UNDERDOPED MANGANITES: CANTED ANTIFERROMAGNETIC ORDERING OR TWO-PHASE FERRO–ANTIFERROMAGNETIC STATE?

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We calculate the energy of charge-carrier-induced canted ordering in conducting layered antiferromagnetic systems with double exchange. The quantum approach to the d-spins is used. In the jellium model the energy of the canted state is lower than the energies of both collinear ferro- and antiferromagnetic states over a certain range of charge carrier densities, beginning with arbitrarily small densities. Nevertheless, the canted state cannot be realized, because it is unstable against charge-carrier density fluctuations. The two-phase ferro–antiferromagnetic state can play the role of an alternative to canting. The case of an intermediate electronic-impurity phase separation is investigated.

1. INTRODUCTION

As is well known, charge carriers in magnetic semiconductors tend to establish ferromagnetic ordering at which their energy is minimal. If the ordering in the undoped semiconductor is antiferromagnetic, then with increasing charge carrier density first a magnetic state intermediate between the ferromagnetic and antiferromagnetic states should appear. At still higher densities, the ordering in the crystal becomes completely ferromagnetic. There are different points of view about the nature of the intermediate state at moderate doping (underdoped samples).

De Gennes [1] assumed canted antiferromagnetic ordering to be an intermediate state of degenerate antiferromagnetic semiconductors. He found, treating the d-spins as classical vectors, that the canting angle should be proportional to the charge carrier density. As an alternative to canting, in Ref. 2 the electronic phase separation model was proposed, according to which a degenerate antiferromagnetic semiconductor with frozen impurities in its ground state is separated into an insulating antiferromagnetic phase and high-conductivity ferromagnetic phases. Later the case of ferro–antiferromagnetic phase separation was considered in systems with mobile impurities and a high magnetic ordering temperature (e. g., oxygen in perovskites [3]). Then not only the charge carriers but also the ionized donors or acceptors are concentrated in the ferromagnetic portion of the crystal (impurity phase separation).

As for experimental verification of these theories, the electronic phase separation theory was confirmed by electric, magnetic and magnetooptic data on EuSe, EuTe, and so on (see Ref. 4). On the other hand, De Gennes [1] interpreted data of neutron studies of the doped lanthanum manganites $La_{1-x}Ca_xMnO_3$ (Ref. 5) as confirmation of canted antiferromagnetic ordering in them. This idea was accepted by many investigators, even those who are engaged in

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neutron studies, and now it is customary to refer to the results of Ref. 5 as providing verification of canted ordering.

In reality, this involves a misunderstanding: Wollan and Koehler [5] arrived just to the opposite conclusion. They pointed out that in principle the superposition of ferro- and antiferromagnetic peaks they observed at $x = 0.18$ can be related to both the canted antiferromagnetic ordering and mixture of the ferro- and antiferromagnetic regions. To choose between these two possibilities, they investigated the behavior of the peaks in the magnetic field. They found that a field of about 4 kOe halves the height of the ferromagnetic peaks but does not influence the height of the antiferromagnetic peaks.

But in the case of canted ordering, the ferromagnetism vector is rigidly related to the antiferromagnetism vector, and the field should rotate these vectors simultaneously. Hence, both the ferro- and antiferromagnetic peaks should vary in intensity simultaneously. In contrast, in case of the phase-separated state, the ferromagnetism and antiferromagnetism vectors are independent. This led Wollan and Koehler [5] to conclude (and this conclusion they expressed in plain words) that the phase separation, rather than canting, takes place in their samples. But the nature of the phase separation remains as yet unknown.

Strictly speaking, a very small canting of the relativistic origin was discovered later [6] in the undoped $LaMnO_3$ but it has nothing in common with the charge-carrier-induced canting proposed in Ref. 1. Its existence was confirmed in Refs. 7 and 8 by neutron investigations of $La_{1-x}Sr_xMnO_3$ and $La_{1-x}Ca_xMnO_3$, respectively. For example, in the former at $x = 0.04$, the ferromagnetic and antiferromagnetic peaks appear simultaneously at the same temperature (136 K), which unequivocally confirms the canted structure. But at $x = 0.125$ the ferromagnetic peaks appear at 230 K and the antiferromagnetic peaks only at 150 K [7].

The most natural explanation of this difference is that the ferromagnetism is not related to the antiferromagnetism as the corresponding regions are spatially separated. In other words, this result can be considered to be consistent with conclusions of Ref. 5. But in Ref. 7 the hypothesis was advanced that as the temperature decreases first the ferromagnetic ordering is established, and then it is replaced by canted antiferromagnetic ordering. Investigations in a magnetic field similar to those carried out in Ref. 5 might address the question of whether the hypothesis of Ref. 7 is adequate.

In Ref. 8, short-range ferromagnetic correlations with a length of several lattice constants were discovered, which were attributed to moving magnetic polarons (ferrons). This result is very important as it directly confirms phase separation: the appearance of ferromagnetic regions inside antiferromagnetic crystals. In our opinion, these correlations should be attributed not to the moving magnetic polarons (ferrons) predicted in Ref. 2: their number is exponentially small, and they are unlikely to be observed in neutron studies. But ferromagnetic correlations can be attributed to ferrons bound to ionized acceptors [2]. Their number is several orders of magnitude larger than the number of free ferrons.

Not only neutron data, but also electric data on manganites conflict with the De Gennes scenario of the appearance of canted antiferromagnetic ordering due to mobile holes. In fact, contrary to the De Gennes assumption, incompletely magnetized materials are not highly conductive but insulating. In addition to Ref. 8, one should also mention other investigations with larger acceptor contents (see Ref. 9). But this is not inconsistent with the properties of the phase-separated semiconductors: at modest charge carrier density they behave like the insulators [2–4].

In the present paper we describe a detailed investigation of the assumed canted layered antiferromagnetic ordering under the double exchange conditions typical of lanthanum

manganites. Unlike that of Ref. 1, our treatment of the magnetic system will not be classical but quantum-mechanical. It will be shown that although in a certain charge-carrier density range the canted antiferromagnetic structure is more energetically favored than the collinear antiferromagnetic and ferromagnetic structures, it is nevertheless not stable against transformation to a nonuniform state. The instability of the uniform state is seen from the fact that the s-electron screening length diminishes with increasing charge carrier density, and formally becomes imaginary at moderate densities.

A new type of ferro-antiferromagnetic phase separation will be considered as a possible alternative to canting. In particular, manganites usually contain not only immobile acceptors (Ca, Sr, and so on) but also mobile acceptors in the form of excess oxygen. The situation intermediate between electronic and impurity phase separation will be considered: in the ferromagnetic portion of the crystal, holes of both immobile and mobile acceptors congregate with the mobile acceptors themselves.

2. DOUBLE-EXCHANGE-INDUCED CANTED ANTIFERROMAGNETIC ORDERING

Canted antiferromagnetic ordering in a layered antiferromagnetic structure will be considered, as this is just the structure realized in lanthanum manganites. The crystalline structure is assumed to be simple cubic.

The charge-carrier energy spectrum for double exchange will be found. It is commonly believed that this limiting case of extremely strong s–d coupling is realized in lanthanum manganites, though some experimental data point to inadequacy of the double exchange (see Ref. 9). Nevertheless, there are other data that support double-exchange scenario in these materials. For example, neutron studies suggest that the magnon spectrum of doped lanthanum manganites corresponds to nearest neighbors, which is inconsistent with standard RKKY indirect exchange [10]. On the other hand [4, 11], this is just the case for indirect exchange in double-exchange systems. We also take note of Ref. 12, in which it was found by optical studies that the Mn e_g^1 band is the highest of the filled bands so that holes only appear in this band.

The treatment is based on the standard s–d model with the Hamiltonian

$$H = -t \sum a_{g\sigma}^* a_{g+\Delta\sigma} - A \sum \left(sS_g \right)_{\sigma\sigma'} a_{g\sigma}^* a_{g\sigma'} - \frac{1}{2} \sum I(f) S_g S_{g+f}, \quad (1)$$

where $a_{g\sigma}^*, a_{g\sigma}$ are the s-electron operators corresponding to conduction electrons or holes located at atom g with the spin projection σ, s is its spin operator, S_g is that of the d-spin of atom g, and Δ is the vector connecting nearest neighbors. The d–d exchange interaction in Eq. (1) is taken in the form ensuring the existence of the ferromagnetically ordered (001) planes with alternating moments. In particular, in the Jahn–Teller systems to which the lanthanum manganites belong, the in-plane d–d exchange can be ferromagnetic, whereas the out-of-plane d–d exchange can be antiferromagnetic [13]. In this case the nearest-neighbor approximation is sufficient.

The double-exchange condition can be formulated mathematically as a requirement that the s-electron band width $W = 2zt$ be small compared to AS, where S is the d spin magnitude and z is the coordination number. The s–d exchange integral A is assumed to be positive. The inequality $W \gg |I|zS^2$ should also be met, as these quantities are of the first and second order in the small d-orbital overlap, respectively.

Unlike Ref. 1, where the d spins were considered as classical, here the d spins will be considered as quantum-mechanical, and the inequality $2S \gg 1$ is not assumed. The quantum approach is necessary to investigate the stability of the canted antiferromagnetic ordering induced by double exchange. The wave function of an s electron in the completely antiferromagnetically ordered crystal is expanded in the eigenfunctions of the s–d exchange Hamiltonian (the second term in Eq. (1)). Such a quantum-mechanical treatment was first carried out in Ref. 14 for a system of two atoms, and by the present author for a system consisting of an arbitrarily large number of atoms [15]. It is assumed that the moments of the two sublattices ($i = 1$ or 2) make angles $\pm\theta$ with the total moment of the crystal.

For any atom, the z axis is aligned with the moment of the sublattice to which the atom belongs. The following eigenfunctions of the s–d exchange Hamiltonian will be used as the basis for the wave function expansion:

$$\Phi_0(\mathbf{g}) = a^*_{\mathbf{g}\uparrow}|0\rangle \prod_{\mathbf{f}} \delta(S^z_{\mathbf{f}}, S),$$

$$\Phi_1(\mathbf{g}) = \frac{1}{\sqrt{2S+1}} \left[a^*_{\mathbf{g}\downarrow} + a^*_{\mathbf{g}\uparrow} S^-_{\mathbf{g}} \right] |0\rangle \prod_{\mathbf{f}} \delta(S^z_{\mathbf{f}}, S),$$

(2)

where $S^- = S^x - iS^y$, $\delta(n, m) = 1$ for $n = m$ and 0 otherwise, and $|0\rangle$ is the s electron vacuum function.

To find the energy to first order in t, the wave function is represented by the linear combination

$$\Psi = \sum_{i=1}^{2} \sum_{\mathbf{g}_i} \left[X(\mathbf{g}_i)\Phi_0(\mathbf{g}_i) + Y(\mathbf{g}_i)\Phi_1(\mathbf{g}_i) \right]. \tag{3}$$

In fact, this is the Ritz variational procedure: in Eq. (3), terms are omitted that correspond to the d spins deviated from the moment of their sublattice in the absence of s electrons at them. These terms correspond to string-like motion of the charge carrier [16], which is of vital importance at $A < 0$ and $S = 1/2$, but is not significant at $A > 0$ [4].

To proceed further, transformation rules for the electron operators from one reference frame to the other are necessary:

$$a(\mathbf{g} + \boldsymbol{\Delta}, \downarrow_{\mathbf{g}+\boldsymbol{\Delta}}) = \cos\theta\, a(\mathbf{g} + \boldsymbol{\Delta}, \downarrow_{\mathbf{g}}) + i\exp(i\mathbf{Qg})\sin\theta\, a(\mathbf{g} + \boldsymbol{\Delta}, \uparrow_{\mathbf{g}}),$$

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(4)

where $\mathbf{Q}$ is the antiferromagnetic wave vector, and the index of the spin projection points to the atom in whose reference frame this projection is measured. We put $\mathbf{g} = (\mathbf{r}, z)$ and denote vectors connecting nearest neighbors in the plane and between the planes by $\boldsymbol{\Delta}$ and $\mathbf{n}$, respectively. Then with allowance for the relationships $t \gg |I|$ and $\mathbf{Q} = \pi(0, 0, 1)$, one obtains from Eqs. (1)–(4) for the s electron energy E_s

$$\left(E_s + \frac{AS}{2} \right) X_{\mathbf{g}} = -t\cos\theta \sum_{\mathbf{n}} X_{\mathbf{g}+\mathbf{n}} - t \sum_{\boldsymbol{\Delta}} X_{\mathbf{g}+\boldsymbol{\Delta}} - \frac{it\sin\theta\, e^{i\mathbf{Qg}}}{\sqrt{2S+1}} \sum_{\mathbf{n}} Y_{\mathbf{g}+\mathbf{n}},$$

$$\left(E_s + \frac{AS}{2} \right) Y_{\mathbf{g}} = -\frac{t\cos\theta}{2S+1} \sum_{\mathbf{n}} Y_{\mathbf{g}+\mathbf{n}} - \frac{t}{2S+1} \sum_{\boldsymbol{\Delta}} Y_{\mathbf{g}+\boldsymbol{\Delta}} - \frac{it\sin\theta\, e^{i\mathbf{Qg}}}{\sqrt{2S+1}} \sum_{\mathbf{n}} X_{\mathbf{g}+\mathbf{n}}.$$

(5)

Putting $X_g = X e^{iqg}$, $Y_g = Y e^{i(q+Q)g}$, and omitting the constant $AS/2$ in Eq. (5), one can rewrite Eq. (5) in the form

$$(E_s + P_k)X = -R_p \cos\theta \ X - \frac{R_p \ \sin\theta}{\sqrt{2S+1}} Y,$$

$$\left(E_s + \frac{P_k}{2S+1}\right) Y = -\frac{R_p \cos\theta}{2S+1} Y + \frac{R_p \ \sin\theta}{\sqrt{2S+1}} X \tag{6}$$

with $q = (k_x, k_y, p)$, $P_k = 2t[\cos(k_x a) + \cos(k_y a)]$, and $R_p = 2t\cos(pa)$.

One obtains from Eqs. (6) the following expression for the electron energy:

$$E_s(kp) = -\frac{(S+1)P_k}{2S+1} - \frac{M R_p}{2S+1} \pm \frac{1}{2S+1} \left[S^2 P_k^2 + (M^2 + 2S + 1)R_p^2 + 2M(S+1)P_k R_p \right]^{1/2}, \tag{7}$$

where $M = S\cos\theta$ is the magnetization per atom, and a is the lattice constant.

As can be seen from Eq. (7), the charge-carrier spectrum consists of two subbands. In complete ferromagnetic ordering, the lower and upper subbands correspond to the total spin projection of an s-electron-loaded atom, equal to $S+1/2$ or $S-1/2$, respectively. At arbitrary magnetization, one of the subbands remains well below the other. As the number of charge carriers is small compared to the number of magnetic atoms, only the low-energy electronic subband matters. If $2S \gg 1$ and $M^2 \gg 2S$, one obtains from Eq. (7) the expression for the s electron energy, which coincides with the result obtained in Ref. 1:

$$E_s(kp) = -P_k - \frac{R_p M}{S}. \tag{8}$$

For arbitrary M and S in the quadratic approximation, this energy can be written in the form ($\hbar = 1$)

$$E(kp) = B + \frac{k^2}{2m_{xy}} + \frac{p^2}{2m_z},$$

$$B = -t \frac{4(S+1) + 2M + \sqrt{Z}}{2S+1},$$

$$\frac{1}{2m_{xy}} = \frac{ta^2}{2S+1}\left[S+1 + \frac{4S^2 + 2M(S+1)}{\sqrt{Z}}\right], \tag{9}$$

$$\frac{1}{2m_z} = \frac{ta^2}{2S+1}\left[M + \frac{2(M^2 + 2S + 1) + 4M(S+1)}{\sqrt{Z}}\right],$$

$$Z = 16S^2 + 4(M^2 + 2S^2 + 1) + 16M(S+1).$$

This result makes it possible to find the magnetization that minimizes the energy of the canted antiferromagnetic ordering. At this stage, keeping in mind that the number ν of s electrons per atom is small, one can put the total energy per atom equal to $E_t = \nu B - IS^2\cos 2\theta$, where B is given by Eq. (9), and I is the interplane d–d exchange integral in the nearest-neighbor approximation. Minimizing E_t with respect to M, one obtains the equation for the equilibrium magnetization, which in the limit $2S \to \infty$ goes over into the De Gennes result [1]:

$$M = \frac{2\nu t}{(2S+1)|I|}\left[1 + \frac{4(S+1) + 2M}{\sqrt{Z}}\right]. \tag{10}$$

In case considered, M is nonzero for all ν. In particular, for large S the magnetization is proportional to ν. From Eq. (10), one obtains the following expression for the relative electron density ν_F at which complete ferromagnetic ordering is established:

$$\nu_F = \frac{|I|S(2S+1)}{4t}\left[1 + \frac{1}{2(3S+1)}\right]^{-1}. \tag{11}$$

Obviously, the inequality $|I|S^2 \ll t$ should hold as the quantities I and t are of the second and first order in the small overlap of d orbitals of neighboring atoms, respectively. For this reason, the inequality $\nu_F \ll 1$ should also hold.

It is interesting to compare results for the layered structure just obtained with the results obtained earlier for a staggered structure [17]. In the latter case, the effective hopping integral for the collinear antiferromagnetic structure is equal to $t/\sqrt{2S+1}$. Hence, it can be rather large even at $2S \gg 1$, keeping in mind that $2S \le 5$ for d shells. But for the layered structure, according to Eq. (9), it is equal to $t/4S$ for $2S \gg 1$, i.e., it is really small. This justifies the De Gennes approach [1].

Another drastic difference between these two structures is the fact that for the staggered structure, canting is energetically favored starting not at some arbitrarily low charge-carrier density, but at some finite value. At lower densities, staggered antiferromagnetic collinear ordering is at least relatively stable, whereas layered collinear ordering is unstable at all densities.

3. INSTABILITY OF THE CANTED ANTIFERROMAGNETIC ORDERING

So far we have shown that a range of charge-carrier densities exists in which canted antiferromagnetic ordering is more energetically favored than the collinear antiferromagnetic or ferromagnetic ordering. But this does not necessarily ensure the stability of a canted structure in magnetic systems with an isotropic exchange interaction. In what follows, it will be proved that in reality, the canted state is absolutely unstable against arbitrarily small fluctuations of electric fields, if the charge carrier density is not too low. Hence, the results of the preceding section, which attest to the instability of the collinear antiferromagnetic and ferromagnetic states in a certain ν range, do not ensure stability of the canted state in this range.

The fact of its being energetically favored as compared with the collinear ferromagnetic and antiferromagnetic states simply implies the absolute instability of the collinear states, but does not prove the stability of the canted state.

The instability of the canted state may be due to the fact that the band bottom position B depends on the magnetization M and decreases with decreasing M (9). On the other hand, the local magnetization increases with local charge-carrier density (10). Hence, if a local density fluctuation lowers the local band bottom, a local potential well for carriers arises at that location. The carriers tend to increase the local density still more. But there are two factors hindering an increase in the fluctuations: a rise in the kinetic energy of the charge carriers, and the Coulomb interaction between them in the region of their enhanced density. Competition among all these factors determines whether the initial fluctuation will continue to increase or it will begin to decrease. In the former case, the uniform canted state will be destroyed.

Here, as is customary for degenerate semiconductors, the jellium model is used, which is applicable at $\mu \gg e^2 n^{1/3}/\epsilon_0$, where μ is the Fermi energy, $n = \nu a^3$ is the charge-carrier density, and ϵ_0 is the dielectric constant. In the jellium model, instability of the canted state

against fluctuations should be manifested mathematically by the screening length becoming imaginary. It means that any arbitrarily small electric field makes the uniform state unstable. This field can be caused by a fluctuation of the charge-carrier density, i.e., one may speak of instability against the density fluctuations. This points to the tendency for the system to go over into a nonuniform state, i.e., to a phase separation. Certainly, an imaginary screening length is a sufficient but not a necessary condition for instability of the uniform state.

The screening length for the canted state will be calculated in the Born–Oppenheimer approximation. This means that the magnetization $M(\mathbf{r})$ and the band bottom position $B(\mathbf{r})$ are smoothly varying functions of the coordinates. This is justified by the fact that the typical length over which they change is the screening length $1/\kappa$, which greatly exceeds the lattice constant a in degenerate semiconductors. As both these quantities depend on $\mathbf{r}$ via $n(\mathbf{r})$, one may put

$$B(\mathbf{r}) = B + \frac{dB}{dM}\frac{dM}{dn}\delta n(\mathbf{r}),$$

$$n(\mathbf{r}) = n + \delta n(\mathbf{r}), \qquad \delta n(\mathbf{r}) = \sum n(\mathbf{q})e^{i\mathbf{q}\mathbf{r}},$$

(12)

where B and n are the average values of the corresponding quantities.

The requirement of constant electrochemical potential in the presence of an external electrostatic field with potential $\Phi(\mathbf{q})$,

$$\mu(\mathbf{r}) + B(\mathbf{r}) + e\phi(\mathbf{r}) = \mathrm{const},$$

(13)

after linearization with respect to $\delta n(\mathbf{r})$ takes the form

$$\frac{d\mu}{dn} + e\phi(\mathbf{q}) + B(\mathbf{q}) = 0, \qquad \phi(\mathbf{q}) = \frac{\Phi(\mathbf{q})}{\epsilon(\mathbf{q})},$$

(14)

where the Fermi energy μ is measured from the bottom of the band.

Using Eq. (12), one obtains the relationship between the internal field $\phi(\mathbf{q})$ and the corresponding fluctuation of the electron density:

$$n(\mathbf{q}) = -\frac{dn}{d\mu}\frac{e\phi(\mathbf{q})}{1-\Gamma},$$

(15)

where the magnetoelectric constant Γ is introduced:

$$\Gamma = -\frac{dB}{dM}\frac{dM}{dn}\frac{dn}{d\mu}.$$

(16)

In what follows, the standard pattern for calculating the screened potenial is used. One introduces the field $\delta\phi(\mathbf{q})$ created by the s electrons polarized by the external field:

$$\delta\phi(\mathbf{q}) = \phi(\mathbf{q}) - \frac{\Phi(\mathbf{q})}{\epsilon_0} = \left[1 - \frac{\epsilon(\mathbf{q})}{\epsilon_0}\right]\phi(\mathbf{q}).$$

(17)

With allowance for Eq. (15), the Poisson equation takes the form

$$q^2\delta\phi(\mathbf{q}) = -\kappa^2\phi(\mathbf{q}),$$

(18)

where

$$\kappa^2 = \frac{4\pi e^2}{\epsilon_0 (1 - \Gamma)} \frac{dn}{d\mu}.$$

As can be seen from Eqs. (17) and (18), the quantity $1/\kappa$ is just the screening length. Obviously, with increasing Γ, the screening length decreases and becomes imaginary when the magnetoelectric constant Γ exceeds unity. For the jellium model used when the compensating charge of ionized impurity is assumed to be distributed uniformly, the condition $\Gamma = 1$ can be considered necessary for the stability of the canted structure. Hence, the problem consists in obtaining an explicit expression for this quantity in the canted structure.

First, the quantity $dn/d\mu$ will be found. We introduce the effective mass of the density of states, m_{dos}, according to the standard procedure for semiconductors with an anisotropic effective mass, as in Eq. (9). To obtain an expression for m_{dos}, the following equation for the density of states is used:

$$g(E) = \frac{Na^3}{(2\pi)^3} \int\limits_{-\pi/a}^{\pi/a} dk_x dk_y dp \; \delta \left(\frac{k_x^2 + k_y^2}{2m_{xy}} + \frac{p^2}{2m_z} - E \right). \tag{19}$$

This expression can be obtained from the expression for the density of states when $\pi^2/2m_z a^2 > \mu$. If the inequality does not hold, one should consider the s electron motion to be two-dimensional. But this «ultraclassical» case emerges only when $2S \to \infty$, and for this reason it is purely of academic interest as $2S \leq 5$ for d-shells, and hence at fairy low densities the condition just mentioned is satisfied.

As follows from Eq. (19), the Fermi energy is given by

$$\mu = \frac{(6\pi^2 n)^{2/3}}{2m_{dos}}, \qquad m_{dos} = (m_{xy}^2 m_z)^{1/3}, \tag{20}$$

where according to Eq. (9), the quantity m_{dos} is a function of M, and thus of n.

To make subsequent calculations more transparent, we first consider the case in which Eq. (8) is valid ($M^2 \gg 2S + 1 \gg 1$). Then

$$m_{dos} = m \left(\frac{S}{M} \right)^{1/3}, \qquad \frac{1}{2m} = ta^2,$$

$$B = -4t - \frac{2tM}{S}, \qquad M = \frac{4\nu t}{(2S+1)|I|} = \frac{S\nu}{\nu_F}, \tag{21}$$

and one obtains from Eqs. (16) and (21)

$$\Gamma = \frac{2}{(6\pi^2)^{2/3} \nu_F^{2/3}}. \tag{22}$$

As can be seen from Eq. (22), the magnetoelectric constant Γ exceeds unity at $\nu_F < 0.05$. Hence, the canted antiferromagnetic ordering at $M^2 \gg 2S + 1$ is absolutely unstable for such ν_F. But this is not the case for $0.05 < \nu_F \ll 1$.

In the opposite limiting case, $2S \gg 1$ and $M \ll 2S$, one finds by a similar calculation

$$\Gamma = \frac{3\nu^{1/3}}{(6\pi^2)^{2/3} \nu_F}. \tag{23}$$

We see from Eq. (23) that when $\nu \to 0$, canted ordering remains at least relatively stable.*

Similar qualitative conclusions were drawn in Ref. 9 about stability of the canted structure in a staggered antiferromagnet, although the case of very low ν is meaningless for them: at such densities collinear antiferromagnetic ordering is energetically more favorable than canted ordering. But in case of staggered ordering, a more realistic model with randomly distributed point impurities can be used instead of the jellium model to investigate the stability of the canted structure [9].

In this model one takes into account that a charge carrier is attracted to the ionized impurity not only by the Coulomb force but also by the force related to the magnetization-dependent location of the bottom of the band (the expression for which is similar to Eq. (9) for B). This force arises because in the vicinity of an impurity the charge-carrier density is higher than its average value. Hence, according to an expression for M similar to Eq. (10), the same is true for the magnetization. As the total force attracting the charge carrier to the impurity exceeds the Coulomb force, the condition for Mott delocalization of the donor electrons is more stringent in the case of canted ordering, than in case of collinear ordering.

For this reason, canting can be unstable against localization of the charge carriers. But canted antiferromagnetic ordering was obtained under the assumption of delocalized charge carriers, which means that this assumption is invalid. Hence, the uniform canted ordering is unstable. Mathematically, the condition of Mott delocalization leads to the stability condition $\Gamma < 1$, instead of $\Gamma = 1$ as in the jellium model.

Unfortunately, a theory of Mott delocalization in anisotropic systems is lacking at present, so it is impossible to use this approach for a layered structure. One must merely be aware that $\Gamma = 1$ is a sufficient (and not a necessary) condition for instability of the canted structure. Nevertheless, as seen from Eq. (22), in typical cases the margin of stability is very large.

4. MIXED ELECTRONIC–IMPURITY PHASE SEPARATION

We now study phase separation as an alternative to canting. As electronic and impurity phase separation were already investigated in Refs. 2 and 3, here we study a special situation that is likely to be typical of manganites. It will be assumed that two types of acceptors (donors) are present in the crystal: immobile (Ca, Sr, etc.) and mobile (oxygen). Mixed impurity–electronic ferro–antiferromagnetic phase separation should then occur. It is characterized by the fact that the ferromagnetic phase becomes the places where holes of the immobile acceptors and holes of the mobile acceptors congregate with these ionized mobile acceptors. The holes and mobile acceptors are absent from the antiferromagnetic portion of the crystal.

This type of phase separation is of special interest for the following reason. The main difference between electronic and impurity phase separation lies in the fact that the local electric charge is nonzero in the former case and zero in the latter. Indeed, in electronic phase separation the positions of the impurity atoms are frozen. For this reason, the concentration of charge carriers in a certain phase leads to its becoming charged, and to the opposite charge of the other phase, due to the remaining ionized impurity atoms. Coulomb forces tend to mix both phases, but surface forces limit the mixing. If the crystal is isotropic, the phase of the smaller volume («minor phase») consists of small droplets several nanometers in size embedded in the host («major phase») [2, 4].

As for impurity phase separation, here there are no Coulomb forces, since the local charges of the nonuniformly distributed electrons (holes) are balanced everywhere by the charge of

ionized donors (acceptors). Nevertheless, the tendency to phase mixing exists here too: it reduces elastic forces resulting from the difference in the elastic moduli of the two phases. As a result, the minimum energy corresponds to a plane-parallel geometry (alternating layers of the two phases), but under typical conditions their size is several orders of magnitude larger than the radius of the droplets in the electronic phase separation [9]. As the Coulomb forces are much stronger than the elastic forces, in mixed phase separation the former should determine the geometry of the system as well.

To calculate the energy of the phase-separated state, a variational procedure will be used. It generalizes the procedure developed in Ref. 2. It is assumed that the minor phase consists of spheres of radius R arranged periodically inside the major phase. The second variational parameter is the ratio of volumes of the antiferromagnetic and ferromagnetic phases: $w = = V_A/V_F$. If the minor phase is highly conductive, the electronic part of the wave function at $T = 0$ is taken in the form of the antisymmetrized product of the single-electron wave functions $\psi(\mathbf{r})$ corresponding to the free motion of an electron inside a spherical region of radius R,

$$\Psi = \frac{1}{\sqrt{N_e!}} \, \mathrm{Det}\left[\psi_k(\mathbf{R}_i - \mathbf{r}_{ni})\right], \qquad (24)$$

where $\mathbf{R}_i$ is the location of the center of the ith sphere, $\mathbf{r}_{ni}$ is the location of the nth electron inside the ith sphere, and N_e is the total number of electrons. In the ground state the indices k of the single-electron states correspond to the single-electron energies E_k below the Fermi energy μ.

Dirichlet boundary conditions are used for each sphere. This is justified even for fairly shallow potential wells if $\sqrt{2m(U - E_k)}R \gg 1$, where U is the potential-well depth and m is the electron effective mass. The wave function (24) is accurate at radii less than the screening length in ferromagnetic ordering. At larger R, it gives the upper bound on the energy of the phase-separated state.

If $\sqrt{2m\mu}\,R \gg 1$, the Born–Oppenheimer approximation can be used to calculate the electron kinetic energy E_K. In this approximation, a memory of the spatial quantization of the electron motion remains in the form of the surface electron energy E_S, which be added to the bulk energy E_B,

$$E_K = E_V + E_S, \qquad (25)$$

$$E_V = \frac{3}{5}\mu(n)n(1 + w)^{2/3}V, \qquad \mu(n) = \frac{(6\pi^2 n)^{2/3}}{2m}, \qquad (26)$$

$$E_S = \beta \left(\frac{\pi}{6}\right)^{1/3} \frac{5E_V}{16n^{1/3}(1 + w)^{1/3}R}, \qquad (27)$$

where $n = n_A + n_O$ is the mean hole (or electron) density. It is composed of the densities n_A and n_O associated with immobile acceptor ions, and excess oxygen, respectively. Further, $n(1 + w)$ is the charge-carrier density inside the ferromagnetic phase, V is the total volume of the sample, $\beta = 3$ if the ferromagnetic phase is the minor one, with volume $V/(1 + w)$.

The Coulomb energy is calculated using elementary electrostatics. For ferromagnetic spheres one obtains

$$E_C = \frac{2\pi n_A^2}{5\epsilon_0} e^2 R^2 f(w)V,$$

$$f(w) = 2w + 3 - 3(1 + w)^{2/3}. \qquad (28)$$

In this case, in which the major phase is ferromagnetic and antiferromagnetic droplets are embedded in the host, the surface energy is given by Eq. (27) with $\beta = 3w$ and the Coulomb energy is given by Eq. (28), in which the function $f(w)$ must be replaced by the function

$$g(w) = w \left[2 + 3w - 3w^{1/3}(1 + w)^{2/3} \right]. \tag{29}$$

In the same nearest-neighbor approximation as before, the d–d exchange energy is

$$E_{dd} = \left[\frac{D - HS}{(1 + w)v} - \frac{H^2 S^2 w}{4Dv(1 + w)} \right], \qquad D = 2|I|S^2, \tag{30}$$

where $v = a^3$ is the unit cell volume and H is the external magnetic field. The first term in Eq. (30) represents an increase in d–d exchange energy due to replacement of antiferromagnetic ordering by ferromagnetic; the second term is the energy of the antiferromagnetic phase in the field.

Finally, we present the s electron energy difference E_U between the ferromagnetic and antiferromagnetic state, which one easily obtains from Eq. (7):

$$E_U = -2(t - t_A)nV, \qquad t_A = t\frac{2S}{2S + 1} \left(\sqrt{1 + \frac{2S + 1}{4S^2}} - 1 \right). \tag{31}$$

We now minimize the total energy

$$E_t = E_V + E_S + E_C + E_{dd} + E_U.$$

As seen from Eqs. (25)–(31), only the surface energy E_S and Coulomb energy E_C depend on R. This makes it possible to minimize the total energy with respect to R in explicit form. In ferromagnetic droplets, the optimized energy and radius are

$$E_R \equiv (E_S + E_C)_{opt} = \left(2^{-2/3} + 2^{1/3} \right) \left(\frac{9m^2}{160\pi} \right)^{1/3} \frac{e^{2/3}n^{2/3}\mu^{4/3}(n)f^{1/3}(w)(1 + w)^{2/9}}{\zeta_0^{1/3}}, \tag{32}$$

$$R_{opt}^3 = \frac{135\pi^2\zeta_0(1 + w)^{1/3}}{32m^2e^2\mu(n)f(w)}, \tag{33}$$

where the effective dielectric constant corresponding to the mixed phase separation is

$$\zeta_0 = \epsilon_0 \left(1 + \frac{n_O}{n_A} \right)^2. \tag{34}$$

Energy minimization with respect to w must be carried out numerically. But if the energy E_R is low, it only weakly influences the optimum value of w, which is determined mainly by E_V and E_{dd} in this case. One then obtains for $H \ll D$

$$\frac{V_F}{V} = \frac{1}{1 + w} = \left[\frac{3\mu(1/v)}{5(D - HS)} \right]^{3/5} nv. \tag{35}$$

As seen from Eqs. (33)–(35), at fixed total charge-carrier density n, the volume of ferromagnetic droplet increases quadratically with the relative weight of the impurity phase separation n_O/n_A

(Eq. (34)). Hence, here the size of ferromagnetic droplets can be considerably larger than in pure electronic phase separation. Thus, these droplets can be manifested not by small-angle neutron scattering but by well-formed ferromagnetic peaks. As such peaks were observed in Ref. 5, one of the possible reasons for their appearance might be mixed phase separation.

According to Eq. (33), the droplet size decreases with increasing w. Hence, according to Eq. (35), the volume of the ferromagnetic part of the crystal also increases with the field. For this reason, beginning with a certain field strength, droplets should begin to make contact with one another, and the charge carriers acquire the ability to move freely from one droplet to another. This means that the magnetic-field-induced transition from the insulating state to the high-conductivity state occurs in the sample as a whole, and can be considered as a manifestation of the giant magnetoresistance.

We note here some other recent publications on phase separation in manganites. First, Ref. 18 is a continuation of Ref. 19. In these papers a simplified treatment is carried out as compared with Ref. 2 and the present paper: the Coulomb interaction and interphase surface energy are not taken into account (the authors of Refs. 18 and 19 are likely not to be acquainted with Ref. 2 and subsequent publications of the present author). Calculations in Ref. 18 are carried out only for the ground state, assuming double exchange. Different dimensionalities are treated, beginning with an one-dimensional system and proceeding to an infinite-dimensional system.

One can also consider the appearance of charge-ordered stripes in $La_{1-x}Ca_xMnO_3$ with $x > 0.5$ as a special sort of phase separation. This pattern of phase separation takes the form of extremely stable pairs of $Mn^{3+}O_6$ stripes separated periodically by stripes of undistorted $Mn^{4+}O_6$ octahedra [20]. Some comments on this subject are given in Ref. 21, but they do not pretend to be a theory of this interesting and complicated phenomenon.

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