PHYSICAL REVIEW VOLUME 164, NUMBER 2 10 DECEMBER 1967

Magnetic Study of the Manganate Phases: $CaMnO_3$, $Ca_4Mn_3O_{10}$, $Ca_3Mn_2O_7$, Ca_2MnO_4

J. B. MacChesney, H. J. Williams, J. F. Potter, and R. C. Sherwood
Bell Telephone Labaratories, Murray Hill, New Jersey

(Received 24 April 1967)

Two series of manganate phases have been prepared and their magnetic properties measured. The first series consists, in addition to $CaMnO_3$, of three phases having layered structures. In these, tetravalent magnanese ions are contained in single or multiple perovskite layers which are separated from each other by nonmagnetic calcium-oxygen layers. Magnetic exchange of the type Mn^{4+}-O-Mn^{4+} is disrupted between layers, and decreased Néel temperatures were expected to result. In a second series of phases, the size of of the $CaMnO_3$ unit cell was increased by partial substitution of strontium for calcium. Increased separation of manganese ions produced by this means was expected to reduce Néel temperatures. However, contrary to these expectations, Néel temperatures remained approximately constant for the first series of phases and increased for the second.

I. INTRODUCTION

CONDITIONED by the success and almost universal acceptance of the concept of superexchange in explaining magnetic interactions of the transition metal oxides, the magnetician's first impulse is to invoke this when considering perovskite phases containing 3*d* transition metal ions. Thus we sought to apply this concept to the magnetic properties of a series of manganate (tetravalent manganese) compounds. This series is based upon the perovskitelike structure of $CaMnO_3$. With increased calcium fraction, three related phases are formed. In these Mn^{4+} ions are contained in either single or multiple perovskite layers which are separated from each other by interleaved calcium-oxygen layers. The consequence of these structures is that 180° exchange persists within these layers, but is prevented or at least drastically reduced between layers.

The implication of such a structural series to exchange parameters is obvious if one considers the molecular field approximation for the Néel temperature T_n:

$$kT_n \approx -\tfrac{2}{3} z J_{\mathrm{ex}} S(S+1).$$

Here z is the number of nearest-neighbor magnetic ions of spin S and J_{ex} the exchange integral. This equation predicts decrease of Néel temperature in proportion to the decrease in the number of nearest-neighbor manganese ions capable of participating in 180° exchange, provided J_{ex} remains constant.

The dependency of the exchange integral upon cell geometry leads to another implication of superexchange. As discussed by Goodenough,[1] this should be sensitive to the separation between Mn^{4+} ions if other exchange parameters are maintained constant. Therefore, it was expected that enlargement of the perovskite unit cell by substitution of larger *A*-site cations for calcium would cause a decrease in Néel temperatures.

In the present work we have prepared two series of polycrystalline specimens whose magnetic properties we anticipated would conform to the foregoing premises. In the first case, starting with $CaMnO_3$,[2] by increasing the calcium content, tetragonal phases $Ca_4Mn_3O_{10}$,[3] $Ca_3Mn_2O_7$,[4] and Ca_2MnO_4[5] were synthesized. The second series were formed by partial substitution of divalent strontium (radius 1.18 Å) for divalent calcium (radius 1.06 Å) of $CaMnO_3$. Solid solution phases up to the composition $Ca_{0.75}Sr_{0.25}MnO_3$ were prepared with significant enlargement of the unit-cell parameters.

Decreased Néel temperatures, anticipated for both series, were not found. The apparent anomalous behavior is explored in this article, and an explanation of it is pursued by Goodenough in the following article.

II. EXPERIMENTAL

Starting mixtures were prepared by conventional ceramic techniques. Pellets pressed from these powders were fired in air and then annealed at high oxygen pressures to maximize the tetravalent manganese concentrations. Most specimens responded well to annealing at low temperatures, as can be attained in conventional hydrothermal apparatus.[6] However, $Ca_3Mn_2O_7$ required higher temperatures which could only be attained in an internally heated pressure vessel. The experimental conditions employed in the preparation, along with the measured crystallographic parameters and chemical analyses for the tetravalent manganese concentration, are given in Table I. Chemical analyses, by the procedure described previously,[7] were used to determine the tetravalent manganese concentration shown in these tables. Lattice constants were determined by Debye-Scherer and diffractometer patterns were obtained using Cr $K\alpha$ radiation and were

---

[1] J. B. Goodenough, following paper, Phys. Rev. **164**, 785 (1967).

[2] E. O. Wollan and W. C. Koehler, Phys. Rev. **100**, 545 (1955).

[3] C. Brisi and M. Lucco-Borlera, J. Inorg. Nucl. Chem. **27**, 2129 (1965).

[4] C. Brisi, Ann. Chem. (Rome) **51**, 1399 (1961).

[5] S. N. Ruddlesden and D. Popper, Acta Cryst. **10**, 538 (1951); C. Brisi and M. Lucco-Borlera, Atti. Acad. Sci. Torino **96**, 805 (1961–62).

[6] O. F. Tuttle, Am. J. Sci. **246**, 628 (1948).

[7] J. B. MacChesney, R. C. Sherwood, and J. F. Potter, J. Chem. Phys. **43**, 1907 (1965).

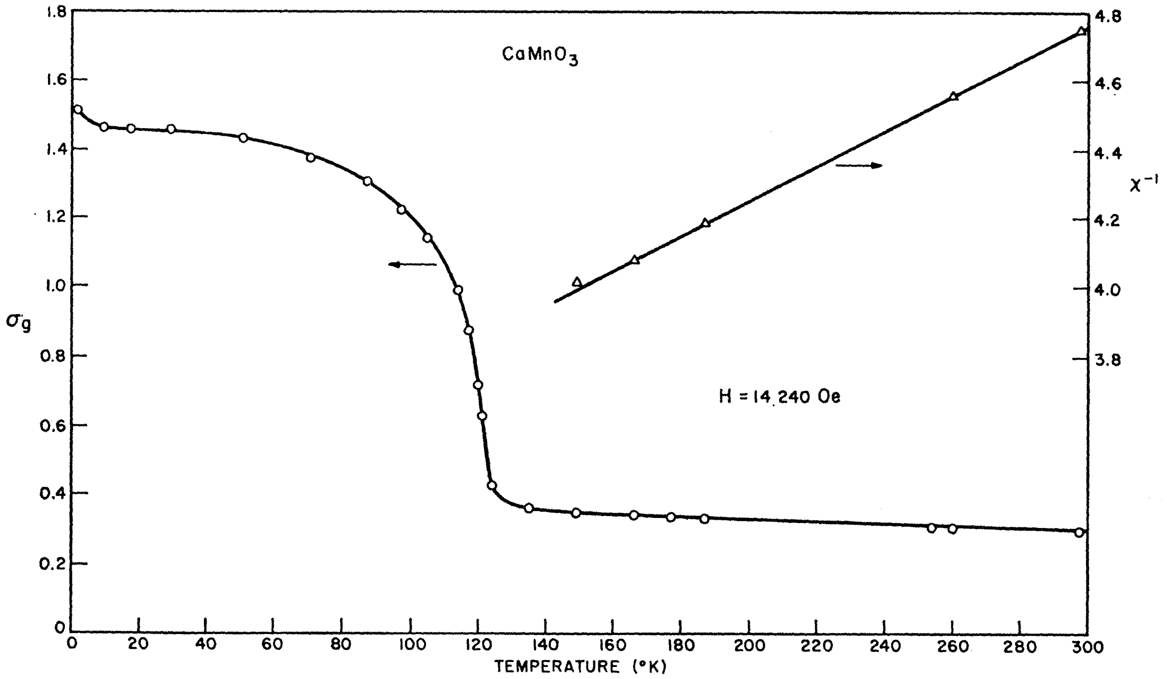

FIG. 1. Magnetization (emu/g) versus temperature for $CaMnO_3$.

refined by the method of Mueller, Heaton, and Miller.[8] Measurements of magnetization versus temperature were obtained using a pendulum magnetometer.[9] Resistivity measurements were made at room temperature and at liquid-nitrogen temperature. The four-probe technique was used for specimens having low resistance ($<10^6\Omega$), while two probe measurements were made for higher resistance specimens.

III. RESULTS

The results are summarized in Table I, which is divided into three sections: The first describes the experimental conditions employed in specimen preparation, the second gives unit cell spacings, and the third salient electrical and magnetic properties. Magnetic measurements are further detailed by diagrams of magnetization versus temperature, Figs. 1–6. The first four represent measurements for the phases $CaMnO_3$, $Ca_4Mn_3O_{10}$, $Ca_3Mn_2O_7$, and Ca_2MnO_4. It is to be noted that Néel temperatures—obtained either from inflections or maxima of the σ-versus-T curves—all occur within the temperature range 110–125°K. These curves further indicate that the first two phases are weakly ferromagnetic and the latter two antiferro-

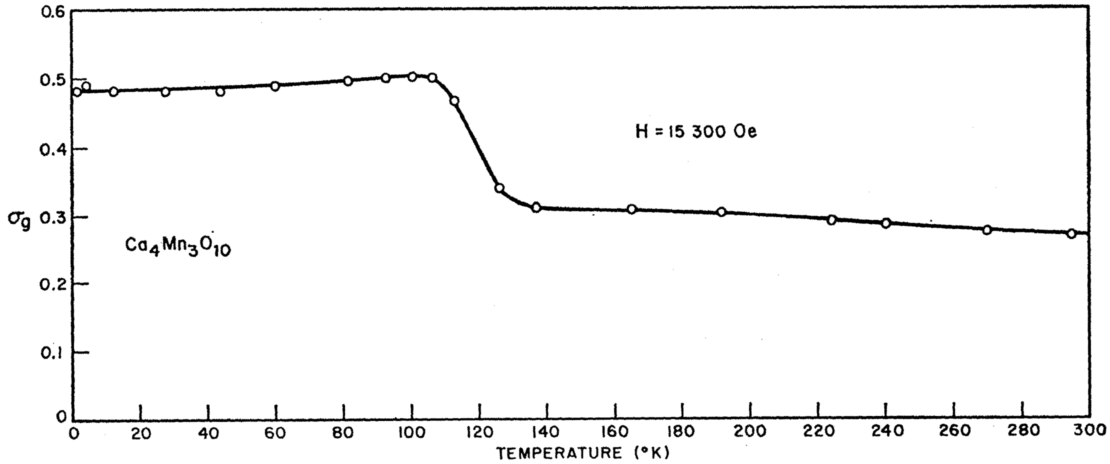

FIG. 2. Magnetization (emu/g) versus temperature for $Ca_4Mn_3O_{10}$.

---

[8] M. H. Mueller, L. Heaton, and K. T. Miller, Acta Cryst. **13**, 828 (1960).

[9] R. M. Bozorth, H. J. Williams, and D. E. Walsh, Phys. Rev. **103**, 572 (1956).

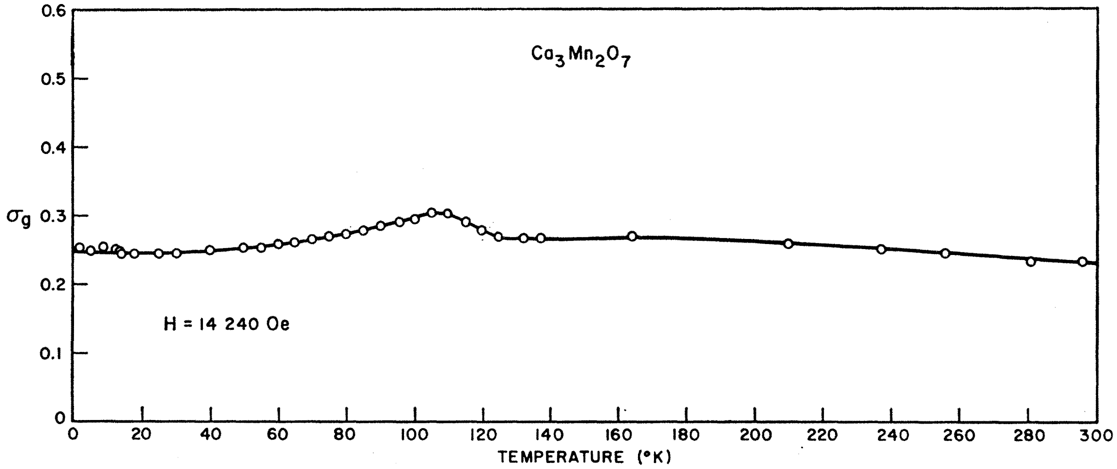

FIG. 3. Magnetization (emu/g) versus temperature for $Ca_3Mn_2O_7$.

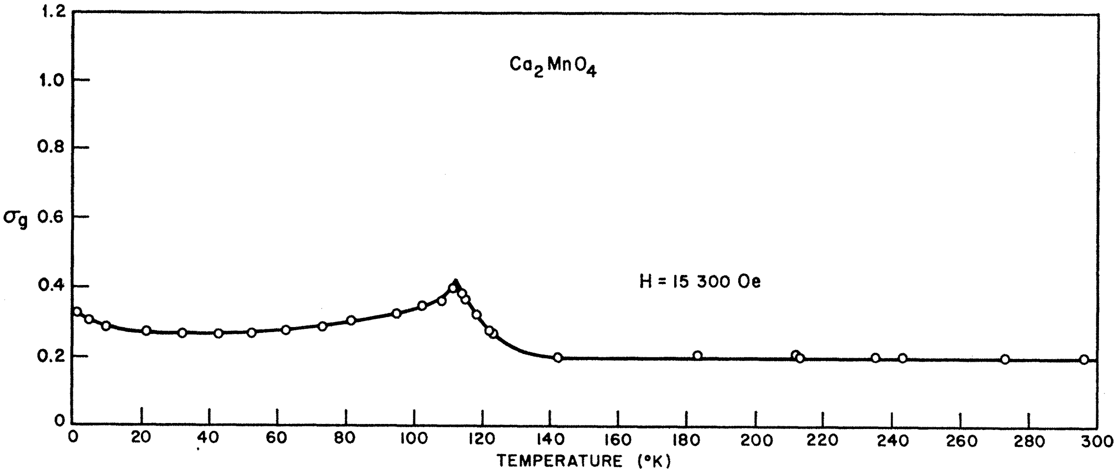

FIG. 4. Magnetization (emu/g) versus temperature for Ca_2MnO_4.

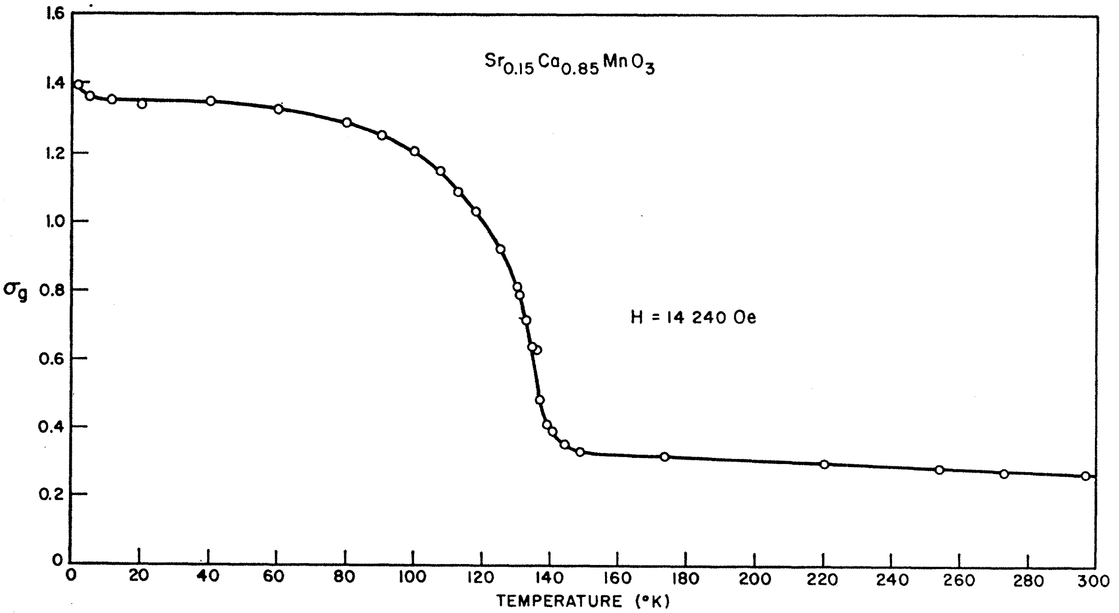

FIG. 5. Magnetization (emu/g) versus temperature for strontium-substituted specimen $Ca_{0.85}$ $Sr_{0.15}MnO_3$.

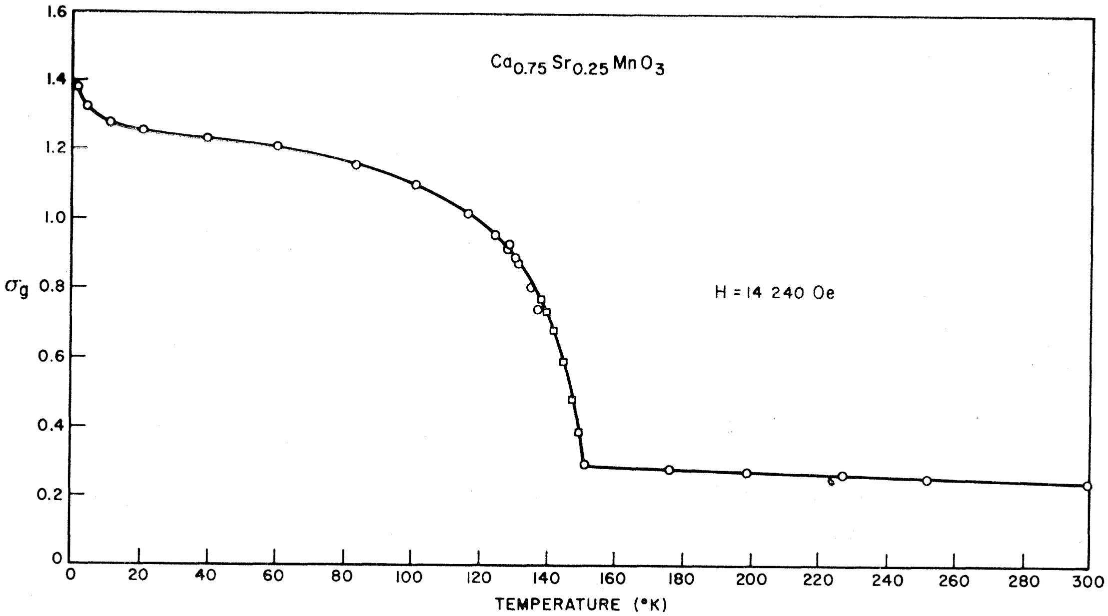

Fig. 6. Magnetization (emu/g) versus temperature for $Ca_{0.75}Sr_{0.25}MnO_3$.

magnetic below T_n. The similarity between $CaMnO_3$ and $Ca_4Mn_3O_{10}$ is preserved above T_n; both are presumed to exhibit Curie-Weiss behavior at temperature sufficiently above the Néel temperature. Magnetization values for Ca_2MnO_4 (see note added in proof) and probably $Ca_3Mn_2O_7$, on the other hand, appear temperature-independent in this region.

Figures 5 and 6 show curves of magnetization versus temperature for the strontium-substituted specimens. Here, weak ferromagnetism exhibited by $CaMnO_3$ (presumably resulting from the anisotropy imposed by orthorhombic distortion) is preserved, but it is to be noted that there is a significant rise in Néel temperature which is roughly proportional to the strontium substitution and concomitant enlargement of the unit cell.

IV. DISCUSSION

Before discussing the results, let us consider in a bit more detail the structures of these phases which are pictured in Fig. 7. First observe—in the case of the layered structures—that in addition to the insertion of nonmagnetic calcium-oxygen layers between single or multiple perovskite layers, the positions of manganese ions alternate between the edge and center of the unit cell. Thus, no oxygen ion (of the nonmagnetic layer) is shared between manganese ions of adjacent perovskite layers. It follows then that there can be no 180° superexchange interactions along this direction. Therefore, in this structural series, the number of exchange interactions per manganese ion must decrease from 6 for the perovskite phase to $5\frac{1}{3}$, 5, and finally 4 for Ca_2MnO_4. This would be expected to decrease the Néel temperature from 123°K for $CaMnO_3$ to $\frac{2}{3}$ that value for Ca_2MnO_4.

Just this type of behavior has been observed for the potassium nickel fluorides, $KNiF_3$[10] and K_2NiF_4.[11] Here, analogy to $CaMnO_3$ and Ca_2MnO_4 is valid because the comparable phases have identical structures. The type of magnetic order exhibited by K_2NiF_4 has

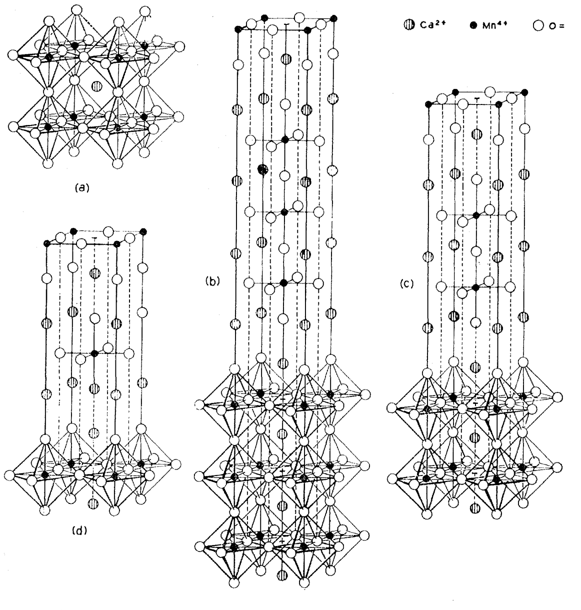

Fig. 7. Drawing showing structure of phases discussed in the text. For simplicity the slight orthorhombic distortion of $CaMnO_3$ has been ignored and the perovskite pseudocell pictured in (a); $Ca_4Mn_3O_{10}$ is shown in (b); $Ca_3Mn_2O_7$ in (c); and Ca_2MnO_4 in (d).

---

[10] R. L. Martin, R. S. Nyholm, and N. C. Stephenson, Chem. Ind. (London) **3**, 38 (1956).

[11] F. Legrand and R. Plumier, Phys. Status Solidi **2**, 317 (1962).

been determined by neutron diffraction.[11] It was found that the spins of the nickel ions were aligned antiparallel within the (001) lattice plane and that exchange between adjacent planes of ions is presumably extremely weak or nonexistent. Of even more relevance to the present study, they also found that the Néel temperature of this phase was 180°K, almost exactly $\frac{2}{3}$ that of $KNiF_3$ (275°K).

To account for this seeming contradiction, the thesis can be advanced that manganates would not show this behavior if the strength of the magnetic exchange increased along the series from $CaMnO_3$ to Ca_2MnO_4 in such a manner as to compensate for the decreased number of interactions per manganese ion. There is some reason to expect this since it is observed in Table I that the *a*-lattice[12] dimensions decrease along the series reaching their lowest value for Ca_2MnO_4. It was just to test this assumption that we prepared the strontium-substituted specimens.

It is apparent that the lattice spacings of these are increased as intended, while the symmetry of $CaMnO_3$ is preserved throughout the range of composition investigated. However, the expected decrease in Néel temperature did not follow; in fact, Néel temperatures increased.

Of course, the question can always be asked: Why consider superexchange? Does not double exchange offer a more plausible mechanism for these materials? Certainly the phases discussed are not particularly good insulators (see Table I), and canting of opposed magnetic sublattices[13] required by the type of exchange gives a possible explanation for the appearance of parasitic ferromagnetism.

However, there are problems here also. First of all, the spontaneous moment determined in the present investigation for a sample consisting of essentially all tetravalent manganese is much larger than that reported by Yudin *et al.*,[14] for a specimen containing a significant trivalent manganese concentration. Presumably, by this mechanism, the moment should be proportional to the number of carriers, i.e., the Mn^{3+} concentration, and the magnitude of the moments should be reversed. Even neglecting this contradiction, however, it is difficult to understand how applications of this mechanism will alleviate the dilemma involving the layered structures. As formulated by de Gennes,[13] the contribution of double exchange energy to the total exchange energy must be small and would not be thought to compensate for the reduced number of interactions. Although a more detailed consideration of double exchange is warranted, it appears to offer no immediate solution to the problem at hand.

TABLE I. Specimen preparation and characterization.

		Preparation conditions					Lattice constants		Néel temperature	Resistivity	
	% Mn^{4+}	Sint. temp. air (°C)	Firing temp. air (°C)	Anneal. temp. oxygen (°C)	Oxygen pressure (psi)	Anneal. time (h)	*a* (Å)	*b* (Å)	*c* (Å)	T_n (°K)	$\rho_{298°K}$ (Ω cm)	$\rho_{78.5°K}$ (Ω cm)
$CaMnO_{2.98}$	96	1100	1250	400	14 500	154	5.270±0.002 (3.729[a])	5.275±0.002	7.464±0.002	123	1.6	3.2×10^3
$Ca_{0.85}Sr_{0.15}MnO_{2.98}$	96	1200	1350	400	14 000	168	5.291±0.002 (3.744[a])	5.296±0.002	7.488±0.002	139	...	...
$Ca_{0.75}Sr_{0.25}MnO_{2.98}$	96	1175	1350	400	14 500	112	5.304±0.002 (3.753[a])	5.302±0.002	7.488±0.002	150	0.65	7.2×10^3
$Ca_4Mn_3O_{9.96}$	97	1130	1350	508	10 000	156	3.724±0.002	...	26.90±0.01	125	1.5×10^1	1.1×10^4
$Ca_3Mn_2O_{6.97}$	97	1100	1350	1320	3 200	16	3.709±0.002	...	19.44±0.01	110[b]	1.4×10^3	6.6×10^{10}
$Ca_2MnO_{4.0}$	99.6	1100	1350	740	17 000	168	3.667±0.002	...	12.063±0.01	114	1.0×10^4	9.7×10^8

[a] Perovskite pseudocell. [b] Transition temperature poorly defined.

---

[12] The comparison becomes a bit more obvious if we compare the *a*-lattice dimensions of the layered specimens with that of the perovskite pseudocell which is found to be 3.729 Å.

[13] P. G. DeGennes, Phys. Rev. **118**, 141 (1960).

[14] V. M. Yudin, A. I. Gavrilishina, M. V. Artem'eva, M. F. Brazhina, Fiz. Tverd. Tela **7**, 2292 (1965) [English transl.: Soviet Phys.—Solid State **7**, 1856 (1966)].

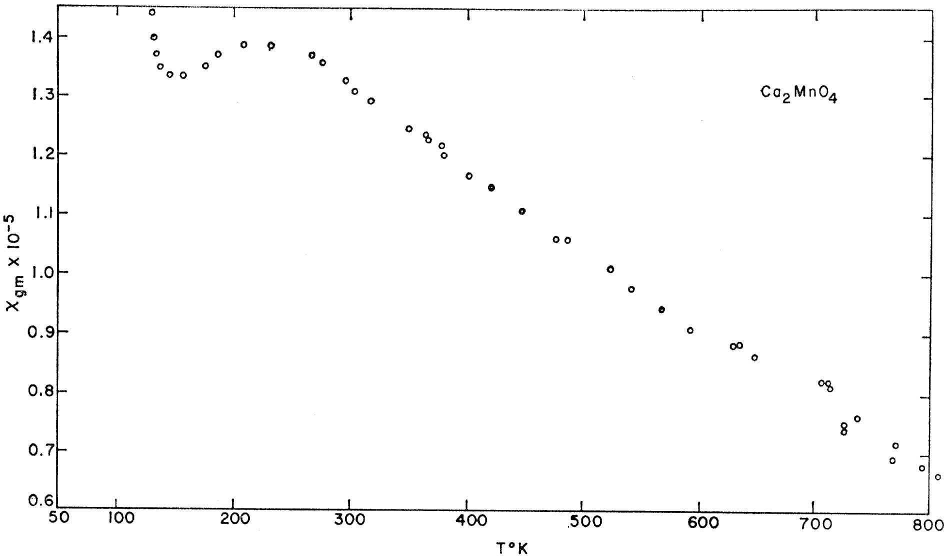

FIG. 8. Susceptibility-versus-temperature data of Ca_2MnO_4 taken by Davis (see Ref. 18). These measurements extend the data on this specimen, shown in Fig. 4, to higher temperature.

At this point, conceding that our results are enigmatic, we have chosen to abandon further search for their explanation in favor of a more careful scrutiny of our experimental data. At least we hope to assure the reader that we have considered some of the more obvious pitfalls and can neglect these. Our concern is with whether the specimens are monophasic, whether the manganese ion is in the tetravalent state, and whether the peaks observed in the magnetization should be considered as Néel temperatures.

Concerning the first question, $CaMnO_3$ or MnO, whose Néel temperatures are near 120°K, conceivably could be present in the layer structured specimens and give rise to the observed peaks in magnetization. In answer to this, it can first be stated on chemical grounds that the presence of MnO is unlikely. At the temperatures at which these specimens were annealed, the equilibrium oxygen pressure necessary for the stable existence of the MnO phase[15] is more than 20 orders of magnitude lower than that employed. If $CaMnO_3$ were present, on the other hand, it would have to comprise 20% of specimen $Ca_4Mn_3O_{10}$ to account for the observed thermal-magnetization curve. This quantity would certainly give rise to discernible diffraction peaks on x-ray photographs.

The valence state of the manganese is established by the analysis for oxidizing power of the specimens. Although wet chemical analyses tend to be imprecise ($\pm 1\%$ Mn^{4+}), they are reliable. Independent evidence that tetravalent manganese is the dominant species present and that these ions are responsible for the observed magnetic order is given by electron-paramagnetic-resonance experiments of Gossard.[16] He studied the Ca_2MnO_4 and $CaMnO_3$ phases, along with that of MnO. Here it is important to realize that in the event the expected tetravalent state of manganese occurs in Ca_2MnO_4 and $CaMnO_3$, the ground-state configuration should be the orbital singlet $^4A_2$ state, with a magnetic moment of 3 Bohr magnetons per manganese ion. At temperatures above the Néel temperatures, these ions would be expected to give rise to a paramagnetic resonance at a frequency corresponding to the spin-only value of $g=2$. Such behavior was indeed observed, with Ca_2MnO_4 showing a resonance of $g=2.00\pm0.01$ and $CaMnO_3$ a resonance at $g=2.00\pm0.02$ in fields of 17 000 G. Observed resonance linewidths were 615 ± 30 G and 1420 ± 60 G, respectively, at room temperature, and in both cases (as in MnO), the resonances broadened at lower temperatures, becoming unobservable below the previously stated Néel temperatures. Disappearance of these resonances confirms the occurrence of magnetic ordering, while the observed g value is consistent with the occurrence of the tetravalent valence state of manganese in an octahedral environment.

The assumption that the Néel temperature is synonymous with the peak or inflection in the magnetization curve may not be strictly correct. It is quite common for the Néel temperature, denoting the breakup of long-range magnetic order, to occur a few degrees below the peak curves of magnetization versus temperature. This effect can be exaggerated in the case of two-dimensional structures such as that of K_2NiF_4, where the persistence of short-range order can be deceptive. In the latter case, susceptibility measurements by Srivastava[17] show a broad maxima some 50–70°K above the ordering temperature determined by neutron diffraction.[11] The $Ca_3Mn_2O_7$ and Ca_2MnO_4 phases of the present investigation could be similar.

---

[15] C. Klingsberg and R. Roy, J. Am. Ceram. Soc. **45**, 620 (1960).

[16] A. C. Gossard (private communication).

[17] K. G. Srivastava, Phys. Letters **4**, 55 (1964).

V. CONCLUSIONS

Magnetization measurements have been made on two series of phases related structurally to the perovskite phase $CaMnO_3$. In the first of these, nonmagnetic layers are present between single or multiple perovskite layers. Magnetic exchange between perovskite layers—across these nonmagnetic layers—is severely weakened and should result in lowered magnetic-ordering temperatures. This, however, appears not to be the case; the apparent Néel temperatures for all phases are nearly the same. A second series of specimens was prepared by partial substitution of strontium for calcium. This resulted in enlargement of the perovskite unit cell. Again lowered Néel temperatures were expected but were not found. On the contrary, Néel temperatures increased with increases in cell size. The reason for this behavior is not apparent from cursory examination of superexchange theory.

Note added in proof. Subsequent to the completion of this work J. L. Davis[18] of these Laboratories has extended to higher temperatures the susceptibility measurements of Ca_2MnO_4. These show (Fig. 8) a weak broad maximum at temperatures between 200° and 250°K and are in agreement with the expectations voiced by Lines[19] in another paper.

ACKNOWLEDGMENTS

The authors are indebted to A. C. Gossard for spin-resonance measurements, to M. E. Lines, E. M. Gyorgy, and L. G. Van Uitert for informative discussions, and to J. M. Longo of the Lincoln Laboratory, Lexington, Massachusetts, for pointing out the reference to the $Ca_4Mn_3O_{10}$ phase.

---

[18] J. L. Davis (private communication).

[19] M. E. Lines, Phys. Rev. **164**, 736 (1967).

PHYSICAL REVIEW VOLUME 164, NUMBER 2 10 DECEMBER 1967

Localized versus Collective *d* Electrons and Néel Temperatures in Perovskite and Perovskite-Related Structures

John B. Goodenough

Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts*

(Received 24 April 1967)

It is pointed out that a simple, localized-electron antiferromagnet having one electron per localized orbital interacting via 180° superexchange with similar orbitals on z near-neighbor cations via an overlap integral Δ has a Néel temperature

$$kT_n \approx z\{q_t b_t^2 + q_e b_e^2\}(S+1)/S,$$

where q_t, q_e are inversely proportional to electrostatic energies associated with electron transfers; $b_t \sim \epsilon_0 \Delta_t$ and $b_e \sim \epsilon_0' \Delta_e$ are the one-electron transfer integrals of states having t_{2g} and e_g symmetry, respectively. On the other hand, a collective-electron antiferromagnet having a half-filled band that is split in two by the magnetic ordering would have a kT_N that decreased with increasing bandwidth, and hence increasing Δ. This provides a criterion for distinguishing the two cases: $dT_N/dp > 0$ for localized-electron antiferromagnetism and $dT_N/dp < 0$ for collective-electron antiferromagnetism, where p is the hydrostatic pressure. It is therefore surprising that $dT_n/da_0 > 0$, where a_0 is the cation-anion-cation separation, in the systems $Ca_{1-x}Sr_xMnO_3$, $A^{3+}FeO_3$, and $A^{3+}CrO_3$, since independent data indicate that the d electrons are localized. This fact is attributed to changes in A-O covalent bonding that cause Δ to increase with the more basic A cation for a given lattice parameter. The relatively small changes in T_N with z in the series $CaMnO_3$, $Ca_4Mn_3O_{10}$, $Ca_3Mn_2O_7$, and Ca_2MnO_4, where geometric considerations alone determine the relative magnitudes of Δ, are shown to be consistent with $dT_N/da_0 < 0$. However, it is pointed out that the magnitude of this geometrical contribution, which should approach a maximum at the localized-electron$\rightleftarrows$collective-electron transition, suggests there may be a change from localized d electrons in $CaMnO_3$, to collective d electrons in Ca_2MnO_4. The fact that the paramagnetic susceptibility obeys a Curie-Weiss law in $CaMnO_3$, but appears to be temperature-independent in Ca_2MnO_4, supports this view.

I. INTRODUCTION

FROM the Néel molecular-field theory of antiferromagnetism for a simple two-sublattice structure having only intersublattice exchange interactions, the Néel temperature T_N is given by the expression

$$kT_N \approx -\tfrac{2}{3} z J_{\mathrm{ex}} S(S+1), \qquad (1)$$

where z is the number of nearest magnetic neighbors to a magnetic cation of spin S and $J_{\mathrm{ex}} < 0$ is the exchange parameter entering the Heisenberg exchange Hamiltonian

$$\mathcal{H}_{\mathrm{ex}} = -\sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j = zNJ_{\mathrm{ex}}S^2, \qquad (2)$$

where N is the number of magnetic cations. Such a Heisenberg Hamiltonian has been rationalized for the

---

* Operated with support from the U.S. Air Force.