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Localized model for systems with double-exchange coupling*

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Magnetic spins in crystals of mixed valence can simultaneously experience two kinds of coupling: the superexchange and the double exchange. The latter coupling, first invoked by Zener and further worked out by Anderson and Hasegawa, is mediated by additional electrons or holes introduced into the system. In the present paper an effective site-spins interaction Hamiltonian for double exchange is formulated. This Hamiltonian involves ascending powers of the bilinear interaction $\vec{S}_i \cdot \vec{S}_j$. The highest power is determined by the value of the site spin. Thus, for spin-$\frac{1}{2}$ the double exchange interaction looks like the ordinary Heisenberg-type coupling. Spin-1 Hamiltonian contains also a biquadratic coupling. Spin-$\frac{3}{2}$ includes a bicubic interaction, spin-2 a biquartic one, etc. It is argued that a localized description of systems with the double exchange is usually sufficient. The phase diagrams are entirely different from the one predicted by the semiclassical (large-spin) band theory proposed by de Gennes. The critical concentrations of the carriers are evaluated at $T = 0$ K in the mean-field-theory approximation. An applied magnetic field is shown to have little influence on the strength of the double-exchange coupling. Spin configurations in the presence of the field are also discussed. Finally, a spin-wave theory for such systems is constructed.

I. INTRODUCTION

Twenty six years ago Jonker and Van Santen[1] discovered some intriguing magnetic and conductivity properties in the compounds $(\mathrm{La}_{1-x}M_x)\mathrm{MnO}_3$, where M denotes the atoms of Ca, Sr, or Ba. For finite values of x, those exceeding, say 9%, a significant increase in the conductivity and a nonvanishing spontaneous magnetization were observed. The occurrence of a net magnetization was confirmed by the neutron diffraction experiments of Wollan and Koehler,[2] who detected a simultaneous presence of antiferromagnetic and ferromagnetic lines at several concentrations of calcium atoms.

These unusual properties certainly stem from the fact that the compounds are in the state of mixed valence. Consider, for instance, $\mathrm{La}^{3+}\mathrm{Mn}^{3+}\mathrm{O}_3$, i.e., the compound with $x = 0$. Now, if some three-valent La ions are replaced by two-valent Ca ones, then some of the Mn^{3+} ions, of configuration $(3d)^4$ have to be transformed into Mn^{4+}. As a result holes, which can carry the electric current, appear in the system. On the other hand the replacement of Ca by La, in the compound with $x = 1$, leads to introduction of mobile electrons.

The puzzling existence of the ferromagnetic moment in crystals of mixed valence has been explained by Zener[3] who has shown that the hopping carriers supply an effective coupling mechanism for the manganese spins. This coupling favors an essentially ferromagnetic spin configuration, as explained in Sec. II, and has been named "double exchange."

A thorough analysis of the double-exchange interaction between two spins has been worked out by Anderson and Hasegawa.[4] This analysis is outlined in Sec. III. Their theory is formulated in terms of two parameters b and J_I, the first of which characterizes the hopping rate of the carrier between the sites, and the second describes the exchange coupling of the carrier to the site spins. Since the compounds in question are only weakly conductive, the carriers move through the crystal very slowly, so the condition $J_I >> b$ has to be satisfied. The authors have pointed out that the coupling is entirely different from the usual exchange interaction, but they have not succeeded in deriving an effective Hamiltonian.

The third and apparently the last, up to now, paper on the subject is due to de Gennes.[5] He has realized that the constant b is in addition bigger than the superexchange coupling constant between the site spins, which simplifies the form of the effective interaction. de Gennes constructs a semiclassical large site-spin theory for a crystal with exchange and double-exchange couplings. In the semiclassical limit the energy of the carrier migrating between two sites is proportional to the cosine of half of the angle between the spins. This is very unlike the angular dependence found for the direct or superexchange. Since the coupling energy in a crystal is shared between the carriers, de Gennes is of the opinion that this energy cannot be written as a sum of terms relating the ionic spins by pairs. As a consequence he formulates his theory in terms of a band picture and he adopts a tight-binding approximation for the carrier's wave function. This theory leads to the conclusion that at $T=0$ K the system will be either in a canted or a ferromagnetic phase, depending on the concentration of the carriers.

The above band model for double exchange is certainly satisfying from the solid-state-physics-concepts point of view. However it seems to be difficult to work with in the manifestly quantum-mechanical case of a finite spin. Our contention is that in the highly localized limit $J_l >> b$, when the band of the allowed energies of the carrier is very narrow, the band model is not necessary, as long as we are interested in the effective spin coupling. In this very limit the Hamiltonian should be a sum of pair interactions. This is because for $J_l >> b$ the carriers move through the crystal sporadically and the coupling extends only small distances. In one respect the situation is like that in the Ruderman-Kittel-Kasuya-Yosida[6] interaction in rare-earth metals; namely, the conduction-band electrons supply there an effective pairwise coupling of the site spins.

In the present paper we derive a quantum Hamiltonian for double exchange between two magnetic sites. This is done in Sec. IV. It turns out that the coupling has the form of a polynomial which contains consecutive powers of the scalar product of the two site-spins operators. The order of this polynomial depends on the value of the spin. The coupling, though primarily ferromagneticlike, contains therefore in general also biquadratic, bicubic, biquartic, etc., interactions. In the limit of large spin the semiclassical results are obtained.

In Sec. V the influence of a magnetic field on the double-exchange coupling is discussed and it is shown not to be essential. In Sec. VI the Hamiltonian for a layer-type N-spin system is formulated as a sum of pair Hamiltonians. The random nature of the carriers-supplied couplings is treated within a framework of the mean-field theory. The limit of small carrier concentrations is assumed. When no carriers are present the system is an antiferromagnet. The system is taken to possess some uniaxial anisotropy.

In Sec. VII a mean-field analysis is performed on the ground-state of spin-$\frac{1}{2}$ through 2 antiferromagnets with double exchange. The results are entirely different from those predicted for the large-spin crystals. In particular the spin-$\frac{1}{2}$ system is never in a canted phase; it is either antiferromagnetic or ferromagnetic. In general, and the spin-1 system seems to be the most regular one, at $T=0$ K the system can be in any of the four following phases: For sufficiently small concentrations the antiferromagnetic phase is stable. For somewhat bigger concentrations a canted phase appears. The system is still very much like an antiferromagnet except that the sublattices cant off the anisotropy axis. For even bigger concentrations a second canted phase, as we call it, is stable. In this phase the sublattice configuration looks like in the spin-flop phase of an antiferromagnet. A further increase in concentration produces a ferromagnetic phase. However in the case of a spin-2 system this phase is never reached in the absence of a magnetic field. The stability regions in the presence of the magnetic field are also discussed in this section.

In Sec. VIII the problem of a ferromagnet with double exchange is investigated. It turns out that for spins smaller than 2 the ferromagnetic phase is always stable. However in the case of spin 2 a canted phase appears for concentrations above some critical value. In Sec. IX the layer-type antiferromagnet of $S \leq 2$ with double exchange is analyzed and an estimate of the constant b is given. A spin-wave theory for such systems is constructed in Sec. X.

Finally, in the Appendix some of the results for spin-$\frac{5}{2}$, -3, -$\frac{7}{2}$, and -4 systems are presented. Even for such large spins the phase diagrams do not qualitatively turn into the one predicted by de Gennes. The reason for this is that de Gennes does not treat the exchange and double exchange contributions to the Hamiltonian on an equal footing; namely, the large-spin limit is performed on the double-exchange part only.

II. MECHANISM OF DOUBLE EXCHANGE

To be specific consider, after Anderson and Hasegawa,[4] two magnetic sites of $Ca^{2+}Mn^{4+}O_3$. Assume that the three d_{xy}, d_{yz}, d_{xz} electrons are strongly coupled and give a net spin vector of $\frac{3}{2}$. The two magnetic sites are separated by an oxygen atom with two p valence electrons. The p electrons can leave the ground-state configuration and move onto the manganese sites which give rise to the superexchange Heisenberg-type interactions between the magnetic spins.[7,8]

Now, if one of the Mn^{4+} atoms is replaced by Mn^{3+} the cluster will acquire one additional electron d_{z^2}. This electron will be coupled ferromagnetically or antiferromagnetically to the core spin by means of the direct exchange of strength J_l. The coupling tends to confine the electron on the magnetic site. However, since J_l is not infinite, the electrón can leave the site and the cluster starts to resonate between the two configurations: with the additional electron to the left or to the right of the oxygen atom. As a result the extra electron will hop between the sites with some frequency b (at least when the site spins are forced to be aligned parallel, as explained later). The hopping is not a direct one, since it is carried through the oxygen electrons.

There are several mechanisms by means of which the transfer of the electron takes place:

(a) The first-order process, invoked by Zener,[3] is an exchange-type interaction, which can be schematically written

$$\mathrm{Mn}^{4+}\ \underset{2\uparrow,3\downarrow}{\mathrm{O}}\ \underset{1\uparrow}{\mathrm{Mn}^{3+}} \rightarrow \underset{2\uparrow}{\mathrm{Mn}^{3+}}\ \underset{1\uparrow,3\downarrow}{\mathrm{O}}\ \mathrm{Mn}^{4+}\ ,$$

where 1,2,3 label the additional electron and the oxygen valence electrons. This process consists of two simultaneous motions (hence the name "double exchange"): the transfer of the electron from the right Mn atom to the central O and the transfer of an electron from the central O to the left Mn. The energy required for the process is proportional to the overlap between the *p* and *d* wave functions[4] and the effective contribution to the transfer constant *b* has a form of the exchange integral.

(b) The second-order process, introduced by Anderson and Hasegawa[4], in which there is one electron on the oxygen in the intermediate state

$$\mathrm{Mn}^{4+}\ \underset{2\uparrow,3\downarrow}{\mathrm{O}}\ \underset{1\uparrow}{\mathrm{Mn}^{3+}} \rightarrow \underset{2\uparrow}{\mathrm{Mn}^{3+}}\ \underset{3\downarrow}{\mathrm{O}}\ \underset{1\uparrow}{\mathrm{Mn}^{3+}} \rightarrow \underset{2\uparrow}{\mathrm{Mn}^{3+}}\ \underset{1\uparrow,3\downarrow}{\mathrm{O}}\ \mathrm{Mn}^{4+}\ .$$

(c) Another second-order process (but of less importance) which can enhance *b* will follow the pattern with no electrons on the oxygen in the intermediate state

$$\mathrm{Mn}^{4+}\ \underset{2\uparrow,3\downarrow}{\mathrm{O}}\ \underset{1\uparrow}{\mathrm{Mn}^{3+}} \rightarrow \underset{2\uparrow}{\mathrm{Mn}^{3+}}\ \mathrm{O}\ \underset{1\uparrow,3\downarrow}{\mathrm{Mn}^{2+}} \rightarrow \underset{2\uparrow}{\mathrm{Mn}^{3+}}\ \underset{1\uparrow,3\downarrow}{\mathrm{O}}\ \mathrm{Mn}^{4+}\ .$$

(d) The last mechanism is higher-order processes which involve the core electrons.

All of these processes have the effect of moving the extra electron from one magnetic site to the other without changing the spin orientation of the hopping electron. This property of the transfer has been proved by Anderson and Hasagawa in the case of processes (a) and (b) by means of the Serber method.[9] However, for all of these processes, this can be readily established on the basis of the spin conservation and the Pauli principle: the initial and final states of the oxygen have to be singlets.

Since the electron is polarized by the direct exchange with one of the site spins and the polarization is not changed on hopping, the new mechanism tends to align the site spins ferromagnetically. However, we will see that the interaction carried through the hopping electron, though primarily of ferromagnetic features, is in reality more complex.

The above picture of the double-exchange mechanism is insensitive to the fact whether the hopping carrier is an electron or perhaps a hole. The latter situation occurs when in the crystal of $\mathrm{LaMn^{3+}O_3}$ some $\mathrm{Mn^{3+}}$ ions are replaced by $\mathrm{Mn^{4+}}$.

III. ENERGY OF THE HOPPING ELECTRON

Let the spin of the hopping electron be denoted by $\vec{s}$ and the site spins by $\vec{S}_1$ and $\vec{S}_2$, respectively. Let the site-spin quantum numbers be the same and equal to S.

Now, when the electron is on a site, the site can be either in the state with total spin $S+\frac{1}{2}$ or $S-\frac{1}{2}$. If this is the first site the corresponding wave functions will be denoted, after Anderson and Hasegawa, by $d_1\alpha$ and $d_1\beta$, respectively. If this is the second site: by $d_2\alpha'$ and $d_2\beta'$.

The Hamiltonian for the cluster of two sites and of the electron can be divided into the superexchange part and $\mathcal{H}^c$, which consists of the direct exchange energy of the site electron plus, qualitatively, the energy of hopping. The diagonal matrix elements of H^c are

$$\langle d_1\alpha|\mathcal{H}^c|d_1\alpha\rangle = -J_l S\ , \tag{3.1a}$$

$$\langle d_1\beta|\mathcal{H}^c|d_1\beta\rangle = J_l(S+1)\ , \tag{3.1b}$$

$$\langle d_2\alpha'|\mathcal{H}^c|d_2\alpha'\rangle = -J_l S\ , \tag{3.1c}$$

$$\langle d_2\beta'|\mathcal{H}^c|d_2\beta'\rangle = J_l(S+1)\ , \tag{3.1d}$$

the other one-site matrix elements vanish, and the transfer matrix elements are

$$\langle d_1\alpha|\mathcal{H}^c|d_2\alpha\rangle = b\ , \tag{3.2a}$$

$$\langle d_1\alpha|\mathcal{H}^c|d_2\beta\rangle = 0,\ \text{etc.}, \tag{3.2b}$$

where $d_2\alpha$ ($d_2\beta$) is a sum of projections of the states α' and β' on the state $\alpha(\beta)$ on the second site. In order to explain this more precisely, note that we have here a problem of addition of three spins $\vec{S}_1$, $\vec{S}_2$, and $\vec{s}$. The addition can be performed in three ways:

(a) First one combines the first site spin and the electronic spin and subsequently couples this net spin with the second site spin

$$\vec{S}_1+\vec{s}=\vec{S}_1{}',\quad \vec{S}_1{}'+\vec{S}_2=\vec{S}_0\ , \tag{3.3a}$$

where S_0 denotes the net spin for the cluster.

(b) First one combines the spins of the second site and of the electron and then adds the first site spin

$$\vec{S}_2+\vec{s}=\vec{S}_2{}',\quad \vec{S}_2{}'+\vec{S}_1=\vec{S}_0\ . \tag{3.3b}$$

(c) First one couples the site spins and then combines this with the electronic spin

$$\vec{S}_1+\vec{S}_2=\vec{S}_t,\quad \vec{S}_t+\vec{s}=\vec{S}_0\ . \tag{3.3c}$$

Note that α and β are eigenstates of $\vec{S}_1{}'$, and α' and β' are eigenstates of $\vec{S}_2{}'$. These two sets of states are not independent since in any of the eigenstates of $\vec{S}_0$ the scalar products $\langle\alpha|\alpha'\rangle$, $\langle\beta|\alpha'\rangle$, etc., are proportional to an appropriate Wigner function. In particular in the semiclassical limit of large S, the scalar products reduce to trigonometric functions

$$|\alpha\rangle = |\alpha'\rangle \cos\tfrac{1}{2}\theta + |\beta'\rangle \sin\tfrac{1}{2}\theta \ , \tag{3.4a}$$

$$|\beta\rangle = -|\alpha'\rangle \sin\tfrac{1}{2}\theta + |\beta'\rangle \cos\tfrac{1}{2}\theta \ , \tag{3.4b}$$

where θ is the angle between the site spins, so Eqs. (3.2) express the fact that the transfer mechanisms connect parallel states. This can be graphically summarized as in Fig. 1.

Now one can write the matrix elements of $\mathcal{H}^c$ in the basis of the states $d_1\alpha$, $d_1\beta$, $d_2\alpha'$, and $d_2\beta'$. Anderson and Hasegawa prove that in the limit of $|J_l| >> |b|$ the lowest two energies are

$$E = -|J_l|S \pm |b|[(S_0+\tfrac{1}{2})/(2S+1)] \ , \tag{3.5}$$

where S_0 denotes possible eigenvalues of S_0. These can take only half-integer value from $\frac{1}{2}$ to $2S+\frac{1}{2}$. In the semiclassical picture the coefficient multiplying $|b|$ turns into $\cos\frac{1}{2}\theta$. The signs of J_l and b are immaterial, so from now on these two quantities will be taken as positive.

In the limit of $J_l >> b$, a crystal composed of N spins should be describable in terms of localized interactions. In the opposite limit, which was also worked out by the two authors, itinerant models would describe the crystal. Here we will deal with the former case as it is the situation encountered in Jonker and Van Santen experiments.

Unlike the usual exchange problem the energies (3.5) do not depend on the eigenvalues of $\vec{S}_t$; instead they are labeled by quantum numbers S_0. In addition S_0 determines two values for the energies. The second difference especially leads Anderson and Hasegawa to believe that such coupling energy cannot be expressed as an effective site-site interaction and no quantum Hamiltonian for double exchange was formulated.

de Gennes,[5] however, points out that in the compounds under study b is much larger than the superexchange coupling, of strength J, between the site spins. On the basis of Wollan-Koehler experiments on $La_{1-x}Ca_xMnO_3$, with x between 0.09 and 0.22, he estimates b to be equal to $64J$ (spin 2). We will see that b should be probably bigger by at least a factor of 2. Therefore in the limit $J_l >> b >> J$ only the minus states of (3.5) are appreciably occupied and the plus sign energies can be neglected. This is true in the range of temperatures which do not much exceed the critical temperature. If b were comparable to J, the omission of the plus-sign states would be justified for temperatures much smaller than the critical one (Néel or Curie temperature).

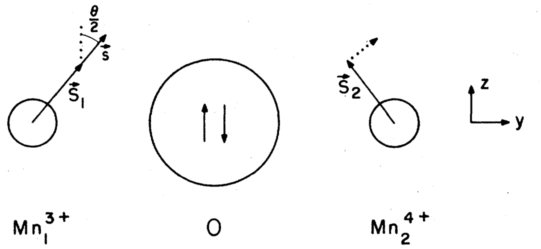


FIG. 1. Model for double exchange.

A heuristic argument why b should be usually bigger than J seems to us to be as follows. The superexchange coupling is a result of transitions to the excited states of the ionic configuration while the hoppings described by b express the ground-state wavefunction oscillations "from left to right," and therefore should be dominant.

IV. DOUBLE-EXCHANGE HAMILTONIAN

The energies (3.5) can be actually written in terms of the net site-spins eigenvalues S_t. To see this note that S_0 can take either $S_t+\frac{1}{2}$ or $S_t-\frac{1}{2}$ values so

$$E = -J_lS - b(S_t+1)/(2S+1), \quad S_0 = S_t+\tfrac{1}{2} \tag{4.1a}$$

or

$$E = -J_lS - bS_t/(2S+1), \quad S_0 = S_t-\tfrac{1}{2}, \quad S_t \neq 0 \ . \tag{4.1b}$$

For $S_t \neq 0$ the energies (4.1b) differ from (4.1a) merely by a constant. When formulating the Hamiltonian we could take into account this ambivalency in the energy eigenvalues by introducing a fictituous spin of $\frac{1}{2}$ which would discern the two series of levels. However, as long as we are interested in the effective coupling of the site spins, we do not need the fictitious spin to consider, since it does not interact with the site spins. For any S_t the effective site-spin coupling energy is therefore given by (4.1a).

Now, the eigenvalues S_t are uniquely determined by the eigenvalues of $\vec{S}_1\cdot\vec{S}_2$:

$$S_t = -\tfrac{1}{2} + \tfrac{1}{2}[1+8S(S+1)+8\vec{S}_1\cdot\vec{S}_2]^{1/2} \ , \tag{4.2}$$

which can be readily established by calculating $(\vec{S}_t)^2$. Hence the effective site-site double-exchange (de) Hamiltonian is

$$\mathcal{H}_{12}^{\rm de} = -[b/2(2S+1)] \times [1+8S(S+1)+8\vec{S}_1\cdot\vec{S}_2]^{1/2} \ , \tag{4.3}$$

where the constant terms have been omitted. In the semiclassical limit (4.3) becomes simply $-b\cos\frac{1}{2}\theta$.

Hamiltonian (4.3) holds for any value of spin, but for a given S it can be simplified in the following way. The square root in (4.3) can be expanded into an infinite series of consecutive powers of $\vec{S}_1\cdot\vec{S}_2$. However, not all of these powers are independent. In particular in the case of spin-$\frac{1}{2}$,

$$(\vec{S}_1\cdot\vec{S}_2)^2=\tfrac{3}{16}-\tfrac{1}{2}\vec{S}_1\cdot\vec{S}_2\ , \tag{4.4a}$$

in the case of spin 1,

$$(\vec{S}_1\cdot\vec{S}_2)^3=2+\vec{S}_1\cdot\vec{S}_2-2(\vec{S}_1\cdot\vec{S}_2)^2\ , \tag{4.4b}$$

etc. This allows one to replace (4.3) by a finite order polynomial in $\vec{S}_1\cdot\vec{S}_2$. In the case of spin-$\frac{1}{2}$ the polynomial will contain a constant and a bilinear term $\vec{S}_1\cdot\vec{S}_2$. For spin 1 the polynomial will be of the second order, for spin-$\frac{3}{2}$—of the third order, for spin 2—of the fourth order, etc. Hence the double-exchange Hamiltonian takes the form [equivalent to (4.3) within a constant]

$$\begin{aligned}\mathcal{H}_{12}^{\text{de}}=-b\tilde{\mathcal{H}}_{12}^{\text{de}}\equiv-b[&J_0^{(S)}+J_1^{(S)}\,\vec{S}_1\cdot\vec{S}_2\\&-J_2^{(S)}(\vec{S}_1\cdot\vec{S}_2)^2-J_3^{(S)}(\vec{S}_1\cdot\vec{S}_2)^3\\&-J_4^{(S)}(\vec{S}_1\cdot\vec{S}_2)^4-\cdots]\ .\end{aligned} \tag{4.5}$$

The coefficients $J_n^{(S)}$ are established by matching the eigenvalues of (4.5) to the possible eigenvalues of $S_t/(2S+1)$. For example, if $S=2$ then $S_t/(2S+1)$ may be equal to 0, $\frac{1}{5}$, $\frac{2}{5}$, $\frac{3}{5}$, and $\frac{4}{5}$. In the state with $S_t=0$, $\vec{S}_1\cdot\vec{S}_2$ becomes -6, so we receive the equation

$$0=J_0^{(2)}-6J_1^{(2)}-6^2J_2^{(2)}+6^3J_3^{(2)}-6^4J_4^{(2)}\ . \tag{4.6}$$

In the similar way the remaining four equations for $J_n^{(2)}$ are obtained. The results of such calculations are as follows:

$S=\frac{1}{2}$:

$$\begin{aligned}&J_0^{(1/2)}=\tfrac{3}{8},\quad J_1^{(1/2)}=\tfrac{1}{2},\\&J_2^{(1/2)}=J_3^{(1/2)}=\cdots=0\ ;\end{aligned} \tag{4.7}$$

$S=1$:

$$\begin{aligned}&J_0^{(1)}=\tfrac{10}{18},\quad J_1^{(1)}=\tfrac{1}{6},\quad J_2^{(1)}=\tfrac{1}{18},\\&J_3^{(1)}=J_4^{(1)}=\cdots=0\ ;\end{aligned} \tag{4.8}$$

$S=\frac{3}{2}$:

$$\begin{aligned}&J_0^{(3/2)}=\tfrac{141}{256},\quad J_1^{(3/2)}=\tfrac{61}{960},\quad J_2^{(3/2)}=\tfrac{1}{720},\\&J_3^{(3/2)}=-\tfrac{1}{180},\quad J_4^{(3/2)}=\cdots=0\ ;\end{aligned} \tag{4.9}$$

$S=2$:

$$\begin{aligned}&J_0^{(2)}=\tfrac{3}{5},\quad J_1^{(2)}=\tfrac{163}{2100},\quad J_2^{(2)}=-\tfrac{7}{1800},\\&J_3^{(2)}=\tfrac{1}{900},\quad J_4^{(2)}=\tfrac{1}{2520},\quad J_5^{(2)}=\cdots=0\ .\end{aligned} \tag{4.10}$$

The coefficients $J_n^{(S)}$ for $S=\frac{5}{2}$, 3, $\frac{7}{2}$, and 4 are presented in the Appendix.

Note that the bilinear term is invariably ferromagneticlike, in agreement with the physical picture attached to the double exchange. However the coupling is actually more complex. Except for the spin-$\frac{1}{2}$ case, it produces also biquadratic interactions of various signs. If $S\geqslant\frac{3}{2}$ the bicubic coupling appears, etc. Although the coefficients of the terms $(\vec{S}_1\cdot\vec{S}_2)^n$ essentially decrease with n, the larger powers are by no means negligible since they are accompanied by S^{2n}. In Sec. VI we shall see that the biquadratic, bicubic, etc., couplings may lead to canted sublattice configurations.

Finally note that the possibility of expressing S_t by the square root, as in Eq. (4.2) may be another source of biquadratic exchange interactions which have been detected in some magnetic systems without mixed-valence chemical structure.

V. EFFECT OF THE MAGNETIC FIELD

An applied field H_0 primarily aligns the site spins, but it also polarizes the hopping electron or the hopping hole. The energies (3.5) are thus modified. We can take into account this polarization only in the framework of the semiclassical picture and when the field points in the z direction, as depicted in Fig. 1. We will show that these are not serious limitations.

If the electron is in the state $d_2\alpha'$ ($d_2\beta'$), it means (semiclassically) that it is parallel (antiparallel) to the second site spin and therefore the electronic spin makes the angle of $\frac{1}{2}\theta$ with the z axis. As a result Eqs. (3.1a) and (3.1c) acquire the additional term

$$-\mu_B H_0\cos\tfrac{1}{2}\theta\ , \tag{5.1a}$$

while Eqs. (3.1b) and (3.1c) increase by

$$+\mu_B H_0\cos\tfrac{1}{2}\theta\ , \tag{5.1b}$$

where μ_B denotes the Bohr magneton, and $\hbar=1$. If the hole is the double-exchange carrier, the signs of (5.1) are reversed. These equations are written in the usually adopted convention that spins of negatively charged particles tend to follow the field direction.

The semiclassical solution of the eigenvalue problem as in Sec. III leads to the replacement of b by an effective transfer constant $\tilde{b}$, where

$$\tilde{b}=b\ \pm\mu_B H_0\ . \tag{5.2}$$

The upper sign holds for electron and the minus sign for the hole. The presence of the electronic carrier enhances the ferromagnetic properties of the double-exchange coupling when the field is applied.

The polarization correction is substantial only if $\mu_B H_0$ becomes comparable to b. Since b is assumed to be much larger than the superexchange coupling constant J, the correction is meaningful at large values of H_0, when the site spins are certainly pointing parallel to the field, and therefore, when the semiclassical picture should be adequate.

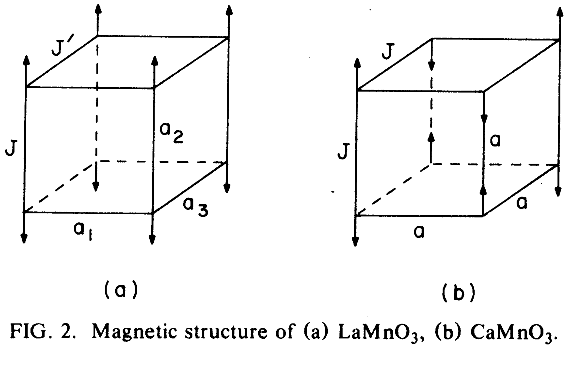
Next consider a situation with the spins in a canted configuration (more precisely we should speak of a canted sublattice-magnetization configuration which can be achieved in a crystal composed of N spins) but with the field pointing in the y direction. Now the semiclassical analysis introduces $\pm\mu_B H_0 \sin\frac{1}{2}\theta$ to (3.5) for either sign of the carrier. This correction does not have the form of the effective double-exchange coupling and it is difficult to handle. However the configuration as described above is stable (see Sec. VII) for fields very much smaller than b, when the correction of this kind can be completely neglected.

VI. N-SPIN HAMILTONIAN

Let us again confine our attention to $La_{1-x}Ca_xMnO_3$. This compound crystallizes in a perovskite-type structure. The magnetic lattice structure has been determined by Wollan and Koehler[2] in neutron diffraction experiments for selected values of x. In particular when $x=0$ or 1 the magnetic unit cell is shown in Fig. 2. The orientations of spins with respect to the lattice, displayed in this figure, are to be taken qualitatively since they are not entirely clear.

$CaMnO_3$ is a spin-$\frac{3}{2}$ cubic antiferromagnet with $a=7.465$ Å at 80 K. On the other hand $LaMnO_3$, with $S=2$, has a slightly monoclinic antiferromagnetic-layer-type structure. This means that each site spin is coupled ferromagnetically to z' neighboring spins in the same layer and antiferromagnetically to z spins in the adjacent layers. The ferromagnetic exchange integral is called J' and the antiferromagnetic one J. The magnetic lattice parameters at 80 K ($T_N=141$ K) are $a_1 \approx a_3 = 7.973$ Å, $a_2=7.693$ Å, and $\beta=92°7'$. Since a_2 is shorter than a_1 and a_3 it seems likely that there exists some uniaxial anisotropy field in the a_2 direction. This system can also distinguish the cubic components of the crystalline field, but we will neglect this effect.

When the concentration x ranges between 0 and 1, double-exchange coupling mediated either by holes or by electrons appears in the system. This is however accompanied by several side effects. One of these is that the average magnetic lattice parameters change their values. Especially dramatic changes occur in the a_1 and a_3 directions where the lengths (in the unit magnetic cell) differ by 0.5 Å between the $x=0$ and $x=1$ situations. As a result the coupling constants J,J' and the corresponding transfer constants b,b' (the hopping rate in a layer may be in general different than between layers) are themselves functions of concentration. One has therefore to deal with average Hamiltonian parameters. In particular, at some concentration which is probably close to $x=0.5$, an exchange inversion transition apparently takes place: the ferromagnetic $J'(x)$ turns into the antiferromagnetic $J(x)$.



(a) (b)

FIG. 2. Magnetic structure of (a) $LaMnO_3$, (b) $CaMnO_3$.

A phenomenological model for exchange inversion transition for systems without double-exchange coupling has been worked out by Kittel[10] and further elaborated by Jarrett.[11] In such a transition interactions with phonons are of fundamental importance. They turn out also to be responsible for a temperature hysteresis at the transition. A microscopic analysis of the whole transformation path between $LaMnO_3$ and $CaMnO_3$ seems therefore to be a complicated task. The theory presented in this paper will apply only to systems with small concentrations of holes or electrons, when the site spins can be considered as fixed rigidly in a lattice.

In the small-concentration limit the interactions between the carriers can also be neglected.

A theory of magnetic order in a layer-type antiferromagnet with double exchange has been constructed by de Gennes.[5] He considers the limit of large S when the double exchange coupling is proportional to $b\cos\frac{1}{2}\theta$. de Gennes treats the carrier wave function in a tight-binding approximation. Subsequently he assumes that in the small-concentration region the carriers occupy merely the bottom of the band, which corresponds to their uniform distribution in the lattice. The ground state of the system is found by minimizing the total energy. It turns out that at $T=0$ K, and for sufficiently small concentrations, the sublattices are in a canted configuration with a canting angle

$$\cos\tfrac{1}{2}\theta = bx/4JS^2 \ . \tag{6.1}$$

If the concentration exceeds $4JS^2/b$ the spins are aligned ferromagnetically. de Gennes points out that condition (6.1) is also obeyed by other than two-sublattice arrangements. However, the presence of anisotropy is expected to stabilize the two-sublattice configuration. de Gennes presents also an involved mean-field theory for the system at finite temperature. The exchange and double-exchange energies appear to decrease with temperature at different rates. The resulting phase diagram (in the absence of an anisotropy) is shown in Fig. 3, but we shall see in the Appendix that even for large spins this diagram is incorrect.

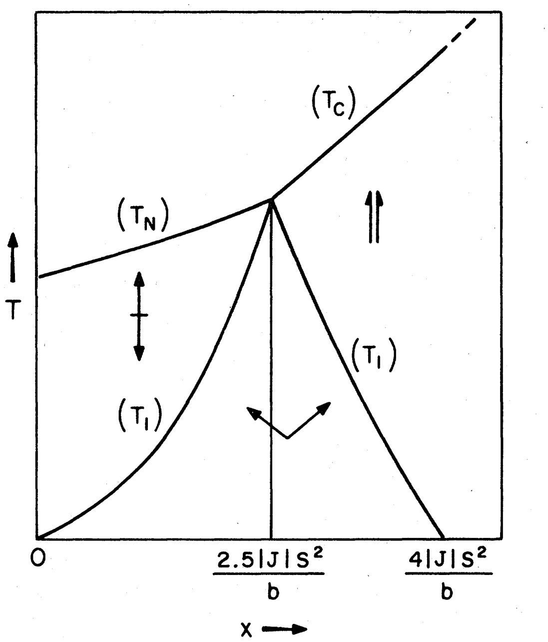


FIG. 3. Phase diagram for a spin layer antiferromagnet in the de Gennes (Ref. 5) theory.

In the framework of his semiclassical theory, de Gennes discusses two additional side effects of the introduction of carriers: creation of bound-states carrier impurity, and self-trapping of the carriers. We shall accept his conclusion that these localized distortions do not alter the average spin configurations significantly (as, for example, both bound and unbound carriers participate in the double-exchange mechanism).

As explained in Sec. I, the above band model is not necessary in the highly localized limit $J_l >> b$, when we are interested in the effective spin coupling. In Sec. IV we have found a Hamiltonian for two sites. Since the carriers move very slowly through the crystal, the double-exchange part of the Hamiltonian for the N-spin system should be a sum of pair interactions. Our argument recalls therefore the standard direct-exchange N-spin Hamiltonian derivation in which one first (i) compares the energies of a direct-exchange electron in its singlet and triplet states, then (ii) one constructs an effective Hamiltonian for a pair of site spins, and finally (iii) one composes the total Hamiltonian from the pair contributions.

In order to simplify the problem we make an additional assumption, equivalent to the one employed by de Gennes, that the carriers are distributed uniformly in the crystal. In this way we obtain a mean-field-type Hamiltonian which serves as a first-approximation description. This fails, however, to be a good approximation in experiments which involve times comparable with $\hbar b^{-1}$.

With the pair double-exchange Hamiltonian (4.5) the total Hamiltonian for the two sublattice layer-type system becomes

$$\mathcal{H} = 2J \sum_{\langle lm \rangle} \vec{S}_l \cdot \vec{S}_m - 2J' \sum_{\langle ll' \rangle} \vec{S}_l \cdot \vec{S}_{l'} - 2J' \sum_{\langle mm' \rangle} \vec{S}_m \cdot \vec{S}_{m'} - 2x\tilde{b} \sum_{\langle lm \rangle} \tilde{\mathcal{H}}_{lm}^{\mathrm{de}} - 2x\tilde{b}' \sum_{\langle ll' \rangle} \tilde{H}_{ll'}^{\mathrm{de}}$$
$$- 2x\tilde{b}' \sum_{\langle mm' \rangle} \tilde{\mathcal{H}}_{mm'}^{\mathrm{de}} - D \sum_l (S_l^z)^2 - D \sum_m (S_m^z)^2 - \sum_l \vec{H} \cdot \vec{S}_l - \sum_m \vec{H} \cdot \vec{S}_m \ , \tag{6.2}$$

where D denotes the uniaxial anisotropy constant, H is $g\mu_B H_0$, with g being the appropriate Landé factor. If H points in the direction which bisects the angle between two sublattices, then $\tilde{b}$ is given by Eq. (5.2), otherwise (and if $H=0$) $\tilde{b}$ is understood to coincide with b. In Eq. (6.2), x denotes the concentration of carriers which mediate the double-exchange coupling. The factor of 2 in the double-exchange terms follows from the fact that the summations in (6.2) are performed over $\frac{1}{2}N$ sites: if we were summing over N ions each of them would carry a weight x; in the summation over $\frac{1}{2}N$ sites the weight $2x$ has to be attributed to each ion.

Hamiltonian (6.2) describes a simple antiferromagnet if $J' = b' = 0$. On the other hand it applies to a ferromagnet with double exchange if $J = b = 0$.

We shall see in Sec. IX that in some instances the layer-type structure has to be actually analyzed in terms of a four-sublattice model.

VII. MEAN-FIELD GROUND STATE OF AN ANTIFERROMAGNET WITH DOUBLE EXCHANGE

A. Stability conditions

Consider the two-sublattice Hamiltonian (6.2) and set $J' = b' = 0$. Assume the system is at $T = 0$ K and the concentration x is sufficiently small so J and b are roughly constant. Let the two sublattices make the angles ϕ and ψ, and the magnetic field the angle ξ, with the anisotropy (z) axis respectively, as shown in Fig. 4. The plane in which this figure is drawn is determined by the direction of the magnetic field. If the magnetic field vanishes the plane of the sublattices orientation is understood as stabilized by an infinitesimal transverse field.

If the spin does not exceed 2, the mean-field expression for the energy of the antiferromagnet with double exchange reads (the constant $J_0^{(S)}$ − term is omitted)

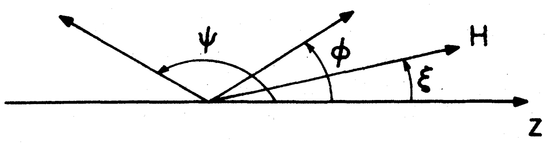


FIG. 4. Two-sublattice configuration.

$$
\begin{aligned}
e \equiv 2E(\psi,\phi)/N = 2z(J - x\tilde{b}J_1^{(S)})S^2\cos(\psi-\phi) &+ 2x\tilde{b}J_2^{(S)}zS^4\cos^2(\psi-\phi) \\
&+ 2x\tilde{b}J_3^{(S)}zS^6\cos^3(\psi-\phi) \\
&+ 2x\tilde{b}J_4^{(S)}zS^8\cos^4(\psi-\phi) \\
&- DS^2\cos^2\phi - DS^2\cos^2\psi \\
&- HS\cos(\phi-\xi) - HS\cos(\psi-\xi) \ .
\end{aligned} \tag{7.1}
$$

We shall assume that the anisotropy constant D is small in comparison with J. For the spin-$\frac{1}{2}$ systems D is effectively zero since the lowest spin that can distinguish uniaxial anisotropy is 1.

The equilibrium conditions are

$$\frac{\partial e}{\partial \phi} = 0 \ , \tag{7.2}$$

$$\frac{\partial e}{\partial \psi} = 0 \ . \tag{7.3}$$

The stability conditions are

$$\frac{\partial^2 e}{\partial \phi^2} > 0 \tag{7.4}$$

and

$$
\begin{vmatrix} \dfrac{\partial^2 e}{\partial\phi^2} & \dfrac{\partial^2 e}{\partial\phi\partial\psi} \\ \dfrac{\partial^2 e}{\partial\phi\partial\psi} & \dfrac{\partial^2 e}{\partial\psi^2} \end{vmatrix} = \left[\frac{\partial^2 e}{\partial\phi^2}\right]^2 - \left[\frac{\partial^2 e}{\partial\phi^2} - 2D^2\cos 2\phi - HS\cos(\phi-\xi)\right]^2 > 0 \ . \tag{7.5}
$$

Consider now the $H=0$ situation in detail. If the equilibrium conditions (7.2) and (7.3) are added side by side, we obtain the equation $\sin 2\phi = -\sin 2\psi$. It means that for $H=0$ four possible sublattice configurations are allowed: (i) $\phi=0$, $\psi=\pi$, which corresponds to the antiferromagnetic phase; (ii) $\psi=\pi-\phi$: the first canted phase; (iii) $\psi=-\phi$: the second canted phase; and (iv) $\phi=0$, $\psi=0$: the ferromagnetic phase. The stability of the above phases depends on concentration and is determined by Eqs. (7.4) and (7.5). Note that in the absence of anisotropy the differentiation between the two canted phases is meaningless.

B. Antiferromagnetic phase

This phase is stable for sufficiently low concentrations. The existence of the antiferromagnetic configuration was ruled out in the de Gennes theory. However, if we consider a two-site problem, then if the contribution from the double exchange is very small, the two sites will be in a configuration with $S_t=0$, which constitutes a nucleus for the antiferromagnetic arrangement.

The antiferromagnetic phase becomes unstable at some concentration x_1 which satisfies the condition

$$2x_1bz = (2zJ+D)(A_1^{(S)})^{-1} \ , \tag{7.6a}$$

where

$$A_1^{(S)} = J_1^{(S)} + 2J_2^{(S)}S^2 - 3J_3^{(S)}S^4 + 4J_4^{(S)}S^6 \ . \tag{7.6b}$$

The constant $A_1^{(S)}$ is equal to $\frac{1}{2}$, $\frac{5}{18}$, $\frac{37}{240}$, and $\frac{199}{2100}$ for spins $\frac{1}{2}$, 1, $\frac{3}{2}$, and 2, respectively. In the case of the four values of spin, the larger the spin the longer this phase is stable, as the double-exchange contribution to the effective bilinear exchange diminishes with spin.

C. First canted phase

This phase is not allowed for spin $\frac{1}{2}$ due to the lack of the biquadratic, etc., interactions. For the higher three values of spin the canting angle is determined by the equation

$$
\begin{aligned}
2zJ + D - 2bxz(J_1^{(S)} &+ 2J_2^{(S)}S^2\cos 2\phi \\
&- 3J_3^{(S)}S^4\cos^2 2\phi + 4J_4^{(S)}S^6\cos^3 2\phi) = 0 \ .
\end{aligned} \tag{7.7}
$$

The larger the angle, the larger the transverse spontaneous moment in the system.

On lowering the concentration ϕ vanishes at $x=x_1$. Thus the transition from the first canted phase to the antiferromagnetic one is of the second order.

Consider now the upper boundary of the first canted phase. In the case of spins 1 and $\frac{3}{2}$ the biquadratic constant $J_2^{(S)}$ is positive and $J_3^{(S)}$ is nonpositive, so the stability condition (7.4), which reads

$$
\begin{aligned}
\frac{\partial^2 e}{\partial\phi^2} = DS^2\cos 2\phi &+ 4xbzS^4\sin^2 2\phi \\
&\times (J_2^{(S)} - 3S^2J_3^{(S)}\cos 2\phi + 6S^4J_4^{(S)}\cos^2 2\phi) > 0
\end{aligned} \tag{7.8}
$$

is satisfied as long as ϕ does not exceed 45°. The first canted phase ends therefore at the concentration x_2:

$$2x_2bz = (2zJ+D)(J_1^{(S)})^{-1}, \quad S = 1, \tfrac{3}{2} \ . \tag{7.9}$$

In the case of $S=2$, $J_2^{(2)}$ is negative and $J_3^{(2)}$ is positive. As a result the second derivative, (7.8) becomes negative at an angle which is smaller than 45°. In the limit of negligible anisotropy the critical angle is

$$\cos 2\phi_2 = \frac{J_3^{(2)} + [(J_3^{(2)})^2 - \frac{8}{3} J_2^{(2)} J_4^{(2)}]^{1/2}}{4J_4^{(2)} S^2} , \qquad (7.10)$$

which corresponds to $\phi = 28.69°$. The critical concentration is then

$$2x_2 bz = (2zJ + D) A_2^{-1}, \quad S = 2 , \qquad (7.11a)$$

where

$$A_2 = J_1^{(2)} + 2J_2^{(2)} S^2 \cos 2\phi_2 - 3J_3^{(2)} S^4 \cos^2 2\phi_2 + 4J_4^{(2)} S^6 \cos^3 2\phi_2 = 0.061 . \qquad (7.11b)$$

The concentration x_2, as given by (7.11a) is 1.56 times as large as x_1 for spin 2.

At the transition point the effective bilinear coupling becomes ferromagnetic and a further increase in concentration produces a configuration with an acute angle between sublattices and therefore with the spontaneous moment along the z axis.

D. Second canted phase

Again, at $H = 0$, this phase is not allowed for $S = \frac{1}{2}$. For higher spins the canting angle is specified now by the equation

$$-2zJ + D + 2xbz (J_1^{(S)} - 2J_2^{(S)} S^2 \cos 2\phi - 3J_3^{(S)} S^4 \cos^2 2\phi - 4J_4^{(S)} S^6 \cos^3 2\phi) = 0 , \qquad (7.12)$$

and the second derivative can be expressed in a form similar to (7.8) except for the change in sign of the bicubic contribution.

Consider first the lower boundary of this phase. In the case of spins 1 and $\frac{3}{2}$ the instability takes place at 45°, i.e., at a concentration $x_{2'}$:

$$2x_{2'} bz = (2zJ - D)(J_1^{(S)})^{-1}, \quad S = 1, \ \frac{3}{2} . \qquad (7.13)$$

In the case of spin 2 this angle is not reached. Instead the maximal angle allowed $\phi_{2'}$ is determined by Eq. (7.10) in which the sign of the $J_3^{(2)}$ term is reversed. This result holds for very small anisotropy and yields $\phi_{2'} = 39.54°$. The corresponding critical concentration is

$$2x_{2'} bz = (2zJ - D) S_{2'}^{-1}, \quad S = 2 , \qquad (7.14a)$$

where

$$A_{2'} = J_1^{(2)} - 2J_2^{(2)} S^2 \cos 2\phi_{2'} - 3J_3^{(2)} S^4 \cos^2 2\phi_{2'} - 4J_4^{(2)} S^6 \cos^3 2\phi_{2'} = 0.081 . \qquad (7.14b)$$

The concentration $x_{2'}$ is smaller than x_2 by 0.76 if $S = 2$, but if $S = 1$ or $\frac{3}{2}$ the two critical concentrations differ by the anisotropy term only. We conclude that the transition between the first and the second canted phases involves a hysteresis so it is of the first order.

Consider next the upper boundary for the second canted phase. If such a boundary exists, it marks a transition to the ferromagnetic phase.

In the case of spin 1, the angle ϕ smoothly diminishes to zero on increasing the concentration. The ferromagnetic phase is reached at a concentration x_3, which is defined by

$$2x_3 bz = (2zJ - D)(J_1^{(1)} - 2J_2^{(1)})^{-1}, \quad S = 1 , \qquad (7.15)$$

and it is three times as large as $x_{2'}$.

In the case of spin $\frac{3}{2}$ the ferromagnetic configuration is not achieved from the second canted phase in a continuous fashion. This is because $J_3^{(3/2)}$ is negative and larger in magnitude than $J_2^{(3/2)}$ which leads to the negativeness of the second derivative for ϕ smaller than some angle ϕ_3. Note that for $S = \frac{3}{2}$ the lower energy solution of the Eq. (7.12) is

$$\cos 2\phi = \frac{-J_2^{(3/2)}}{3J_3^{(3/2)} S^2} + (3S^2)^{-1} \left[\left(\frac{J_2^{(3/2)}}{J_3^{(3/2)}} \right)^2 + \frac{3(D + 2xbzJ_1^{(3/2)} - 2zJ)}{2xbzJ_3^{(3/2)}} \right]^{1/2} . \qquad (7.16)$$

This solution becomes complex at concentrations exceeding that $x = x_3$ for which the square root in (7.16) vanishes. The critical angle is then equal to 43.94° and it differs from 45° merely by 1.06°. Thus the concentration x_3 only slightly exceeds x_2 and is given by

$$2x_3 bz = (2zJ - D) A_3^{-1}, \quad S = \frac{3}{2} , \qquad (7.17a)$$

where

$$A_3 = \frac{(J_2^{(3/2)})^2 + 3J_1^{(3/2)} J_3^{(3/2)}}{3J_3^{(3/2)}} = \frac{137}{2160} . \qquad (7.17b)$$

At $x = x_3$ the stability condition (7.5) is broken and the system undergoes a first order transition to the ferromagnetic phase. The second canted phase is yet, for $S = \frac{3}{2}$, highly unlikely to be observed, as is explained in Sec. VII F.

In the case of $S = 2$ there is no upper boundary for the second canted phase as a function of concentration. The ferromagnetic phase turns out to be unstable and it is never reached. On increasing the concentration, however, the canting angle does not diminish indefinitely. To see this note that in the limit of $xb >> Jz$, the $-2zJ + D$ term in the equilibrium condition (7.12) can be neglected. The asymptotically reached angle ϕ_3 is therefore equal to 13.47°

($\cos 2\phi_3 = 0.891\,45$). The allowed angles in the second canted phase range thus between 13.47° and 39.54°.

E. Ferromagnetic phase

The analysis of the condition (7.5) leads to the conclusion that the ferromagnetic phase is stable for concentrations larger than $x_{3'}$ with

$$2x_{3'}bz = (2zJ - D)(A_{3'}^{(S)})^{-1} , \tag{7.18}$$

provided

$$S^{-2}\frac{\partial^2 e}{\partial \phi^2} = -2zJ + 2xbzA_{3'}^{(S)} + 2D > 0 , \tag{7.19}$$

where

$$A_{3'}^{(S)} = J_1^{(S)} - 2J_2^{(S)}S^2 - 3J_3^{(3)}S^4 - 4J_4^{(S)}S^6 . \tag{7.20}$$

The constant $A_{3'}^{(S)}$ is equal to $\frac{1}{2}$, $\frac{1}{18}$, $\frac{17}{120}$, and $\frac{-97}{2100}$ for $S = \frac{1}{2}$, 1, $\frac{3}{2}$, and 2, respectively. Since for $S = 2$ $A_{3'}^{(2)}$ is negative, the condition (7.19) is never fulfilled and, as already mentioned, the ferromagnetic phase is not achieved.

For $S = \frac{3}{2}$, $x_{3'}$ lies in the stability region for the first canted phase and it is in fact very close to the upper boundary for the antiferromagnetic phase, x_1.

If $S = 1$ the transition between the second canted phase and the ferromagnetic one is continuous.

Finally, if $S = \frac{1}{2}$ the transition between the antiferromagnetic and ferromagnetic phases is continuous as a function of x. This is due to the absence of any single-ion anisotropy in that case.

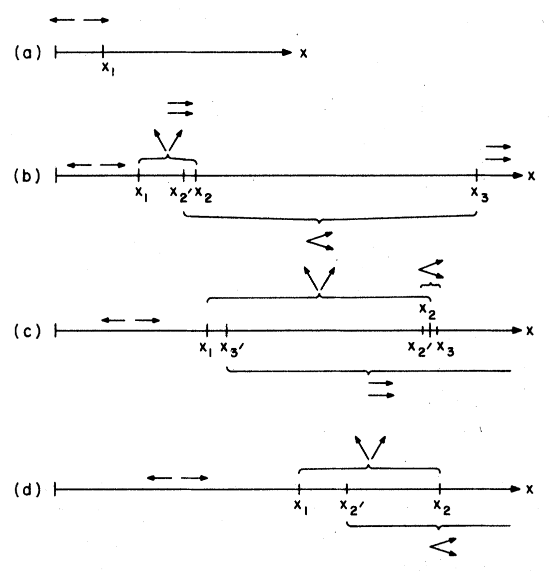


FIG. 5. Phase diagrams at $T = 0$ K for (a) $S = \frac{1}{2}$, (b) $S = 1$, (c) $S = \frac{3}{2}$, and (d) $S = 2$.

TABLE I. Summary of our results on phase boundaries.

	$S = \frac{1}{2}$	$S = 1$	$S = \frac{3}{2}$	$S = 2$
$2x_1bz$	$4zJ$	$3.6(2zJ + D)$	$6.49(2zJ + D)$	$10.55(2zJ + D)$
$2x_2bz$	$\cdots$	$6(2zJ + D)$	$15.74(2zJ + D)$	$16.39(2zJ + D)$
$2x_{2'}bz$	$\cdots$	$6(2zJ - D)$	$15.74(2zJ - D)$	$12.35(2zJ - D)$
$2x_3bz$	$\cdots$	$18(2zJ - D)$	$15.77(2zJ - D)$	$\cdots$
$2x_{3'}bz$	$4zJ$	$18(2zJ - D)$	$7.06(2zJ - D)$	$\cdots$

F. Summary, $H = 0$

The results of our discussion on phase boundaries are summarized in Table I. The phase diagrams are schematically shown in Fig. 5.

The variety of the phase diagrams is a result of the diversity in signs and magnitudes of the double exchange concentration-dependent bilinear, biquadratic, bicubic, and biquartic interactions.

As explained in Sec. VI the Hamiltonian we have been analyzing is meaningful for small concentrations. If the transfer constant b is sufficiently larger than J, then the systems can follow all of the stages of the appropriate phase diagrams in the small x region. Otherwise the theory is reliable in the first one, or perhaps two, phases.

The second canted phase, in the case of spin $\frac{3}{2}$, is nevertheless very improbable to be observed. It has rather to be thought of as a virtual configuration (or a metastable one). The reason for this is that x_3 is well in the stability region of the ferromagnetic phase. In addition x_3 almost coincides with the upper boundary x_2 for the first canted phase. For not too small anisotropy constant D, x_3 is actually lower than x_2.

G. Configurations in the presence of a parallel magnetic field

(a) If at $H = 0$ the system is in the antiferromagnetic phase, then at

$$H_{\mathrm{AF}\to\mathrm{SF}} = 2SD^{1/2}(2zJ + D - 2xbzA_1^{(S)})^{1/2} , \tag{7.21}$$

the antiferromagnetic phase ceases to be stable and a first-order transition to the spin-flop phase (which is the field-induced second canted phase) takes place. At so small values of H the carriers polarization have no influence on the double-exchange coupling.

The spin-flop phase becomes unstable, on decreasing H, at

$$H_{\mathrm{SF}\to\mathrm{AF}} = 2SD^{1/2}(2zJ - D - 2xbzA_1^{(S)}) \times (2zJ + D - 2xbzA_1^{(S)})^{1/2} . \tag{7.22}$$

The above result has been derived under the assumption that (i) the concentration is small in comparison with x_1, and (ii) $D/Jz << 1$. These assumptions make the canting angle to be close to 90° in the vicinity of the antiferromagnetic phase. Indeed, when $x=0$, the cosine of this angle is proportional to $(D/2zJ)^{1/2}$.

In the spin-flop region the canting angle is determined by the equation

$$H=2S\cos\phi[2zJ-D+2x\tilde{b}z(-J_1^{(S)}+2J_2^{(S)}S^2\cos2\phi+3J_3^{(S)}S^4\cos^2 2\phi+4J_4^{(S)}S^6\cos^3 2\phi)] \ . \tag{7.23}$$

When this angle vanishes the spin-flop phase undergoes a second-order transformation into the paramagnetic phase (or the field-induced ferromagnetic phase). This happens at

$$H_{\mathrm{SF}\to P}=2S(2zJ-D-2xbzA_3^{(S)})\times(1\pm g^{-1}4xzSA_3^{(S)})^{-1} \ , \tag{7.24}$$

where g is the Landé factor for the site spins, $A_3^{(S)}$ is defined by (7.20), and the upper (lower) sign holds for electronic (hole) carriers. The term including the Landé factor takes into account the polarization correction. In comparison with a purely antiferromagnetic system, the double exchange diminishes $H_{\mathrm{SF}\to P}$ except for the spin-2 case, when the critical field is enhanced.

(b) If at $H=0$ the system is in the first canted phase, then under the influence of the field the sublattices will start to rotate towards the z axis, until they reach the spin-flop phase. The critical field required to cause such a transition is of the order of the anisotropy field. When H achieves another critical value, given by (7.24), the system will be found in the paramagnetic phase.

(c) If at $H=0$ the system is in the second canted phase, then with the applied field it will undergo a single second order transition to the paramagnetic phase. This happens at H also equal to (7.24).

H. Configurations in the presence of a perpendicular magnetic field

If at $H=0$ the system is either in the ferromagnetic or the second canted phase, then a field which is, roughly speaking, smaller than the anisotropy field will rotate the sublattices towards the field. For bigger fields the system will be in the spin-flop phase (or a field-induced first canted phase).

The antiferromagnetic system ($x \leq x_1$) will be in the spin-flop phase even at arbitrarily small values of H.

The spin-flop phase transforms into the paramagnetic one at $H=H^{\perp}_{\mathrm{SF}\to P}$, which is given by an expression similar to (7.24) except for the change in sign in the anisotropy term.

VIII. MEAN-FIELD GROUND STATE OF A FERROMAGNET WITH DOUBLE EXCHANGE

In this section we set $J=b=0$ in Hamiltonian (6.2). The mean-field expression for the energy is now like (7.1) with J and $\tilde{b}$ replaced by $-J'$ and $\tilde{b}'$, respectively. On inspection of the correspondingly adjusted equation (7.19) we conclude that if S is equal to $\frac{1}{2}$, 1, or $\frac{3}{2}$, the ferromagnetic phase is stable at any concentration. However, if $S=2$, the ferromagnetic phase is stable for x not exceeding x_4:

$$2x_4b'z=-(2zJ'+D)(A_3^{(2)})^{-1}=21.65(2zJ'+D) \ . \tag{8.1}$$

On increasing the concentration beyond x_4 the sublattices open up. The transition to the second canted phase is a continuous one. To see this note that the concentration x_4 coincides with the $\phi=0$ solution of the modified equation (7.12). This equation possesses solutions in the domain of small angles only, when the expression in the brackets is negative. In this domain the maximal canting angle of 13.47° is reached (ϕ_3 of Sec. VII D) for: $xb' >> J'$. There is no subsequent transition to the first canted or antiferromagnetic phases, for the primary effect of the double exchange is to strengthen the ferromagneticlike bilinear coupling.

In the large-S de Gennes theory the canted phase is not allowed. When a parallel field is applied to the spin-2 system at $x > x_4$, it will force the sublattices to point in the z direction if it exceeds

$$H_4=2S(-2zJ'-D-2xb'zA_3^{(2)})\times(1)\pm g^{-1}4xzSA_3^{(2)})^{-1} \ . \tag{8.2}$$

Again the upper sign holds for electronic carriers. The critical field H_4 vanishes when $x=x_4$.

IX. LAYER-TYPE ANTIFERROMAGNET WITH DOUBLE EXCHANGE

Now the system is described by the complete Hamiltonian (6.2). In the spin-2 crystal $(\mathrm{La}_{1-x}\mathrm{Ca}_x)(\mathrm{Mn}^{3+}_{1-x}\mathrm{Mn}^{4+}_x)\mathrm{O}_3$, J' is probably much smaller than J (for sufficiently small x) since J' is about to invert its sign. On the other hand it seems likely that b' is of the same order of magnitude as b. The critical concentration x_4 is therefore probably smaller than x_1.

Beyond x_4 the system has to be then described in terms of a four-sublattice model since the sublattices coupled by J' open up. If $x > x_1$ canting in two mutually perpendicular planes should take place. However, the canting angle of the ferromagnetically coupled sublattices is small, as it reaches 13.47° only asymptotically. A two-sublattice model should be therefore sufficient at not too big concentrations.

The experimental evidence on $(\mathrm{La}_{1-x}\mathrm{Ca}_x)(\mathrm{Mn}_{1-x}^{3+}\mathrm{Mn}_x^{4+})\mathrm{O}_3$ (Ref. 2) seems to suggest that at $x=9\%$ and probably also at somewhat smaller concentrations, a canted configuration is present. The occurrence of the ferromagnetic lines in the neutron diffraction pattern should be due to the canting of the antiferromagnetically coupled sublattices. de Gennes, on the basis of the large-spin theory, estimates $b \approx 64J$. If we take this value of b (and neglect anisotropy) we get $x_1 \approx 16\%$. We conclude that de Gennes underestimates b by at least a factor of 2. However, further experimental evidence is certainly necessary to check our model.

A mean-field analysis for systems with double exchange at finite temperatures seems to be involved. This analysis should be formulated in terms of interacting multipoles, as is done for spin-1 systems with biquadratic exchange.[12] In these systems effective dipolar and quadrupolar couplings enter the expression for the free energy.

X. SPIN WAVES IN SYSTEMS WITH DOUBLE EXCHANGE

A semiclassical spin-wave theory for small wave vectors has been worked out be de Gennes.[5] In this section we shall derive spin-wave energies for the spin-$\frac{1}{2}$ through -2 systems for any wave vector. These results may be of importance in an analysis of magnetic-resonance experiments.

A. Spin-wave Hamiltonian

Consider the layer-type system described by the Hamiltonian (6.2) with the magnetic field applied along the z axis. Assume the concentration x is sufficiently small so that the canting of the ferromagnetically coupled spins, if any in the spin-2 system, is negligible. In other words, we are discussing the two-sublattices configurations.

In any of these configurations (in particular: $\psi=\pi$, $\phi=0$; $\psi=\pi-\phi$; $\psi=-\phi$; $\psi=\phi=0$) the spins in the rotated reference system x', y', z' are related to the fixed reference system x,y,z in the following way: for the first sublattice,

$$S_l^x = S_l^{x'} \ , \tag{10.1a}$$

$$S_l^y = S_l^{z'}\sin\phi + S_l^{y'}\cos\phi \ , \tag{10.1b}$$

$$S_l^z = S_l^{z'}\cos\phi - S_l^{y'}\sin\phi \ ; \tag{10.1c}$$

and for the second one,

$$S_m^x = S_m^{x'} \ , \tag{10.2a}$$

$$S_m^y = S_m^{z'}\sin\psi + S_m^{y'}\cos\psi \ , \tag{10.2a}$$

$$S_m^z = S_m^{z'}\cos\psi - S_m^{y'}\sin\psi \ . \tag{10.2c}$$

The z' directions are parallel to the respective sublattice magnetizations so they are the proper quantization axes. The x', y', z' spin components can be expressed in terms of the Holstein-Primakoff[13] bosons as follows:

$$S_l^{z'} = S - a_l^\dagger a_l \ , \tag{10.3a}$$

$$S_l^{y'} = i(\tfrac{1}{2}S)^{1/2}(a_l^\dagger - a_l) + i[4(2S)^{1/2}]^{-1} \times (a_l^\dagger a_l a_l - a_l^\dagger a_l^\dagger a_l) + \cdots \ , \tag{10.3b}$$

$$S_l^{x'} = (\tfrac{1}{2}S)^{1/2}(a_l^\dagger + a_l) - [4(2S)^{1/2}]^{-1} \times (a_l^\dagger a_l a_l + a_l^\dagger a_l^\dagger a) + \cdots \ , \tag{10.3c}$$

and similarly for $S_m^{z'}$, $S_m^{y'}$, and $S_m^{x'}$ except that the a_l bosons are replaced by b_m bosons. The scalar product $\vec{S}_l \cdot \vec{S}_m$ therefore becomes

$$\vec{S}_l \cdot \vec{S}_m = S^2\cos(\psi-\phi) + \Delta_{lm}(\psi-\phi) \ , \tag{10.4}$$

where

$$\Delta_{lM}(\psi-\phi) = \tilde{\Delta}_{lm}(\psi-\phi) + \Delta_{lm}^{\mathrm{III}}(\psi-\phi) + \Delta_{lm}^{\mathrm{IV}}(\psi-\phi) + \cdots \ , \tag{10.5a}$$

with

$$\tilde{\Delta}_{lm}(\psi-\phi) = iS(\tfrac{1}{2}S)^{1/2}\sin(\psi-\phi)(a_l^\dagger - a_l + b_m - b_m^\dagger) - S\cos(\psi-\phi)(a_l^\dagger a_l + b_m^\dagger b_m) + \tfrac{1}{2}S[\cos(\psi-\phi)+1](a_l^\dagger b_m + b_m^\dagger a_l) + \tfrac{1}{2}S[1-\cos(\psi-\phi)](a_l^\dagger b_m^\dagger + a_l b_m) \ , \tag{10.5b}$$

$$\Delta_{lm}^{\mathrm{III}}(\psi-\phi) = -i(\tfrac{1}{2}S)^{1/2}\sin(\psi-\phi)[b_m^\dagger a_l^\dagger a_l - a_l^\dagger a_l b_m - a_l^\dagger b_m^\dagger b_m + b_m^\dagger b_m a_l + \tfrac{1}{4}(a_l^\dagger a_l a_l - a_l^\dagger a_l^\dagger a_l - b_m^\dagger b_m b_m + b_m^\dagger b_m^\dagger b_m)] \ , \tag{10.5c}$$

and

$$\Delta_{lm}^{\mathrm{IV}}(\psi-\phi) = \cos(\psi-\phi)a_l^\dagger a_l b_m^\dagger b_m - \tfrac{1}{8}[1-\cos(\psi-\phi)](b_m^\dagger a_l^\dagger a_l^\dagger a_l + a_l^\dagger a_l a_l b_m + a_l^\dagger b_m^\dagger b_m^\dagger b_m + b_m^\dagger b_m b_m a_l) - \tfrac{1}{8}[1+\cos(\psi-\phi)](b_m^\dagger a_l^\dagger a_l a_l + a_l^\dagger a_l^\dagger a_l b_m + a_l^\dagger b_m^\dagger b_m b_m + b_m^\dagger b_m^\dagger b_m a_l) \tag{10.5d}$$

The operator $\Delta_{lm}(\psi-\phi)$ describes deviations from the mean-field ground state. These deviations are small in the low-temperature region.

The double-exchange coupling involves the subsequent powers of $\vec{S}_l\cdot\vec{S}_m$ and therefore subsequent powers of $\Delta_{lm}(\psi-\phi)$. It seems very difficult to calculate the exact form of $\Delta^n_{lm}(\psi-\phi)$ since all of the terms (up to infinite order) of the Holstein-Primakoff expansion for $S^{y'}$ and $S^{x'}$ contribute to the linear, quadratic, cubic, quartic, etc., terms of $\Delta^n_{lm}(\psi-\phi)$. However, it is well known[14,15] that the rigorous Dyson[16] results on the excitation spectrum in a ferromagnet at low temperatures are reproduced by the Holstein-Primakoff representation if expressions (10.3b) and (10.3c) are thought of as formal expansions in S^{-1} so that only the leading-powers-of-S coefficients are meaningful in each order term in the Hamiltonian. We assume that this is the case also in systems with the double exchange. Otherwise, if we included in $\Delta^n_{lm}(\psi-\phi)$ [calculated on the basis of operators explicitly shown in (10.3)] the terms arising from commutators, when the normal ordering is introduced, the results, especially in the spin-1 system, would be dramatically divergent from those predicted by the mean-field theory. In other words the Holstein-Primakoff representation cannot be taken literally and the rule of the thumb is that all the commutator terms are meaningless. The same line of reasoning was implicitly adopted in the Iwashita and Uryû[17,18] spin-wave theory for systems with a biquadratic exchange.

We conclude that the relevant terms in $\Delta^2_{lm}(\psi-\phi)$ are

$$\Delta^2_{lm}(\psi-\phi)=[\Delta^2_{lm}(\psi-\phi)]^{\mathrm{II}}+[\Delta^2_{lm}(\psi-\phi)]^{\mathrm{III}}+[\Delta^2_{lm}(\psi-\phi)]^{\mathrm{IV}}+\cdots\quad, \tag{10.6a}$$

where

$$\begin{aligned}[\Delta^2_{lm}(\psi-\phi)]^{\mathrm{II}}=S^2[1-\cos^2(\psi-\phi)]&\times[a_l^\dagger a_l+b_m^\dagger b_m+a_l^\dagger b_m^\dagger\\&+a_lb_m-a_l^\dagger b_m-b_m^\dagger a_l-\tfrac{1}{2}\\&\times(a_l^\dagger a_l^\dagger+a_la_l+b_m^\dagger b_m^\dagger+b_mb_m)]\quad,\end{aligned} \tag{10.6b}$$

and $[\Delta^2_l(\psi-\phi)]^{\mathrm{III}}$ denotes the cubic terms, while $[\Delta^2_l(\psi-\phi)]^{\mathrm{IV}}$ denotes the quartic ones. All of the linear terms in $\Delta^2_{lm}(\psi-\phi)$ are irrelevant as they arise from commutators and therefore they are by one order in S smaller than the linear terms in $S^2\cos(\psi-\phi)\tilde{\Delta}_{lm}(\psi-\phi)$ [note $(\vec{S}_l\cdot\vec{S}_m)^2=S^4\cos^2(\psi-\phi)+2S^2\cos(\psi-\phi)\Delta_{lm}+\Delta^2_{lm}$]. Note also that for parallel or antiparallel configurations of sublattices $[\Delta^2_{lm}(\psi-\phi)]^{\mathrm{II}}$ vanishes.

Similarly the only meaningful terms in $\Delta^3_{lm}(\psi-\phi)$ are cubic, quartic, etc., and in Δ^4_{lm} quartic and of higher orders.

In the harmonic approximation the resulting spin-wave Hamiltonian has the form

$$\begin{aligned}\mathcal{H}\approx{}&E_0+I_1(\psi-\phi)\sum_{\langle lm\rangle}\tilde{\Delta}_{lm}(\psi-\phi)+I_2(\psi-\phi)\sum_{\langle lm\rangle}[\Delta^2_{lm}(\psi-\phi)]^{\mathrm{II}}-2(J'+x\tilde{b}'A_3^{(S)})\left(\sum_{\langle ll'\rangle}\tilde{\Delta}_{ll'}(0)+\sum_{\langle mm'\rangle}\tilde{\Delta}_{mm'}(0)\right)\\&+2iDS(\tfrac{1}{2}S)^{1/2}\left(\sin\phi\cos\phi\sum_l(a_l^\dagger-a_l)+\sin\psi\cos\psi\sum_m(b_m^\dagger-b_m)\right)+DS\left((3\cos^2\phi-1)\sum_l a_l^\dagger a_l+(3\cos^2\psi-1)\sum_m b_m^\dagger b_m\right)\\&+\tfrac{1}{2}DS\left(\sin^2\phi\sum_l(a_l^\dagger a_l^\dagger+a_la_l)+\sin^2\psi\sum_m(b_m^\dagger b_m^\dagger+b_mb_m)\right)+i(\tfrac{1}{2}S)^{1/2}H\left(\sin\phi\sum_l(a_l^\dagger-a)+\sin\psi\sum_m(b_m^\dagger-b_m)\right)\\&+H\left(\cos\phi\sum_l a_l^\dagger a_l+\cos\psi\sum_m b_m^\dagger b_m\right)\quad,\end{aligned} \tag{10.7}$$

where $\tilde{\Delta}_{ll'}(0)\,(\tilde{\Delta}_{mm'}(0))$ has the structure of $\tilde{\Delta}_{lm}(0)$ with b_m's (a_l's) replaced by $a_{l'}$'s ($b_{m'}$'s) since the excitations within the same sublattice are sufficiently described by one set of bosons. The constant E_0 coincides with the mean-field expression for the energy and the coefficients $I_1(\psi-\phi)$ and $I_2(\psi-\phi)$ are defined as

$$\begin{aligned}I_1(\psi-\phi)=2J-2x\tilde{b}\,[J_1^{(S)}&-2S^2\cos(\psi-\phi)J_2^{(S)}\\&-3S^4\cos^2(\psi-\phi)J_3^{(S)}\\&-4S^6\cos^3(\psi-\phi)J_4^{(S)}]\end{aligned} \tag{10.8}$$

and

$$\begin{aligned}I_2(\psi-\phi)=2x\tilde{b}\,[J_2^{(S)}&+3S^2\cos(\psi-\phi)J_3^{(S)}\\&+6S^4\cos^2(\psi-\phi)J_4^{(S)}]\quad.\end{aligned} \tag{10.9}$$

In antiferromagnetic and ferromagnetic (or paramagnetic) phases, $[\Delta^2_{lm}(\psi-\phi)]^{\mathrm{II}}$ does not contribute to the Hamiltonian. On the other hand, when $D=H=0$, in the canted phases the $\tilde{\Delta}_{lm}(\psi-\phi)$ terms do not appear and $[\Delta^2_{lm}(\psi-\phi)]^{\mathrm{II}}$ is entirely responsible for the intersublattice exchange and double-exchange dynamics. The reason for this is as follows. The canting angle is determined from the condition of vanishing of the linear terms, which corresponds to a no-torque situation. The resulting equations for the angle coincide with the mean-field expressions like (7.7), (7.2), and (7.23). Now, in the absence of D and H, this condition makes the entire coefficient I_1 equal to zero, so $[\Delta_{lm}^2(\psi-\phi)]^{\mathrm{II}}$ becomes important.

Let us introduce the Fourier-transformed (magnon) operators

$$a_k=(\tfrac{1}{2}N)^{-1/2}\sum_l a_l e^{-ikr_l}, \quad \text{etc.}$$

With the linear terms vanishing the magnon Hamiltonian becomes

$$\begin{aligned}\mathcal{H} \approx \sum[&\mathcal{A}_\phi(k)a_k^\dagger a_k+\mathcal{A}_\psi(k)b_k^\dagger b_k\\ &+\tfrac{1}{2}\mathcal{B}_\phi(a_k^\dagger a_{-}^\dagger k+a_k a_{-k})\\ &+\tfrac{1}{2}\mathcal{B}_\psi(b_k^\dagger b_{-k}^\dagger+b_k b_{-k})\\ &+\mathcal{C}_1\gamma(k)(a_k^\dagger b_k+b_k^\dagger a_k)\\ &+\mathcal{C}_2\gamma(k)(a_k^\dagger b_{-k}^\dagger+a_k b_{-k})] \ , \end{aligned} \tag{10.10}$$

where

$$\begin{aligned}\mathcal{A}_\phi(k)=&-I_1(\psi-\phi)Sz\cos(\psi-\phi)\\ &+I_2(\psi-\phi)S^3z[1-\cos^2(\psi-\phi)]\\ &+2S(J'+x\tilde{b}'A_3^{(S)})(z'-\gamma(k))\\ &+DS(3\cos^2\phi-1)+H\cos\phi \ , \end{aligned}\tag{10.11a}$$

$$\mathcal{B}_\phi=SD\sin^2\phi-I_2(\psi-\phi)S^3z[1-\cos^2(\psi-\phi)] \ , \tag{10.11b}$$

$$\begin{aligned}\mathcal{C}_{1,2}=&\tfrac{1}{2}I_1(\psi-\phi)S[1\pm\cos(\psi-\phi)]\\ &\mp I_2(\psi-\phi)S^3[1-\cos^2(\psi-\phi)] \ , \end{aligned}\tag{10.11c}$$

and $\mathcal{A}_\psi(\mathcal{B}_\psi)$ is equal to $\mathcal{A}_\phi(\mathcal{B}_\phi)$ with ϕ and ψ interchanged. The coefficient $\gamma(k)$ is defined as

$$\gamma(k)=\sum_\delta e^{ik\delta} \ , \tag{10.11d}$$

where γ's are positions of the intralayer nearest neighbors. Analogously $\gamma'(k)$ involves summations over the nearest neighbors within the same layer.

B. Spin-wave energies

(a) First consider the antiferromagnetic phase. Here $\mathcal{B}_\phi=\mathcal{B}_\psi=\mathcal{C}_1=0$. The energies of the two branches of spin-wave excitations are

$$\begin{aligned}\omega_{1,2}(k)=2S\{[&z(J-xbA_1^{(S)})\\ &+(J'+xb'A_{3'}^{(S)})(z'-\gamma'(k))+D]^2\\ &-\gamma^2(k)(J-xbA_1^{(S)})^2\}^{1/2}\pm H \ . \end{aligned}\tag{10.12}$$

These energies are minimal at $k=0$ and the magnons of the lower branch go soft at $H=H_{\mathrm{AF}\to\mathrm{SF}}$ given by Eq. (7.21). In particular, if $H=0$, this happens at $x=x_1$ [Eq. (7.6a)].

(b) Next consider the first canted phase at $H=0$. In this phase $\mathcal{A}_\psi=\mathcal{A}_\phi$, $\mathcal{B}_\psi=\mathcal{B}_\phi$, and all of the coefficients have to be evaluated at $\psi=\pi-\phi$. The two branches of energies are

$$\begin{aligned}\omega_{1,2}(k)=\{[&\mathcal{A}_\phi(k)\pm\mathcal{C}_1\gamma(k)]^2\\ &-[\mathcal{C}_2\gamma(k)-\mathcal{B}_\phi]^2\}^{1/2} \ , \end{aligned}\tag{10.13}$$

and the phase boundaries coincide with those obtained in Sec. VII C. In particular, if $S=1$ or $\frac{3}{2}$, the ω_1 magnons soften at 45°. For the thermodynamical properties of systems with biquadratic exchange (which is formally equivalent to the $S=1$ double-exchange systems) in the second canted phase we refer the reader to the article by Iwashita and Uryû.[17]

(c) In the second canted phase (or in the spin-flop phase) the energies have the form similar to (10.13) except that the coefficients $\mathcal{A}_\psi=\mathcal{A}_\phi$, $\mathcal{B}_\psi=\mathcal{B}_\phi$, $\mathcal{C}_{1.2}$ have to be evaluated at $\psi=-\phi$.

(d) Finally, in the ferromagnetic (or paramagnetic) phase $\mathcal{B}_\psi=\mathcal{B}_\phi=\mathcal{C}_2=0$. The two branches of energies merge into one (the distinction between the two sublattices becomes irrelevant):

$$\begin{aligned}\omega(k)=&-2S(J-x\tilde{b}A_{3'}^{(S)})[z-\gamma(k)]\\ &+2S(J'+x\tilde{b}A_{3'}^{(S)})[z'-\gamma'(k)]+2DS+H \ . \end{aligned}\tag{10.14}$$

If the concentration x is outside the ferromagnetic region, then the minimum of energy occurs at $\gamma(k)=-z$, $\gamma'(k)=+z$. An instability develops at H given by (7.24), which marks a transition from the paramagnetic phase to the spin-flop phase. At $H=0$ the mode is stable for $x \geqslant x_{3'}$.

In all this section it has been assumed that in the spin-2 system the canting of spins coupled by J', if any, is insignificant so $J'+x\tilde{b}'A_{3'}^{(S)}$ is taken to be positive. However, if such a canting does occur, the magnon energies would split slightly. In particular at sufficiently strong fields that make the sublattices coupled by J to be aligned parallel but the sublattices coupled by J' still cant (if the values of J,J',b,b' allow for this) the energy (10.14) would take the form (10.13) with $\gamma(k)$ replaced by $\gamma'(k)$. The extra term $\mathcal{C}_2\gamma'(k)-\mathcal{B}_\phi$ is negligible for small canting angles. However, in general, the spin-2 system energies actually split further into four branches whenever x exceeds x_4, as given by Eq. (7.25).

The cubic terms in the spin-wave Hamiltonian are responsible for the temperature renormalization of the canting angle, whereas the quartic ones give rise to the renormalization of energies. For instance the paramagnetic phase boundary should have a $T^{3/2}$ dependence.[19] Moreover, in the presence of an orthorhombic anisotropy or (and) in systems with a transversally anisotropic exchange coupling the T^2 law is likely to be observed.[20]

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APPENDIX

The coefficients $J_n^{(S)}$ in the double-exchange Hamiltonian (4.5) are for $S=\frac{5}{2}$, 3, $\frac{7}{2}$, and 4 (in $3d$ materials $S \leqslant \frac{5}{2}$) as follows:

$S=\frac{5}{2}$:

$$J_0^{(5/2)}=0.6366,\quad J_1^{(5/2)}=0.3453\times10^{-1},\quad J_2^{(5/2)}=0.7928\times10^{-2}\;,$$

$$J_3^{(5/2)}=0.6000\times10^{-3},\quad J_4^{(5/2)}=-0.1579\times10^{-3}\;,\quad J_5^{(5/2)}=-0.2057\times10^{-4}\;;$$

$S=3$:

$$J_0^{(3)}=0.6063,\quad J_1^{(3)}=0.1798\times10^{-1},\quad J_2^{(3)}=0.2493\times10^{-2},\quad J_3^{(3)}=-0.1213\times10^{-2},$$

$$J_4^{(3)}=-0.3237\times10^{-4},\quad J_5^{(3)}=0.1287\times10^{-4},\quad J_6^{(3)}=0.8463\times10^{-6}\;;$$

$S=\frac{7}{2}$:

$$J_0^{(7/2)}=0.6396,\quad J_1^{(7/2)}=0.1884\times10^{-1},\quad J_2^{(7/2)}=0.7557\times10^{-3},\quad J_3^{(7/2)}=0.1339\times10^{-3},$$

$$J_4^{(7/2)}=-0.2105\times10^{-4},\quad J_5^{(7/2)}=-0.2304\times10^{-7},\quad J_6^{(7/2)}=0.1272\times10^{-6},\quad J_7^{(7/2)}=0.4312\times10^{-8}\;;$$

$S=4$:

$$J_0^{(4)}=0.6653,\quad J_1^{(4)}=0.6254\times10^{-2},\quad J_2^{(4)}=0.4921\times10^{-2}\;,$$

$$J_3^{(4)}=0.1358\times10^{-3},\quad J_4^{(4)}=-0.7604\times10^{-4},\quad J_5^{(4)}=-0.6507\times10^{-5}\;,$$

$$J_6^{(4)}=0.7956\times10^{-7},\quad J_7^{(4)}=0.2255\times10^{-7},\quad J_8^{(4)}=0.5771\times10^{-9}\;.$$

The antiferromagnetic phase is stable [Eq. (7.6)] provided

$$A_1^{(S)}=J_1^{(S)}+\sum_{n=2}^{2S}(-1)^n nJ_n^{(S)}S^{2(n-1)}>0\;. \tag{A1}$$

The constant $A_1^{(S)}$ is equal to 0.066, 0.0503, 0.0536, and 0.0441 for $S=\frac{5}{2}$, 3, $\frac{7}{2}$, and 4, respectively. The corresponding critical concentrations are therefore $2x_1bz/(2zJ+D)=15.15$, 19.90, 18.64, and 22.66.

On the other hand the ferromagnetic phase is stable [Eqs. (7.18) and (7.10)] if

$$A_3^{(S)}=J_1^{(S)}-\sum_{n=2}^{2S}nJ_n^{(S)}S^{2(n-1)}>0\;. \tag{A2}$$

The coefficients $A_3^{(S)}$ are equal to 0.1762, −0.272, −0.094, and −1.270 for the four spins in question. It means that a $S=\frac{5}{2}$ system with the antiferromagnetic exchange coupling will reach the ferromagnetic phase. The lower boundary of this phase is $2x_{3'}bz/(2zJ-D)=5.67$. However, the higher spin systems will never close down. We expect that for spins even higher than 4 this will also be the case for the following reason. Inspection of Table I and of the results presented in this Appendix leads to the conclusion that the higher the spin then, essentially, the more the phase boundaries are shifted towards the bigger concentrations (at fixed J and b). This is not at all surprising. The larger the spin the less is the system influenced by the hopping carriers and then the antiferromagnetic exchange dominates the properties of the system. Thus when $S \geqslant 3$ (and also if $S=2$) the ferromagnetic arrangement disappears from the phase diagram.

In ferromagnets with the double exchange (Sec. VIII) the two sublattice configurations will be present at concentrations exceeding x_4 of Eq. (8.1). The numerical coefficient in (8.1) is replaced by 3.68, 10.64, and 0.79 for $S=3$, $\frac{7}{2}$, and 4, respectively.

Note added in proof. According to G. Matsumoto [J. Phys. Soc. Jpn. 29, 606 (1970)] the magnetic properties of $LaMnO_3$ are more complex. In this compound the Dzialoshinski-Moriya spin coupling has been found. In addition, the single-ion anisotropy turns out to be composed of the uniaxial, cubic, and orthorhombic parts. The overall easy direction is, however, as taken in our paper. The NMR and magnetization measurements on the polycrystalline $La_{1-x}Ca_xMnO_3$ samples, with x ranging from 0.005 to 0.3, have also been reported by Matsumoto [J. Phys. Soc. Jpn. 29, 615 (1970)]. A substantial spontaneous magnetization appears for $x \gtrsim 7\%$ at the liquid-nitrogen temperature. Some small moment is also observed below 7%. This should be due to the presence of the Dzialoshinski-Moriya interaction. The magnetization data, taken in the vicinity of $\frac{1}{2}$ of the Néel temperature, are not conclusive on which of the two theories, de Gennes's and ours, is correct.

K. Kubo and N. Ohata [J. Phys. Soc. Jpn. 33, 21 (1972)] have proposed another theory of double exchange. Their theory is based on a canonical transformation of the *s-d* model Hamiltonian, and it is more concerned with the electronic properties (like resistance) of the system.

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