Anomalous spin susceptibility and magnetic polaron formation in the double exchange systems

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The magnetic susceptibility and spin-spin correlation of the double-exchange model for doped manganites are investigated through the Monte Carlo calculations on the three-dimensional lattice model. Deviations of the susceptibility from the Curie-Weiss behavior above the ferromagnetic ordering temperature \(T_c\) seem to indicate a formation of local ferromagnetic clusters in the vicinity of \(T_c\), which is consistent with recent electron paramagnetic resonance experiments for \(La_{2/3}Ca_{1/3}MnO_3\). A further analysis of the spin-spin correlations show the ferromagnetic cluster size to be three-to-four lattice spacings, suggesting that the charge carriers may form magnetic polarons.

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I. INTRODUCTION

Recent interests in mixed-valence manganites with the chemical compositions of \(R_{1-x}A_xMnO_3\) (where \(R=\) rare earth; \(A=\) Ca, Sr, Ba) are largely ascribed to their potential technological applications. The most notable feature of these materials is an extremely large change of resistivity under the application of a magnetic field near ferromagnetic ordering temperature \(T_c\), which is known as colossal magnetoresistance (CMR). A metal-insulator (MI) transition accompanied by the ferromagnetic-paramagnetic phase transition is occurred near \(T_c\). The strong connection between the MI transition and the ferromagnetic spin alignment has been understood in terms of the double-exchange (DE) mechanism. The conduction electrons in the \(e_g\) orbital of Mn\(^{3+}\) ions are hopping in the background of Mn\(^{4+}\) \((t_{2g})\) ion spins with an experience of a strong on-site Hund’s rule coupling, thereby leading to an effective hopping integral of the form \(t \cos(\theta_{ij}/2)\) where \(\theta_{ij}\) is the relative angle between Mn\(^{4+}\) ions.

Although the electron-lattice interaction arising from the dynamic Jahn-Teller distortion is considered to be important for the understanding of overall trends of CMR phenomena, the lattice polaron formation is incomplete to explain the transport properties in connection with the observed CMR phenomena. Contrary to the above approach, it is suggested that the \(e_g\) carriers can be trapped by spin-disorder scattering due to the local deviations of the ferromagnetic surroundings, resulting in the formation of magnetic polarons in the vicinity of \(T_c\). Indeed, a lot of theoretical works have demonstrated that the magnetic polaron formation plays a crucial role in CMR phenomena in the paramagnetic state.

From the experimental point of view, much efforts have been devoted to understand their unique magnetic features in the paramagnetic state. For instance, the high temperature inverse susceptibility for \(La_{0.7}Ca_{0.3}MnO_3\) is smaller than expected from the Curie-Weiss law at low magnetic field \(H < 0.1\) T. The deviation of susceptibility from Curie-Weiss law is also found in the layered material of \(La_{1.35}Sr_{1.65}Mn_2O_7\), suggesting the formation of ferromagnetic cluster above \(T_c\). Recent electron paramagnetic resonance (EPR) study revealed that EPR signals decrease exponentially at temperatures slightly above \(T_c\), which results in an enormous enhancement of the effective spins of about \(\sim 30\) per formula unit. Moreover, small angle neutron scattering experiments estimated the size of the ferromagnetic cluster in the paramagnetic state to be about 12Å. There has also been an increasing realization which manifest the importance of the magnetic fluctuations that is beyond the mean-field prediction in the paramagnetic state of the doped perovskite manganites.

The main purpose of this paper is to elucidate the characteristic features of the ferromagnetic polaron in the vicinity of \(T_c\). In order to account for the spin fluctuation effects accurately, we adopt a Monte Carlo method for the DE model on the three-dimensional (3D) lattice. We found that the temperature dependence of inverse susceptibility deviates from the expected Curie-Weiss behavior, which is in good agreement with experimental observations. Also, the activation energy estimated from the non-Curie-Weiss part of the susceptibility coincides with that of EPR measurements for \(La_{2/3}Ca_{1/3}MnO_3\). From these results together with the calculated spin-spin correlation, we suggest that charge carriers above \(T_c\) form the ferromagnetic cluster with the size of three-to-four lattice spacings.
II. MODEL AND CALCULATIONS

One of the simplest models for the description of the paramagnetic-ferromagnetic phase transition in doped manganites is a single-orbital DE model Hamiltonian. In the strong Hund’s coupling limit \((J_H \to \infty)\), it can be written as

\[ \mathcal{H} = -\sum_{\langle ij \rangle} \left( t_{ij} c_i^+ c_j + \text{h.c.} \right) - h \sum_i S_i^z, \]

where the operator \( c_i^+ \) creates a spinless conduction electron at site \( \vec{R}_i \), and \( h \) is an external magnetic field. The hopping amplitude in the strong Hund’s coupling limit is characterized by the diagonalization of the \((L^3 \times L^3)\) hermitian matrix for each given spin configuration \( \{ \theta_i, \phi_i \} \), we obtain the \( L^3 \) eigenvalues denoted by \( \epsilon_\alpha(\theta_i, \phi_i) \). Thus the resulting partition function becomes

\[ Z = \prod_i^{L^3} \left( \int_0^\pi d\theta_i \sin \theta_i \int_0^{2\pi} d\phi_i \right) L^3 \prod_{\alpha=1} L^3 (1 + e^{-\beta (\epsilon_\alpha - \mu)}) \]

Now, we can apply a Monte Carlo integration procedure for the summation over the configuration angles \( \{ \theta_i, \phi_i \} \) of localized spins using a standard Metropolis algorithm. The actual calculations are performed for 3D cubic lattices \( L^3 = 6^3 \) with periodic boundary conditions in spatial directions. Typically, we take 5000 Monte Carlo steps per site for statistical average. Thermodynamic quantities of interest are obtained directly from the thermal average of spin configurations and the eigenvalues of Hamiltonian. The carrier density \( \langle n \rangle \approx 0.5 \), i.e., the hole density \( x = 1 - \langle n \rangle \), obtained by fixing \( \mu = 0.0 \).

III. RESULTS

Before studying the magnetic fluctuation effects, we first investigate the nature of the magnetic transition in the ferromagnetic state. Figure 1 shows the temperature \((T)\) dependence of the magnetization, \( M = \langle \sum_i S_i^z \rangle / L^3 \), denoted by solid squares. As clearly shown in Fig. 1, the magnetization drops sharply when the ferromagnetic ordering temperature reaches to \( T_c \approx 0.125t \) and the so-called ferromagnetic-to-paramagnetic transition takes places near \( T_c \). The dashed line represents the mean-field prediction of DE model by Kubo and Ohata, leading to \( M = M_0 \left[ 1 - T/|T_c| \right]^{1/2} \) with \( M_0 = \sqrt{5}/T_c \) for \( S = 2 \) as \( T_c \) is approached. This magnetic transition is closely related to the other transition of apparently different character, i.e., the \( T \)-dependence of resistivity. The obtained Monte Carlo result, however, varies more slowly than that of the mean-field prediction of DE model. Moreover it is noted that the magnetization data can be fitted with a power law of \( M(T) \sim |T_c - T|^\beta \) just below \( T_c \). The solid line in the Fig. 1 is a fitting curve, yielding \( \beta = 0.32 \pm 0.01 \). This value of the exponent \( \beta \) is very close to that of La\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\) single crystal and 3D Heisenberg class which is \( \beta = 0.33 \) in the vicinity of \( T_c \). Above \( T_c \), however, our calculated result of \( M \) is different from zero due to the finite-size effects. The similar results are also obtained by using different Monte Carlo methods for a larger size of unit cells \( 20 \times 20 \times 20 \).
Now we turn to study the magnetic fluctuation effects in the paramagnetic state. The magnetic susceptibility directly measures the magnetic fluctuation as shown in the following equation:

\[
\chi = \frac{\partial M}{\partial h} = \frac{\partial}{\partial \mu N h} \text{Tr} e^{-\beta(\mu N h - \sum_i S_i^z)} = \frac{\langle M^2 \rangle - \langle M \rangle^2}{T}. \tag{5}
\]

Figure 2 provides \(\chi\) as a function of \(T/T_c\) denoted by open squares. With increasing temperature, \(\chi\) increases to a maximum near \(T_c\) and then quickly decreases above \(T_c\). It should be noted that the susceptibility is well described by a power law of \(\chi \sim |T - T_c|^{-\gamma}\) as \(T\) approaches close to the critical temperature \(T_c\), in the paramagnetic state, where the critical fluctuations are dominant. The inset of Fig. 2 shows \(\ln(\chi)\) vs. \(\ln(|T - T_c|)\) curve, yielding the exponent \(\gamma = 0.92 \pm 0.01\) and the dashed line in the Fig. 2 is a fitting curve. This value of the critical exponent \(\gamma\) is smaller than those of the experimental suggestion of 1.22 for \(\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3\) and the mean-field theory of Curie-Weiss law which is \(\gamma = 1\). However, it is not unreasonable if we take account of the fact that the present value is determined only from the finite size cluster calculation with no scaling analysis.

\[d(\chi^{-1})dT\text{ in the high temperature regime of a typical itinerant ferromagnetic such as nickel (}\ T_c = 623 \text{ K}\) is known to be temperature-dependent. In order to understand the spin entities in the paramagnetic state, we plot \(1/\chi\) vs. \(T/T_c\) in Fig. 3. In the high-temperature region of \(T > 2.5T_c\), the corresponding \(1/\chi\) follows a linear Curie-Weiss behavior where each spin has a non-interacting magnetic moment. The solid line is the fitting curve of the Curie-Weiss law, \(\chi \approx C/(T - \Theta)\), yielding the mean-field Curie temperature \(\Theta = 0.5T_c\) and \(C = 0.0008\). However, starting from and below \(2T_c\), \(1/\chi\) shows a distinct deviation from the expected Curie-Weiss law, suggesting a possible presence of short-range ferromagnetic clusters due to the spin fluctuations above \(T_c\). This feature are consistent with observations in the recent experimental measurements on the single crystal of \(\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3\) and the thin film of \(\text{La}_{0.6}\text{Y}_{0.07}\text{Ca}_{0.33}\text{MnO}_3\) and the layered material of \(\text{La}_{1.35}\text{Sr}_{1.65}\text{MnO}_3\) in low magnetic field \(h < 0.1\ T\). For the high magnetic field, however, \(1/\chi\) becomes larger than the one expected from the Curie-Weiss law, indicating a suppression of ferromagnetic fluctuation due to the carrier delocalization and magnetic ordering by the applied magnetic field.

Assuming that ferromagnetic clusters exist, one should see an effective moment which is larger than that of the appropriate average of Mn\(^{3+}\) and Mn\(^{4+}\) moments. From the consideration that \(P\) neighboring sites with ferromagnetically aligned spins form a spin polaron of the spin \((S_1 + P S_2)\) due to the double exchange mechanism, the effective spin for the fluctuation effects becomes:

\[S_{\text{eff}}^2 = x(S_1 + P S_2)(S_1 + P S_2 + 1) + (1 - x - P x)S_2(S_2 + 1),\]

where \(S_1\) and \(S_2\) identify the spin of Mn\(^{4+}\) and Mn\(^{3+}\) species, respectively. This estimation of the square of total spin will become larger than the one without spin polaron formation, i.e., \(P = 0\) case, and consequently the inverse susceptibility will be smaller compared to the Curie-Weiss law. These features are consistent with our current Monte Carlo results as well as other results of the exact diagonalization study in which the effective spins of \(e_g\) carriers gate from 1/2 to 7 and the EPR experiments above \(T_c\). Thus, it is reasonable to interpret that the spin polarized carriers form ferromagnetic polarons with each individual cluster retaining a large magnetic moment.
find that \( \Delta \chi \) the Curie-Weiss law as \( \Delta \chi \equiv \chi - C/(T - \Theta) \). In the intermediate temperature region of \( T_c < T \lesssim 2.5T_c \), we find that \( \Delta \chi \) can be fit by the following form

\[
\Delta \chi = \chi_0 \exp(E_a/T)
\]  

(6)

where \( E_a \) is an activation energy which scales to the \( T_c \).

It is interesting to compare our Monte Carlo results with the outcomes from the EPR measurements. For this purpose we define the deviation of susceptibility from the Curie-Weiss law as

\[
\Delta \chi = \chi - C/(T - \Theta).
\]

For a comparison with our result of \( \Delta \chi \), we obtain from EPR measurement is approximately \( 7T_c \) which is slightly smaller than that obtained from the \( \Delta \chi \) for fixing \( T > 2T_c \) and, in particular, almost 15% of the maximum at \( T_c \). Furthermore, the short-range ferromagnetic correlation is clearly seen in the intermediated regime of \( T_c < T \lesssim 2T_c \). The size of the ferromagnetic surroundings is of the order of \( 3 \sim 4 \) lattice spacing distances, i.e., 12Å~16Å if we consider a size of lattice as 4Å, which is in good agreement with recent neutron scattering. Moreover, a simple estimation of the ferromagnetic correlation length, \( \sigma \approx (at/T)^{3/2} \), in terms of a ferromagnetic spin-polaron picture has been introduced by Varma. At the temperature range of paramagnetic state, in particular at room temperature \( \sim 300 \) K, the size of the spin polaron is estimated to be a few lattice size for \( t \approx 0.2 \) eV, which agrees with the current results. It implies that the spin-polarized carriers can be trapped into a local ferromagnetic surroundings due to the spatially fluctuating spin correlations, resulting in the formation of the magnetic polaron in the paramagnetic phase.

Finally, we estimate the effective sizes of the ferromagnetic clusters in the paramagnetic state. Figure 5 shows the log of intensity as a function of \( I \equiv \chi - C/(T - \Theta) \), yielding \( E_a = 10T_c \) which corresponds to 0.22 eV for \( t = 0.17 \) eV, when \( \chi_0 = 9 \times 10^{-6} \) is used.

It is interesting to note that the EPR intensity decreases exponentially above \( T_c \) and has a strong correlation with the deviation of the magnetic susceptibility. For a comparison with our result of \( \Delta \chi \), the log of intensity as a function of \( 1000/T \) for \( La_{1-x}Ca_{x/3}MnO_3 \) (\( T_c \approx 270 \) K) from Ref. [18] is shown in the inset of the Fig. 4. The shape of the \( T \)-dependence of EPR intensity is quite similar to the Monte Carlo result of \( \Delta \chi \) for \( La_{2/3}Ca_{1/3}MnO_3 \) (\( T_c \approx 270 \) K) from Ref. [18].
Using Monte Carlo methods, we have studied the magnetic fluctuation effects near and above $T_c$ within the framework of DE model. We found that the temperature dependence of the susceptibility shows a sharp peak near $T_c$, and the inverse susceptibility displays non-Curie-Weiss behavior above $T_c$. The activation energy obtained from the deviation of susceptibility from the Curie-Weiss behavior is consistent with the EPR measurements. These results clearly demonstrate the formation of the magnetic polaron with short-range ferromagnetic ordering in the paramagnetic state. Moreover, the ferromagnetic correlation length is estimated to be $3 \sim 4$ lattice spacings which is in good agreement with recent neutron scattering experiments. From the results, it is suggested that the magnetic polaron formation is responsible for the magnetic transition and the magneto-transport properties in doped CMR manganites.

IV. CONCLUSIONS

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