Spin Excitation Spectrum of La$_{1-x}$A$_x$MnO$_3$

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(Received

As an effective model to describe perovskite-type manganates (La,A)MnO$_3$, the double-exchange model on a cubic lattice is investigated. Spin excitation spectrum of the model in the ground state is studied using the spin wave approximation. Spin wave dispersion relation observed in the inelastic neutron scattering experiment of La$_{0.7}$Pb$_{0.3}$MnO$_3$ is reproduced. Effective values for the electron bandwidth as well as Hund’s coupling is estimated from the data.

KEYWORDS: perovskite-type manganate, LaMnO$_3$, double-exchange model, metallic ferromagnetism, spin wave
Due to the colossal magnetoresistance (CMR) \[1, 2, 3\] and other related phenomena, perovskite-type manganates \((R,A)\text{MnO}_3\) have recently been investigated intensively. Here, A-site ions \(R\) and \(A\) are trivalent rare-earth and divalent alkaline-earth ions, respectively. There exist renewed interests in these materials not only due to their potential ability for application but also from the viewpoint of strong correlation effects in 3d transition-metal oxides which is one of the most challenging problem in the field of the condensed matter physics.

Under appropriate hole doping, the system becomes a metallic ferromagnet, \[4, 5, 6\] which is explained by the double-exchange mechanism. \[7, 8\] As an effective model to describe these materials, the double-exchange model

\[
\mathcal{H} = -t \sum_{\langle ij \rangle, \sigma} \left( c_i^{\dagger} \sigma c_j \sigma + h.c. \right) - \frac{J_H}{S} \sum_i S_i \cdot \sigma_i
\]  

(1)

has been proposed. Here \(t\) and \(J_H\) are the electron transfer energy and Hund’s coupling between electrons and localized spins, respectively. The electron spin is represented by the Pauli matrices, while \(S_i\) describe the localized spins. The localized spins are considered to represent Mn \(t_{2g}\) electrons with \(S = 3/2\) while itinerant electrons mainly occupy the Mn \(e_g\) orbitals.

The double-exchange model correctly describes several properties of \(\text{La}_{1-x}\text{Sr}_x\text{MnO}_3\) \[9,10\] such as the doping dependence of the Curie temperature \(T_c\) \[11\] and the universal curve of CMR near \(T_c\). \[12, 13\] However, the double-exchange model does not explain anomalous temperature dependence in the Drude weight observed in the optical measurement of \(\text{La}_{1-x}\text{Sr}_x\text{MnO}_3\) at \(T \ll T_c\). \[14\] Effects of other interactions and degrees of freedom which are present in 3d electron systems such as Coulomb repulsions, lattice distortions, orbital degeneracies and anisotropies of orbitals are not treated in this model. Millis et al. \[15\] have argued that if a polaron effect due to strong Jahn-Teller type electron-lattice coupling is included in the double-exchange model, it leads to better agreements with transport properties around \(T_c\) in doped manganates. It is important to study whether these effects not treated in the model essentially changes the properties of the model or are able to be taken into account by the renormalization of parameters \(t\) and \(J_H\). In order to gain insights of the behaviors of these materials, it seems to be necessary to clarify to what extent the double-exchange model correctly describes the thermodynamical properties of perovskite manganates.

Recently, spin wave dispersion relation of doped manganates has been measured by the neutron inelastic scattering experiments. For \(\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3\), \[16\] the spin wave dispersion relation at \(T = 27\text{K}\) is given by \(\omega_q = \Delta + D_s(q/a)^2\), where \(D_s \simeq 12.5\text{meV}\) is the spin stiffness obtained from the least-squares fitting. The spin gap probably due to anisotropies is \(\Delta \simeq 0.7\text{meV}\), while the lattice constant is observed as \(a \simeq 3.9\text{Å}\). For \(\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3\), \[17\]
the observed dispersion relation fits well in the form
\[ \omega_q = \Delta + E_{sw} \frac{3 - \cos q_x - \cos q_y - \cos q_z}{6}, \tag{2} \]
which has been pointed out to be reproduced by a ferromagnetic Heisenberg model with nearest-neighbor spin exchange couplings. Here, the least-squares fit gives the spin wave bandwidth \( E_{sw} \approx 106 \text{meV} \) and the gap \( \Delta \approx 2.5 \text{meV} \).

In this paper, we calculate the spin excitation spectrum of the double-exchange model, and compare the results with recent data of the neutron inelastic scattering experiments. We use the spin wave approximation in the ground state, which has been introduced in the limiting case of \( J_H = \infty \) by Kubo and Ohata. We make estimates of the effective electron bandwidth and the Hund’s coupling in these materials. The spin wave dispersion is an important measure to study the coherence of the electrons in the double-exchange systems. We may obtain informations about the electronic states of doped manganates at low temperatures as well as their changes when temperature is raised, by comparing the results of the calculation with experiments.

Using the spin wave operators in the ferromagnetic state,
\[ S_i^+ \approx \sqrt{2} S a_i, \quad S_i^- \approx \sqrt{2} S a_i^\dagger, \quad S_i^z = S - a_i^\dagger a_i, \tag{3} \]
the Hamiltonian of the double-exchange model is described by fermion and spin wave operators in the form
\[
\mathcal{H}_{sw} = \sum_k \left( (\varepsilon_k - J_H) c_{k\uparrow}^\dagger c_{k\uparrow} + (\varepsilon_k + J_H) c_{k\downarrow}^\dagger c_{k\downarrow} \right) \\
+ J_H \sqrt{\frac{2}{SN}} \sum_{q_k} \left( a_{q\downarrow}^\dagger a_{q\downarrow} c_{k+q\uparrow} c_{k\downarrow} + a_{q\uparrow} c_{k+q\uparrow}^\dagger c_{k\downarrow} \right) \\
+ J_H \frac{1}{SN} \sum_{q_{k1}q_{k2}\sigma} \sigma a_{q1\downarrow}^\dagger a_{q2\uparrow} c_{k-\sigma q1\sigma} c_{k-\sigma q2\sigma}. \tag{4} \]
We restrict ourselves to the lowest order terms of the \( 1/S \) expansion at \( T = 0 \). We consider the case of \( J_H \) being finite but sufficiently large so that electrons are also completely polarized, i.e. \( n_\uparrow = n \) and \( n_\downarrow = 0 \), at \( T = 0 \). The electron concentration is described as \( n = 1 - x \). We assume a simple cubic lattice with nearest-neighbor electron hoppings so that we have
\[ \varepsilon_k = -2t (\cos k_x + \cos k_y + \cos k_z). \tag{5} \]
For perovskite manganates, estimates of the electron bandwidth and the on-site Hund’s coupling being a few eV has been made by the first-principle calculations. However, we consider that \( t \) and \( J_H \) in this model are the effective parameters which could be strongly renormalized from the bare value due to other interactions present in the real systems. These parameters should be determined from comparisons with experiments.
The spin wave self-energy in the lowest order of $1/S$ expansion, which is schematically illustrated in Fig. 1, is given by

$$\Pi(q, \omega) = \frac{1}{SN} \sum_k (f_{k\uparrow} - f_{k+q\downarrow}) \times \left( J_H + \frac{2J_H^2}{\omega + \varepsilon_k - \varepsilon_{k+q} - 2J_H} \right),$$

where $f_{k\sigma}$ is the Fermi distribution function. We have $f_{k\downarrow} = 0$ from the assumption. The spin wave dispersion relation $\omega_q$ is obtained self-consistently as a solution of the equation $\omega_q = \Pi(q, \omega_q)$. Since $\Pi \propto 1/S$, the lowest order $1/S$ expansion gives $\omega_q = \Pi(q, 0)$. Therefore, the spin wave dispersion is described as

$$\omega_q = \frac{1}{2SN} \sum_k f_{k\uparrow} \frac{J_H(\varepsilon_{k+q} - \varepsilon_k)}{J_H + (\varepsilon_{k+q} - \varepsilon_k)/2}.$$

In Fig. 2, we show the spin wave dispersion relation at $x = 0.3$ for various values of $J_H/t$. As the value of $J_H$ becomes comparable with the electron bandwidth, we see the softening of the spin wave dispersion since the effective coupling between spins become weak.

At $J_H \to \infty$, we have

$$\omega_q \approx \frac{1}{2SN} \sum_k (\varepsilon_{k+q} - \varepsilon_k)f_{k\uparrow}$$
Fig. 2. Spin wave dispersion relation at $x = 0.3$. Curves are for $J_H/t = \infty, 24, 12$ and $6$ from top to bottom.

\[
E_{sw} = \frac{3 - \cos q_x - \cos q_y - \cos q_z}{6}.
\]

where $E_{sw}$ is the spin wave bandwidth given by

\[
E_{sw} = \frac{6t}{SN} \sum_k f_{k\uparrow} \cos k_x.
\]

The dispersion relation (9) is the same as those in a ferromagnetic Heisenberg model with nearest-neighbor spin exchanges.

The above correspondence can be understood as follows. We consider a perfectly spin polarized state at $T = 0$ and then twist a spin at site $i_0$. In the case of the strong coupling limit $J_H \gg t$ where electrons with spins anti-parallel to the localized spins of the same site are disfavored, the electron at site $i_0$ is localized because it has different spin orientation to the localized spins in neighboring sites. Therefore, in this limit the effective spin-spin interaction is short ranged. As $J_H/t$ increases, electrons become more localized so the range of effective interaction becomes shorter. It is in a sharp contrast to the weak coupling limit where the RKKY long range interaction with power law decay is mediated by the coherent
motion of electrons. As long as we restrict ourselves to the single magnon excited states at $T = 0$, the double-exchange model in the strong coupling limit is mapped to the Heisenberg model with short-range interactions.

![Spin wave dispersion relation of La$_{0.7}$Pb$_{0.3}$MnO$_3$(squares). Curves are calculated by fitting data at $J_H/t = 12$ (dotted curve) and $J_H/t = \infty$ (solid curve).](image)

Now we compare the results with experiments. In Fig. 3, we plot the data of the neutron inelastic scattering experiment [17] together with the fitting curves in the form

$$\omega_{\text{fit}}(q) = \Delta + \omega_q,$$

where $\omega_q$ is obtained at $x = 0.3$ as a function of $J_H$ and $t$ from eq. (7). It has been pointed out that the dispersion relation in La$_{0.7}$Pb$_{0.3}$MnO$_3$ fits well in the cosine-band form with $E_{sw} = 0.1055\text{eV}$ and $\Delta = 0.0025\text{eV}$. [17] As shown previously, the double-exchange model at $J_H/t \to \infty$ gives the same dispersion relation, with the electron hopping energy $t = 0.18\text{eV}$. At $J_H/t = 12$, which is in the intermediate coupling region, we have a better fit to the data at $t = 0.26\text{eV}$ and $\Delta = 0.004\text{eV}$. Thus we see that the dispersion relation
of the spin wave obtained experimentally is reproduced by the double-exchange model in a realistic parameter region $J_H/t \gtrsim 12$ and $t \sim 0.2\text{eV}$.

![Fig. 4. Magnon bandwidth $E_{sw}$ (solid curve) and the spin stiffness $D_s$ (dashed line) at $x = 0.3$.](image)

For La$_{0.7}$Sr$_{0.3}$MnO$_3$, the hopping energy $t$ is estimated as follows. The spin stiffness of La$_{0.7}$Sr$_{0.3}$MnO$_3$ is obtained experimentally as $D_s \simeq 12.5\text{meV}$. From the model calculation, we expand eq. (7) at $q \to 0$ and obtain the spin stiffness. On a cubic lattice with the electron dispersion relation (5), we have $\omega_q = D_s q^2$ where the spin stiffness constant $D_s$ is given by

$$D_s = \frac{t}{2S N} \sum_k f_{k\uparrow} \left( \cos k_x - \frac{2t}{J_H} \sin^2 k_x \right).$$

(12)

In Fig. 4, we show the spin stiffness $D_s$ at $x = 0.3$ as a function of $J_H/t$, together with the spin wave bandwidth $E_{sw} \equiv \omega_{q=Q} - \omega_{q=0}$. At $S = 3/2$, we have $D_s < 0.04t$ for finite $J_H/t$. Then we have the estimated value as $t \gtrsim 0.3\text{eV}$.

Let us now investigate the effective electron hopping energy at $T \sim T_c$. From the above effective parameters for La$_{0.7}$Pb$_{0.3}$MnO$_3$, we calculate the Curie temperature and make a
comparison with experiments. In order to obtain $T_c$ in the double-exchange model, we apply the infinite-dimensional approach. For details of the calculation, readers are referred to ref. [11]. Here we simply use the result for the semicircular density of states where the bandwidth is taken to be equal to the value on the cubic lattice, $W \equiv 6t$. In the case $J_H/t = 12$ or $J_H/W = 2$, we obtain $T_c^\infty = 0.146t$ at $x = 0.3$. Then, the previous value $t \sim 0.26eV$ obtained from the fitting gives $T_c^\infty \sim 440K$. Experimentally, we observe $T_c^{\text{exp}} = 355K$ in La$_{0.7}$Pb$_{0.3}$MnO$_3$. Since spatial fluctuations which are absent in infinite-dimensional approaches reduce $T_c$, we consider that the parameters determined at $T = 0$ may also describes $T_c$ for La$_{0.7}$Pb$_{0.3}$MnO$_3$ in a consistent way. Thus, the double-exchange model with a fixed parameters $t$ and $J_H$ simultaneously accounts for the spin wave dispersion relation at the low temperature region and the Curie temperature $T_c$.

There exists no substantial change in the electronic hopping energy at $T \sim T_c$ and $T \sim 0$ in these perovskite manganates. The value of $t$ estimated above is comparable with those obtained from the first-principle calculation. Therefore, in these compounds, we consider that the renormalizations of electron coherence due to dynamical lattice distortions and other elementary excitations are not so large and do not have substantial temperature dependences. As long as La$_{0.7}$Pb$_{0.3}$MnO$_3$ is concerned, the double-exchange model alone seems to describe the spin excitation properties adequately.

It has been known that Sr- and Pb-doped lanthanum manganates have wider bandwidth compared to other compounds in this family of materials. [4] At $x = 0.3$, the above manganates are far from the phase boundaries of insulator-metal transition or structural transition and are metallic even in the paramagnetic phase. Since the double-exchange model reproduces the thermodynamical properties of these compounds, we consider that the effect of coherent motions of electrons dominantly determine the thermodynamical properties of these relatively wide-banded compounds in the metallic region, indeed. Effects of Coulomb interactions and Jahn-Teller type distortions may cause renormalization of electron hopping energy and Hund’s coupling, but they seem to be irrelevant to the low energy properties. Further systematic studies of the other bandwidth-controlled manganates will show us how and in what condition these residual interactions become relevant.

We note here the relation between the present calculation and the approach by Kubo and Ohata. [18] They have considered the double-exchange model in the strong Hund’s coupling limit $J_H/t = \infty$. The Hamiltonian is given by

$$\mathcal{H'} = -t \sum_{\langle i,j \rangle, \sigma, \sigma'} \langle \hat{c}^\dagger_{i\sigma} (\hat{P}_i \hat{P}_j)_{\sigma\sigma'} c_{j\sigma'} + h.c. \rangle,$$

where $\hat{P}_i = \hat{P}(S_i)$ is the projection operator to the electronic state with a spin parallel to the localized spin at $i$-th site $S_i$. At the first and the second order expansion of $1/S$, the
present approach in the limit $J_H/t \to \infty$ and the spin wave approximation for the projected Hamiltonian \(^{[13]}\) give equal results for the spin wave dispersion in the single magnon excited state at $T = 0$. Although the interaction vertices are proportional to $J_H$, the spin wave self energy at $J_H/t \to \infty$ does not show singularities but converges to those obtained at $J_H/t = \infty$, at least up to the second order of $1/S$ expansions. Therefore, in the low order $1/S$ expansions, the present approach for finite $J_H/t$ seems to be valid even in the large Hund’s coupling region. Details on higher order expansions with respect to $1/S$ will be reported elsewhere.

To summarize, we have calculated the spin wave dispersion relation of the double-exchange model using the spin wave approximation. Comparison with the neutron scattering experiment data in La$_{0.7}$Sr$_{0.3}$MnO$_3$ and La$_{0.7}$Pb$_{0.3}$MnO$_3$ has been performed. Spin wave dispersion relation throughout the Brillouin zone in La$_{0.7}$Pb$_{0.3}$MnO$_3$ is reproduced qualitatively. Values of the electron bandwidth as well as Hund’s coupling is estimated from the spin wave bandwidth and the spin stiffness. The double-exchange model consistently describes the spin wave dispersion relation and the Curie temperature of La$_{0.7}$Pb$_{0.3}$MnO$_3$.

Acknowledgments

The author would like to thank Y. Endoh and Y. Tokura for fruitful suggestions. This work was supported by a Grant-in-Aid for Encouragement of Young Scientists from the Ministry of Education, Science and Culture.

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