P-wave Pairing and Colossal Magnetoresistance in Manganese Oxides

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Abstract

We point out that the existing experimental data of most manganese oxides show the *frustrated* p-wave superconducting condensation in the ferromagnetic phase in the sense that the superconducting coherence is not long enough to cover the whole system. The superconducting state is similar to the A_1 state in superfluid He-3. The sharp drop of resistivity, the steep jump of specific heat, and the gap opening in tunneling are well understood in terms of the p-wave pairing. In addition, colossal magnetoresistance (CMR) is naturally explained by the superconducting fluctuations with increasing magnetic fields. The finite resistivity may be due to some magnetic inhomogeneities. This study leads to the possibility of room temperature superconductivity.

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1. INTRODUCTION

Recently, much attention has been paid to the manganese oxides since the observation of colossal magnetoresistance (CMR).[1-4] The nearly half-metallic nature of ferromagnetic phase was also reported.[5-8] In addition, the layered manganite was found.[9] These systems are strongly correlated and show antiferromagnetic-ferromagnetic transition and metal-insulator transition simultaneously. These phenomena were explained by the double exchange mechanism.[10-12] However, there is still no consensus as to the theoretical understanding because of the strong interaction between spin, charge, and lattice degrees of freedom.[13,14]

In this letter, we propose a *frustrated* p-wave superconducting state for the ferromagnetic phase of manganese oxides. In fact, the existing experimental data seem to manifest the p-wave superconducting condensation. In this scenario, colossal magnetoresistance (CMR) is naturally explained by the superconducting fluctuations with increasing magnetic fields. The superconducting state is similar to the well-known A_1 state which is realized in the superfluid He-3.[15] Only majority spin up electrons are paired. Because of a strong Hund coupling between the e_g conduction electrons and $S = 3/2$ core spins formed by the t_{2g} electrons, the ferromagnetism appears and the conduction electrons are highly spin-polarized in the ground state. If the majority spin up electrons are paired by the currently unknown mechanism, the energy of the ground state will be even lower. Presumably, both the electron-phonon interaction and the magnetic interaction contribute significantly. The gap parameter is very anisotropic and has point nodes at the points of intersection of the Fermi surface with the spontaneous anisotropy axis. Whereas the minority spin electrons may be localized.[5,12] But depending on the doping level, there are some minority spin electrons in the extended $t_{2g}\downarrow$ band. Hence they are also paired. The resulting p-wave superconducting state will be similar to the ABM state.[16]

The apparent finite resistivity may be caused by the *frustrated* p-wave pairing condensation, since the domain wall structures of the ferromagnetic phase and the existence of the localized minority spin electrons limit the superconducting coherence seriously. The possible existence of the canted phase[12] and the electronic phase separation[17] will also give rise to the finite resistivity. A similar finite resistivity was found in very narrow superconducting metal wires where the superconducting condensation is also frustrated.[18]

In Section 2 we critically reinvestigate the existing experimental data of resistivity, specific heat, and tunneling. Other data will be considered elsewhere. Because the superconducting behaviors are mostly screened to some extent, we need to analyze the existing data with caution. The possible p-wave superconducting states are described in Section 3. In Section 4 we discuss how to make good room temperature superconductors for practical applications.

2. REINVESTIGATION OF EXPERIMENTAL DATA

It is amazing that the p-wave superconducting condensation in manganese oxides was unnoticed until now even though there are so many experimental manifestations of the existence of the p-wave pairing.[1–4,6,7,9,19–24] It is crucial to notice that the apparent finite resistivity is caused by some extrinsic reasons not by the intrinsic reasons. The possible causes of the nonzero resistivity are the following:

(1). If the ferromagnetic phase forms the domain wall structures, the p-wave superconducting phase coherence is established in each domain and the anisotropic superconducting domains are coupled by the Josephson coupling. Then, this leads to the strong cancellation of the supercurrents as well as the finite resistivity.

(2). The minority spin electrons coming from the both Mn 3d and O 2p orbitals may hinder the supercurrents and give rise to the finite resistivity.

(3). The homogeneous canted phase developed by de Gennes[12] or the coexistence of ferromagnetic (FM) and antiferromagnetic (AF) microdomains[17] will certainly give rise to the finite resistivity.

(4). Finally, since supercurrents in A_1-like state are very anisotropic, they may not be easily

observable as in the case of the A phase of superfluid He-3.[15]
More conclusive proof of the p-wave pairing in manganese oxides is the steep jump of the specific heat and the gap opening in tunneling.[6,21–24]

2.1 Resistivity and CMR

In this Section we consider the resistivity data.[19,20] Almost all data show the abrupt decrease of the resistivity by several orders when the temperature is decreasing from the transition temperature T_c. But it appears that the $T = 0$ resistivity does not vanish and is $\sim 10\mu\Omega cm$ for good samples. The main obstacle to the realization of the superconductivity in manganese oxides is the apparent finite resistivity. Considering the possibility of *frustrated* p-wave pairing, the crucial point is not the finite value of the resistivity but the abrupt drop of the resistivity as a function of the temperature. Notice the similarity between the finite resistivity of very narrow superconducting metal wires and that of manganese oxides.[18] People think that if superconducting and normal electrons are coexisting, the resistivity will be zero because of the short-circuiting behavior of the superconducting electrons. However, in this case the superconducting coherence may be seriously limited by the domain wall structures, the effect of the minority spin electrons, and some magnetic inhomogeneities.

Figures 1 (a) and (b) show the temperature dependence of the magnetization and the resistivity of a single crystal of $La_{0.65}(PbCa)_{0.35}MnO_3$ (LCPMO), respectively.[19] Data are due to Liu et al..[19] The transition temperature T_c is $300K$. It is obvious that the ferromagnetic-to-paramagnetic transition and the metal-insulator transition occur simultaneously. The long tail of the resistivity seems to be due to the disorder caused by the co-doping of Pb and Ca. The maximum CMR was observed exactly at T_c, which indicates the close relation between superconductivity and CMR. In this type of p-wave superconducting state, T_c is increasing for strong magnetic fields because the ferromagnetic domain size is increasing by the alignment of the $S = 3/2$ core spins. Accordingly, the concomitant superconducting fluctuations lead to enhanced conductivity and CMR. Figure 1 (c) also shows the temperature dependence of the resistivity of $La_{0.72}Ca_{0.25}MnO_z$ (LCMO) measured by Chahara et al..[20] It appears that these data also indicate the p-wave superconducting condensation.

2.2 Specific Heat

The second evidence for the p-wave pairing in manganese oxides is found in the electronic specific heat measurements.[21,22] The observed steep jump of the electronic specific heat means the second order phase transition of the electronic state. But the T^3 law near $T = 0$ was not confirmed clearly. The reason is certainly related with the apparent finite resistivity. It appears that the *frustrated* p-wave superconducting electrons and normal electrons are coexisting. Note that the minority spin electrons and holes caused by divalent ion doping also contribute to the specific heat near $T = 0$.

Figure 2 (a) shows the specific heat data of $La_{0.8}Ca_{0.2}MnO_3$. Data are due to Tanaka and Mitsuhashi.[21] The broken line denotes a lattice heat capacity. It is clear that the electronic transition is of second order as noted by the authors, which is consistent with ferromagnetic-metal-to-p-wave superconductor transition. Figure 2 (b) shows the electronic specific heat divided by temperature, C/T, for $x = 0.33$ $La_{1-x}Ca_xMnO_3$ sample.[22] Data are from Ramirez et al..[22] Again we find a steep jump of the specific heat. Since both the electronic and magnetic transitions occur at the same time, the specific heat change also includes the magnetic contribution. Note that the shape of the specific heat change should be symmetric with respect to T_c if only the magnetic transition had occurred.

2.3 Tunneling

The final evidence for the p-wave pairing superconducting state is provided by the tunneling data.[6,23,24] The quasiparticle density of states (DOS) for the ABM or A_1 state is parabolic at low energies. It also shows divergences as the energy is approached to the maximum gap energy Δ_o both from below or above. The theoretical DOS will be shown in Fig. 5 (b).

Figure 3 (a) shows the normalized conductance versus the sample bias voltage for $La_{0.7}Ca_{0.3}MnO_3$ (LCMO). Data are from Wei, Yeh and Vasquez.[23] They observed the density of states of an epitaxial film sample of ferromagnetic LCMO by scanning tunneling spectroscopy. It is noteworthy that this figure is very similar to the DOS of the ABM and the A_1 states. The two peaks at $\sim \pm 0.4V$ imply that the maximum Cooper pair binding energy equals to $\sim 0.4eV$. The energy is huge enough to give rise to the p-wave superconducting state with $T_c = 260K$. The pronounced peaks at $\sim \pm 1.75V$ may be related with the exchange-split, spin-polarized peaks in the density of states calculated by Pickett and Singh.[5] In other words, these are half-metallic peaks. Figure 3 (b) shows the dynamic conductance dI/dV vs bias V at $T = 4.2K$ of magnetic tunnel junctions of $La_{0.67}Sr_{0.33}MnO_3$. Data are due to Lu et al..[6] Notice the depletion of the DOS at the zero bias. If we disregard some background contribution, this curve seems to show the zero DOS at the Fermi level, which agrees with the DOS of the p-wave pairing state. In fact, Hudspeth et al.[24] clearly observed the depletion in the conductance of LCMO films at the Fermi level with decreasing temperature. The parabolic shape of the conductance curve is also consistent with the DOS of the ABM and the A_1 states. Since the transition temperature T_c is $347K$, the peaks may appear at $\sim \pm 0.53V$ in view of Fig. 3 (a).

3. FRUSTRATED P-WAVE SUPERCONDUCTING STATE

Now we discuss the theoretical model for the p-wave superconducting state which may be realized in manganese oxides. Since the double exchange model and the related strong interaction between spin, charge, and lattice degrees of freedom are not solvable yet, our discussion is rather qualitative. We don't discuss the mechanism of the p-wave pairing either. Presumably, the strong electron-phonon interaction and the ferromagnetic interaction lead to the p-wave superconducting condensation in manganese oxides. Nevertheless we can explain the experimental data of the specific heat and the quasiparticle density of states (DOS) in terms of the A_1 state or the ABM state, because they are determined entirely by the topology of the zero gap. In this case even the crystal structure does not play an important role. On the other hand, if the mobile minority spin electrons exist for some doping concentrations,[5,7] the ABM state may be more appropriate.

3.1 Frustration

The frustration may be caused by the domain wall structures of the ferromagnetic phase and the coexisting minority spin electrons. Figure 4 (a) shows the domain wall separating domains. The spins of the superconducting electrons in the left domain are pointing upward, whereas those of the electrons in the right domain are pointing downward. In the transition region, the conduction electrons may become normal because the spin directions of the core t_{2g} electrons are strongly varying. The two superconducting domains are coupled by the Josephson-like coupling. Then, the supercurrents decay after passing the transition region and consequently the finite resistivity is obtained. Figure 4 (b) shows the effect of the minority spin electrons localized randomly. The spins of the Cooper pair electrons are canted by the spins of the minority electrons.[25] Then the quasiparticles near the nodes will be excited and lead to the finite resistivity. On the other hand, superconductivity is also possible in the canted phase.[25] However, the condensation energy will be much smaller than that of the ferromagnetic case and the quasiparticles are easily excited by any perturbation. Recently, Allodi et al.[17] reported the possibility of intrinsic phase separation of the holes into FM microdomains. This may also lead to the frustrations and the finite resistivity.

3.2 A_1 State and ABM State

In the ferromagnetic phase the majority spin electrons are free to move, whereas minority spin electrons may be localized. Therefore, only majority (up) spin electrons are paired since the pairing interaction for the localized electrons will be exponentially small.[26,27] The resulting p-wave superconducting wavefunction is given,

$$\tilde{\phi}_P = \prod\nolimits'_{\vec{k}} (u_{\vec{k}} + v_{\vec{k}} a^{\dagger}_{\vec{k}\uparrow} a^{\dagger}_{-\vec{k}\uparrow})|0>, \tag{1}$$

where the product over $\vec{k}$ is restricted to a half-space and $a^{\dagger}_{\vec{k}\uparrow}$ creates a majority spin electron at the e_g conduction band. Because of the Fermi statistics, we have

$$u_{-\vec{k}} = u_{\vec{k}}, \qquad v_{-\vec{k}} = -v_{\vec{k}}. \tag{2}$$

The gap parameter for the A_1 state is given by

$$\Delta^{\uparrow\uparrow}_{\vec{k}} = \Delta_o sin\theta_{\vec{k}} e^{i\phi_{\vec{k}}}, \tag{3}$$

where $\theta_{\vec{k}}$ and $\phi_{\vec{k}}$ are the polar and azimuthal angles of $\vec{k}$. Notice that the gap vanishes at two points along $\hat{k}_z = \hat{\mathbf{l}}$ with $\mathbf{l}$ denoting the angular momentum. In the presence of the mobile minority spin electrons, the gap parameter of the ABM state is given by

$$\Delta^{\uparrow\uparrow}_{\vec{k}} = \Delta_o sin\theta_{\vec{k}} e^{i\phi_{\vec{k}}}, \quad \Delta^{\downarrow\downarrow}_{\vec{k}} = \Delta'_o sin\theta_{\vec{k}} e^{i\phi_{\vec{k}}}, \tag{4}$$

where Δ'_o is not always the same as Δ_o.

Since the specific heat and the density of states for the A_1 state and the ABM state show the qualitatively same behaviors, we consider those of the ABM state with $\Delta'_o = \Delta_o$. The single-particle excitation energy is given by

$$E_{\vec{k}} = \sqrt{\epsilon^2_{\vec{k}} + \Delta^2_o sin^2\theta_{\vec{k}}}. \tag{5}$$

Accordingly, the specific heat is found to be

$$\begin{aligned} C_V &\equiv T\frac{dS}{dT} \\ &= \frac{1}{2T^2}\sum_{\vec{k}}[E^2_{\vec{k}} - \frac{T}{2}\frac{d\Delta^2_{\vec{k}}}{dT}]sech^2\frac{E_{\vec{k}}}{2T}, \end{aligned} \tag{6}$$

where S denotes the entropy. In the low temperature limit, one finds

$$C_V = 3.5(\gamma T_c)(\frac{T}{T_c})^3, \tag{7}$$

where $\gamma = C_n/T$. C_n is the normal specific heat. The specific heat jump for the ABM state is given by

$$\frac{\Delta C_V}{C_n} \cong 1.19. \tag{8}$$

(For the A_1 state the jump is 0.74.[15]) The normalized single-particle density of states (DOS), $N(E)/N_o$, was found to be[16]

$$\frac{N(E)}{N_o} = \frac{|E|}{2\Delta_o} ln \left| \frac{E+\Delta_o}{E-\Delta_o} \right|, \tag{9}$$

where N_o is the normal DOS. The $N(E)$ is parabolic, that is, $N_o(E/\Delta_o)^2$, near the Fermi energy and becomes infinite at $E = \Delta_o$.

Figures 5 (a) and (b) show the specific heat and the normalized density of states, $N(E)/N_o$, for the ABM state with the transition temperature $T_c = 100K$. Comparing with Figs. (2) and (3), the agreements between our theoretical curves and experimental data are excellent. It is reasonable to conclude that the p-wave pairing superconducting condensation is realized in manganese oxides. However, the superconducting behaviors are almost screened by domain wall structures, the existence of the localized minority spin electrons, the canted phase, and the coexistence of the FM and AF microdomains.

3.3 A_1-like State in cubic crystalline symmetry

In manganese oxides, the Mn ions form a cubic lattice. The group theoretical classification of p-wave pairing superconducting states under cubic symmetry has been already done.[28−32] The superconducting classes with ferromagnetic properties are obtained from three dimensional representations of the cubic group. They are $D_3(E)$ and $D_4(E)$ classes from three-dimensional representations F_1 and F_2.[29] The phases $D_3(E)$ have zeros at the points of intersection of the Fermi surface with a three-fold axis, whereas the phases $D_4(E)$ have zeros at the points of intersection of the Fermi surface with a four-fold axis. $D_3(E)$ and $D_4(E)$ phases are eight-fold and six-fold degenerate, respectively. These superconducting states resemble the A phase of He-3. On the other hand, manganese oxides seems to be coverted to a rhombohedral structure with the Jahn-Teller effect.[33] The corresponding p-wave superconducting classes have also been investigated.[34] ¿From these states we may obtain proper A_1-like and ABM-like p-wave pairing superconducting states which may be realized in manganese oxides. More details will be reported elsewhere.

4. DISCUSSION

More studies are required to check whether the *frustrated* p-wave pairing superconducting condensation is really realized in manganese oxides. When analyzing the experimental data, it is important to take into account the screening effect caused by domain wall structures, minority spin electrons, and other magnetic inhomogeneities. The magnetic properties of manganese oxides need to be reinvestigated. In particular, NMR experiments probing the spin dynamics may provide the specific information on the structure of the p-wave superconducting state. The collective modes such as sound modes and spin-wave modes may also give a clue to the existence of the p-wave pairing. The effects of magnetic fields are particularly interesting, since they give rise to CMR and metal-insulator transition in some samples.[35] The spin-polarized tunneling experiment[6] should be done up to higher bias voltages to find the gap opening.

Let us discuss how we can make good room temperature superconductors. It depends on how we eliminate the frustrations and make a good single crystal with one single magnetic domain and 100 % spin polarization near the Fermi level. It is also desirable for the minority spin electrons to have a large insulating gap which results in the complete disappearance of the minority spin DOS near the Fermi surface. In other words, we need a perfect half-metallic ferromagnet. The local spin distortions caused by any possible bound or self-trapped states of the carriers should be eliminated since they give rise to the canting of the Cooper pair spins and limit the superconducting coherence seriously. If we overcome the above problems, it is highly likely that we can make almost room temperature superconducting manganese oxides which have the zero temperature resistivity smaller than that of the good Cu samples by a factor of more than a thousand.

5. CONCLUSION

We have proposed the *frustrated* p-wave pairing superconducting state to explain CMR, the sharp drop of resistivity, the steep jump of specific heat, and the gap opening in tunneling of manganese oxides. The p-wave pairing state is similar to the A_1 state in superfluid He-3. The apparent finite resistivity may be caused by the domain wall structures of the ferromagnetic phase, the coexisting minority spin electrons, the canted phase, and the possible existence of the FM and AF microdomains. If we eliminate the above problems, the resistivity of manganese oxides will be smaller than that of good Cu samples by a factor of more than a thousand. This study opens up the possibility of room temperature superconductivity.

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FIGURES

FIG. 1. (a) The temperature dependence of the magnetization of a single crystal of LPCMO, taken from Liu et al. (Ref. 19). The Curie temperature T_c is $300K$. (b) The resistivity vs temperature in zero field and in a 5.5-T field, taken from Liu et al. (Ref. 19). (c) The temperature dependence of the resistivity at zero field, taken from Chahara et al. (Ref. 20).

FIG. 2. (a) The temperature dependence of specific heat of monoclinic $\mathrm{La_{0.8}Ca_{0.2}MnO_3}$. (After Tanaka and Mitsuhasi Ref. 21.) The broken line denotes a lattice specific heat calculated by a Debye model. (b) specific heat divided by temperature, C/T for $x = 0.33$ $\mathrm{La_{1-x}Ca_xMnO_3}$ with lattice contribution subtracted. (After Ramirez et al. Ref. 22.)

FIG. 3. (a) STM spectroscopy data at 77K, plotted as the normalized conductance $(dI/dV)/(\overline{I/V})$ vs the bias voltage V, taken from Wei et al. (Ref. 23). (b) dynamic conductance dI/dV vs bias V at $T = 4.2K$ of a magnetic tunnel junction, taken from Lu et al. (Ref. 6).

FIG. 4. (a) The triplet Cooper-pairs in the domain wall structures of the ferromagnetic phase. (b) a Cooper pair in the presence of the minority spin electrons localized randomly.

FIG. 5. (a) Specific heat vs temperature for the ABM state. The transition temperature T_c is 100K. (b) the density of states vs energy divided by the maximum gap parameter, E/Δ_o, for the ABM state.