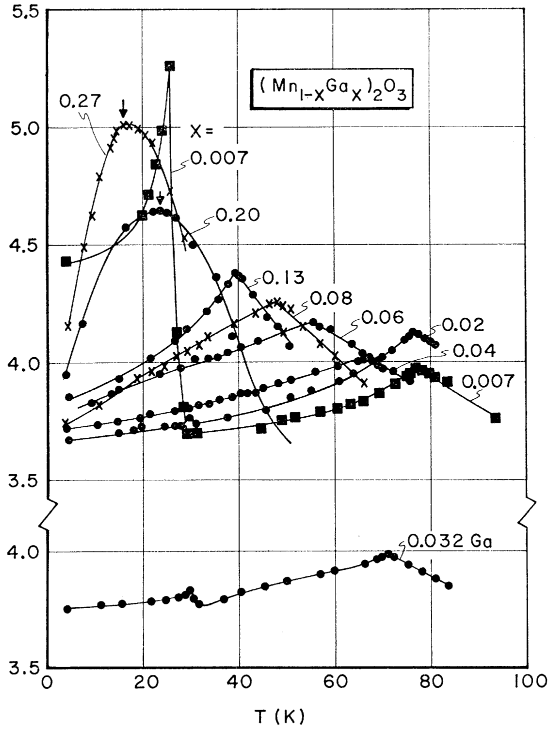

FIG. 7. Susceptibility χ_n (in Bohr magnetons per Oe, per formula unit) versus temperature.

perature T_{N1}. It was expected that some further clarification of this relation would result from the investigation reported here. This does not appear to be the case; the systems of substituted Mn_2O_3 appear to be more complex than anticipated.

It was expected that the temperature of the crystallographic transition from the cubic to orthorhombic phase for a given value of x would decrease with increasing substituent ion size. This implies that the value of x, beyond which all solid solutions are cubic down to 0 K, would increase with decreasing ion size. These relations do actually hold for Sc^{3+} and Cr^{3+} substitution—that is, the Sc^{3+} ion is considerably larger than the Fe^{3+} ion, the Cr^{3+} is somewhat smaller than the Fe^{3+} ion, and the plots of T_t versus x (Fig. 3) satisfy expectation. But the results for Ga^{3+} ion substitution (Fig. 3) are anomalous: The Ga^{3+} ion is slightly smaller than the Fe^{3+} ion, but in *relation to the cubic-to-orthorhombic transition*, as a function of composition, it behaves like a larger ion. It is possible that site preference plays a role, but we cannot use Mössbauer-effect spectroscopy to determine site occupancy in this case. Neutron diffraction or perhaps single-crystal x-ray diffraction could elucidate this role. We have not made such investigations as yet.

In the case of the $(Mn_{1-x}Fe_x)_2O_3$ system, the Néel temperatures T_{N1}, determined from χ versus T, plotted against x, showed where the solid solutions were cubic down to 0 K (see Fig. 5 of Ref. 3); this occurred at $x=0.09$, the same value at which $T_t=0$ K. For Sc^{3+} ion substitution such a relation cannot be determined because of the low solid solubility (maximum x) of Sc^{3+} in Mn_2O_3. For Ga^{3+} ion substitution, there is an inflection in T_{N1} versus x at about $x=0.06$, and it may be that this indicates the value of x at which the transition from orthorhombic to cubic occurs at 0 K. This would agree quite well with the value derived from T_t versus x (Fig. 3).

For values of $x \geqslant 0.08$, T_{N1} versus x for Ga^{3+} ion substitution is almost a straight line, which when extrapolated to $T_{N1}=0$, gives $x=0.38$. This implies that, if it were possible to make it, a 38-at.% (or greater) replacement of Mn^{3+} by Ga^{3+} (a diamagnetic ion), prevents magnetic order at any temperature. This is in contrast to the Fe^{3+} ion substitution, which at first rapidly lowers the transition temperature T_{N1} with increasing x to $x=0.09$, then increases it slightly (with increasing x) in the cubic phase (see Fig. 6).

It seems that *any* substitution other than Fe^{3+} *sharpens* the higher-temperature transition in contrast with that of Mn_2O_3 itself, and either broadens or eliminates the low-temperature transition (Figs. 4, 5, and 7).

In the rare-earth perovskitelike crystals,[9] both the Ga^{3+} and Cr^{3+} are smaller than the Fe^{3+} ions. The difference in size, however, between Fe^{3+} and Ga^{3+} is greater than that between Ga^{3+} and Cr^{3+}. As expected, this is seen to be the case when these ions are substituted for Mn^{3+} in Mn_2O_3 (Fig. 2 and Ref. 3). It appears that these smaller ions both raise T_{N2}; however, there are two anomalies. The curve of T_{N2} versus x (Fig. 6) shows that T_{N2} for 0.10 Cr^{3+} substitution should be 63 K, but no low-temperature transition is observed. We have seen that there is an extreme tendency for these low-temperature transitions to be broadened in the specimens prepared by solid-state reaction as well as by increased substitution; these may be the causes for our not observing this transition in the 0.10 Cr^{3+} specimen.

The situation in the $(Mn_{1-x}Ga_x)_2O_3$ system is, however, even more disturbing. In the $(Mn_{1-x}Cr_x)_2O_3$ system the increase in T_{N2} with increasing x is monotonic. In the former system, T_{N2} is the same for both $x=0.02$ and $x=0.032$. When $x=0.04$, the transition is not observed. The specimens with $x=0.032$ and 0.04 were both single crystals obtained by flux growth, whereas the specimen for $x=0.02$ was prepared by solid-state reaction, so that difference in method of preparation is not the answer.

In the system $(Mn_{1-x}Sc_x)_2O_3$, T_{N2} appears to be lowered by increasing x, but not by as much as for Fe^{3+} ion substitution, at least to $x=0.01$. However, T_{N2} is not observed (see Fig. 4) for the specimen with $x=0.015$ in this system. Both the specimen with

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[9] S. Geller, Acta Cryst. 10, 248 (1957).

$x=0.01$ and the one with $x=0.015$ were prepared by solid-state reaction. Thus, in this system it is probable that a T_{N2} for $x=0.015$ is not observed, because of the method of preparation of the specimen.

One of the most challenging aspects of the results of these investigations is to understand why the substitution of Fe^{3+} has such a devastating effect on the Néel temperature in the orthorhombic phase. In fact, it has almost the same effect as the substitution of diamagnetic Ga^{3+} ion. The results of Cr^{3+} ion substitution give a clue to the solution of this problem.

Ordinarily, one expects the strongest superexchange interactions in oxides to occur between Fe^{3+} ions. There are few cases in which substitutions of any other ion for Fe^{3+} ion in the same structural system produces an increase in Néel or Curie temperature. The only one we know[10] is the substitution of V^{5+} for Fe^{3+} ion and the simultaneous substitution of 2 Ca^{2+} for 2 Y^{3+} in YIG. Substitution of Cr^{3+} for Fe^{3+} ion in YIG lowers the Curie temperature[11]; it lowers the Néel temperature when substituted for Fe^{3+} ion in $CaFe_2O_4$.[12] However, substitution of Cr^{3+} for Mn^{3+} in Mn_2O_3 does not affect T_{N1} as drastically as Fe^{3+} ion substitution. At 12 cation-percent Cr^{3+} ion, T_{N1} is only reduced to 68 K. T_{N1} for 8% Cr^{3+} ion substitution is 71 K, while it is down to 42 K for 8% Fe^{3+} ion substitution.

It is known from Mössbauer-effect spectroscopy that in the cubic structure, Fe^{3+} ions show a preference for the higher-symmetry cation sites.[3,13] These ions must remain preferentially in the sites derived from the cubic structure. It seems rather unlikely that site preference would be the major cause of the difference in results between Cr^{3+} and Fe^{3+} ion substitution.

The explanation that appeals to us involves the electronic structure of the atoms. While the coordination in this structure is very far from regular, it is likely that the crystal field splitting is such that the t_{2g} orbitals are lowest in energy. We have suggested elsewhere[1] that Mn_2O_3 chooses the structure related to bixbyite as opposed to the corundum structure, because of the Jahn-Teller distortion of the Mn^{3+}, which is somehow more easily accommodated by the Mn_2O_3 structure. The results imply that in this structure, empty e_g orbitals are particularly important to the magnetic interactions, probably because of their effect on interaction geometry. The Cr^{3+} with two empty e_g orbitals is more compatible with the Mn^{3+} ion than is any ion with a filled, half-filled, or completely empty d shell.

Note added in proof. Another paper (by S. G.) related to this work, entitled "Structures of α-Mn_2O_3, $(Mn_{0.983}Fe_{0.017})_2O_3$ and $(Mn_{0.37}Fe_{0.63})_2O_3$ and Relation to Magnetic Ordering" is to be published in Acta Crystallographica.

ACKNOWLEDGMENTS

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[10] S. Geller, G. P. Espinosa, H. J. Williams, R. C. Sherwood, and E. A. Nesbitt, J. Appl. Phys. **35**, 570 (1964).

[11] M. A. Gilleo and S. Geller, Phys. Rev. **110**, 73 (1958).

[12] L. M. Corliss, J. M. Hastings, and W. Kunnmann, Phys. Rev. **160**, 408 (1967).

[13] E. Banks, E. Kostiner, and G. K. Wertheim, J. Chem. Phys. **45**, 1189 (1966).