Role of Orbitals in Manganese Oxides - Ordering and Fluctuation

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Abstract

We study the manganese oxides from the viewpoint of the strongly correlated doped Mott insulator. The magnetic ordering and the charge transport are governed by the orbital degrees of freedom, and their dimensionality is controlled by the anisotropic transfer integrals between the $e_g$ orbitals. As $x$ increases the magnetic structure is predicted to change as $A \to F \to A \to C \to G$ ($F$: ferromagnet, $A$: layered antiferromagnet, $C$: rod-type antiferromagnet, $G$: usual antiferromagnet), in agreement with experiments. Especially the orbital is aligned as $d_{x^2-y^2}$ in the metallic $A$ state, which explains the quasi 2D transport and no canting of the spin observed experimentally.

Next we discuss the ferromagnetic state without the orbital ordering due to the quantum fluctuation. Here the interplay between the electron repulsion
and the Jahn-Teller electron-phonon interaction $E_{LR}$ is studied with a large $d$ model. In addition to this strong correlation, we propose that the dynamical phase separation could explain the specific heat as well as the various anomalous physical properties, e.g., resistivity, photo-emission, etc.

I. INTRODUCTION

The interplay between the magnetism and transport properties is one of the main issues in the physics of the strongly correlated electronic systems. Doped manganites $R_{1-x}A_x\text{MnO}_3$ ($R=$La, Pr, Nd, Sm; $A=$ Ca, Sr, Ba) have recently attracted considerable interests from this viewpoint in connection to the colossal magnetoresistance (CMR). It has been believed that the most fundamental mechanism for this CMR is the double exchange interaction, which has been studied long time ago \cite{1,2,3}. However recent systematic experimental studies have revealed the vital role of the orbital degrees of freedom, which is the subject of this paper.

In the parent compound $R\text{MnO}_3$, the valence of the Mn ion is $\text{Mn}^{3+}$ with the configuration $d^4$. Due to the crystal field the five $d$-orbitals split into two $e_g$-orbitals ($x^2-y^2, 3z^2-r^2$) and three $t_{2g}$-orbitals ($xy, yz, zx$). According to Hund’s rule the four electrons occupy three $t_{2g}$-orbitals and one of the $e_g$-orbitals with parallel spins. Then the $e_g$-electron has the orbital degrees of freedom in addition to the spin ones. When the holes with concentration $x$ are doped, the vacancies in the $e_g$-orbitals are introduced which induces the ferromagnetism due to the double exchange interaction and the charge transport. However there are several experimental facts which cannot be explained in the simple double exchange models. One is the rich phase diagrams which is studied theoretically in Section II and the other is the anomalous features in the ferromagnetic metallic phase described in Section III. All these issues are closely related to the orbital degrees of freedom, which control the dimensionality of the electronic systems and whose quantum fluctuation gives rise to the orbital liquid and orbital Kondo effect. Section IV is devoted to the conclusions where the possibility and implications of the dynamical phase separation are mentioned.
II. PHASE DIAGRAM

We set up the three-dimensional cubic lattice consisting of the manganese ions. Two kinds of the $e_g$ orbital ($\gamma, \gamma'$) are introduced in each site, and the $t_{2g}$ electrons are treated as the localized spin with $S = 3/2$. The Hamiltonian without the JT coupling is given as follows [4–7],

$$H = \sum_{<ij>,\sigma,\gamma,\gamma'} \left( t^{\gamma' \gamma}_{ij} d^\dagger_{i\gamma\sigma} d_{j\gamma'\sigma} + \text{h.c.} \right) + U \sum_i n_{i\gamma\uparrow} n_{i\gamma\downarrow} + U' \sum_i n_{ia} n_{ib} + I \sum_{i,\sigma,\sigma'} d^\dagger_{ia\sigma} d_{ib\sigma'} d_{ia\sigma'} d_{ib\sigma} + J_H \sum_i \vec{S}_i \cdot \vec{S}_t^{2g} + J_s \sum_{<ij>} \vec{S}_t^{2g}_i \cdot \vec{S}_t^{2g}_j. \quad (1)$$

d^\dagger_{i\gamma\sigma}$ is the operator which creates an electron with spin $\sigma(=\uparrow, \downarrow)$ in orbital $\gamma(=a, b)$ at site $i$, and $\vec{S}_i$ is the spin operator for the $e_g$ electron defined by $\vec{S}_i = \frac{1}{2} \sum_{\gamma\gamma'} \sum_{\sigma\sigma'} d^\dagger_{i\sigma\gamma} \vec{\sigma}_{\gamma\gamma'} d_{i\sigma\gamma'}$. The first term describes the electron transfer between $\gamma$ orbital at site $i$ and $\gamma'$ orbital at the nearest-neighbor site $j$. The value of $t^{\gamma' \gamma}_{ij}$ is estimated by considering the oxygen 2$p$ orbitals between the nearest Mn-Mn pair, and is represented by $c^{\gamma' \gamma}_{ij} t_0$, where $c^{\gamma' \gamma}_{ij}$ is the numerical factor depending on the orbitals [5]. $t_0$ is estimated to be $0.72eV$, which we choose the unit of energy below ($t_0 = 1$) [4]. The second line shows the electron-electron interaction terms where $U$, $U'$ and $I$ is the intra-, inter-orbital Coulomb interactions, and inter-orbital exchange interaction, respectively. This interaction can be rewritten as $-\alpha \sum_i \left( \vec{S}_i(\tau) + \frac{J_H}{2m} \vec{S}_t^{2g}(\tau) \right)^2 - \beta \sum_i \vec{T}_i(\tau)^2$ [6]. Here the spin operator $\vec{S}_i$ and the iso-spin operator $\vec{T}_i = \frac{1}{2} \sum_{\gamma'\gamma} \sum_{\sigma'\sigma} d^\dagger_{i\sigma'\gamma'} \vec{\sigma}_{\gamma'\gamma} d_{i\sigma\gamma}$ for the orbital degrees of freedom are introduced, and the two positive coefficients $\alpha$ and $\beta$, which are defined by $\alpha = 2U/3 + U'/3 - I/6$ and $\beta = U' - I/2$, represent the interaction to induce the spin and iso-spin moments, respectively. The last line is the sum of the Hund coupling and the AF interaction between the nearest neighboring $t_{2g}$ spins. Here we adopt the mean field approximation by introducing the order parameters $\langle \vec{S}_i \rangle$, $\langle \vec{S}_t^{2g} \rangle$, and $\langle \vec{T}_i \rangle$. These order parameters are determined to optimize the mean field energy at zero temperature. For both spin and orbital, the four types of the ordering are considered, that is, the ferromagnetic (F-type) ordering, where the order parameters are uniform, and the three AF-like orderings, i.e.,
the layer-type (A-type), the rod-type (C-type) and the NaCl-type (G-type) AF orderings. Hereafter, types of the orderings are termed as, for example, (spin:C), and so on.

In Fig. 1, we present the calculated phase diagram in the case of $\alpha = 8.1$, $\beta = 2.5$, which is relevant to the actual manganese oxides. In each region, the spin structure is specified by the letter F,A,C,G and the orbital configuration by picture. The important results are the followings.

[1] There occurs the crossover from the superexchange dominated region for small $x$ ($x < 0.3$) to that of the double exchange interaction for large $x$ ($x > 0.3$). The former region could not be reproduced by the analysis without Coulombic repulsion. In this respect, the spin F state up to $x \sim 0.4$ in the phase diagram is mostly due to the superexchange interaction.

[2] Because of the anisotropy of the transfer integral between the $e_g$-orbitals, the most natural orbital configuration expected from the double exchange interaction is $(x^2 - y^2)$ with the two dimensional electronic dispersion. This corresponds to the A phase for $0.15 < x < 0.45$. In this case the interlayer transfer is forbidden, and the spin A-type structure is stabilized by $J_s$. No spin canting is expected in this case.

[3] Similarly the spin C structure is accompanied by the $3z^2 - r^2$ orbital which gives the 1D-like dispersion along the $c$-axis. Hence the spin and orbital structure is closely correlated through the dimensionality of the electronic dispersion. From this viewpoint, the orbitals have more degrees of freedom in the ferromagnetic state. This suggests the large orbital fluctuation in the spin F state as discussed in the next section.

We now discuss the comparison between the mean field phase diagram in Fig. 1 and the experiments. At the moment, a value of $J_S$ cannot be estimated accurately, but there are two rough estimates. One is from the Néel temperature $T_N = 130K$ for CaMnO$_3$ ($x = 1.0$) which suggest $J_S = T_N / 7.5 \cong 1.7meV \cong 0.0023t_0$ in the mean field approximation. The fluctuations lower $T_N$, and hence increase the estimate for $J_S$. Another estimate is obtained from the numerical calculations for LaMnO$_3$ ($x = 0.0$), which suggests $J_S \cong 8meV \cong 0.011t_0$. Although $J_S$ might depend on $x$ in real materials, we tentatively fix $J_S$ to be $0.009t_0$. 

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represented by the broken line in Fig. 1. Then the spin structure changes as $A \rightarrow F \rightarrow A \rightarrow C \rightarrow G$, as $x$ increases, which is in good agreement with the experiments [10, 12]. Another implication to the experimental results is about spin:A phase appearing around $x > 0.5$. In Nd$_{1-x}$Sr$_x$MnO$_3$, the ferromagnetic metallic phase is realized up to about $x = 0.48$ and the CE-type AF structure with the charge ordering tunes up [9, 10]. With further increasing of $x$, the metallic state with spin:A again appears at about $x = 0.53$, and the large anisotropy in the electrical resistivity is observed in this phase. The similar metallic phase accompanied with spin:A is also reported in Pr$_{1-x}$Sr$_x$MnO$_3$ [11]. The spin canting is not observed experimentally [9–11] as predicted above in this Spin:A metal, in contrast to the Spin:A in the small $x$ region which has been discussed by de Gennes [3].

Summarizing this section we have studied the phase diagram of La$_{1-x}$Sr$_x$MnO$_3$ in the plane of $x$ (hole concentration) and $J_s$ (AF exchange interaction between the $t_{2g}$ spins) in the mean field approximation. The global features can be understood in terms of the interplay between the superexchange interaction and the double exchange one which is considerably modified with taking the orbital degrees of freedom into account. The dimensionality of the energy band attributed to the orbital structure plays an essential role to determine the phase boundary. The orbital structure in the ferromagnetic phase is sensitive to changes of the carrier concentration and the energy parameters. This is because the spin structure does not forbid the kinetic energy gain for any direction, and the orbitals have more freedom. This enhances the fluctuation of the orbital degrees of freedom. Actually the orbital fluctuation has been studied in the slave-fermion formalism, and it has been found that the orbitals remain a liquid down to the low temperature due to the fluctuation among the three directions of the $x^2 - y^2$-type ordering [3]. What quenches the entropy of the system is the quantum tunneling between the different orbital configurations, which could be regarded as the orbital-Kondo effect. This will be studied in the next section.
III. ORBITAL FLUCTUATION

Experimentally there are several anomalous features in the low temperature ferromagnetic phase below $T_c$.

[a] In the neutron scattering experiment no temperature dependent phonon modes have been observed [13]. The recent Raman scattering experiment also shows that the Jahn-Teller phonons (especially their frequencies) are temperature independent and insensitive to the ferromagnetic transition at $T_c$ [14]. [b] The photo-emission spectra show a small discontinuity at the Fermi edge even at $T << T_c$, which suggests some interactions still remain strong there [15]. [c] The optical conductivity $\sigma(\omega)$ at $T << T_c$ is composed of two components, i.e., the narrow Drude peak ($\omega < 0.02\text{eV}$) and the broad incoherent component extending up to $\omega \sim 1\text{eV}$ [16]. The Drude weight is very small, which seems to be consistent with the photo-emission spectra.

[d] The low temperature resistivity $\rho(T)$ can be fitted by

$$\rho(T) = \rho_0 + AT^2,$$ 

where $A$ is a large constant of the order of $500\mu\Omega\text{cm}/\text{K}^2$ [17], again suggesting the strong electron correlation.

[e] Contrary to the case of resistivity [d], the coefficient of $T$-linear specific heat is very small with $\gamma = 2\text{mJ}/\text{K}$, which violates the Kadowaki-Woods law for these compounds [18].

Although [e] is difficult to reconcile with [a]-[d], we consider the latter as the evidence for the strong correlation and orbital fluctuation even at $T \ll T_c$. Because the spins are perfectly aligned at $T \ll T_c$, the only remaining degrees of freedom are the orbital ones. In this section, we study a large $d$ model [19] for the ferromagnetic state including both the electron-electron interaction $U$ and the Jahn-Teller coupling $g$ [20]. This model takes care of the following two respects, (i) including the electron-electron interaction, (ii) including the quantum fluctuations. Especially the latter is essential to describe the low temperature Fermi liquid state, which is described by the Kondo peak in the large $d$ limit [19]. The strong
electron-electron interaction with the reasonable magnitude of the Jahn-Teller coupling explains both the large isotope effect and [a]. Moreover, the features of strong correlation [b]-[d] are at least consistent with the large $U$ picture although [e] still requires another physics, which we will discuss in the next section. We start with the Hubbard-Holstein model for the ferromagnetic state.

$$H = - \sum_{i,j,\alpha,\alpha'} t_{ij}^{\alpha\alpha'} c_{i\alpha}^\dagger c_{j\alpha'} + U \sum_i n_{i\uparrow} n_{i\downarrow} - g \sum_i Q_i (n_{i\uparrow} - n_{i\downarrow}) + \frac{1}{2} \sum_i \left( \frac{P_i^2}{M} + M \Omega^2 Q_i^2 \right),$$

where the spin indices $\alpha = \uparrow, \downarrow$ correspond to the orbital degrees of freedom as $\uparrow = d_{x^2-y^2}$ and $\downarrow = d_{3z^2-r^2}$, and the real spins are assumed to be perfectly aligned. We consider only one Jahn-Teller displacement mode $Q_i$ for each site, while there are two modes $Q_{2i}, Q_{3i}$ in the real perovskite structure [21]. However this does not change the qualitative features obtained below. The Jahn-Teller mode is assumed to be an Einstein phonon with a frequency $\Omega$. The transfer integral $t_{ij}^{\alpha\alpha'}$ depends on a pair of orbitals $(\alpha, \alpha')$ and the hopping direction. These dependences lead to the various low lying orbital configurations, and thus they suppress the orbital orderings in the ferromagnetic state. Actually there is no experimental evidence for the orbital orderings, e.g., the anisotropies of the lattice constants and/or transport properties in the ferromagnetic state. Then we assume that no orbital ordering occurs down to the zero temperature due to the quantum fluctuations, and the transfer integral is assumed to be diagonal for simplicity, i.e., $t_{ij}^{\alpha\alpha'} = t_{ij} \delta_{\alpha\alpha'}$. This means that the ground state is a Fermi liquid with two degenerate bands at the Fermi energy. In order to describe this Fermi liquid state, we employ the large-$d$ approach where the model Eq.(3) is mapped to the impurity Anderson model with the self-consistent condition [19]. This approach has been applied to the manganese oxides to study Hund’s coupling by Furukawa [22] and to study the additional Jahn-Teller coupling by Millis et al. [23]. The action for the effective impurity model is given by

$$S = \int_0^\beta d\tau \int_0^\beta d\tau' c_{\alpha}(\tau) G^{-1}_0(\tau - \tau') c_{\alpha}(\tau')$$
\[ + \int_0^\beta d\tau \left[ U n_\uparrow(\tau) n_\downarrow(\tau) - g Q(\tau)(n_\uparrow(\tau) - n_\downarrow(\tau)) \right] + \int_0^\beta d\tau \frac{M}{2} \left[ (\partial_\tau Q(\tau))^2 + \Omega^2 Q(\tau)^2 \right], \]  

where \( G_0^{-1}(\tau - \tau') \) is the dynamical Weiss field representing the influence from the surrounding sites. The self-consistency condition is that the on-site Green’s function \( G(i\omega_n) = (G_0(i\omega_n)^{-1} - \Sigma(i\omega_n))^{-1} \) should be equal to the Hilbert transform of the density of states \( D(\varepsilon) \) as

\[
G(i\omega_n) = \int d\varepsilon \frac{D(\varepsilon)}{i\omega_n + \mu - \Sigma(i\omega_n) - \varepsilon}. \tag{5}
\]

We take the Lorentzian density of states \( D(\varepsilon) = t/(\pi(\varepsilon^2 + t^2)) \) because there is no need to solve the self-consistency equation in this case, and the Weiss field is given by

\[
G_0^{-1}(i\omega_n) = i\omega_n + \mu + i t \text{sign} \omega_n. \tag{6}
\]

The only unknown quantity is the chemical potential \( \mu \), which is determined by the electron number. The determination of chemical potential requires some numerical calculations, but our discussion below is not sensitive to the location of the chemical potential. Then we take \( \mu \) as the parameter of our model, and the problem is now completely reduced to that of a single impurity. Now we introduce a Stratonovich-Hubbard (SH) field \( \xi(\tau) \) to represent the Coulomb interaction \( U \). Then the action is given by

\[
S = \sum_{\omega_n}(i\omega_n + \mu + i t \text{sign} \omega_n)c_\alpha^\dagger(\omega_n)c_\alpha(\omega_n)
+ \int_0^\beta d\tau \left[ \frac{\Delta^2}{U} \xi(\tau)^2 + \frac{M}{2} \left[ (\partial_\tau Q(\tau))^2 + \Omega^2 Q(\tau)^2 \right] + \xi(\tau)Q(\tau) - \Delta \xi(\tau) - g Q(\tau))(n_\uparrow(\tau) - n_\downarrow(\tau)) \right], \tag{7}
\]

where \( \Delta = (t^2 + \mu^2)/t \) and \( \xi(\tau) \) is the test field to measure the phonon correlation function. At this stage the electron is coupled with the linear combination of the SH field \( \xi(\tau) \) and the phonon \( Q \) as \( \eta(\tau) \equiv \xi(\tau) + \frac{\Delta}{U} Q(\tau) \). Then the effective action can be derived as

\[
S = \sum_{\omega_n} \left[ (i\omega_n + \mu + i t \text{sign} \omega_n) c_\alpha^\dagger(\omega_n)c_\alpha(\omega_n) - \Delta \eta(i\omega_n)(n_\uparrow(-i\omega_n) - n_\downarrow(-i\omega_n)) \right]
+ \sum_{\omega_n} \frac{1}{2M(\omega_n^2 + \Omega^2)} \left[ -\zeta(i\omega_n)\zeta(-i\omega_n) + \frac{2\Delta^2}{U} M(\omega_n^2 + \Omega^2) \eta(i\omega_n)\eta(-i\omega_n) \right]
+ \frac{2g\Delta}{U} \eta(i\omega_n)\eta(-i\omega_n) \right] \tag{8},
\]
where $\tilde{\Omega} = \Omega \sqrt{U_{\text{eff}}/U}$. The effective interaction $U_{\text{eff}}$ is the sum of the Coulomb repulsion $U$ and the lattice relaxation energy $E_{LR} = g^2/(2M\Omega^2)$ as $U_{\text{eff}} = U + 4E_{LR}$. The phonon Green’s function $d(i\omega_n) = \langle Q(i\omega_n)Q(-i\omega_n) \rangle$ is given by

$$d(i\omega_n) = \frac{1}{M(\omega_n^2 + \tilde{\Omega}^2)} + 4 \left( \frac{g\Delta/U}{M(\omega_n^2 + \tilde{\Omega}^2)} \right)^2 \chi_\eta(i\omega_n),$$

where $\chi_\eta(i\omega_n) = \langle \eta(i\omega_n)\eta(-i\omega_n) \rangle$ is the orbital susceptibility of the electronic system. The first term is the usual phonon Green’s function with the renormalized frequency $\tilde{\Omega}$, which is higher than the bare $\Omega$. This $\tilde{\Omega}$ does not depend on the electron response function and hence temperature independent. When $U \ll E_{LR}$, $\tilde{\Omega}$ is much larger than $\Omega$ and the first term of Eq.(9) is irrelevant in the phonon frequency region $\omega \sim \Omega \sim 0.1eV$. In the opposite limit $U \gg E_{LR}$, the renormalization of the phonon frequency is small. The second term depends on the temperature (Kohn anomaly) and shows the characteristic lineshape with the broadening. From the above consideration together with the experimental fact that no temperature dependence of the phonon frequency has been observed, we conclude that the Coulomb interaction $U$ is larger than the lattice relaxation energy $E_{LR}$.

Now let us study the electronic system in detail. Following the analysis in section III C of ref. [24], the quantum fluctuation between two orbital configurations gives rise to the orbital Kondo effect with the Kondo temperature $T_K$. We obtain an estimate for the Kondo temperature as

$$T_K \sim t \exp\left[ -\frac{RU_{\text{eff}}}{\Delta} \right].$$

where

$$R = 2x\sqrt{1 + 4y^{-1}}, \text{ for } y >> 1/\max(x, x^2)$$

$$R = \sqrt{1 + \frac{2}{3}x^2(4 + y)}, \text{ for } y << 1/\max(x, x^2).$$

Here we have introduced the dimensionless variables $x = E_{LR}/\Omega$ and $y = U/E_{LR}$. The main conclusion here is that when $x > 1$, i.e., $E_{LR} > \Omega$, the reduction factor $R$ is proportional
to $x$ even in the limit $U \gg E_{LR}$. This is because the overlap of the phonon wavefunction enters the tunneling matrix element even when the Coulomb interaction is dominating.

This Kondo temperature $T_K$ gives the effective bandwidth $B$ in the large-$d$ model, and the effective mass enhancement is estimated as $m^*/m = t/T_K \sim \exp\left(\frac{R U_{\text{eff}}}{\Delta}\right)$. This strong mass enhancement manifests itself in the physical quantities as follows. The orbital susceptibility $\chi_\eta(i\omega_n \to \omega + i\delta)$ has a peak at $\omega = 0$ with the peak height of the order of $\eta_0^2/T_K$ and with the width of the order of $T_K$. The specific heat coefficient $\gamma$ should be proportional to $B^{-1}$, while the coefficient $A$ of $T^2$ in Eq.(2) scales as $A \propto B^{-2}$. The ferromagnetic transition temperature $T_c$ is expected to be proportional to $B$, and hence we expect a large isotope effect when $R > 1$. In other words, the large isotope effect does not rule out the large Coulomb interaction $U$. The edge of the photoemission spectrum at the Fermi energy and the Drude weight are reduced by the factor $m/m^*$. As mentioned above, many experiments except for those of specific heat seem to suggest that the manganese oxides in their ferromagnetic state belong to the strongly correlated region. Then it is natural that the large isotope effect is observed. The band width is rather difficult to pin down accurately, but a rough estimate from $A$ in eq.(2) is $B \sim 0.1 eV$, which is comparable to $\Omega$. This suggests that the suppression is not extremely large. Another experimental fact is that the temperature independent Jahn-Teller phonon is observed at the frequency near the original one $\Omega$, which means that $U$ is larger or at least of the order of $E_{LR}$. Then we conclude that the relative magnitude of the energy scales is $\Omega < E_{LR} < U$ for the ferromagnetic phase in the manganese oxides. The small specific heat coefficient necessitates the physical mechanisms which have not been included in our model, which will be discussed in the next section.

Summarizing this section, we have studied a model of manganese oxides in the ferromagnetic state taking into account both the Coulomb repulsion $U$ and the Jahn-Teller interaction $E_{LR}$. These two interactions collaborate to induce the local orbital moments. In the strong coupling case, i.e., $U_{\text{eff}} = U + 4E_{LR} \gg t$ ($t$ : transfer integral), the overlap of the phonon wavefunctions ($\sim e^{-E_{LR}/\Omega}$) enters the tunneling amplitude between the two minima for the orbital moment. The phonon spectral function consists of two parts, i.e., the sharp peak
at the renormalized frequency $\tilde{\Omega} = \Omega \sqrt{U_{\text{eff}}/U}$ and the broad peak with the width of the order of the band width. These results can reconcile the large isotope effect on $T_c$ and the apparent temperature independent phonon spectrum assuming $U > E_{LR} > \Omega$.

**IV. CONCLUSIONS**

We have studied the vital role of the orbitals in manganese oxides. The most important ingredient is the strong Coulombic interaction, which induces the orbital polarization. This polarization controls the dimensionality of the electronic system when ordered. In the isotropic ferromagnetic state, large orbital fluctuation is expected which gives rise to the quantum liquid state below the orbital Kondo temperature $T_K$. From this viewpoint, the double exchange interaction is switched on below the orbital Kondo temperature $T_K$, and the ferromagnetic transition temperature $T_c$ is roughly identified with $T_K$. This scenario might explain the photoemission experiment which shows that the discontinuity at the Fermi level grows only below $T_c$. However there still remain several puzzles as follows. (i) the small specific heat, (ii) violation of the Kadowaki-Woods relation, (iii) absence of the quasi-particle peak in the angle-resolved photoemission spectra in double layered manganese oxides, (iv) the residual resistivity larger than the Mott limit. One possible explanation for these is the (dynamical) phase separation. The phase separation occurs when the total energy $E(x)$ as a function of the hole concentration $x$ has more than two minima and it is possible to draw a common tangential line. This is found to occur for several models. Here we want to point out that when the bandwidth strongly depends on the orbital configuration, the $x$-dependence of it naturally gives rise to the phase separation. In reality the long range Coulomb interaction will suppress the phase separation, but which still remain as a fluctuation, i.e., dynamical one. Suppose phase separation occurs, and assume that $r$ is the metallic fraction while $1 - r$ is the insulating fraction. Now we relate the observed physical quantities to the metallic ones and the fraction $r$. The $T$-linear specific heat $\gamma_{\text{obs}} T$ is reduced by the factor $r$, and hence $\gamma_{\text{obs}} = r \gamma_{\text{metal}}$. Concerning the resistivity, the percolating path
will lower the capacitance energy when the voltage is applied, and the observed resistivity is enhanced by the factor $1/r$, i.e., $\rho_{\text{obs}}(T) = \rho_{\text{metal}}(T)/r$. Therefore the Kadowaki-Woods ratio is related to

$$\left(\frac{A}{\gamma^2}\right)_{\text{obs}} = r^{-3}\left(\frac{A}{\gamma^2}\right)_{\text{metal}}. \quad (13)$$

The observed ratio is $10^2$ times larger than the universal ratio, and if we attribute this discrepancy to the factor $r$, we obtain $r \approx 0.2$. This also suggests $\gamma_{\text{metal}} \approx 14mJ/mol$, which means that the mass enhancement is $\sim 10$. Furthermore the Drude weight is reduced by $r$ in addition to the mass enhancement, and is expected to be about $1/50$ of the noninteracting value in agreement with experiment. The residual resistivity is enhanced by $1/r$ and can be larger than the Mott limit. Roughly speaking, the Hall constant, on the other hand, is not modified by the phase separation. The extremely large noise might be also related to the dynamical fluctuation of the phase separation. Thus the phase separation seems to explain many puzzles in the manganese oxides. However the detailed studies including the time/length scale of the fluctuation are left for future investigations.

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REFERENCES

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

[2] P. W. Anderson, and H. Hasegawa, Phys. Rev. 100, 675 (1955).

[3] P. G. de Gennes, Phys. Rev. 118, 141 (1960).

[4] S. Ishihara, J. Inoue, and S. Maekawa, Physica C 263, 130 (1996), and Phys. Rev. B 55, 8280 (1997).

[5] S. Ishihara, M. Yamanaka, N. Nagaosa, Phys. Rev. B 56, 686 (1997).

[6] R. Maezono, S. Ishihara and N. Nagaosa, Phys. Rev. B 57, R21822 (1998).

[7] R. Maezono, S. Ishihara and N. Nagaosa, to be published in Phys. Rev. B 58, November (1998).

[8] E. O. Wollan, and W. C. Koehler, Phys. Rev. 100, 545 (1955).

[9] H. Kawano, R. Kajimoto, H. Yoshizawa, Y. Tomioka, H. Kuwahara , and Y. Tokura, Phys. Rev. Lett. 78, 4253 (1997).

[10] H. Kuwahara, T. Okuda, Y. Tomioka, T. Kimura, A. Asamitsu and Y. Tokura, Mat. Res. Soc. Sym. Proc. 494, 83 (1998).

[11] Y. Tomioka (unpublished).

[12] Y. Moritomo, T. Akimoto, A. Nakamura, K. Ohoyama, and M. Ohashi, Phys. Rev. B 58, 5544 (1998).

[13] M.C.Martin, G.Shirane, Y.Endoh, K.Hirota, Y.Moritomo, Y.Tokura, Phys. Rev. 53, 14285 (1996).

[14] K.Yamamoto and Y.Tokura, private communications.

[15] D.D.Sarma et al., Phys. Rev. B53, 6874 (1996).
[16] Y.Okimoto \textit{et al.}, Phys. Rev. Lett. \textbf{57}, 109 (1995).

[17] A.Urushibara \textit{et al.}, Phys. Rev. B\textbf{51}, 11103 (1995).

[18] B.Woodfield, M.L.Wilson, and J.M.Byers, Phys. Rev. Lett. \textbf{78}, 3201 (1997); T.Okuda and Y.Tokura, Private communications.

[19] For a review see A.Georges \textit{et al.}, Rev. Mod. Phys. \textbf{68}, 13 (1996).

[20] N. Nagaosa, S. Murakami, and H.C.Lee, Phys. Rev. B \textbf{57}, R6767 (1998).

[21] J.Kanamori, J. Appl. Phys.\textbf{31}, 14S (1960).

[22] N.Furukawa, J. Phys. Soc. Jpn \textbf{63}, 3214 (1994).

[23] A.J.Millis, R.Mueller, and B.I.Shraimain, Phys. Rev. B\textbf{74}, 5389; 5405 (1996).

[24] D.R.Hamann, Phys. Rev. \textbf{2}, 1373 (1970).
Figure captions

Figure 1. Mean field phase diagram as a function of the carrier concentration \( (x) \) and the antiferromagnetic interaction between \( t_{2g} \) spins \( (J_S) \). The energy parameters are chosen to be \( \tilde{\alpha} = 8.1 \) and \( \tilde{\beta} = 6.67 \). Schematic orbital structure in the each phase is also shown. Dotted line \( (J_S = 0.009) \) well reproduces the change of the spin structure experimentally observed.
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