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SUBJECT: **A THEORY OF PEROVSKITE-TYPE MANGANITES (La,M(II))$MnO_3$**

To: Group 63

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Abstract:

Semicovalence and its effects on indirect magnetic-exchange interactions are reviewed and applied to the manganites. These considerations lead to qualitative predictions which are in complete accord with the following experimentally observed facts, where x is taken as the percentage of manganese ions which are $Mn^{4+}$: (1) At $x = 0$, $LaMnO_3$ is an orthorhombic perovskite-type lattice with $a_1 = a_3 > a_2$. The ratio $a_2/a_3$ increases to 1 at $x = 1/4$, and for $0.4 < x < 0.75$ the lattice is tetragonal. For $x > 0.75$ the lattice is cubic. (2) At $x = 0$ the lattice is composed of ferromagnetic layers parallel to a (110) face perpendicular to the $a_2$ axis; these layers are stacked antiferromagnetically. As x increases to 1/4, the lattice becomes ferromagnetic. For $x > 0.4$ various antiferromagnetic phases form, the magnetic configurations varying with x. (3) In the range $0.25 \leq x \leq 0.35$ the saturation moment corresponds to ferromagnetically coupled spin-only values of the manganese ions; it drops off sharply toward zero around $x = 0.1$ and $x = 0.5$. (4) The electrical resistivity is a minimum and the Curie temperature a maximum at $x \approx 0.3$. (5) The maximum Curie temperature increases markedly from (La,Ca)$MnO_3$ to (La,Sr)$MnO_3$ and (La,Ba)$MnO_3$.

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## I. INTRODUCTION

In 1950 Jonker and van Santen[1,2] measured the electric resistivity, the saturation magnetization, and the Curie temperature of the perovskite-type systems $La_{(1-x)}M_x MnO_3$, where M was $Ca^{2+}$, $Sr^{2+}$, or $Ba^{2+}$. They found that for $0.25 \leq x \leq 0.35$ the magnetization assumed a value corresponding to a ferromagnetic alignment of the manganese ions, each ion contributing a "spin-only" value for its atomic moment. The Curie temperature reached a maximum at $x \approx 0.3$; these temperatures were approximately 270 K, 375 K, 350 K for Ca, Sr, and Ba, respectively. Above the Curie temperature the electric resistivity, $\rho$, increased with decreasing temperature T, the materials acting like normal semiconductors. At the Curie temperature, however, there was an anomalie in the log $\rho$ vs 1/T plot which was so pronounced in the interval $0.2 \leq x \leq 0.4$ that the slope of the curve changed sign, the material acting like a metallic conductor. Since the ferromagnetism of these compounds is directly correlated with their electric resistivity, the maximum Curie temperature of any $(La,M^{2+})MnO_3$ system might be expected to vary inversely with lattice parameter. It is interesting to note that the maximum Curie temperature for $(La,Sr)MnO_3$ is roughly 100 C higher than that for $(La,Ca)MnO_3$, which has a smaller lattice parameter, and 25 C higher than that for $(La,Ba)MnO_3$, which has a larger lattice parameter.

Recently Koehler and Wollan[3] have made neutron-diffraction studies of the system $La_{(1-x)}Ca_x MnO_3$, this system having the advantage that it forms solid solutions of a perovskite-type phase for all values of x. They have observed that for $x < 0.05$* there is a single antiferromagnetic phase which consists of ferromagnetic (100) planes arranged in antiparallel layers. They refer to this magnetic lattice as Type A. Also the crystal lattice is an orthorhombic perovskite type with $a_1 = a_3 > a_2$, the difference $(a_1 - a_2)$ decreasing with x from 0.26 Å $(a_2/a_3 = 0.995)$ at $x < 0.05$ to zero at $x = 0.25$.

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1. G.H. Jonker and J.H. van Santen, Physica 16, 337 (1950)
2. J.H. van Santen and G.H. Jonker, Physica 16, 599 (1950)
3. W.C. Koehler and F.O. Wollan, Paper Presented at Conference on Ferrimagnetism, 11-12 Oct. 1954, U.S. Naval Ordnance Laboratory

* It should be noted that due to easy oxidation of the manganese, it is possible to have a large percentage of $Mn^{4+}$ ions in a sample which has a one-to-one ratio of La and Mn atoms. In the rest of this paper x will refer to the percentage of Mn ions which are $Mn^{4+}$.

Within the range $0.25 \leq x \leq 0.35$ the neutron-diffraction patterns can be relatively unambiguously interpreted from a model of complete ferromagnetic alignment of the manganese atomic moments. This result is in complete agreement with measurements of saturation magnetization by Jonker and van Santen; the ferromagnetic lattice is referred to as Type B. The crystallographic lattice corresponding to ferromagnetic alignment is cubic.

In the $Mn^{4+}$ range $0.1 < x < 0.25$ the neutron-diffraction patterns behave as if there were two magnetic phases present, Types A and B, although the x-ray patterns indicate but a single crystallographic phase.

At $x = 0.4$ there is again an indication of the presence of two magnetic phases, the one ferromagnetic and the other antiferromagnetic. The neutron-diffraction patterns are difficult to interpret in the region $0.4 < x < 0.9$. In one sample with $x = 0.7$ an antiferromagnetic phase, referred to as Type C, was definitely established. This phase consisted of an ordering of $Mn^{3+}$ and $Mn^{4+}$ ions in alternate (100) planes with each atom antiferromagnetically coupled to its four like neighbors, ferromagnetically coupled to its two unlike neighbors. This specimen appeared, crystallographically, to be tetragonal.

At $x = 1$ the lattice is unambiguously cubic with an antiferromagnetic coupling between each $Mn^{4+}$ ion and its six near-neighbor $Mn^{4+}$ ions. This magnetic lattice is referred to as Type G.

Zener[4] has suggested that the correlation between ferromagnetism and electric resistance in these systems is due to double exchange, a mechanism whereby a $Mn^{3+}$ and a $Mn^{4+}$ ion which are located on opposite sides of an $O^{2-}$ ion are indirectly coupled, a ferromagnetic alignment permitting degeneracy between the states $Mn^{3+}-O^{2-}-Mn^{4+}$, $Mn^{4+}-O^{2-}-Mn^{3+}$ and therefore representing both the low-energy state and the condition

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[4] C. Zener, Phys. Rev. 82, 403 (1951)

for lowest electric resistivity. If this mechanism is responsible for the ferromagnetic alignment of the manganese-ion moments, however, it would appear that the maximum Curie temperature for ferromagnetic alignment and the minimum electric resistivity should occur at $x = 0.5$ instead of at $x = 0.3$, as observed. Either the double-exchange mechanism does not apply to the perovskite crystals or there is some additional mechanism present. It is the purpose of this present paper to suggest an additional mechanism which will not only explain the correlation of ferromagnetism and minimum electric resistivity at $x = 0.3$, but will also explain the antiferromagnetic structures referred to as Types A, C, and G. It will be shown that this mechanism can also account for the crystallographic distortions from cubic symmetry.

## II. SEMICOVALENCE

In a previous paper[5] the importance of homopolar bonding in the spinel-type lattices was emphasized. It was qualitatively shown how homopolar bonding influences cation ordering and how the spinel-type-lattice distortions to tetragonal symmetry may result from the formation of four square, homopolar bonds and two linear, ionic bonds about $Cu^{2+}$, $Mn^{3+}$, or $In^{3+}$ ions in octahedral sites. A new concept for chemical bonding in lattices containing transition elements, viz. semicovalence, was also introduced. It was suggested that semicovalence could stabilize different ions in different types of lattice sites; it was also shown that the customary concepts of superexchange[6] must be modified if semicovalence exists. Since it is believed that the perovskite-type manganites can be explained by semicovalence and its influence on indirect exchange mechanisms, this concept is briefly reviewed below.

If an ionic model for a lattice is assumed, it is presumed that the atomic electron orbitals provide a fairly accurate description for the electrons in the lattice. It has previously been assumed that the transition-element cations in oxide lattices are ionically bound;

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[5] J. B. Goodenough and A.L. Loeb, Phys. Rev. (to be published)

[6] H. A. Kramers, Physica 1, 182 (1934); P.W. Anderson, Phys. Rev. 79, 350 (1950); J. H. Van Vleck, J. phys. et radium 12, 262 (1951)

therefore although various authors[7] have considered the perturbations of the cation d orbitals caused by internal electric fields, there has been no serious consideration of the perturbations of the empty cation orbitals. The empty cation orbitals are assumed to have so much higher an energy than either the cation d orbitals or the anion p orbitals that they have no influence on the state of the electrons.

Such an assumption is extremely dangerous. Because of the strong perturbations of neighboring atoms on one another, the empty energy levels correspond to lattice orbitals, not atomic orbitals, and these lattice orbitals may have energies which are nearly degenerate with the atomic d orbitals. A qualitative table has been given[5] in which the most stable hybrid orbitals were listed for various transition-element cations. Because of extreme steric hindrance in a close-packed lattice, the most stable of the cation hybrid orbitals may not overlap appreciably the neighboring anion orbitals. In such a case the empty lattice orbital may have little effect on the state of the electrons in the solid. However, if the most stable of the empty cation orbitals strongly overlap the full orbitals of neighboring anions, the anion p electrons may spend some of their time in the cation orbitals. The amount of electron sharing between cation and anion depends, of course, on the relative stabilities of the cation and anion orbitals. The degree of electron sharing is a measure of the homopolar bonding.

The full anion p orbital which overlaps an empty cation orbital contains two electrons of opposite spin. In ordinary homopolar bonding each of these electrons has an equal probability of being shared by the cation. If the cation has a net magnetic moment, however, these electrons will not have an equal probability of being shared by the cation. Because of the presence of exchange forces, that anion electron whose spin is parallel to the net cation spin will spend more time on the cation than that with antiparallel spin. This is in accordance with

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[7] H. A. Bethe, Ann. Physik 3, 133 (1929); J.H. van Santen and J.S. van Wieringen, Rec. trav. chim. 71, 420 (1952)

Hund's rule if it is imagined that the d shell is extended by the s and p orbitals when an atom is in a lattice where hybrid orbitals are formed. Because a single electron predominates in this bond, it is called semi-covalent.

Although the superexchange model is based on the nonionic character of a lattice, it is usually assumed that the s and p orbitals are of no relevance; the electron which is excited from an anion to a neighboring transition-element cation is said to go into a cation d orbital. According to this model it is the antiparallel electron which is excited whenever the d shell is half or more filled, the parallel electron whenever the d shell is less than half full. Also in the superexchange model only one anion electron can be excited at a time so that two cations on opposite sides of an anion are coupled parallel if their d shell is less than half full, antiparallel if the d shell is half or more filled. Whereas semicovalence assumes that the exchange energy is greater than the energy difference between the lattice-orbital and the d-orbital energy levels, superexchange usually assumes the opposite.

This difference between semicovalence and the superexchange model leads to different predictions for the indirect couping between the cation moments in an oxide lattice. According to the superexchange model, for example, $Mn^{3+}$ or $Mn^{4+}$ ions, which have d shells which are less than half full, should couple ferromagnetically if they are on opposite sides of an $O^{2-}$ ion. With such a model it is impossible to interpret the experimental results of Koehler and Wollan[3]. It will be shown below, however, that the semicovalent concept is compatible with both the magnetic coupling and the lattice distortions which are observed.

## III. SEMICOVALENCE AND INDIRECT Mn-Mn MAGNETIC EXCHANGE

In order to give an interpretation of the system $(La,Ca)MnO_3$, it is first necessary to outline the model of Mn-O bonding and Mn-Mn magnetic exchange on which this interpretation is based.

First it is assumed that $Mn^{3+}$, with an outer-electron configuration $d^4$, hybridizes stable ($dsp^2$) lattice orbitals. These lattice orbitals are square and coplanar. The reason for their stability is the availability of but a single empty d orbital. The tetragonality of hausmannite, $Mn_3O_4$, with axial ratio $c/a > 1$ is experimental evidence that this hypothesis is valid.[5] It is further assumed that $Mn^{4+}$, with outer-electron configuration $d^3$, hybridizes stable ($d^2sp^3$) lattice orbitals, two empty d orbitals being available. These lattice orbitals are octahedral and can therefore simultaneously point toward all six oxygen near neighbors if the $Mn^{4+}$ ion is in an octahedral site, as it is in $(La,Ca)MnO_3$. The preference of $Cr^{3+}$ for octahedral coordination when in a spinel lattice is experimental evidence that cations with outer-electron configuration $d^3$ do hybridize ($d^2sp^3$) orbitals which are stable enough to effect the cation-anion bonds.[5,8]

There are essentially three kinds of indirect exchange interactions which must be distinguished, that between like cations each of which has a stable, empty lattice orbital pointing toward their common anion, that between like cations of which only one has an empty lattice orbital pointing toward the anion, and that between unlike cations. Since the manganese ions are always on opposite sides of their common anion in the perovskite-type lattice, angular considerations are always ideal for indirect coupling.

If an $O^{2-}$ ion has each of the wings of a full p orbital overlapped by stable, empty cation orbitals, a covalent bond can be formed on either side with equal probability. Since only a single anion electron plays the predominant bonding role when the cation has a net magnetic moment, the most stable configuration is for one p electron to predominate in the bond on one side, the other on the other side. Since the p electrons are antiparallel, in accordance with the Pauli Exclusion Principle, and since the bonding electron is parallel to the net spin of the bonded cation, the two cations are coupled antiferromagnetically. This is called Case 1 and is schematically illustrated in Table I.

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[8] E. W. Gorter, "Saturation Magnetization and Crystal Chemistry of Ferrimagnetic Oxides," Thesis, University of Leiden (1954)

Since two semicovalent bonds are involved, the strength of the magnetic coupling, on a relative scale, is designated moderate.

If, on the other hand, the $O^{2-}$ ion has only one of its p-orbital wings overlapped by an empty cation orbital, a single covalent bond is formed. Although this bond may be coordinate covalent, with both electrons participating in the bond, the electron whose spin is parallel to the net spin of the bonded cation will be the more active bonding electron. This means that an anion which bonds covalently to a transition-element cation carries a net electron spin which is antiparallel to that of the bonded cation. This net anion spin interacts antiferromagnetically with its electrovalently bonded cation on the opposite side, and the two cations are thereby coupled ferromagnetically. This is Case 2 and is also illustrated schematically in Table I. Because the direct exchange via the electrovalent bond is weak, this magnetic interaction is designated weak on the scale of relative strengths. Case 2 is possible if the bonded cations are $Mn^{3+}$ since a $Mn^{3+}$ ion can extend empty lattice orbitals towards only four of its six neighboring $O^{2-}$ ions, its stable orbital being square. It should be noted that this is an example of ferromagnetic coupling which is not correlated with a low electrical resistivity.

Case 3 of Table I represents the coupling of unlike cations via a common anion. Zener[4] has already pointed out that in such an instance the system can be stabilized by the admixture of the two degenerate states $Mn^{4+}$-$O^{2-}$-$Mn^{3+}$ and $Mn^{3+}$-$O^{2-}$-$Mn^{4+}$. This admixture can occur only if the two cations are coupled ferromagnetically. If the two p-orbital wings of the anion are overlapped by cation orbitals, the magnetic coupling is relatively strong. However, it may happen that an electron ordering takes place such that the state $Mn^{4+}$-$O^{2-}$-$Mn^{3+}$ is not degenerate with the state $Mn^{3+}$-$O^{2-}$-$Mn^{4+}$. Any electronic ordering inhibits double exchange; a large electronic-ordering energy could conceivably induce antiferromagnetic coupling between a $Mn^{4+}$ and a $Mn^{3+}$ ion. If, however, the $Mn^{3+}$ ion of an ordered lattice has no empty orbital pointing toward the $O^{2-}$ ion, the $Mn^{3+}$-$Mn^{4+}$ coupling will be ferromagnetic in the same way as the $Mn^{3+}$ ions are in Case 2. Because of the possibility of admixing states whose energies differ only by the electron-ordering energy, this coupling will be stronger than Case 2, but weaker than the disordered Case 3.

## IV. INTERPRETATION OF THE SYSTEM (La,Ca) $MnO_3$

Attention is focused first on the manganese ions of this system since these are believed to cause the properties which are peculiar to all the manganites $(La^{3+}M^{2+})\ MnO_3$. The effect of the large cations will be deferred until the end of this section. Furthermore, it is assumed that the lowest zero-point energy of a system is that which permits the largest number of covalent, or semicovalent, manganese-oxygen bonds.

### A. The Case x = 1.

In the ideal case of $x = 1$, all the manganese ions are $Mn^{4+}$ and every Mn-O bond can be semicovalent. The $Mn^{4+}$-$Mn^{4+}$ coupling corresponds, therefore, to Case 1, and each $Mn^{4+}$ ion is antiferromagnetically coupled to its six near-neighbor cations as shown in Fig. 1. This is just the magnetic lattice which was observed by Koehler and Wollan for $CaMnO_3$ with $x > 0.96$. It corresponds to their Type-G magnetic lattice. Since all the Mn-O bonds are identical, cubic symmetry is predicted for the lattice. This was also observed.

Although the experimental results agree with those predicted in a straightforward manner from the semicovalent model, they are the opposite of the prediction from a superexchange model. Since the d shell is less than half full, ferromagnetism should result if superexchange is the correct mechanism.

### B. The Case x = 0.

In the ideal case of $x = 0$, all the manganese ions are $Mn^{3+}$ and only 2/3 of the Mn-O bonds can be covalent or semicovalent. One possible arrangement of these bonds would be an ordering of all the coplanar bonds in a (100) plane. Then each $Mn^{3+}$ ion in a plane would be coupled antiferromagnetically to its four coplanar near-neighbors, but there would be no magnetic coupling between planes. It is immediately seen that such a magnetic configuration is less probable than the one pictured in Fig. 2 where all of the $O^{2-}$ ions are bonded covalently in at least one direction. Let the $a_2$ axis be a (100) direction in which semicovalent bonds are formed on both sides of the oxygen ions, and let the alternate planes perpendicular to this direction be called A and B planes, respectively. Then the A-B coupling corresponds to Case 1 and is everywhere antiferromagnetic. Within a plane the coplanar bonds will so order that each oxygen in the plane has only one of its p-orbital wings overlapped by the empty ($dsp^2$) orbitals of a $Mn^{3+}$ ion. Semicovalence can be formed on only one side of the $O^{2-}$ ions in this plane, and ferromagnetic coupling between the $Mn^{3+}$ ions within the plane results (Case 2). This leads to completely cooperative coupling in which the A and B planes are ferromagnetic within themselves but antiferromagnetically aligned with respect to each other. This is just the Type-A magnetic lattice of Koehler and Wollan which was observed for $LaMnO_3$ with $x < 0.05$.

Further, the bonds along the $a_2$ axis are different than those in an A or B plane, that is along the $a_1$ and $a_3$ axes. Since it is reasonably assumed that the configuration with two semicovalent bonds per $O^{2-}$ ion is more stable than that with one covalent bond per $O^{2-}$ ion, the more stable $a_2$- axis bonds should be shorter than the $a_3$- axis or $a_1$- axis bonds. Again the crystallographic measurements of Koehler and Wollan substantiate this model.

### C. The Case $x = 0.5$

If $x = 0.5$, there are just as many $Mn^{3+}$ ions as $Mn^{4+}$ ions present. Since these ions are statistically distributed throughout the lattice, it is not possible to assume that there is an ordering of 1/2 $Mn^{3+}$ and 1/2 $Mn^{4+}$ ions in every unit cell. However, the largest number of such unit cells will be found at $x = 0.5$. In this case there can be a great deal of short-range ordering of the $Mn^{3+}$ and $Mn^{4+}$ ions. If short-range order occurs, there will be fairly large regions of long-range order also. The optimum conditions for covalent-bond formation occur if there is an ordering of $Mn^{3+}$ and $Mn^{4+}$ ions in alternate (100) planes. Under these conditions coplanar ($dsp^2$) orbitals of the $Mn^{3+}$ ions can order themselves parallel to the $Mn^{3+}$ planes so that each $Mn^{3+}$ ion is coupled antiferromagnetically to its four coplanar $Mn^{3+}$ neighbors, the oxygen ions of this plane each forming two semicovalent bonds. Similarly the $Mn^{4+}$ ions will be coupled antiferromagnetically with each of their four coplanar $Mn^{4+}$ neighbors since every $Mn^{4+} - O^{2-}$ bond in that plane is semicovalent. The $O^{2-}$ ions between a $Mn^{3+}$ plane and a $Mn^{4+}$ plane can, however, form covalent, or semicovalent, bonds with only the $Mn^{4+}$ ions so that every $Mn^{4+} - O^{2-} - Mn^{3+}$ interaction is ferromagnetic. This type of ordering leads to the magnetic configuration of Fig. 3a, which corresponds to Koehler and Wollan's Type C. Furthermore the difference in bonding between like and unlike ions should cause a distortion to tetragonal symmetry. Although Type C corresponds to an ordered Case 3 for the $Mn^{4+} - Mn^{3+}$ spin interaction, some admixing of states probably occurs. This bond is therefore more stable than that of Case 2. However, since the amount of admixture depends upon the unknown electron-ordering energy, it is not possible to qualitatively predict whether the axial ratio of the tetragonal phase should be $c/a < 1$ or $c/a > 1$.

It should be noted that the ordering of $Mn^{3+}$ and $Mn^{4+}$ ions into alternate planes requires only an electron ordering and can therefore be accomplished at relatively low temperatures. The only restriction to complete ordering is the randomness of the $La^{3+}$, $M^{2+}$ distribution, a randomness which would require ionic diffusion to eliminate.

In the above discussion it has been tacitly assumed that the electron ordering of Fig. 3a is the most stable configuration. However, it might well be asked why the electron ordering of Fig. 3b, which would result in ferromagnetic coupling, is not stronger, especially if the Case 3 magnetic coupling is stronger than that of Case 1 or Case 2. It must be realized, however, that the strength of the Case-3 bond depends upon the amount of admixture of degenerate states. In the ordered lattice of Fig. 3b the only state of the system which is degenerate with the one shown is when every $Mn^{3+}$ and $Mn^{4+}$ ion interchange simultaneously. Whenever two $Mn^{4+}$ ions are near neighbors, they couple antiferromagnetically (Case 1), so a random mixture of $Mn^{3+}$ and $Mn^{4+}$ introduces forces which oppose a ferromagnetic alignment. The ordered structure of Fig. 3a is completely cooperative and should therefore represent the lowest energy state of the system.

It is possible, however, that at higher temperatures the entropy of a disordered configuration will stabilize the ferromagnetic lattice. Although this possibility is apparently not realized in the (La,Ca)$MnO_3$ system, Jonker and van Santen[1] have found anomalous saturation magnetization vs. temperature curves for $La_{0.4}Sr_{0.6}MnO_3$ which can be qualitatively accounted for if a disordered phase is stable at the high temperatures, an ordered phase at low temperatures.

### D. The Range $0 < x < 0.5$

If a $Mn^{4+}$ ion is placed on one of the lattice sites of the cell illustrated in Fig. 1, all six, instead of just four, of the oxygen ions around that site can form semicovalent bonds. Since four of the six bonds favor a similar magnetic coupling to that with only $Mn^{3+}$ ions present, the spin of the $Mn^{4+}$ ion remains parallel to that of the $Mn^{3+}$ ion that it replaced. Since there is now a $Mn^{4+}$ ion coupled ferromagnetically to a plane of $Mn^{3+}$ ions, the exchange coupling between the $Mn^{4+}$ and its four coplanar $Mn^{3+}$ neighbors with parallel spin is enhanced by the double-exchange mechanism of Case 3. This results in a greater mobility of the bonding electron which is reflected in a decreased electrical resistivity.

Although a single $Mn^{4+}$ ion in a lattice of $Mn^{3+}$ ions may not upset the bonding structure sufficiently to destroy the spin coupling represented by Type A, it does reduce the stability of this ordered arrangement. As more $Mn^{4+}$ ions are added, the electrical resistivity and the stability of the Type-A lattice are further reduced. Since the $Mn^{4+}$ ions disturb the exchange interactions so that they are no longer cooperative, the Type A lattice is replaced by a disordered lattice as x is increased beyond about 0.1. In the disordered lattice the $Mn^{4+}$-$Mn^{3+}$ interaction predominates; the double-exchange mechanism is strongest when the $Mn^{4+}$ and $Mn^{3+}$ ions can be interchanged without altering the energy of the total system. Wherever the $Mn^{4+}$-$Mn^{3+}$

interaction predominates, the magnetic coupling is ferromagnetic.

As an indication of the manner in which the lattice becomes ferromagnetic as x is increased, it is instructive to look at two hypothetical structures for $x = 0.125$ in which the $Mn^{4+}$ ions are assumed ordered into a simple cubic array with one $Mn^{4+}$ ion per unit cell. In Fig. 4a the cation orbitals are so ordered that the magnetic-exchange interactions are completely cooperative. It represents a ferrimagnetic lattice with a saturation moment of 1 Bohr magneton per molecule. Such an ordered lattice would be cubic. In Fig. 4b it is assumed that even in the ordered lattice the $Mn^{4+} - Mn^{3+}$ interactions corresponding to Case 3a are stronger than those corresponding to Case 3b. This lattice is ferrimagnetic with a saturation moment of 15/8 Bohr magnetons per molecule. Any disordered state should have a saturation moment of at least this amount.*

Similarly a possible ordered structure for the case $x = 0.25$ can be imagined (see Fig. 5). As in the ordered phase of Fig. 4b, the $Mn^{4+} - Mn^{3+}$ interactions are reduced by electron ordering so that a disordered phase is probably the most stable just below the Curie temperature. The purpose of showing Fig. 5 is to indicate that even the ordered phase is ferromagnetic if $x = 0.25$. One can qualitatively predict, therefore, that the saturation magnetization should increase with x at least as rapidly as is indicated in Fig. 6.

As the number of $Mn^{4+}$ ions is increased beyond $x = 0.25$, there is an increasing probability that $Mn^{4+}$ ions are near neighbors. Between $0.25 \leq x \leq 0.375$, $Mn^{4+} - Mn^{4+}$ interactions, which are antiferromagnetic, can be avoided so that ferromagnetic coupling should prevail. For $x > 0.375$, however, there are necessarily regions of the lattice which contain at least 1/2 $Mn^{4+}$ ions. In these regions the lattice orders as shown in Fig. 3a rather than as shown in Fig. 3b so that an antiferromagnetic phase begins to form. Consequently the saturation magnetization drops off

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* If there is a transition at low temperatures from regions of a disordered ferromagnetic phase to regions of an ordered ferrimagnetic phase, the saturation magnetization vs. temperature curve should show an anomalie at the ordering temperature, the ordered phase having the lower saturation magnetization.

with x, as indicated in Fig. 6, until it is below 1 Bohr magneton per molecule at x = 0.5, only inhomogeneities in the lattice preventing a complete ordering and consequent zero magnetization. The decrease in magnetization is associated with a decrease in the strength of the $Mn^{4+}$- $Mn^{3+}$ interactions, and therefore with an increase in the electrical resistivity. The resistivity at x = 0.5 should not, however, be nearly as high as at x = 0 since both $Mn^{3+}$ and $Mn^{4+}$ ions do exist in the lattice and only the electron-ordering energy barrier needs to be overcome. From Fig. 6 the maximum amount of double exchange should occur for compositions approximately midway between x = 0.1 and x = 0.5. That this is indeed the case is reflected both by a maximum in the Curie temperature and in the metallic characteristics of the low-temperature resistivity vs. reciprocal temperature curves at $x \approx 0.3$.

Finally it should be noted that in the ferromagnetic region all of the Mn-O bonds are equivalent so that the lattice should be cubic.

## E. The Range $0.5 < x < 1$

In the range $0.5 < x < 1$ the lattice remains antiferromagnetic while changing from Type C to Type G. There will always be a mixture of at least two types of magnetic phase in this region so that neutron diffraction patterns should be difficult to interpret. For $x > 0.75$, regions of the crystal may order to give Koehler and Wollan's Type F, which is shown in Fig. 7. Here the $Mn^{4+}$ ions are coupled antiferromagnetically with respect to one another as two near neighbors form semicovalent bonds at opposite sides of their common $O^{2-}$ ion. The $Mn^{4+}$ - $Mn^{3+}$ coupling is ferromagnetic, however, because of double exchange. The magnetic phase Type F should be cubic. Therefore, whenever there is the ordering necessary for Type F to occur as a second phase with Type G, the lattice should be cubic.

## E. The Curie Temperature

The Curie temperature reflects the temperature at which the semicovalent bonds are formed. So far we have considered only the role of the manganese cations. It is now proposed that covalent bonding with the large cations also play a role. The most stable hybrid orbitals of the large cations are tetrahedral ($sp^3$) orbitals. If the large cations form covalent bonds with four of their neighboring twelve oxygen ions, these bonds are in planes which are perpendicular to the edges of the cubes formed by the manganese ions. If a p orbit of an $O^{2-}$ ion is oriented through covalence toward a large cation, it will have a perpendicular p orbit which may lie along a Mn-O-Mn axis. This is the optimum position for either Mn-O covalent-bond formation or for double exchange. It follows, therefore, that the more stable the tetrahedral ($sp^3$) orbital associated with the large cation, the higher the temperature at which the lattice bonds order and the higher the Curie temperature. Since the stability of the $M^{2+}$- O covalent bond increases from $Ca^{2+}$ to $Sr^{2+}$ and $Ba^{2+}$, the increase of 100 C in the maximum Curie temperature can be understood by the model of this paper. Apparently the reduction in Mn-O bond strength with increasing lattice parameter compensates for the increased covalent-bond strength of the large cation on going from (La,Sr) $MnO_3$ to (La,Ba) $MnO_3$.

Further, a comparison of the bonds in magnetic-lattice Type A with those of magnetic-lattice Type G indicates that the Curie temperature of Type G should be higher than that of Type A if the Mn-O bonds alone are considered. If one takes account of the large-cation bonds, however, a lattice containing $La^{3+}$ should have a higher Curie temperature than one containing $Ca^{2+}$. Since $LaMnO_3$ is Type A and $CaMnO_3$ is Type G, the two effects tend to cancel one another. The Curie temperatures of the two lattices are 140 K and 100 K, respectively;[3] the large-cation contribution apparently predominates. Finally it should be noted that the exchange coupling due to semicovalence has a Curie temperature which is considerably lower than that due to double exchange. This is consistent with the qualitative assumption of this paper that double exchange is the stronger magnetic interaction.

### G. Lattice Distortions

It has already been shown that the magnetic lattices referred to as Types B, F, and G should be cubic. Any lattice which is composed of one or a combination of these magnetic phases should therefore be cubic.

Type A, on the other hand, has been shown to have $a_1 = a_3 > a_2$. If only the Mn-O bonds are considered, this lattice should be tetragonal with $c/a < 1$. Since Type A occurs in $LaMnO_3$, however, the covalent character of the La-O bonds cannot be neglected. If the lattice is distorted to tetragonal symmetry with $c/a < 1$, work must be done against the La-O covalent bonds which are most stable if the bonded oxygens are at the corners of a regular tetrahedron. Because $c/a < 1$, the amount of distortion of the La-O bond angle can be reduced by a further distortion of the lattice to orthorhombic symmetry. Thus the observed orthorhombic symmetry of the Type-A $LaMnO_3$ lattice follows directly from covalent considerations.

In the Type-C lattice, considerations of the Mn-O bonds alone have predicted tetragonal symmetry although it has not been possible to predict whether the axial ratio is greater or less than one. Since the $Ca^{2+}$ ion is smaller and has less stable hybrid ($sp^3$) orbitals than $La^{3+}$, the presence of considerable $Ca^{2+}$ should reduce any tendency of the lattice to distort further to orthorhombic symmetry.

The crystallographic predictions which follow from covalent and semicovalent considerations are summarized in Fig. 6.

## V. CONCLUSION

The theory of semicovalence and its influence on magnetic exchange has been reviewed and applied to the manganites $(La^{3+}, M^{2+}) MnO_3$. The influence of covalence is seen to be of significant importance for this perovskite-type system which has previously been assumed to be purely ionic. Whereas the lattice distortions from cubic symmetry, the magnetic interactions, the range of minimum resistivity, and the variation of Curie point with $M^{2+}$ cannot be accounted for on the basis of superexchange or double exchange and an ionic model, a consideration of the role of covalence in the lattice has resulted in qualitative predictions which are in complete accord with observations of all these phenomena. It is therefore concluded that covalence plays a significant role in the perovskite-type lattice just as it does in the spinel-type lattice. It is further concluded that the concept of semicovalence is fundamental to an understanding of the manganites and that these systems are an excellent illustration of the modifications which may be necessary in any superexchange theory which starts with an ionic model as the ground state of the crystalline lattice.

## Acknowledgment

The author wishes to thank Dr. W. C. Koehler for communicating to him the preliminary results of his very interesting experimental study of the (La,Ca)$MnO_3$ system.

Signed: John B. Goodenough
John B. Goodenough

JBG/md

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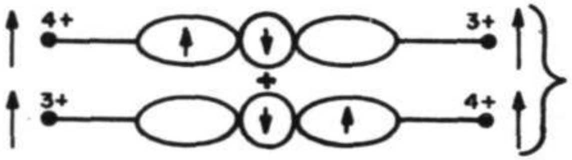
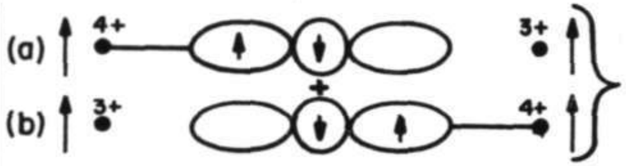
TABLE I. Semicovalent model for the magnetic coupling of manganese ions in manganites $(La,M(II))MnO_3$. N is the number of semicovalent bonds which can be formed by a manganese ion with its six neighboring oxygen ions. In the column for schematic electron-spin configurations the cations, marked 4+ or 3+, have an empty orbital pointing toward the $O^{2-}$ p orbitals if joined by a dash.

| LOW-ENERGY, EMPTY LATTICE ORBITALS | | | |
|---|---|---|---|
| ION | OUTER ELEC. CONFIG. | EMPTY LOW-ENERGY ORBITALS | N |
| $Mn^{4+}$ | $d^3$ | OCTAHEDRAL $(d^2sp^3)$ | 6 |
| $Mn^{3+}$ | $d^4$ | SQUARE $(dsp^2)$ | 4 |

| MAGNETIC COUPLING | | |
|---|---|---|
| SCHEMATIC ELECTRIC-SPIN CONFIGURATIONS | STRENGTH | CASE |
|  | MODERATE | 1 |
|  | MODERATE | 1 |
|  | WEAK | 2 |
|  | STRONG | 3a |
|  | DEPENDS ON (a)-(b) ORDER ENERGY DIFFERENCE | 3b |

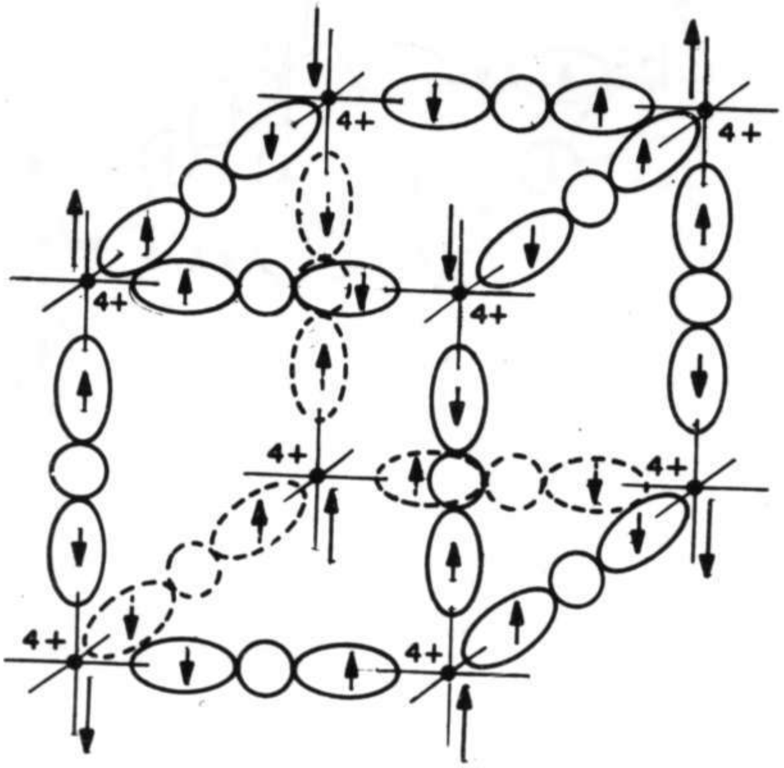


FIG. I

MAGNETIC LATTICE FOR x=1, TYPE G

A-60863

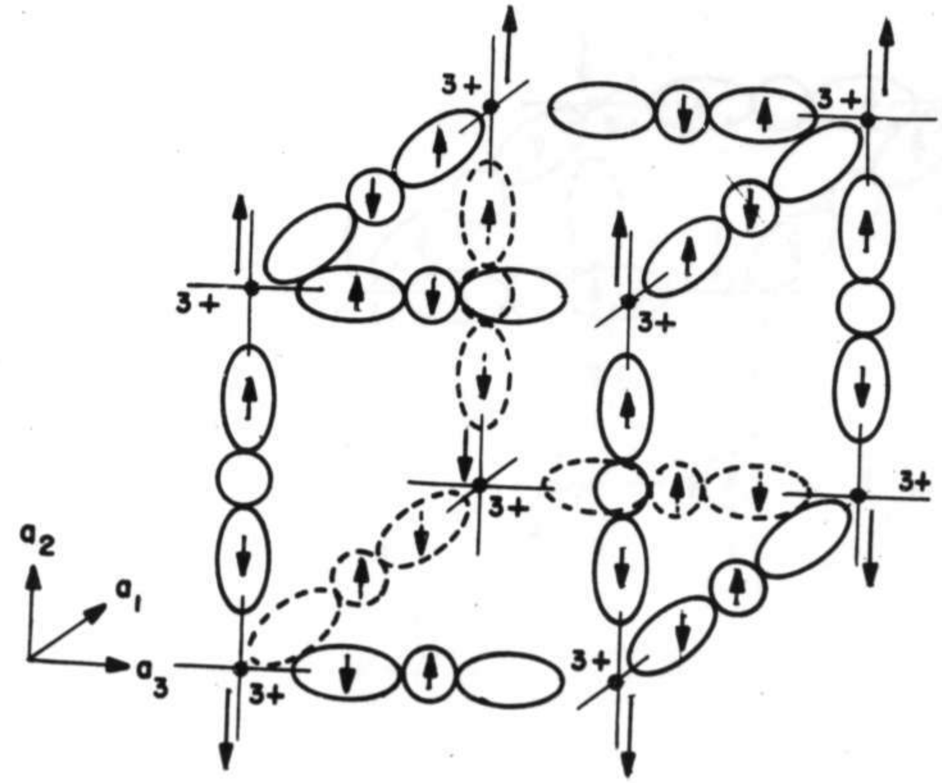


FIG. 2

MAGNETIC LATTICE FOR x=0; TYPE A

A-60861

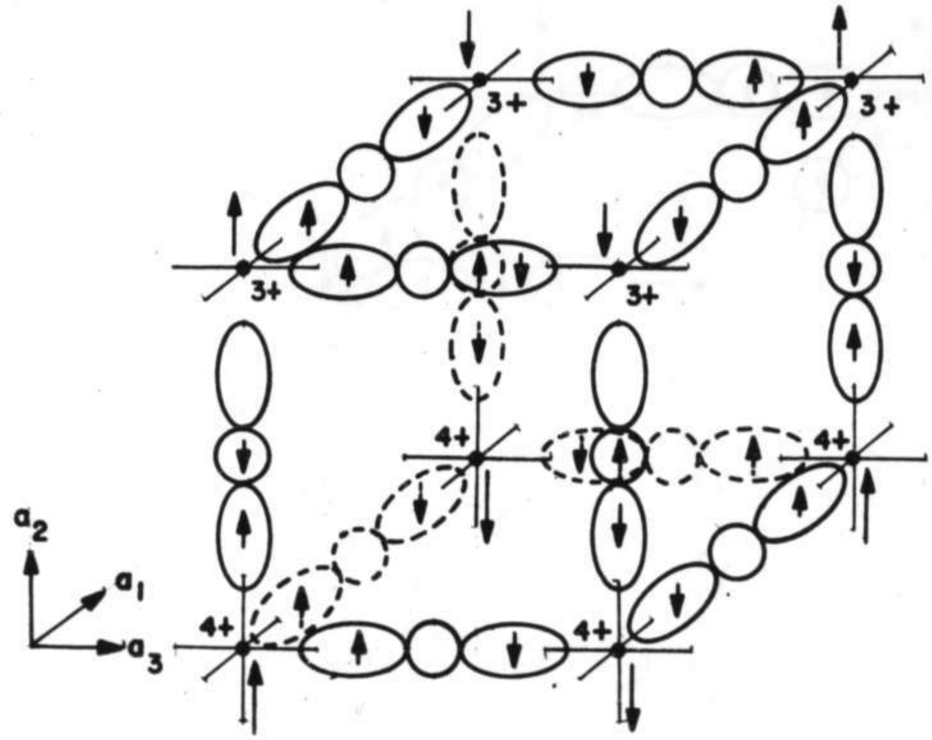


FIG. 3a

MAGNETIC LATTICE FOR x=0.5;TYPE C

A-60862

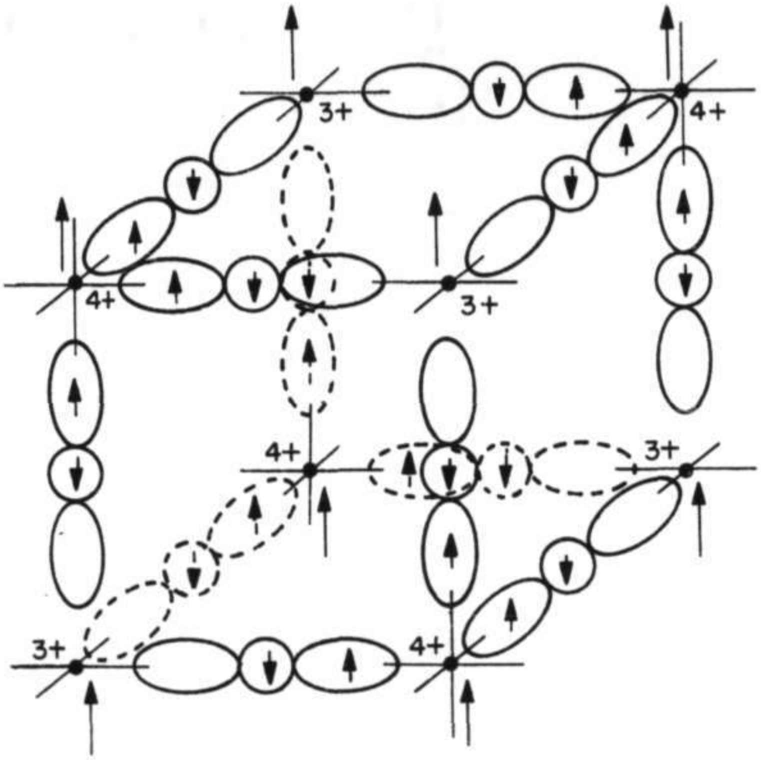
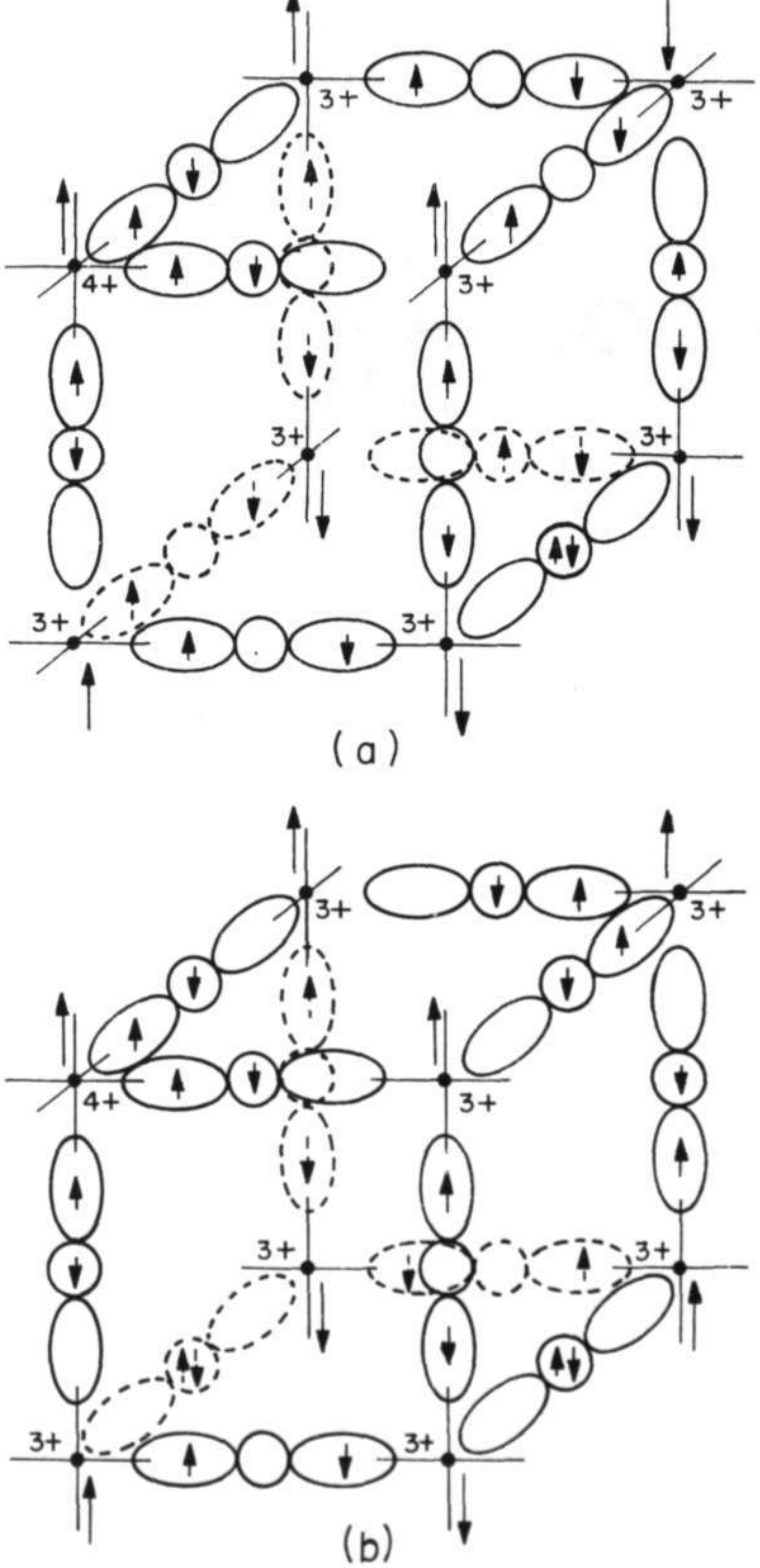


FIG. 3b

ALTERNATIVE ORDERED STRUCTURE
FOR $x = 0.5$; TYPE B

A-60894



(a)

(b)

FIG. 4

ONE OCTANT OF A HYPOTHECTICAL ORDERED STRUCTURE FOR x=0.125. IT IS FERRIMAGNETIC WITH A NET MAGNETIZATION OF (a) 1/8 AND (b) 15/8 BOHR MAGNETONS PER MOLECULE

A-60895

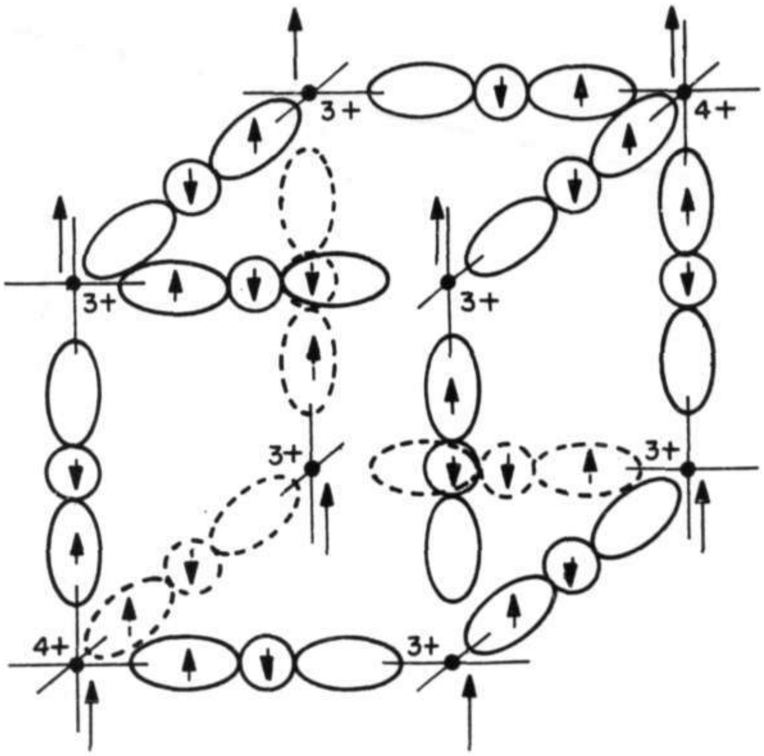


FIG. 5

HYPOTHETICAL ORDERED STRUCTURE FOR
x= 0.25 IT IS FERROMAGNETIC, TYPE B.

A-60896

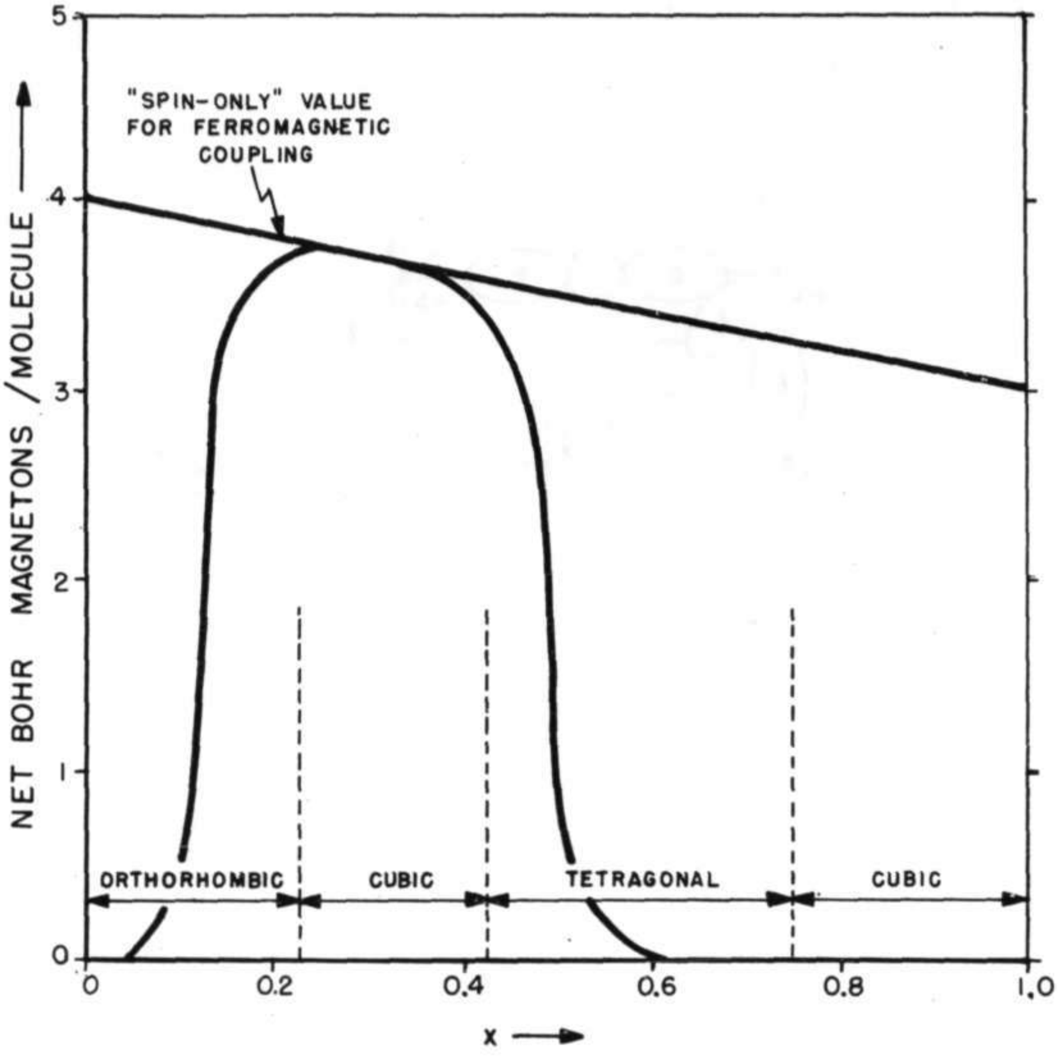


FIG. 6

QUALITATIVE PREDICTION OF VARIATION OF CRYSTALLOGRAPHIC SYMMETRY AND SATURATION MAGNETIZATION WITH FRACTION x OF MANGENESE IONS PRESENT AS $Mn^{4+}$

A-60897

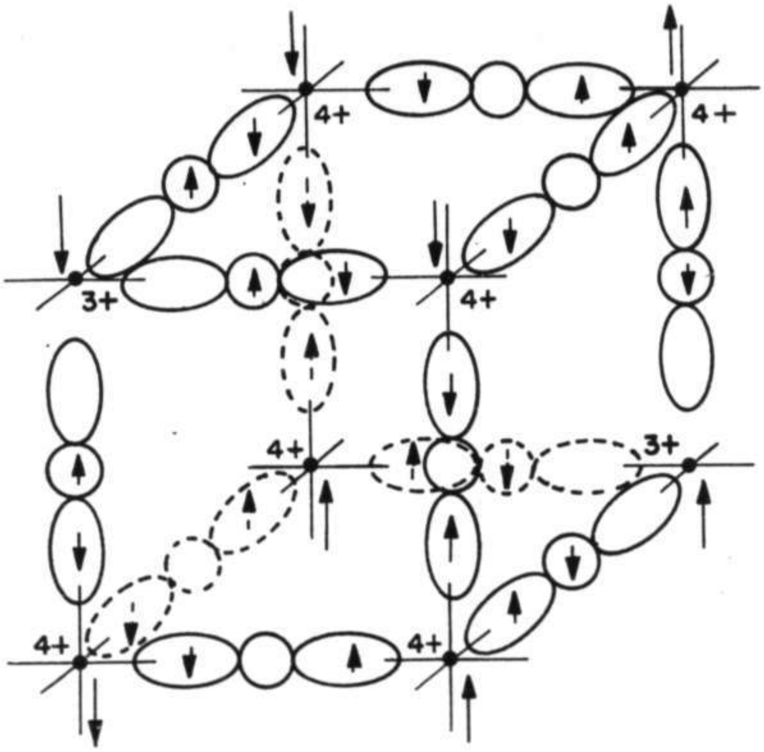


FIG. 7

MAGNETIC LATTICE FOR $x=0.75$; TYPE F

A-60898