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$_2$MnO$_4$. 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.

[18] J. L. Davis (private communication).
[19] M. E. Lines, Phys. Rev. **164**, 736 (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$_x$MnO$_3$, 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$_4$Mn$_3$O$_{10}$, Ca$_3$Mn$_2$O$_7$, and Ca$_2$MnO$_4$, 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$\rightleftharpoons$collective-electron transition, suggests there may be a change from localized d electrons in CaMnO$_3$, to collective d electrons in Ca$_2$MnO$_4$. The fact that the paramagnetic susceptibility obeys a Curie-Weiss law in CaMnO$_3$, but appears to be temperature-independent in Ca$_2$MnO$_4$, 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

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

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

$$\mathcal{3C}_{ex} = -\sum_{ij} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j = zNJ_{ex}S^2, \qquad (2)$$

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

case of localized d electrons by superexchange theory, which gives

$$J_{\text{ex}} = (1/4S^2)\{C-D-E\} < 0, \qquad (3)$$

where

$$C = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \ (e^2/r_{12})\Psi_i{}^*(\mathbf{r}_1)\Psi_j(\mathbf{r}_1)\Psi_j{}^*(\mathbf{r}_2)\Psi_i(\mathbf{r}_2) \quad (4)$$

is the usual direct exchange. For half-filled orthogonal orbitals, C is positive definite. However, for 180° cation-anion-cation interactions, it is always small compared to the two superexchange terms

$$D = z_l b^2/U_{AA} \quad \text{and} \quad E = 2z_l b^2/U, \qquad (5)$$

where z_l is the number of half-filled, localized orbitals per atom having a transfer integral $b \approx \epsilon_0 \Delta$ to a similar orbital on a near-neighbor cation. Here ϵ_0 is a one-electron energy and Δ is the overlap integral for interacting orbitals. The electrostatic energies U and U_{AA} refer, respectively, to the ionization energies for a one-electron transfer from one cation to a near neighbor and for a two-electron transfer from an intermediary anion simultaneously to two near-neighbor cations. Since it is generally anticipated that

$$C \ll D+E, \qquad (6)$$

it follows from Eqs. (1), (3), and (5) that

$$kT_N \approx Az\Delta^2\epsilon_0{}^2/U_T, \qquad (7)$$

where

$$A = z_l(S+1)/3S$$

and

$$U_T{}^{-1} = (2U_{AA})^{-1} + U^{-1}. \qquad (8)$$

Since U_T decreases with the increased screening associated with a larger b, the Néel temperature T_N can unambiguously be expected to decrease with decreasing z and/or Δ.

The perovskite structure, with chemical formula ABX_3, provides an opportunity to check this theoretical prediction, since the only appreciable interatomic exchange interactions are 180° cation-anion-cation interactions between nearest-neighbor cations of a simple-cubic array. Further, if the octahedral-site cations have the d-electron configuration t^3e^0, as in Mn^{4+} or Cr^{3+}, or t^6e^2, as in Ni^{2+}, then only similar half-filled orbitals on neighboring cations interact with one another to give antiferromagnetic coupling. ($A=5/3$ and $4/3$, respectively.) If the octahedral-site cations have the configuration t^3e^2 of Fe^{3+} or Mn^{2+}, it is necessary to sum the contributions from the t and e orbitals separately, so that

$$kT_N \approx (7/5)z\{(\Delta^2\epsilon_0{}^2/U_T)_t + \tfrac{2}{3}(\Delta^2\epsilon_0{}^2/U_T)_e\}. \quad (9)$$

There are other structures, such as the K_2NiF_4 structure, that contain perovskite-type layers that are only weakly coupled to one another, and these provide an opportunity to effectively vary z. Thus, $KNiF_3$ has $T_N = 275°K$ and $z=6$, whereas K_2NiF_4 has $T_N = 180°K$ and $z=4$, as pointed out by others.[1] However, when MacChesney et al. attempted to further check the simple prediction of Eq. (7) in the manganese (IV) oxides, they obtained unexpected results. In the series $CaMnO_3$, $Ca_4Mn_3O_{10}$, $Ca_3Mn_2O_7$, and Ca_2MnO_4, in which z varies from 6 to $5\tfrac{1}{3}$ to 5 to 4, they found $T_N = 123$, 125, (110), 114°K, respectively. Further, in the series $Ca_{1-x}Sr_xMnO_3$, they found $dT_N/da_0 > 0$, where a_0 is the cation-anion-cation separation. These apparent disagreements with the predictions that follow from Eq. (7) suggest that either our naive inference from the theory is incorrect or that the theory is inapplicable. Since good agreement between theory and experiment is obtained for the fluorides $KNiF_3$ and K_2NiF_4, where the Ni^{2+} d electrons are unambiguously localized, there is reason to suspect that a localized-electron theory may not be generally applicable to the manganese (IV) oxides. Independent evidence for this conclusion is presented in Sec. II, where some general properties of spontaneous band antiferromagnetism are also summarized. It is concluded that although localized-electron antiferromagnetism occurs unambiguously in $CaMnO_3$, the conditions for collective-electron antiferromagnetism are approached, and may be reached, in Ca_2MnO_4. In Sec. III it is pointed out that a $dT_N/da_0 > 0$ occurs not only in the system $Ca_{1-x}Sr_xMnO_3$, but also in $A^{3+}CrO_3$ and $A^{3+}FeO_3$, where A is La, a rare-earth ion, or Y. This fact appears to contradict Eq. (7), since geometric factors favor a $d\Delta/da_0 < 0$. It is pointed out how this apparent discrepancy is due to competitive A-O covalent bonding, which favors a $d\Delta/da_0 > 0$ if the variations in a_0 are introduced chemically. It is concluded that the only adequate test of the naive expectation of $dT_N/da_0 < 0$ would be a hydrostatic-pressure experiment.

II. CRITICAL OVERLAP INTEGRAL Δ_c

A. Essential Features of Band Antiferromagnetism

It has been argued elsewhere[2] that there is a critical transfer integral b_c, and hence a critical overlap integral Δ_c, at which the perturbation expansions leading to Eqs. (5) break down. There is also experimental evidence[2,3] that there is an abrupt transition from a localized-electron model, where $\Delta < \Delta_c$, to a collective-electron model, where $\Delta > \Delta_c$. In addition, it follows[4]

[1] F. Legrand and R. Plumier, Phys. Status Solidi 2, 317 (1962); J. B. MacChesney, H. J. Williams, J. F. Potter, and R. C. Sherwood, preceding paper, Phys. Rev. 164, 779 (1967).

[2] J. B. Goodenough, Bull. Soc. Chim. France 4, 1200 (1965); J. Appl. Phys. (to be published).

[3] P. M. Raccah and J. B. Goodenough, Phys. Rev. 155, 932 (1967).

[4] J. B. Goodenough, J. Appl. Phys. 38, 1054 (1967).

that any spontaneous band magnetism occurs in a small interval $\Delta_c < \Delta < \Delta_c{}^m$, where $\Delta_c{}^m$ is the overlap integral corresponding to the maximum bandwidth of allowed energies that will sustain spontaneous band magnetism. Given one electron per interacting orbital and a two-sublattice structure, as in the manganese (IV) oxides studied by MacChesney, *et al.*,[1] or in $KNiF_3$ and K_2NiF_4, or in the perovskites $A^{3+}FeO_3$ and $A^{3+}CrO_3$, then there is antiferromagnetic coupling in the localized-electron limit ($\Delta < \Delta_c$) and band antiferromagnetism in the collective-electron limit ($\Delta_c < \Delta < \Delta_c{}^m$).[4] Further, in the collective-electron limit, a half-filled band may be split in two by antiferromagnetic ordering, so that below T_N the compound may be a semiconductor, as in the localized-electron limit. Our problem is to understand how the magnitude of the spontaneous atomic moment and the exchange energy $\mathcal{3C}_{ex}$ change on passing from the localized-electron to the collective-electron limit and whether the manganese (IV) oxides have a $\Delta \approx \Delta_c$.

Although the theory of collective-electron magnetism is not worked out in the same detail as that for localized-electron magnetism, nevertheless there are a few general features that can be described qualitatively:

(1) Given a half-filled, narrow energy band of collective-electron states, there is a narrow-band Jahn–Teller theorem[5] that states that below some temperature T_t, which increases with decreasing bandwidth, there will be a doubling of the primitive unit cell that splits the band in two, the occupied states being stabilized and the unoccupied states destabilized by the change in translational symmetry. The doubling of the unit cell may be accomplished either by atomic displacements or by magnetic ordering, or by both simultaneously. If the narrow band is a cation-sublattice d band, then the band splitting may be accomplished by atomic motions, as in V_2O_3 and VO_2. However, if the band is a crystalline d band (cation-anion-cation overlap integrals $\Delta_{cac} > \Delta_c$), as in the case of perovskite or perovskite-related structures, then band splitting by atomic motions requires either large atomic displacements, as demonstrated by the PdO structure versus the rocksalt structure of NiO, or smaller displacements that are accompanied by cationic disproportionation, as in $Pd^{2+}Pd^{4+}F_6$. In these cases it may be energetically more favorable to split the band via spontaneous band antiferromagnetism, especially where $\Delta_c < \Delta < \Delta_c{}^m$.

(2) The magnitude of the spontaneous atomic moment of a band antiferromagnet should decrease with increasing bandwidth (or increasing Δ_{cac}), vanishing for $\Delta_{cac} > \Delta_c{}^m$.

(3) The Néel temperature $T_N = T_t$ should decrease with increasing bandwidth (or increasing Δ_{cac}), vanishing for $\Delta_{cac} > \Delta_c{}^m$. Since this property is just opposite

to that for localized electrons, according to Eq. (7), it follows that the maximum Néel temperature should occur where $\Delta \approx \Delta_c$.

(4) Temperature-independent (Pauli) paramagnetism may occur for $T > T_N$, as has been demonstrated in elemental chromium.

B. Evidence for $\Delta \approx \Delta_c$ in Manganese (IV) Oxides

Let us turn now to the evidence for $\Delta \approx \Delta_c$ in the manganese (IV) oxides. Data on the oxides with perovskite structure have been summarized elsewhere.[6] These and additional data for perovskite-related compounds are presented in Table I for oxides of the first-long-period transition elements.

In the perovskite structure, the two relevant overlap integrals are $\Delta_{ccc}{}^\pi = (\Psi_t, \Psi_{t'})$ for localized orbitals of t_{2g} symmetry on either side of an anion and $\Delta_{cac}{}^\sigma = (\Psi_e, \Psi_{e'})$ for localized orbitals of e_g symmetry on either side of an anion, where by geometry

$$\Delta_{cac}{}^\pi < \Delta_{cac}{}^\sigma. \qquad (10)$$

Octahedral-site Mn^{4+} or Cr^{3+} ions have half-filled orbitals of t_{2g} symmetry and empty orbitals of e_g symmetry $(t_{2g}{}^{*3}e_g{}^{*0})$; octahedral-site Ni^{2+} ions have half-filled e_g orbitals and filled t_{2g} orbitals $(t_{2g}{}^{*6}e_g{}^{*2})$; and high-spin Fe^{3+} ions have half-filled t_{2g} and e_g orbitals $(t_{2g}{}^{*3}e_g{}^{*2})$. The asterisk signifies that the orbitals are antibonding with respect to the anion array. For $\Delta_{cac}{}^\pi > \Delta_c$, the localized $t_{2g}{}^*$ orbitals are transformed into collective π^* orbitals; for $\Delta_{cac}{}^\sigma > \Delta_c$ the localized $e_g{}^*$ orbitals into collective σ^* orbitals.[6] Finally, since there must be more covalent mixing with orbitals of higher-valence-state cations, it may be assumed that

$$\Delta_{cac}(4+) > \Delta_{cac}(3+) > \Delta_{cac}(2+). \qquad (11)$$

The most significant feature of Table I is the apparent role of intra-atomic exchange in stabilizing a localized-electron state. In the perovskite phase, $\Delta_{cac}{}^\pi > \Delta_c$ occurs unambiguously if the number of t_{2g} electrons or holes of a given spin can only be $n_t < 2$. If $n_t > 2$, then $\Delta_{cac}{}^\pi < \Delta_c$. Where $n_t = 2$, as in $LaVO_3$, $SrCrO_3$ and $PbCrO_3$, the relationship of Eq. (11) appears to be critical. The distortion in $LaVO_3$ to tetragonal $(c/a < 1)$ symmetry for $T < T_N$ suggests spin-orbit magnetostriction associated with localized $t_{2g}{}^*$ orbitals; the lack of such a distortion in $PbCrO_3$ leaves the situation ambiguous.[5,7] However, the Pauli paramagnetism and metallic conductivity of $SrCrO_3$ clearly indicate collective d electrons. (Note that CrO_2 is metallic as a result of a $\Delta_{cac}{}^\pi > \Delta_c$.[2,8]) However, consistency then requires localized $t_{2g}{}^*$ orbitals in $CaMnO_3$ and the orthochromites $A^{3+}CrO_3$. Similarly, $\Delta_{cac}{}^\sigma < \Delta_c$

[5] J. B. Goodenough, Mat. Res. Bull. **2**, 37 (1967); **2**, 165 (1967).

[6] J. B. Goodenough, J. Appl. Phys. **37**, 1415 (1966).

[7] J. B. Goodenough (unpublished).

[8] D. S. Chapin, J. A. Kafalas, and J. M. Honig, J. Phys. Chem. **69**, 1402 (1965); D. S. Rodbell, J. M. Lommel, and R. C. DeVries, J. Phys. Soc. Japan **21**, 2430 (1966).

JOHN B. GOODENOUGH

TABLE I. Néel temperature, interaction separations, and probable electron configurations for several oxides of first-long-period transition elements with perovskite or perovskite-related structures.

Compound	Electron configuration	T_N(°K)	a_0(Å)[a]	Remarks	Ref.
$SrTiO_3$	$Ti^{4+}:\pi^{*0}\sigma^{*0}$	Ferroelectric	3.91	Superconducting if reduced	b
$CaVO_3$	$V^{4+}:\pi^{*1}\sigma^{*0}$	Pauli[c]	3.76	Metallic, doubled unit cell	d
$SrCrO_3$	$Cr^{4+}:\pi^{*2}\sigma^{*0}$	Pauli	3.82	Metallic	e
$PbCrO_3$	$Cr^{4+}:(\Delta_c<\Delta_{cac}{}^\pi<\Delta_c{}^m)$	210	4.01	Cubic all T	f
$CaMnO_3$	$Mn^{4+}:t_{2g}{}^{*3}\sigma^{*0}$	123	3.73	Curie-Weiss $\chi_m(T>T_N)$	g
$Ca_4Mn_3O_{10}$	$Mn^{4+}:t_{2g}{}^{*3}\sigma^{*0}$	125	3.72	T-dependent $\chi_m(T>T_N)$	g
$Ca_3Mn_2O_7$	$Mn^{4+}:(\Delta_{cac}{}^\pi\approx\Delta_c)$	110[h]	3.71	Weakly T-dependent $\chi_m(T>T_N)$	g
Ca_2MnO_4	$Mn^{4+}:\pi^{*3}\sigma^{*0}$	114	3.67	T-independent $\chi_m(T>T_N)$	g
$SrFeO_3$	$Fe^{4+}:t_\alpha{}^{*3}\pi_\beta{}^{*1}\sigma^{*0}$	134	3.85	T-independent polycrystal ρ, Cubic all T	i
$LaTiO_3$	$Ti^{3+}:\pi^{*1}\sigma^{*0}$	Pauli	3.94	Metallic	j, k
$LaVO_3$	$V^{3+}:t_{2g}{}^{*2}\sigma^{*0}$	137	3.91	Tetragonal $T<T_N$	l
$LaSrVO_4$	$V^{3+}:\pi^{*2}\sigma^{*0}$	Pauli	3.86	Metallic	m
$LaCrO_3$	$Cr^{3+}:t_{2g}{}^{*3}\sigma^{*0}$	320	3.88	Parasitic ferromagnet	k
$LaMnO_3$	$Mn^{3+}:t_{2g}{}^{*3}e_g{}^{*1}$	100	3.85 3.98	Jahn-Teller splitting of $e_g{}^*$	k
$LaFeO_3$	$Fe^{3+}:t_{2g}{}^{*3}e_g{}^{*2}$	750	3.93	Parasitic ferromagnet	k
$LaCoO_3$	$Co^{3+}:t_{2g}{}^{*6}\sigma^{*0}; t_{2g}{}^{*4}e_g{}^{*2}$		3.85	Localized$\rightleftarrows$collective $e_g{}^*$ at 937°C	n
$LaNiO_3$	$Ni^{3+}:t_{2g}{}^{*6}\sigma^{*1}$	Pauli	3.84	Metallic, rhomb. all T	j, k
La_2CoO_4	$Co^{2+}:t_{2g}{}^{*5}e_g{}^{*2}$	520	3.89	Semiconductor	o
La_2NiO_4	$Ni^{2+}:t_{2g}{}^{*6}\sigma^{*2}$	( )[p]	3.86	Metallic above 500°K	q, r, s
La_2CuO_4	$Cu^{2+}:t_{2g}{}^{*6}\sigma^{*3}$	Pauli	3.81	Metallic	o

[a] Room-temperature cation-anion-cation separation.

[b] J. F. Schooley, W. R. Hosler, E. Ambler, J. H. Becher, M. L. Cohen, and C. S. Koonce, Phys. Rev. Letters 14, 305 (1965).

[c] Temperature-independent (Pauli) paramagnetism.

[d] D. B. Rogers (private communication).

[e] B. L. Chamberland (private communication).

[f] W. L. Roth and R. C. DeVries, J. Appl. Phys. 38, 951 (1967).

[g] See Ref. 1.

[h] Néel temperature poorly defined.

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

[j] See Ref. 6.

[k] See Ref. 9.

[l] D. B. Rogers, A. Ferretti, R. J. Arnott, and J. B. Goodenough, J. Appl. Phys. 37, 1431 (1966).

[m] P. M. Raccah (private communication).

[n] See Ref. 3.

[o] J. M. Longo and P. M. Raccah (private communication).

[p] Curie-Weiss law above 200°K, but no long-range magnetic order above liquid-hydrogen temperature.

[q] M. Foex, Bull. Soc. Chim. France 1961, 109 (1961).

[r] G. A. Smolenskii, V. M. Yudin, and E. S. Sher, Fiz. Tverd. Tela 4, 3350 (1962) [English transl.: Soviet Phys.—Solid State 4, 2452 (1963)].

[s] E. Legrand and M. Verschureren, J. Phys. (Paris) 25, 578 (1964).

occurs unambiguously if the total number of unpaired spins is $n_s\geq4$, corresponding to $S\geq2$. (The Jahn-Teller splitting of the $e_g{}^*$ orbitals in $LaMnO_3$ is characteristic of localized electrons.[5]) This means that all the d orbitals are localized in the orthoferrites.

The second significant feature of Table I is the apparent increase in Δ_{cac} on going from the perovskite to the K_2NiF_4 structure: $LaSrVO_4$ is metallic and Pauli paramagnetic, whereas $LaVO_3$ is a localized-electron antiferromagnet. In this structure, even the divalent cations have $\Delta_{cac}{}^\sigma>\Delta_c$ where $S\leq1$. This larger Δ_{cac} is compatible with the smaller cation-anion-cation separations. This fact makes a $\Delta_{cac}{}^\pi>\Delta_c$ in Ca_2MnO_4 consistent with $\Delta_{cac}{}^\pi<\Delta_c$ in $CaMnO_3$. Since the paramagnetic susceptibility is temperature-independent for $T>T_N$ in Ca_2MnO_4 and obeys a Curie-Weiss law in $CaMnO_3$, it is reasonable to assume that indeed $\Delta_{cac}{}^\pi\gtrsim\Delta_c$ in Ca_2MnO_4. The fact that paramagnetic resonance with a $g=2$ could be observed[1] at $T>T_N$ is not inconsistent with band paramagnetism. The

fact that polycrystalline bars were semiconducting[1] $(d\rho/dT<0)$ at all T does not exclude the possibility of narrow π^* bands. Where $\Delta_c<\Delta<\Delta_m$, electron correlations tend to split a half-filled band in two, even above T_N. However, the magnetic susceptibility has only been measured to room temperature, and it may be temperature-dependent at higher temperatures. The temperature-independent interval could reflect intraplanar antiferromagnetic order between T_N and room temperature. Such a situation would indicate an even larger J_{ex} in Ca_2MnO_4 than that inferred from T_N, but it would leave open the question whether $\Delta_{cac}{}^\pi>\Delta_c$ or $\Delta_{cac}{}^\pi<\Delta_c$.

Given this conclusion, the fact that T_N is not reduced from 123 to 110 to 103 to 82°K on going from $CaMnO_3$ to $Ca_4Mn_3O_{10}$ to $Ca_3Mn_2O_7$ to Ca_2MnO_4 can be rationalized. So long as $\Delta_{cac}{}^\pi\leq\Delta_c$ is valid, the model predicts $dT_N/da_0<0$. Since J_{ex} is especially sensitive to the lattice parameter where $\Delta\approx\Delta_c$, reduction in the lattice parameter could compensate for

reduction in z. (J_{ex} should be less sensitive to a_0 in KNiF$_3$ and K$_2$NiF$_4$, where Δ is considerably smaller than Δ_c.)

III. THE SYSTEM Ca$_{1-x}$Sr$_x$MnO$_3$

Given localized electrons in the compound CaMnO$_3$, the increase in T_N with increasing lattice parameter ($dT_N/da_0 > 0$) in the system Ca$_{1-x}$Sr$_x$MnO$_3$ requires explanation, especially as the data on CaMnO$_3$, Ca$_4$Mn$_3$O$_{10}$, Ca$_3$Mn$_2$O$_7$, and Ca$_2$MnO$_4$ have been compatible with a $dT_N/da_0 < 0$. A similar increase in T_N with increasing lattice parameter has been found for the systems A^{3+} FeO$_3$ and A^{3+} CrO$_3$.[9,10] Since the d orbitals at the Fe^{3+} and the Cr^{3+} ions are also localized, according to Table I, this apparent anomaly is common to all the perovskites where the change in cell size is induced chemically. Treves, *et al.*[11] have tried to rationalize the variation in the orthoferrites, which are orthorhombic perovskites, on the basis of changing cation-anion-cation angle, since this angle increases with decreasing lattice parameter in the orthorhombic symmetry. The basis of this argument is that the Δ_{cac} actually decrease with decreasing lattice parameter because of the decreasing cation-anion-cation angle. The fact that the cation-anion-cation angle of orthorhombic CaMnO$_3$ deviates from 180° to give a parasitic ferromagnetism, which disappears in Ca$_3$Mn$_2$O$_7$ and Ca$_2$MnO$_4$, indicates that the dependence of Δ_{cac} on cation-anion-cation angle may make a contribution to the $dT_N/da_0 < 0$. However, the angular deviations from 180° appear to be too small for such a contribution to be significant in these compounds, and they are probably too small in the A^{3+} FeO$_3$ and A^{3+} CrO$_3$ compounds as well. Some more general argument seems to be required.

The overlap integrals are $\Delta_{cac} \sim \lambda^2$, where λ is the covalent-mixing parameter. For the π-bonding and σ-bonding orbitals, it is defined as[6]

$$\Psi_t = N_\pi(f_t + \lambda_\pi\Phi_\pi), \qquad \Psi_e = N_\sigma(f_e + \lambda_\sigma\Phi_\sigma), \qquad (12)$$

where Ψ_t and Ψ_e are crystal-field, localized orbitals of t_{2g} and e_g symmetry, f_t and f_e are the corresponding atomic orbitals, and Φ_π and Φ_σ are the sum of the near-neighbor-anion p_π or s, p_σ orbitals that are mixed with

[9] J. B. Goodenough, *Landolt-Bornstein Tabellen (II)* (Springer-Verlag, Berlin, 1962), Part 9, pp. 2–208.
[10] R. Aléonard, R. Pauthenet, J. P. Rebouillat, and V. Zarubica, Compt. Rend. **262**, 866 (1966).
[11] D. Treves, M. Eibshutz, and P. Coppens, Phys. Letters **18**, 216 (1965).

f_t or f_e via covalence. This means that the contributions to T_N in Eq. (7) from the orbitals of t_{2g} and e_g symmetry are proportional to λ_π^4 and λ_σ^4:

$$kT_N \approx z\{Q_t\lambda_\pi^4 + Q_e\lambda_\sigma^4\}, \qquad (13)$$

where $Q_e = 0$ for the Cr^{3+} and Mn^{4+} ions, but not for the Fe^{3+} ions. The expectation of a $dT_N/da_0 < 0$ arises from geometrical considerations only, which require smaller λ_π and λ_σ with larger lattice parameter a_0. If the changes in lattice parameter are induced by hydrostatic pressure (or by changing structure as in the series CaMnO$_3$ to Ca$_2$MnO$_4$), only these geometric considerations are applicable. However, where they are induced by chemical means, it is necessary to inquire about the influence of the chemical changes on the magnitude of λ_π. (Chemical changes of the large A cation do not influence λ_σ.)

The anion p_π orbitals contained in Φ_π of Eq. (12) are so labeled because they π-bond with the transition-metal B cations of the perovskites A BO$_3$. However, they simultaneously σ-bond with the large A cation, so that there is a competition for covalent mixing between the outer s and p orbitals of the A cations and the d orbitals of t_{2g} symmetry at the B cations. Therefore, the larger the covalent mixing with the A cations, the smaller the magnitude of λ_π for a given a_0. Since the larger cations are known to be more basic (smaller covalent contribution to A-O bond), therefore allowing a larger λ_π for a given a_0, it follows that the chemical influence has an opposite effect on λ_π than the geometrical influence. Experimental data would indicate that the chemical influence is the greater, which is quite reasonable. This point can be readily checked experimentally by studying the change in T_N with pressure. In this case only the geometrical influence is present and z is kept constant, so that a

$$dT_N/dp = (dT_N/da_0)(da_0/dp) > 0 \qquad (14)$$

is unambiguously predicted from Eqs. (7) or (9).

However, note that if a compound exhibits spontaneous band antiferromagnetism rather than localized-electron antiferromagnetism, then

$$dT_N/dp < 0 \qquad (15)$$

is predicted. It follows that, if Ca$_2$MnO$_4$ represents spontaneous band antiferromagnetism, then Eq. (15) should hold, whereas Eq. (14) should apply to CaMnO$_3$, LaCrO$_3$, and LaFeO$_3$.