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Theory of the Role of Covalence in the Perovskite-Type Manganites [La,M(II)]MnO$_3$†

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The theory of semicovalent exchange is reviewed and applied to the perovskite-type manganites [La,M(II)]MnO$_3$. With the hypothesis of covalent and semicovalent bonding between the oxygen and manganese ions plus the mechanism of double exchange, detailed qualitative predictions are made about the magnetic lattice, the crystallographic lattice, the electrical resistivity, and the Curie temperature as functions of the fraction of Mn^{4+} present. These predictions are found to be in accord with recent findings from neutron-diffraction and x-ray data as well as with the earlier experiments on this system by Jonker and van Santen.

I. INTRODUCTION

In a recent paper[1] on the influence of covalent effects in spinel-type structures, it was shown how covalent bonding influences lattice distortions and indirect magnetic-exchange interactions between two magnetic cations separated by an anion. The magnetic interaction was termed semicovalent exchange since it depends upon the concept of semicovalent bonding, a concept which was also introduced in that same paper. Although there are certain similarities between this exchange mechanism and the superexchange mechanism which was first proposed by Kramers[2] in 1934, the two have fundamental differences: in some oxides the two lead to identical predictions, but in others they lead to opposite predictions. The perovskite-type manganites represent a system in which the magnetic moments of the manganese ions are coupled by indirect exchange mechanisms; it is a system for which semicovalent exchange and superexchange give opposite predictions. It is, therefore, a particularly appropriate system for evaluating the merits of the semicovalent-exchange hypothesis, especially as Wollan and Koehler,[3] with the support of x-ray work by Yakel, have just completed a beautiful experimental study of its magnetic and crystallographic lattices as functions of Mn^{4+} content.

In Sec. II, there is a discussion of semicovalence, and in Sec. III there is a restatement of the indirect magnetic coupling between the various manganese ions in a perovskite-type oxide if semicovalence occurs. The effects of covalence on bond length are also pointed out. This discussion is summarized in Table I. The predictions resulting from the superexchange model are contrasted with those from the covalent-bond and semicovalent-exchange models which, in Sec. IV, are applied to the system [La,M(II)]MnO$_3$, where M(II) is Ca^{2+}, Sr^{2+}, or Ba^{2+}. These predictions are summarized in Sec. V and Fig. 6.

II. SEMICOVALENCE

There are three principal contributions to the internal energy of a solid, the electrostatic, electronic, and elastic contributions. In an ideal ionic lattice the electronic contribution is negligible, the principal binding energy coming from the electrostatic term. In a homopolar or metallic lattice the electrostatic term is negligible, the principal binding energy coming from the electronic term.

Previous workers have assumed that the transition-element cations in oxide lattices are ionically bound. Although the superexchange mechanism depends upon the nonionic component of the cation-oxygen bonds, in this model it is presumed that the atomic electron orbitals provide a fairly accurate description for the electrons in the lattice, or that a tight-binding approximation is valid. Whereas various authors[4] 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 their influence on the state of the electrons in the system is qualitatively similar to that of unperturbed empty orbitals.

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[1] 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, and the assumption of ionic bonding is suitable. 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

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[1] J. B. Goodenough and A. L. Loeb, Phys. Rev. **98**, 391 (1955).

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

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

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

amount of electron sharing between cation and anion depends, of course, on the relative stabilities of their 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 an oriented 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 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 semicovalent.

Semicovalence assumes, therefore, that the exchange energy between the shared electron and the cation *d*-shell electrons is greater than the energy difference between the empty lattice orbital and the *d*-orbital energy levels occupied by one electron. It can only occur in those bonds where there is strong overlap of stable, empty cation orbitals and an anion *p* orbital; semicovalent bonds are directed in the same manner as normal covalent bonds. Semicovalence occurs only below the Curie temperature where the net cation magnetic moment is oriented. Above the Curie temperature there is normal coordinate covalence. If the formation of covalent bonding causes a distortion of the lattice from cubic symmetry, there is a transition temperature above which the covalent bonding is not ordered and cubic symmetry results. This transition temperature is above the Curie temperature if the magnetic coupling is due to semicovalent exchange. Normally a distortion of a lattice from cubic symmetry increases the energy gap between the valence and conduction bands so that covalent-bond ordering is a cooperative phenomenon[1] and the ordering temperature can be defined within fairly narrow temperature limits. However, it is possible that covalent-bond ordering may, in some instances, reduce the energy gap between the conduction band and the valence band. In such a case there will not be a well-defined ordering temperature; rather, covalent-bond ordering will occur over a wide temperature range.

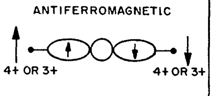
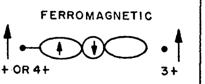
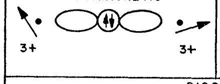
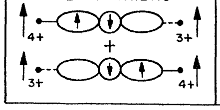
III. Mn—Mn MAGNETIC EXCHANGE

In order to give an interpretation of the system [La,M(II)]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 postulating their stability is the availability of but a single empty *d* orbital. Experimental evidence[1] for this postulate is the tetragonality of hausmannite, Mn$_3$O$_4$, with $c/a>1$. To be consistent with this assumption, it is further postulated that Mn^{4+}, with outer-electron configuration d^3, hybridizes stable (d^2sp^3) orbitals, two empty *d* orbitals being available. These lattice orbitals are octahedral and can therefore point simultaneously toward all six oxygen near neighbors if the Mn^{4+} ion is in an octahedral site, as it is in the perovskite-type manganites [La,M(II)]MnO$_3$. The preference of Cr^{3+} for octahedral coordination when in a spinel lattice is experimental evidence that cations with outer-electron configurations d^3 do hybridize (d^2sp^3) orbitals which are stable enough to effect the cation-anion bonds.[1,5]

TABLE I. Semicovalent model for the magnetic coupling of manganese ions in the perovskite-type 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. T_0 and T_c are the transition temperatures for bond ordering and magnetic ordering, respectively. In the column for schematic electron-spin configurations the cations, marked 4+ and 3+, have an empty orbital pointing toward the O^{2-} *p* orbitals if they are 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

SCHEMATIC ELECTRON-SPIN CONFIGURATIONS	Mn-Mn SEPARATION	TRANSITION TEMPS.	RESISTIVITY	CASE
ORDERED LATTICES				
ANTIFERROMAGNETIC  4+ OR 3+ 4+ OR 3+	SMALLEST	$T_0 > T_c$	HIGH	1
FERROMAGNETIC  3+ OR 4+ 3+	LARGE	$T_0 > T_c$	HIGH	2
PARAMAGNETIC  3+ 3+	LARGEST	$T_c \approx 0$	HIGH	3
DISORDERED LATTICES				
FERROMAGNETIC  4+ 3+ + 3+ 4+	SMALL	$T_0 = T_c$	LOW	4

In the perovskite-type manganites there are three possible Mn—O bonds: a covalent or semicovalent bond if an empty manganese orbital points toward the O^{2-} ion, an ionic bond if the empty Mn^{3+}—(dsp^2) orbitals point away from the O^{2-} ion, or a metallic-like bond if the O^{2-} ion is between a Mn^{3+} and a Mn^{4+} ion in a lattice of disordered Mn^{3+}, Mn^{4+} ions. The first of these bonds is the most stable; it is therefore the shortest bond. The second is the least stable; it is the longest

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[5] E. W. Gorter, Philips Research Repts. 9, 403 (1955).

bond. These bond types are admixed above some transition temperature. The transition from covalent or ionic bonding to admixed bonding is not necessarily associated with a magnetic transition. Judging from the covalent transition[1] in Mn_3O_4 at 1170°C, the covalent-admixed transition should occur well above room temperature in the perovskite-type manganites. Any ionic-admixed transition temperature should also be greater than the Curie temperature. On the other hand a transition from semicovalent to covalent, or from metallic-like to admixed, bonding is accompanied by a magnetic transition. If two or more bond types occur in the same crystal, the long-range magnetic transitions all occur at about the same temperature because of the cooperative character of magnetic ordering.

There are four possible Mn—O—Mn bonding arrangements, and with each of these four arrangements there is a different Mn—Mn separation and a different indirect coupling of the manganese magnetic moments. If both Mn—O bonds can be covalent, the Mn—Mn separation is smallest and the cations couple antiferromagnetically below the Curie temperature, the transition temperature from two semicovalent bonds to partially covalent bonds. It should be noted that it is the same O^{2-} p orbital which extends towards both near-neighbor manganese ions so that above the Curie temperature no one bond is covalent all the time; the two O^{2-} electrons are shared equally with the manganese ions on either side. Below the Curie temperature the bonds are semicovalent, each of the O^{2-} electrons spending the majority of its time on a different side of the O^{2-} ion. Since the two O^{2-} electrons are antiparallel and, by semicovalence, each couples ferromagnetically with the net manganese-ion spin with which it is predominantly associated, the two manganese ions are coupled antiferromagnetically. The Curie temperature is a measure of the exchange-energy gain associated with the ordering of the anion electrons. This argument is summarized in Case 1 of Table I.

If only one Mn—O bond can be covalent, below the covalent-admixed transition one bond is ionic, the other covalent. The Mn—Mn separation is greater than in the case where both bonds can be covalent, and the O^{2-} ion is displaced toward the manganese ion with which it forms the covalent bond. Below the Curie temperature the covalent bond becomes semicovalent so that a net magnetic moment is associated with the O^{2-} ion. This moment is due to the anion electron which participates less in the semicovalent bond; it is therefore antiparallel to the net moment of the manganese ion which is coupled ferromagnetically via semicovalent bonding to the other anion electron. Since there is a direct exchange interaction between the magnetic moment of the anion and that of the neighboring manganese ion which is ionically bound to it, the second manganese-ion moment is also antiparallel to the anion moment, and the two manganese ions are coupled ferromagnetically, as shown in Case 2 of Table I.

If neither Mn—O bond can be covalent, both bonds are ionic. The Mn—Mn separation is largest, and these is no indirect magnetic exchange between the manganere ions. This is illustrated as Case 3 of Table I

Finally, if the anion separates ferromagnetically coupled Mn^{3+} and Mn^{4+} ions in a lattice of disordered Mn^{3+}, Mn^{4+} ions, the state $Mn^{3+}—O—Mn^{4+}$ is degenerate with the state $Mn^{4+}—O—Mn^{3+}$ so that below the Curie temperature ferromagnetic double exchange takes place between the manganese ions, one electron being free to jump through the anion between the two manganese ions to form a metallic-like bond. The double-exchange mechanism was first proposed by Zener.[6] If the Mn^{3+} and Mn^{4+} ions form part of an ordered lattice, however, double exchange is inhibited as the degeneracy is removed. It should also be noted that low electrical resistivity accompanies the double-exchange phenomenon; high electrical resistivity is associated with the other exchange mechanisms even if there is ferromagnetic coupling of the manganese magnetic moments.

These predictions are in sharp contrast to those based on a superexchange model. Although superexchange is also based on the nonionic character of the lattice, it is assumed in this model that the cation s and p orbitals are of little 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 that anion electron which is antiparallel to the net cation spin which is excited whenever the d shell is half or more filled, that electron which is parallel 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 magnetic 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. In this model it is assumed that the exchange energy is smaller than the energy difference between the lattice-orbital and the d-orbital energy levels whereas the opposite is assumed in the semicovalent-exchange model. From such a model the system $[La,M(II)]MnO_3$ should be ferromagnetic for all compositions with a maximum Curie temperature and a minimum electrical resistivity for $x=0.5$, where x is defined as the fraction of manganese ions which are Mn^{4+}. This follows from the fact that both Mn^{3+} and Mn^{4+} ions have d shells which are less than half full and that double exchange should be a more stable mechanism than superexchange. This prediction is not verified by experiment: the ferromagnetic compositional region is only found for $0.2<x<0.4$, and the maximum Curie temperature and minimum electrical resistivity is in the composition $x\approx 0.3$.[7] In the superexchange model there is no way for atoms to couple ferromagnetically in one direction, antiferromagnetically in another as it con-

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

[7] G. H. Jonker and J. H. van Santen, Physica **16**, 337 (1950); J. H. van Santen and G. H. Jonker, Physica **16**, 599 (1950).

tains no anisotropy; similarly the superexchange model cannot account for lattice distortions. Wollan and Koehler[3] have shown that both of these features are required of an adequate model for the system [La,M(II)]MnO$_3$. It can be concluded that superexchange is completely inadequate for this chemical system; it remains to be shown that the covalent and semicovalent-exchange model is adequate.

IV. INTERPRETATION OF THE PEROVSKITE-TYPE SYSTEM [La,M(II)]MnO$_3$

Attention is first focused on the manganese ions of the manganites as these are believed to be primarily responsible for the lattice distortions, magnetism, and electrical-resistivity variations which occur. Discussion of the large-cation effects are deferred until the end of this section. Furthermore, it is assumed that the lowest internal energy of a system is that which permits the largest number of covalent, or semicovalent, manganese-oxygen bonds. Frequent reference will be made to the experimental determinations of Wollan and Koehler.[3] The fraction of manganese ions that are Mn^{4+} is designated by x, and a perovskite-type lattice with manganese ions in octahedral O^{2-} interstices is assumed throughout.

A. Compositions $x=1$

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 of Table I, 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 Wollan and Koehler for CaMnO$_3$ with $x=0.97$. 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.

B. Compositions $0.9<x<1$

If one of the Mn^{4+} ions of a composition with $x=1$ is replaced by a Mn^{3+} ion, the Mn^{3+} ion is surrounded by Mn^{4+} ions of opposite spin to the one it replaced. Since a single Mn^{3+} ion cannot be said to be ordered, it couples ferromagnetically with its six neighbors via double exchange, Case 4 of Table I. (However, because of the antiferromagnetic character of the parent lattice, the extra electron associated with the Mn^{3+} ion does not migrate freely through the lattice as would a single electron in the conduction band of a semiconductor). The generalization then follows that if a small fraction of Mn^{3+} ions are present, these ions should orient themselves antiparallel to the Mn^{4+} ion they replace; this reduces the net moment of the magnetic sublattices to which they belong. The Mn^{3+} ions are randomly distributed, so the two sublattices of the type-G structure are equally reduced; Wollan and Koehler have found this effect by measuring a decrease in the average moment per ion in the antiferromagnetic phase with increasing Mn^{3+} content (see their Fig. 19). This effect should predominate in the compositional region $0.9<x<1$ since the Mn^{3+} ions are essentially isolated and randomly distributed at these low Mn^{3+} concentrations. Further, since the Mn—O bonds of the double-exchange model are isotropic, the cubic structure of the lattice is preserved. Finally, since the double-exchange mechanism is stronger in this system than semicovalent exchange, the Curie temperature may be expected to increase with increasing Mn^{3+} content.

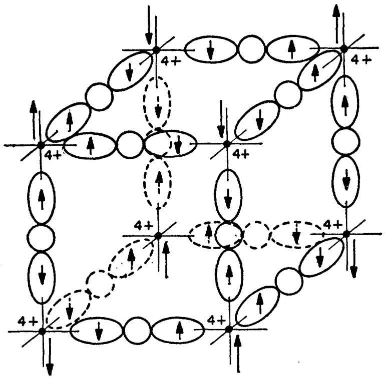

FIG. 1. Magnetic lattice for $x=1$; type G.

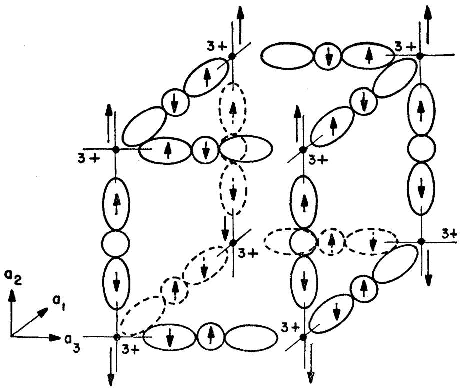

FIG. 2. Magnetic lattice for $x=0$; type A.

C. Compositions $x=0$

In an ideal composition with $x=0$, all the manganese ions are Mn^{3+} and only $\frac{2}{3}$ of the Mn—O bonds can be covalent or semicovalent. The covalent bonds order below some transition temperature in order to reduce the elastic energy associated with the different Mn—Mn separations associated with different bond types. This ordering produces a cooperative elastic strain within the crystal. One possible arrangement of these bonds is an ordering of all the coplanar bonds in (100) planes. In such an arrangement the Mn—O—Mn bonds within a (100) plane correspond to Case 1 of Table I whereas those between (100) planes correspond to Case 3. Such an ordering would produce a large crystalline distortion

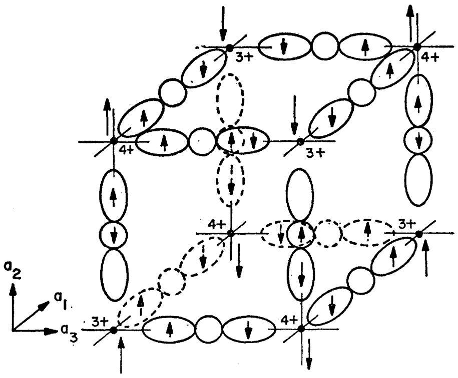

FIG. 3(a). High-energy ordered structure for $x=0.5$; type C.

to tetragonal symmetry with axial ratio $c/a>1$: a similar type of ordering in the spinel lattice[1] of Mn_3O_4 produces an axial ratio $c/a=1.16$. It is immediately seen that in the perovskite structure there is another ordered configuration for the covalent bonds which produces a smaller lattice distortion and is therefore more stable, less energy being expended to distort the cubic symmetry. This configuration is pictured in Fig. 2. In this arrangement all of the O^{2-} ions are bonded covalently in at least one direction: in the (100) planes perpendicular to the a_2 axis the Mn—O—Mn bonds all correspond to Case 2 of Table I whereas all the bonds parallel to the a_2 axis correspond to Case 1. Such an ordering of the covalent bonds produces a lattice distortion with $a_2<a_1=a_3$: however, this distortion is smaller than the former possibility discussed because the Mn—Mn separation in Case 2 is smaller than that in Case 3. If use is made of the axial ratio of Mn_3O_4 and of the lattice parameters $a=8.14$ A, $a_2=7.68$ A of Mn_3O_4 and $LaMnO_3$, respectively, the strain $\Delta\equiv(a_3-a_2)/a_3=0.042$ is calculated.

Further, it was pointed out in the discussion of Case 2 of Table I that the O^{2-} ion is closer to the manganese ion with which it forms a covalent bond than it is to its other neighbor with which it forms an ionic bond. This means that in the planes perpendicular to the a_2 axis the oxygen ions about any Mn^{3+} ion form a rhombus rather than a square. Now a characteristic feature of perovskite-type lattices is a "puckering" of the oxygen octahedra so that the unit cell is double that of the simple perovskite-type structure. This puckering is found, for example, in perovskite itself, $CaTiO_3$.[8] Since the O^{2-} ions in the manganese-containing planes perpendicular to the a_2 axis are bonded covalently to only one of their near neighbors, there is no distortion of covalent-bond angles if "puckering" occurs in this plane. Whereas such a puckering would not destroy the square symmetry of the plane were the manganese ion at the center of a square formation of O^{2-} ions, after puckering the square symmetry is replaced by rhombic symmetry when the manganese ions are at the center of a rhombic formation of O^{2-} ions and the near-neighbor rhombuses alternate the direction of their long axis, as in the case corresponding to Fig. 2. It follows, therefore, that at $x=0$ the lattice may be orthorhombic, rather than tetragonal, with $a_2<a_3=a_1$. The x-ray data reported by Wollan and Koehler in a sample with $x=0.02$ indicates orthorhombic symmetry and $a_2<a_3=a_1$ with the ratio $a_2/a_3=0.965$. An extrapolation of their values to $x=0$ gives the ratio $a_2/a_3=0.959$ with $\Delta=0.041$.

Finally, if the covalent bonds order as in Fig. 2, below the Curie temperature the magnetic coupling within the (100) planes is ferromagnetic, but that between planes is antiferromagnetic, Cases 2 and 1, respectively, of Table I. But this is just the type-A magnetic lattice which is reported by Wollan and Koehler.

It should be noted that the transition temperature for covalent-bond ordering may be much higher than the Curie temperature. The crystalline distortion from cubic symmetry occurs at the transition temperature for covalent-bond ordering; at the Curie temperature the change in lattice parameter is only a second-order effect.

D. Compositions $0<x<0.1$

If a Mn^{4+} ion replaces one of the Mn^{3+} ions of the type-A lattice illustrated in Fig. 2, all six, instead of just four, of the oxygen ions around that site can form covalent bonds. Therefore the addition of Mn^{4+} ions reduces the ratio a_2/a_3 and the transition temperature for covalent-bond ordering is lowered. Further, below the Curie temperature the spin of the Mn^{4+} ion remains parallel to that of the Mn^{3+} ion it replaced since four of the six bonds favor similar magnetic coupling to that with only Mn^{3+} ions present: Mn^{4+}, which is randomly located, couples ferromagnetically with its four neighbors in the (100) plane via double exchange, Case 4. Also it is capable of coupling antiferromagnetically with its two neighbors along the a_2 axis via semicovalent exchange, Case 1. Thus below the Curie temperature the Mn^{4+} ion is constrained to stay in its (100) plane, the antiferromagnetic coupling between planes inhibiting electron transfer from one plane to the other.

It is concluded that the type-A antiferromagnetic lattice should predominate in the compositional region $0<x<0.1$ since the Mn^{4+} ions are essentially isolated

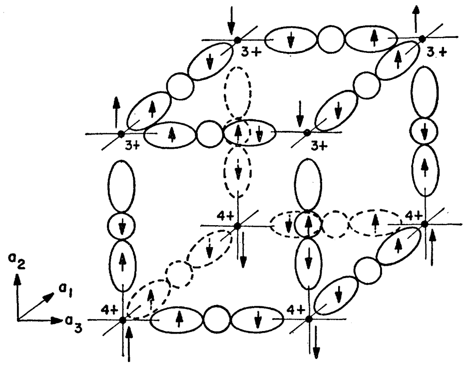

FIG. 3(b). High-energy magnetic lattice for $x=0.5$; type C.

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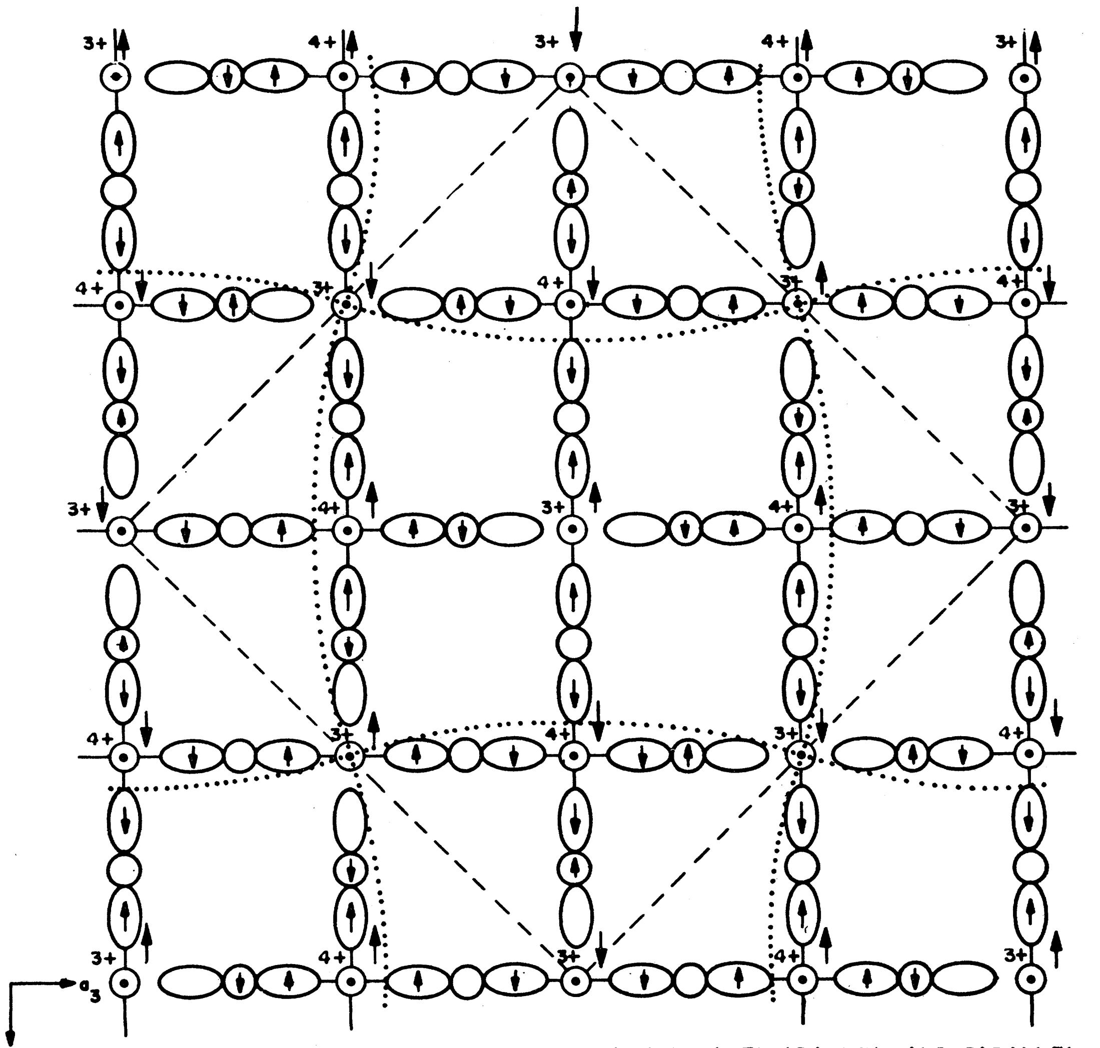
[8] H. D. Megaw, Acta Cryst. 5, 739 (1952).



SUCCESSIVE (100) PLANES ARE ALTERNATELY ANTIPARALLEL AND PARALLEL TO THIS PLANE WITH IDENTICAL BOND CONFIGURATIONS, ROWS OF MANGANESE IONS ALONG a_2 AXIS ARE ALTERNATELY ALL Mn^{3+} AND ALL Mn^{4+} WITH Mn-O-Mn BONDS CORRESPONDING TO CASE 1 OF TABLE I.

FIG. 4. Low-energy magnetic lattice for $x=0.5$; type *CE*.

and randomly distributed at these low values of x. The Curie temperature increases with Mn^{4+} content because of the added possibilities for double exchange. The axial ratio a_2/a_3 increases toward one with the number of bonds in the a_1, a_3 plane which are changed from Case 2 to Case 4 of Table I.

E. Compositions $x=0.5$

If $x=0.5$, there are just as many Mn^{3+} ions as Mn^{4+} ions present. Although the M(II) ions or lattice vacancies which are responsible for the presence of the Mn^{4+} ions may be randomly located, the ready migration of electrons from Mn^{3+} to Mn^{4+} ions makes it possible for ordering of the Mn^{3+} and Mn^{4+} ions to occur. This ordering occurs at transition temperatures which are similar to the covalent-bond ordering temperature since the driving force behind this ordering is due more to covalent-bond formation than Madelung-energy considerations.

At $x=0.5$ there are three possible ordered-bond arrangements which give cooperative lattice strains: these are pictured in Figs. 3(a), 3(b), and 4. They correspond to an ordering of Mn^{3+} and Mn^{4+} ions in alternate (111), (100), or (110) planes, respectively. The electrostatic energies for these three configurations are only slightly different; the elastic energy, however, is markedly reduced for the configuration of Fig. 4. This follows from the fact that in the configurations in Fig. 3 the ratio $(a_3-a_2)/a_3$ corresponds to that for the composition $x=0$, whereas in Fig. 4 this ratio is only half as great since half of the bonds in a (100) plane correspond to Case 1 of Table I. The ordering within the (100) planes gives the optimum electrostatic configuration as well as a cooperative elastic strain which conserves the square symmetry. If the Mn^{3+} ions establish the square symmetry, the Mn^{4+} ions are displaced in the cooperative way indicated by the dotted lines in Fig. 4. Further, there are sufficient covalent bonds in these planes to inhibit a puckering of the oxygen octahedra. From binding-energy considerations it is predicted, therefore, that the covalent bonds order as shown in Fig. 4 and, using the lattice parameters for $x=0$, that the lattice distortion from cubic symmetry is to tetragonal with $c/a=0.979$. This corresponds to a measured value, as reported by Wollan and Koehler, of $c/a=0.974$ at $x=0.58$.

Below the Curie temperature semicovalent bonds are formed to produce completely cooperative magnetic coupling between the manganese ions: the resulting magnetic lattice is just the type-*CE* configuration which was determined by Wollan and Koehler from neutron-diffraction experiments on a sample with $x=0.58$. It is illustrated in Fig. 4.

Finally, it is suggested that if the high-temperature cubic phase is puckered, the energy gap between the conduction band and the valence band might be reduced by a bond-ordering which inhibited a puckering of the lattice. This could account for the lack of a sharp ordering temperature on going from tetragonal to cubic symmetry as reported by Wollan and Koehler.

F. Compositions $x=0.75$

At $x=0.75$, half of the Mn^{3+} ions in any (100) plane of Fig. 4 are replaced by Mn^{4+} ions, and a cooperative elastic strain within the plane can only occur if Mn—O—Mn bonds corresponding to Case 2 of Table I are aligned along the same axis. This is in contrast with the type-*CE* lattice shown in Fig. 4 where the Case-2 Mn—O—Mn bonds are so ordered that square symmetry within the (100) planes is preserved without requiring any Mn—O—Mn bond to be strained. This alignment of the ionic Mn—O bonds means that along two axes all bonds correspond to Case 1 whereas along the third axis half of the bonds correspond to Case 2. Such an ordering of the covalent bonds gives an axial ratio $c/a=1.020>1$ if the lattice parameters for $x=0$ are used to give a measure of the relative Mn—Mn separations for Cases 1 and 2. The measured[3] axial ratio for a sample with $x=0.8$ is $c/a=1.022$. It should be noted that elastic considerations inhibit the location of neighboring Mn^{3+} ions along the *c* axis as such a configuration would introduce a Mn—Mn configuration corresponding to Case 3. If the ions order as shown in Fig. 5, the elastic energies are minimized; each row of manganese ions parallel to the *c*-axis have the same length.

Below the Curie temperature the magnetic exchange interactions are not completely cooperative. Because of the ordering induced by elastic-energy considerations, there are no double-exchange interactions. If the magnetic lattice orders as shown in Fig. 5, one third of the Mn^{4+} ions have only two of their six near-neighbor interactions opposed to the configuration while four favor it, and all other interactions are cooperative. This is the most nearly cooperative coupling possible, and it corresponds to Wollan and Koehler's type-*C* configuration.

G. Compositions $0.5<x<0.75$

If a Mn^{4+} ion replaces a Mn^{3+} ion in the type-*CE* configuration of Fig. 4, the lattice distortion is diminished since the number of covalent bonds in the (100) plane is increased. Also the Mn—Mn separations in the (100) plane are no longer completely cooperative and the covalent-bond ordering temperature is reduced. Experimentally it is observed that the covalent-ordering transition-temperature region decreases from just above room temperature to below room temperature in this compositional range.

Below the Curie temperature the added Mn^{4+} ion is antiparallel to the Mn^{3+} ion it replaces since four out of six of its neighbors favor this magnetic arrangement: it couples ferromagnetically with the Mn^{3+} ions in the two neighboring (100) planes via double exchange, Case 4 of

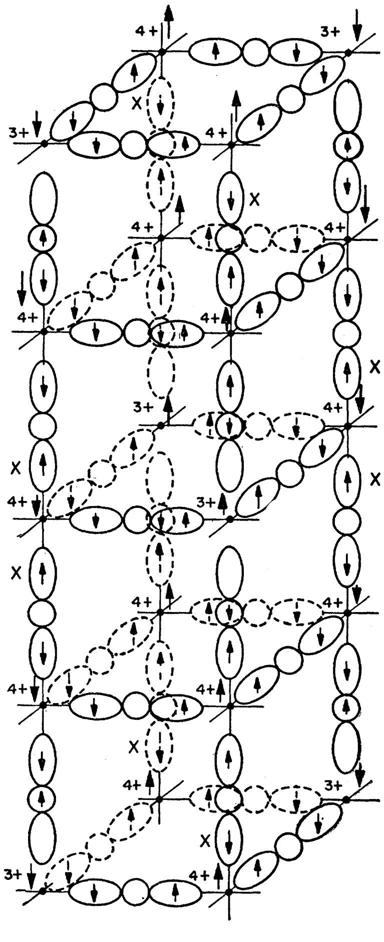


FIG. 5. Magnetic lattice for $x=0.75$; type *C* bonds marked with an *X* are mismatched.

Table I, while the four Mn^{4+} neighbors compete equally via Case 1 for a spin parallel or antiparallel to that of the original Mn^{3+} ion. This corresponds to the experimental conclusions of Wollan and Koehler from neutron-diffraction intensity measurements in patterns from compositions with $0.5<x<0.71$.

At some point between $x=0.5$ and $x=0.75$ there will be a two-phase region in which the modified type-*CE* elastic and magnetic configuration described above is mixed with the type-*C* pattern corresponding to $x=0.75$. This is probably an extremely small region near the composition $x=0.75$ since ordering of the bonds within the (100) planes should be a cooperative phenomenon.

H. Compositions $0.75<x<0.9$

If a Mn^{4+} ion replaces a Mn^{3+} ion in the type-*C* lattice of Fig. 5, the lattice distortion and the covalent-bond transition temperature are reduced; magnetically the Mn^{4+} ion couples parallel to the Mn^{3+} ion it replaces, and the type-*C* magnetic structure is preserved. As more Mn^{4+} ions are added, however, a composition is reached where the elastic forces no longer order the lattice; the structure then becomes cubic with a magnetic configuration corresponding to the modified type-*G* lattice described for compositions $0.9<x<1$. Between the type-*C* and the modified type-*G* lattices there is a two-phase region: this region probably lies within the compositional range $0.85<x<0.9$.

I. Compositions $0.25<x<0.375$

At $x=0.25$ the electrostatic energy is minimized if the Mn^{4+} ions order so as to form a b.c.c. array of cell edge two Mn—O—Mn distances. A subsequent ordering of the covalent bonding which makes every Mn^{4+}—O—Mn^{3+} bond correspond to Case 4 of Table I and every Mn^{3+}—O—Mn^{3+} bond to Case 2 would produce a cooperative elastic strain to rhombohedral symmetry, the Case 4 Mn—Mn separations being smaller than those corresponding to Case 2. Further, there is ferromagnetic coupling throughout and a mechanism for relatively high electric conductivity through the Case 4 bonds.

In such a structure the strength of the double-exchange mechanism is reduced by the electrostatic ordering, the reduction increasing with the polarity difference between the ions designated Mn^{4+} and Mn^{3+}. It is probable, therefore, that at last at higher temperatures the Mn^{4+} ions are randomly distributed throughout the lattice so that the lattice remains cubic even below the Curie temperature where the prevalence of double exchange makes the lattice ferromagnetic.

For the compositional range $0.25<x<0.375$ there is less reason to expect an ordering of the Mn^{4+} ions. The disordered lattice is cubic with a relatively high Curie temperature. Since its bonds are metallic-like, it has a low resistivity. The maximum Curie temperature and minimum electrical resistivity must occur at that composition for which the double-exchange mechanism is optimized; this optimum occurs for that disordered composition which has the largest number of Mn^{3+} ions with one, and only one, Mn^{4+} near neighbor. In an ordered lattice this occurs for $x=0.25$; in a disordered lattice this occurs at an $x>0.25$. Since the double-exchange mechanism requires a disordered arrangement, in the Appendix there is a calculation of the value of x at which there are the largest number of Mn^{3+} ions with one, and only one, Mn^{4+} near neighbor in a random matrix of Mn^{4+} and Mn^{3+} ions. This value is $x=0.31$. Any deviation of the lattice from complete randomness of the Mn^{4+} ions reduces this value toward $x=0.25$. The measurements of Jonker and van Santen[7] indicate a maximum Curie temperature and a minimum resistivity at $x\approx 0.3$.

J. Compositions $0.1<x<0.25$ and $0.375<x<0.5$

The compositional regions between the modified type-*A* and the ferromagnetic phases and between the ferromagnetic and the type-*CE* phases must be two-phase. Therefore within $0.1<x<0.25$ there must be a two-phase region in which the modified type-*A* and the ferromagnetic lattice are both present. The axial ratio a_2/a_3 for the solubility limit of the modified type-*A* lattice will be closer to one than its value at $x=0$; nevertheless it appears it should be possible to detect the two-phase character of this lattice by x-ray as well as neutron-diffraction methods as one phase is cubic, the other is not. Wollan and Koehler have observed the two magnetic phases; they were unable to detect two crystallographic phases within this compositional region.

Similarly within the compositional range $0.375<x<0.5$ there must be a ferromagnetic, cubic phase coexistent with an antiferromagnetic, tetragonal phase. Again only the two magnetic phases have been identified.

K. Effect of the Large Cations

So far only the role of the manganese cations has been considered. The large cations must also influence the lattice structure and the covalent-bond formation. If the bivalent cations which replace the La^{3+} ions are too large, there will be a composition at which the perovskite structure is no longer maintained. This is found[7] for $(La,Sr)MnO_3$ and $(La,Ba)MnO_3$ at concentrations of Sr^{2+} or Ba^{2+} much above 0.5. The series $(La,Ca)MnO_3$ forms solid solutions of perovskite-type structure throughout the entire compositional range.

If the large cations form bonds with considerable covalent character in this structure, this influences the transition temperature from an ordered to disordered covalent-bond arrangement. The most stable hybrid orbitals of the larger cations are tetrahedral (sp^3) orbitals. If the large cations form partially 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 has a perpendicular p orbit which may

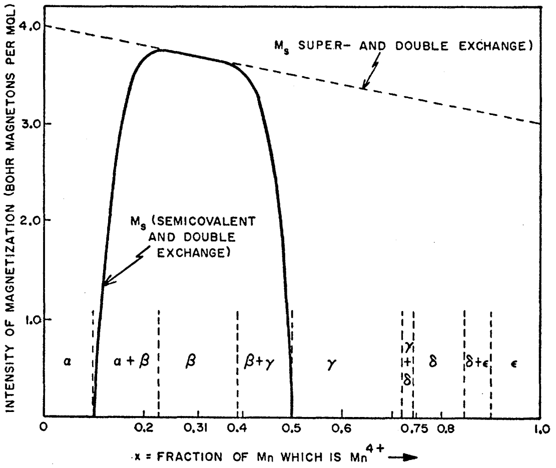


FIG. 6. Predicted intensity of magnetization M_s and phase diagram for the system. [La,M(II)]$\mathrm{MnO_3}$ according to covalent-bond, semicovalent-exchange model.

lie along a Mn—O—Mn axis. This is the optimum configuration 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 or, in the case of ferromagnetism via double exchange, the higher the Curie temperature.

Jonker and van Santen have found a maximum ferromagnetic Curie temperature at $x\approx 0.3$ for Ca-, Sr-, and Ba-substituted manganites; these maximum temperatures are, respectively, 270°K, 375°K, and 350°K. Since the stability of the M^{2+}—O covalent bond increases from $\mathrm{Ca^{2+}}$ to $\mathrm{Sr^{2+}}$ and $\mathrm{Ba^{2+}}$, the increase of 100°C in the maximum Curie temperature can be understood as due to the differing amounts of covalence associated with the large-cation bonds. 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)$\mathrm{MnO_3}$ to (La,Ba)$\mathrm{MnO_3}$.

V. SUMMARY

The predictions of Sec. IV are summarized in Fig. 6 where the compositional regions marked α, $\alpha+\beta$, β, $\beta+\gamma$, γ, $\gamma+\delta$, δ, $\delta+\epsilon$, and ϵ correspond to the following phases:

Phase α:

(i) Orthorhombic ($a_2<a_3=a_1$). At $x=0$ $\Delta\equiv(a_3-a_2)/a_3=0.042$.

(ii) Antiferromagnetic type A with $T_0>T_c=T_c^s$ at $x=0$, where T_0 is the covalent-bond ordering temperature, T_c^s is the Curie temperature for semicovalent exchange.

(iii) As x increases, (a_3-a_2) and T_0 decrease while T_c increases; the $\mathrm{Mn^{4+}}$ ions couple parallel to the $\mathrm{Mn^{3+}}$ ions they replace.

(iv) High resistivity.

Phase $\alpha+\beta$:

(i) Orthorhombic ($a_2<a_3=a_1$) plus cubic.

(ii) Antiferromagnetic type A plus ferromagnetic with $T_0>T_c$ and $T_c^s<T_c<T_c^d$, where T_c^d is Curie temperature for double exchange and $T_c^d>T_c^s$ is assumed.

(iii) As x increases, T_0 decreases toward T_c^d, T_c increases toward T_c^d, and resistivity decreases sharply.

Phase β:

(i) Cubic. (Rhombohedral possible).

(ii) Ferromagnetic with $T_0=T_c\approx T_c^d$.

(iii) Resistivity low.

(iv) Maximum T_c and minimum resistivity at $x=0.31$.

Phase $\beta+\gamma$:

(i) Cubic plus tetragonal ($c/a<1$).

(ii) Ferromagnetic plus antiferromagnetic type CE with $T_0>T_c$ and $T_c^d>T_c>T_c^s$.

(iii) As x increases, T_c decreases toward T_c^s, T_0 and resistivity increase.

Phase γ:

(i) Tetragonal ($c/a<1$) with $(c-a)\approx\Delta/2$ at $x=0.5$.

(ii) Antiferromagnetic type CE with $T_0>T_c=T_c^s$ at $x=0.5$.

(iii) As x increases, $(c-a)$ and T_0 decrease, T_c passes through maximum, and the added $\mathrm{Mn^{4+}}$ ions couple antiparallel to the $\mathrm{Mn^{3+}}$ ions they replace.

(iv) High resistivity.

Phase $\gamma+\delta$:

(i) Tetragonal ($c/a<1$) plus tetragonal ($c/a>1$).

(ii) Antiferromagnetic types CE and C with $T_c>T_c^s$.

(iii) As x increases, T_c decreases and T_0 passes through a minimum value.

(iv) High resistivity.

Phase δ:

(i) Tetragonal ($c/a>1$) with $(c-a)\approx\Delta/2$ at $x=0.75$.

(ii) Antiferromagnetic type C with $T_0>T_c>T_c^s$.

(iii) As x increases, $(c-a)$, T_0, and T_c decrease, and added $\mathrm{Mn^{4+}}$ ions couple parallel to the $\mathrm{Mn^{3+}}$ ions they replace.

(iv) High resistivity.

Phase $\delta+\epsilon$:

(i) Tetragonal ($c/a>1$) plus cubic.

(ii) Antiferromagnetic types C and G with $T_0>T_c>T_c^s$.

(iii) As x increases, T_c decreases and T_0 passes through a minimum.

(iv) High resistivity.

Phase ϵ:

(i) Cubic.

(ii) Antiferromagnetic type G with $T_c\geq T_c^s$.

(iii) As x increases, T_c decreases to T_c^s at $x=1$ and the $\mathrm{Mn^{3+}}$ ions couple antiparallel to the $\mathrm{Mn^{4+}}$ ions they replace.

(iv) High resistivity.

It should be noted that the $Mn^{4+}-O$ bond has been assumed equal in length to the $Mn^{3+}-O$ bond with covalent character. This is a fair approximation if the covalent character of the $Mn^{4+}-O$ bond is less than that in the $Mn^{3+}-O$ bond; the general decrease in T_0 with added Mn^{4+} content is consistent with this hypothesis.

It is concluded, therefore, that at least in the manganites $[La,M(II)]MnO_3$ the theory of superexchange is inadequate whereas the concepts of covalence and semicovalent exchange offer a consistent model for explaining complicated variations with chemical composition of crystal structure and magnetic interactions. These concepts were first developed to account for cation ordering, lattice distortions, and magnetic interactions in spinel-type lattices[1]; their generality demands that they be valid for other crystal types. It is therefore significant that they apply so strikingly to this perovskite-type system.

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APPENDIX

Consider the following problem: assume that when a La^{3+} ion is replaced by a M^{2+} ion, two Mn^{3+} ions become Mn^{4+} and a neighboring La^{3+} becomes La^{2+} so as to minimize the Madelung energy of the configuration. Calculate the fraction of M^{2+} ions necessary to make half the manganese ions Mn^{4+} if the M^{2+} ions replace lanthanum ions randomly and the replacement of a La^{2+} by M^{2+} causes no change in the valencies of the manganese ions. This problem has identical boundary conditions and is mathematically similar to the problem of calculating the fraction of randomly distributed Mn^{4+} ions which gives the largest number of Mn^{3+} ions with one, and only one, Mn^{4+} near neighbor.

Two Mn^{4+} ions are created by the first La^{3+} ion replaced by a M^{2+} ion. When the second lanthanum ion is replaced, the probability that it be a La^{2+} ion is $p_1 = 1/(N-1)$, and that it be a La^{3+} ion is $(1-p_1)$, where N is the total number of lanthanum ions present. When the third lanthanum ion is replaced, the probability that it be a La^{2+} ion is $p_2=(2-p_1)/(N-2)$, and that it be a La^{3+} ion is $(1-p_2)$. When the $(n+1)$th lanthanum ion is replaced, the probability that it be a La^{2+} ion is $p_n=(n-p_{n-1})/(N-n)$, and that it be a La^{3+} ion is $(1-p_n)$. Half the manganese ions are Mn^{4+} when

$$2\left(n-\sum_n \frac{n-p_{n-1}}{N-n}\right)=\frac{N}{2}. \tag{1}$$

When N is large, the summation can be approximated by

$$\sum_n \frac{n}{N-n}\approx N\int_0^x \frac{x'dx'}{1-x'}=-N[x+\log(1-x)], \tag{2}$$

where $x=n/N$. Equation (1) reduces, therefore, to

$$2x=0.25-\log(1-x),$$
$$x=0.31.$$

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Symmetry Properties of the Energy Bands of the Zinc Blende Structure

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The symmetry properties of the one-electron energy bands of a crystal of the zinc blende structure are studied by means of group theory. This is done both with and without the inclusion of spin-orbit coupling. The character tables and compatability tables are obtained for the various irreducible representations of the space group T_d^2 associated with the zinc blende structure. The degeneracies and the gradients of the various possible energy bands are studied at lines and points of symmetry in the Brillouin zone. These results are compared with those for the equivalent energy bands in a crystal of the diamond structure.

I. INTRODUCTION

COMPOUNDS of the zinc blende structure are today assuming positions of increasing importance and interest in solid-state physics. The III–V compounds such as InSb are being intensively studied as semiconductors,[1] while II–VI compounds such as ZnS are used both as photoconductors and as phosphors.[2] There is thus much interest in the nature of the one-electron energy bands in these compounds. Considerable information of a qualitative nature can be deduced about the energy-band maxima and minima in these compounds by means of a judicious combination of symmetry arguments, perturbation theory, and experimental information.[3] Here we propose to determine what can be said

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