Spin and orbital ordering in double-layered manganites

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We study theoretically the phase diagram of the double-layered perovskite manganites taking into account the orbital degeneracy, the strong Coulombic repulsion, and the coupling with the lattice deformation. Observed spin structural changes as the increased doping are explained in terms of the orbital ordering and the bond-length dependence of the hopping integral along c-axis. Temperature dependence of the neutron diffraction peak corresponding to the canting structure is also explained. Comparison with the 3D cubic system is made.

I. INTRODUCTION

Perovskite manganites \((R_{1-x}A_x)_{n+1}Mn_nO_{3n+1}\) (\(R=\)La, Pr, Nd, Sm; \(A=\)Ca, Sr, Ba; \(n=1,2,\infty\)) have recently attracted renewed interests from the viewpoint of the close connection between magnetism and transport. The stability of the perovskite structure enables the preparation of high quality single crystals with systematically changing the carrier density and the bandwidth by controlling \(R\) and \(A\) atoms. In addition, the crystal structure changes from two-dimensional \((n=1,\) single layer) to three-dimensional \((n=\infty,\) cubic) as \(n\) increases. The dimensionality of the electronic structure is controlled also by the spin and the orbital orderings, for example, the transfer along c-axis is forbidden by the anti-parallel spin configuration and/or the \(d_{x^2-y^2}\) orbital ordering. Therefore even in the isotropic \((n=\infty,\) cubic, 113-system) crystal structure, the electronic dispersion can be quasi-two-dimensional (layered antiferromagnetic (spin \(A\)) in \(Pr_{1-x}Sr_x\) MnO3, Nd1−xSr2MnO4, La1−xSr2MnO4) or quasi-one-dimensional (rod type \(AF\) (spin \(C\)) in Nd1−xSr2MnO4). Another important related issue is the spin canting. As discussed by de Gennes, \(A\)-type antiferromagnet near the parent insulator is unstable toward the spin canting when holes are doped. This is because the kinetic energy gain along c-axis wins the energy cost of the \(AF\) exchange interaction for small canting angle. In the metallic \(A\)-type \(AF\) phase mentioned above, however, no spin canting has been observed.

Double-layered manganites with \(n=2\) (327-system) offer an interesting opportunity to study the interplay of the spin, the orbital and the crystal structure in the above-mentioned issues of dimensionality and spin canting. With increasing \(x\), the spin ordering within one double-layer changes from the ferromagnetic one (spin \(F\), \(x=0.3\)) to the spin \(A\) \((x=0.5)\). For \(0.4<x<0.48\) the diffraction peak observed in the neutron-scattering experiments indicates the coexistence of the spin \(F\)- and \(A\)-components at low temperatures, which has been interpreted as the spin canting. However it could be interpreted also in terms of the phase separation, and further theoretical studies are needed. Lattice deformation depending upon \(x\) is also observed, implying active contribution to the spin transition, in comparison with 113-system. In 113-system, there is the one to one correspondence between the crystal deformation and the orbital ordering, e.g., the c-axis contracts in the metallic spin \(A\) state where the \(d_{x^2-y^2}\) ordering occurs. In 327-system, on the other hand, MnO6 octahedra elongates along c-axis during the spin structural change from spin \(F\) to cant, and to spin \(A\). This elongation decreases with increasing \(x\) up to \(x=0.5\) continuously, but even in the spin \(A\) phase a little elongation remains, though this deformation prefers the \(d_{3z^2-r^2}\).

In this paper, we study the spin and the orbital ordering in the double-layered compounds. Possibility of the spin canting is studied for general \(x\), which includes the de Gennes’s canting mechanism as a special case. In the metallic region, the spin \(A\) is locally stable against the spin canting. Spin transition from the spin \(A\) is therefore discontinuous one to the spin canting or to the spin \(F\), depending on the ratio of the transfer integral and the superexchange interaction between \(t_{2g}\) spins. For the spin canting to occur in the metallic region, the small transfer integral along c-axis, i.e., the planer orbital ordering, turned out to be indispensable. The canting angle is sensitive to the bond-length along c-axis. With this mechanism, calculated mean-field phase diagram together with the observed lattice distortions can qualitatively explain the observed \(x\)-dependence and \(T\)-dependence of the spin ordering and also the spin-anisotropy in 327-system.

The plan of this paper follows. In Sec. II, the model and the formulation are given. Results and discussion are presented in Sec. III. Notations used here are standard as in ref. 8.

II. MODEL AND FORMULATION

We start with the Hamiltonian
\[ H = \sum_{\gamma \gamma'} d_{i \gamma}^{\dagger} d_{j \gamma'} + J_H \sum_i \vec{S}_{i \gamma} \cdot \vec{S}_{i \gamma'} - J_S \sum_{\langle ij \rangle} \vec{S}_{i \gamma} \cdot \vec{S}_{j \gamma'} + H_{\text{on site}} + H_{\text{el-ph}}, \]

where \( \gamma = a(d_{z^2-r^2}), b(d_{3z^2-r^2}) \) specifies the orbital and the other notations are standard. The transfer integral \( t_{ij}^{\gamma \gamma'} \) depends on the pair of orbitals (\( \gamma, \gamma' \)) and the direction of the bond \((i, j)\). \( J_H \) is the Hund coupling between \( e_g \) and \( t_{2g} \) spins, and \( J_S \) is the AF coupling between nearest-neighbor \( t_{2g} \) spins. \( H_{\text{on site}} \) represents the on-site Coulomb interactions between \( e_g \) electrons, and is given by:

\[ H_{\text{on site}} = -\sum_i \left( \vec{\beta} T_i^2 \bar{\sigma} + \bar{\alpha} \vec{S}_{e_g i}^{\dagger} \right), \]

where the spin operator for the \( e_g \) electron is defined as \( \vec{S}_{e_g i} = \frac{1}{2} \sum_{\gamma \gamma'} d_{i \gamma}^{\dagger} \bar{\sigma}_{\gamma \gamma'} d_{i \gamma'} \) with the Pauli matrices \( \bar{\sigma} \), while the orbital isospin operator is defined as \( \vec{T}_i = \frac{1}{2} \sum_{\gamma \gamma'} d_{i \gamma}^{\dagger} \sigma_{\gamma \gamma'} d_{i \gamma'} \). Coefficients of the spin and isospin operators, i.e., \( \bar{\alpha} \) and \( \vec{\beta} \), are given by:

\[ \bar{\alpha} = U - \frac{J}{2} > 0, \quad \vec{\beta} = U - \frac{3J}{2} > 0. \]

The minus sign in Eq. (2) means that the Coulomb interactions induce both spin and orbital (isospin) moments. The parameters \( \bar{\alpha}, \vec{\beta}, t_0 \), used in the numerical calculation are chosen as \( t_0 = 0.72 \text{ eV} \), \( U = 6.3 \text{ eV} \), and \( J = 1.0 \text{ eV} \), being relevant to the actual manganese oxides. The electron-lattice interaction is:

\[ H_{\text{el-ph}} = +|g|/r \sum_i \vec{v}_i \cdot \vec{T}_i, \]

where \( g \) is the coupling constant and \( r (\vec{v}_i) \) is the magnitude (direction) of the lattice distortion of the MnO₆-octahedra. Values of \( r \) and \( v \) are taken from the observed elongation along \( c \)-axis in (La₃₋ₓSrₓ)₃Mn₂O₇ \((0.3 < x < 0.4)\), leading to \( r \approx 0.01, \vec{v} // \hat{z} \). We calculate the ground state energy by the meanfield approximation with the two order parameters:

\[ \varphi_S = \langle \vec{S}_{e_g} \rangle + \frac{J_H}{2\bar{\alpha}} \langle \vec{S}_{t_{2g}} \rangle, \]

\[ \varphi_T = \langle \vec{T} \rangle. \]

As the exchange interaction between two double-layers is reported to be less than \( 1/100 \) compared with the intra-double-layer one, we consider an isolated double-layer for which the Brillouin zone contains only two \( k \)-points along \( c \)-axis. We consider four kinds of the spin alignment in the cubic cell: spin \( F \), \( A \), \( C \) and \( G \) (NaCl-type). For spin \( A \), we also consider the possibility of the canting characterized by an angle \( \eta \) which is 0 (\( \pi \)) for spin \( F \) (\( A \)). As for the orbital degrees of freedom, we consider two sublattices \( I \), and \( II \), on each of which the orbital is specified by the angle \( \theta_{I, II} \) specifies:

\[ |\theta_{I, II}\rangle = \cos \frac{\theta_{I, II}}{2} |d_{x^2-y^2}\rangle + \sin \frac{\theta_{I, II}}{2} |d_{3z^2-r^2}\rangle. \]

We also consider four types of orbital-sublattice ordering, i.e., \( F, -A, C, G \)-type in the cubic cell. Henceforth, we often use a notation such as spin \( A \), orbital \( G \) \((\theta_I, \theta_{II})\) etc. Denoting the wave vector of the spin (orbital) ordering as \( \vec{q}_S \) \((\vec{q}_T) \), the ground state energy is given as a function of the spin ordering (\( \eta \), \( \vec{q}_S \)), the orbital ordering \((\theta_I, \theta_{II}, \vec{q}_T)\), and the lattice distortion (\( g, r, \vec{v} \)).

**III. RESULTS AND DISCUSSIONS**

**A. Phase diagram without canting and lattice distortion**

Figure 1. shows the phase diagram at zero temperature in the plane of the doping concentration \( x \) and the AF interaction between \( t_{2g} \) spins \((J_S)\), without the electron-lattice coupling \((g = 0)\). Orbital shape is represented by \( p \)- (planar, orbital \( F \) \((0,0)\), i.e., \( d_{z^2-r^2} \)) and \( n \)- (non-planar, orbital \( G \) \((100,100)\) around \( x = 0.1 \) and orbital \( A \) \((-40,40)\) around \( x = 0.7 \)) hereafter. The possibility of the spin canting is not taken into account, i.e., \( \eta = 0 \) or \( \pi \). For \( J_S = 0 \), spin \( F \) is the most stable for almost the whole region of \( x \), except around \( x = 0 \). This ferromagnetism comes from the superexchange interaction between \( e_g \) spins for small \( x \) \((x \sim 0.1)\), and from the double-exchange interaction for larger \( x \) \((x \sim 0.7)\). Nonmonotonic behavior with double peaks \((x = 0.1, 0.7) \) of the phase boundary between spin \( F \) and \( A \) \((J_S(FA))\) is then attributed to the cross-over from the super- to the double-exchange interaction, similarly to the case of the 113-system. We identify the spin transition from spin \( F \) to spin \( A \) with increasing \( x \) observed experimentally for \( 0.3 < x_{\exp} < 0.3 \) with that around \( x \approx 0.15 \) when \( J_S \approx 0.006 \text{ eV} \) (for example, arrow (a) or (b) in Fig. 1). This value of \( J_S \) is roughly of the same order in magnitude as the 113-case. Depicted orbital alignment is the one optimized at each point of the phase diagram. For most of the phase diagram, \( d_{x^2-y^2} \) is the most stable one reflecting the two-dimensional nature of the double-layered structure. The spin \( C \) phase completely disappears. One might regard this self-evident because of the two-dimensionality. This, however, is not so trivial because the valency along \( c \)-axis can still lower the energy by the bonding/anti-bonding splitting for the double-layered structure.
B. Spin canting

We now study the spin canting between spin \( F \) and \( A \). First we consider the possibility of the spin canting with fixed \( J_S = 0.004 \text{ eV} \), shown as the arrow (a) in Fig. 1.

\[
\text{FIG. 2.}
\]

The \( x \)-dependence of the optimized canting angle \( \eta \) is shown in Fig. 3. The electron-lattice coupling is not considered (\( g = 0 \)). The canting angle changes continuously from \( \pi \) (spin \( A \), \( x = 0 \)) to zero (spin \( F \), \( x \sim 0.1 \)), corresponding to the spin canting around the parent insulator. In this region, the orbital alignment almost remains that for \( x = 0 \) (orbital \( G (100,-100) \)), implying that the ordering is still dominated by the superexchange interaction in this region. This is consistent with the interpretation that the peak of the phase boundary \( J_S(FA) \) around \( x = 0.1 \) is attributed to the superexchange interaction. Coexisting double-exchange interaction due to the introduced carriers competes with \( J_S \), leading to the spin canting seen for \( 0 < x < 0.1 \) in Fig. 2 through the conventional mechanism a la de Gennes for 113-system. Battle et al. observed the coexistence of the spin \( F \) and \( A \) by the powder diffraction of the poly-crystal sample \( \text{La_2SrMn_2O_6} \) \( x = 0 \). This can be explained by small amount of carriers introduced by the oxygen deficiencies which brings about the spin canting by this mechanism for small \( x \) region, as reproduced in Fig. 2. When \( x \) goes beyond \( x \sim 0.125 \), \( \eta \) discontinuously changes from zero to \( \pi \), corresponding to the first-order transition from spin \( F \) to spin \( A \). This behavior without canting is due to the discontinuous orbital transition. With increasing the double-exchange interaction for \( x > 0.1 \), the orbital discontinuously changes from orbital \( G (100,-100) \) to orbital \( F (0,0) \), i.e., \( d_{xz-\gamma^2} \), in order to maximize the kinetic energy gain. With fixed \( J_S \) as in Fig. 2, the spin transition between spin \( F \) and \( A \) is accompanied with this orbital transition (\( n \)-spin \( F \) to \( p \)-spin \( A \)). Therefore, the spin canting observed for \( 0.4 < x_{exp.} < 0.5 \) in the single-crystal samples cannot be reproduced in Fig. 2.

In order to explain this experimental observation, we look for the possible mechanisms for the continuous change of spin/orbital structure starting from the \( p \)-spin \( A \). One possibility is to change the orbital wave function via the coupling to the lattice. In 327-system, the lattice constant \( c \) is longer than \( a, b \), which prefers \( d_{xz-\gamma^2} \) compared with \( d_{x^2-\gamma^2} \), and \( c \) changes as \( x \). This corresponds to the ‘‘magnetic field’’ to the orbital pseudo-spin, and tends to enhance the transfer along \( z \)-direction and hence the spin canting.

\[
\text{FIG. 3.}
\]

In Fig. 3 shown the phase diagram in the plane of \( x \) and \( gr \) (\( g : \) coupling constant, \( r : \) elongation along \( c \)-axis). This \( gr \) corresponds to the ‘‘orbital magnetic field’’ to prefer \( d_{x^2-\gamma^2} \). Here \( J_S \) is fixed to be 0.004 eV which is comparable to the value appropriate for 113-system. The \( p \)-spin \( A \) state (shaded in Fig. 3(a)) is surrounded by the discontinuous ‘‘orbital spin-flop’’ transition. This is because the ‘‘orbital magnetic field’’ \( gr \) is applied not perpendicularly but anti-parallel to the \( d_{x^2-\gamma^2} \)-direction. Therefore it seems unlikely that the spin canting occurs between the \( p \)-spin \( A \) and spin \( F \) with different orbital structures, e.g., the arrow (a) in Fig. 1.

We now look for the possibility of the spin canting with the orbital structure fixed to be \( d_{xz-\gamma^2} \), i.e., the arrow (b) in Fig. 1. The corresponding \( J_S \) value might appear to be too small (~ 0.0002 eV), but \( J_S \) is very sensitive to the bond-length \( l \) (\( J_S \sim l^{-14} \) as discussed later), and the lattice elongation along \( c \)-axis suggests smaller value of \( J_S \) in 327-system compared with 113. Furthermore, the \( x \)-dependence of \( l \) induces the \( x \)-dependence of \( J_S \) and the arrow (b) in Fig. 1 has finite vertical component. Another remark is that even though the orbital pseudospin \( \tilde{T}_e \) is fully polarized along \( d_{xz-\gamma^2} \)-direction, the wavefunction is the hybridized one with \( d_{xz-\gamma^2} \) and \( d_{x^2-\gamma^2} \).

Namely the \( d_{xz-\gamma^2} \) has the weight \( \sim (t_0/\tilde{\beta})^2 \), which induces the effective transfer \( t_z \) between layers. However \( t_z \) is much smaller than \( t_0 \), which is crucial to the spin canting as discussed below.

\[
\text{FIG. 4.}
\]

In Fig. 4 shown the energy as a function of the angle \( \eta \) between the spins of two layers for several values of \( J_S \). Spin \( F \) for \( J_S = 0 \) is due to the above-mentioned double-exchange interaction with the weight \( \sim (t_0/\tilde{\beta})^2 \). For \( J_S = 0.42-0.5 \text{ meV} \), the optimized angle \( \eta \) is the intermediate between \( \eta = 0 \) and \( \eta = \pi \), and the canting state is realized. Therefore we conclude that the spin canting occurs between \( p \)-spin \( A \) and \( p \)-spin \( F \) states when \( J_S \) changes.

\[
\text{FIG. 5.}
\]

In order to study further this canting state, we introduce a simplified model shown in Fig. 5. We assume that the spin polarization is perfect, i.e., all the electron spins are aligned along the ordered direction. Therefore we consider the spinless fermions. The density of states is taken to be a constant \( N_F \) for each layer. We take the hole-picture, and \( x \) holes are occupying this constant density of states from the bottom. These two bands are split into bonding and anti-bonding ones with the splitting \( \Delta = t_z \cos \frac{2\pi}{3} = t_z \xi \). The kinetic energy gain \( \Delta E_{\text{kin}}(\xi) \) is given by

\[
\Delta E_{\text{kin}}(\xi) \sim \begin{cases} -t_z^2 \cdot N_F \cdot \xi^2 & \text{for } \xi < \xi_c \equiv \frac{t_0}{N_F \cdot t_z} \\ -t_z \cdot x \cdot \xi & \text{for } \xi > \xi_c \end{cases}, \quad (7)
\]

while the energy cost of the exchange interaction is
$J_S \cos \eta = J_S (2\xi^2 - 1)$. The lower line of Eq. 4 is obtained by de Gennes, and if this holds the canting always occurs. The new aspect here is that $\Delta E_{kin}(\xi) \propto \xi^2$ when the splitting $\Delta = t_z \xi$ is smaller than the Fermi energy $\epsilon_F = x/N_F$ and both the bonding and anti-bonding bands are occupied. Therefore the spin $A$ structure $(\xi = 0, \eta = \pi)$ is at least locally stable when $2J_S > t^2_z N_F$. This condition can be satisfied when the orbital is almost $d_{2z-y^2}$ and $t_z$ is much reduced from $t_0$. For general orbital configuration $t^2_z N_F$ is order of magnitude larger than $J_S$. Now we look for the optimized $\xi$ to minimize the total energy $\Delta E(\xi) = \Delta E_{kin}(\xi) + \Delta E_{ex}(\xi)$. When $\xi > 1$ ($x > t_z N_F$), only the upper line of Eq. (4) is relevant and $\Delta E = (2J_S - t^2_z N_F) \cdot \xi^2$. Therefore $\xi$ jumps from 1 (spin $F$) to 0 (spin $A$) as $J_S$ increases across $t^2_z N_F/2$.

FIG. 6.

When $\xi_c < 1$, the optimized $\xi$ as a function of $J_S$ is given in Fig. 1. As $J_S$ increases, the spin structure changes as spin $F$ ($J_S < t_z x/4$) → spin canting ($t_z x/4 < J_S < t^2_z N_F/4$) → spin canting with fixed canting angle ($t^2_z N_F/4 < J_S < t^2_z N_F/2$) → spin $A$ ($t^2_z N_F/2 < J_S$. Note that the canting angle continuously evolves from spin $F$, but jumps at the transition to the spin $A$. Summarizing, $x < t_z N_F$ and $t_z x/4 < J_S < t^2_z N_F/2$ are the condition for the occurrence of the spin canting. Considering $N_F \sim 1/t_0$, and $J_S$ is about two orders of magnitude smaller than $t_0$, this condition is satisfied only when $t_z$ is much reduced from $t_0$ and $x$ is small. Spin canting state does not appear in Fig. 2 because of the large $t_z$ for $n$-spin $F$.

Spin canting observed in the metallic region $0.4 < x_{exp} < 0.5$ implies therefore the planer orbital in this region. This is consistent with the spin easy axis observed within the $ab$-plane in this region because the planar orbital leads to this anisotropy of the easy axis according to the spin Hamiltonian derived by Matsumoto taking into account the spin-orbit interaction. The observed spin transition from $F$ to $A$ with increasing $x$ should therefore corresponds to that from $p$-spin $F$ to $p$-spin $A$ in Fig. 1, for which the increase in $J_S$ with increasing $x$ is needed (arrow (b) in Fig. 1).

This $x$-dependence of $J_S$ can be explained in terms of the bond-length dependence of the inter-layer hopping integral. According to the pseudo-potential theory, the hopping integral between the $d$ orbitals depends on the bond length $l$ as $t \propto l^{-7}$, leading to $\xi_0 \propto (t_z)^{2} / (t_2^z)^{2} \propto l^{-7}$, where $l_c$ denotes the bond-length along $c$-axis. The observed lattice contraction along $c$-axis with increasing $x$, therefore, gives rise to the decrease of $\xi_0$, leading to the spin structure changes from spin $F$ to cant, and to spin $A$. $J_S \propto (t_2^z)^{2} \propto l^{-14}$ increases due to this lattice contraction along $c$-axis, which can explain the $x$-dependence of $J_S$ needed for the change from $p$-spin $F$ to $p$-spin $A$, as shown by the arrow (b) in Fig. 1.

The neutron-diffraction experiments have revealed that the samples with the spin canting at zero temperature ($0.4 < x_{exp} < 0.48$) become the spin $A$ at higher temperatures. This can also be explained in terms of the lattice deformation as follows. The observed lattice contraction along $c$-axis with increasing temperature brings about the decrease of $\xi_0 \propto t_z/J_S \propto l^{-7}$, leading to the spin transition toward the spin $A$ discontinuously. Hirota et al. also attributed this $T$-dependent spin transition to the lattice deformation.

As shown above, the observed lattice deformation plays an important role to explain the spin transition. In our scenario, the bond-length dependence of the inter-layer hopping is the most important mechanism which relates the lattice- and the electron-systems. One might, however, attribute it rather to the Jahn-Teller type electron-lattice interaction through the electro-static coupling (in other word, the “orbital magnetic field”). In this scenario, the lattice contraction along $c$-axis reduces the hybridization of $d_{2z-y^2}$ orbital as $x$ increases, namely the stabilization of $d_{2z-y^2}$ which prefers spin $A$. According to this scenario, the temperature dependence of the spin canting mentioned above is also explained by the change in the hybridization of $d_{2z-y^2}$ which is brought about by the temperature-dependent lattice elongation. This scenario, however, results in the decrease of the inter-layer hopping as $x$ ($T$) increases, being opposite to our scenario, where little change in the orbital ordering and the increase of the inter-layer hopping $t_z \propto l^{-7}$ during the spin transition are predicted. Main distinction between these two scenarios is whether such a large change in the hybridization of $d_{2z-y^2}$ occurs during the spin transition or not. As seen in Fig. 2 and Fig. 3, however, the spin transition should be of the first order without canting if it is accompanied with the large change in the orbital. Experimentally, the spin easy axis falls onto $ab$-plane discontinuously around $x_{exp} = 0.32$ (spin $F$) and the spin transition from $F$ to cant, and to spin $A$ occurs with this easy axis being unchanged. This behavior implies that the hybridization of $d_{2z-y^2}$ decreases discontinuously before the spin transition, and during the transition the wave-function is almost planar as $d_{2z-y^2}$, namely the transition is between $p$-spin $F$ and $p$-spin $A$ with canting. Though, even in this case, the “orbital magnetic field” brings about a little change in the hybridization of $d_{2z-y^2}$ via the change of the weight mentioned before, $(t_0 / \tilde{\beta})^2 \rightarrow (t_0 / (\tilde{\beta} - gr))^2$, it is a minor correction comparing with the sensitively changing bond-length dependence, $t^2 \propto l^{-7}$, $J_S \propto l^{-14}$.

For the spin canting, $\xi_0 = t^2 x/4J_S < 1$, and hence the planer orbital during the spin transition turned out to be essential. In 133-system, the spin $F$ phase neighboring the metallic spin $A$ has the quasi-three-dimensional orbital ordering for the realistic parameters in the mean field theory. Therefore the canting does not occur because the orbital structures are different between spin $A$ and $F$, and the transition between them is always discon-
tinuous. In the real 113-system no anisotropy has been reported in the spin \(F\) state, and there is a theoretical suggestion of the orbital liquid state for the spin \(F\) metallic region. In any case the orbital state is different from the \(d_{xz-y^2}\) in the metallic spin \(A\) state. In 327-case, the layered crystal structure brings about the two-dimensional orbital anisotropy, reflecting the interplay of the dimensionality of the crystal structure and that of the orbital ordering.

FIG. 7.

Figure 7 summarizes our interpretation of the experiments (notations \(x_{th}\) and \(x_{exp.}\) are used to prevent the confusion due to the quantitative discrepancy of \(x\) between the calculations and the experiments). The hatched region corresponds to the spin canting phase due to the planar orbital for the \(p\)-spin \(F\). \(J_\parallel (FA)\) is the phase boundary with the first-order transition between spin \(F\) (or canting) and spin \(A\). Spin \(F\) phase at \(x_{exp.} \approx 0.32\) corresponds to the \(n\)-spin \(F\) phase. With increasing \(x\), spin \(F\) changes from \(n\)- to \(p\)- with the orbital transition into \(d_{xz-y^2}\) around \(x_{th.} \sim 0.125\). This transition is of the first-order, leading to the discontinuous reorientation of the spin easy axis from being along \(c\)-axis into within the \(ab\)-plane by considering the spin-orbit interaction. This explains the observed spin anisotropy where the easy axis, pointing parallel to the \(c\)-axis for \(x_{exp.} = 0.32\), discontinuously turns onto the \(ab\)-plane at \(x_{exp.} \sim 0.32\) for \(T \lesssim 100\) K. The \(p\)-spin \(F\) phase around \(x_{th.} \gtrsim 0.125\) cants readily within the \(ab\)-plane because of the decrease in \(\xi_0 \propto \ell^2\) due to the contraction of the bond-length along \(c\)-axis with increasing \(x\), and then discontinuously jumps to the \(p\)-spin \(A\), corresponding to the observation for \(0.4 < x_{exp.} < 0.5\).

In conclusions, we have studied the spin and the orbital ordering in 327-system, taking the orbital degrees of freedom and the strong Coulombic repulsion into account. Observed \(x\)-dependence of the spin ordering and its anisotropy were qualitatively explained in terms of the orbital ordering and the observed lattice deformation along \(c\)-axis. The observed temperature dependence of the spin structure is also explained by the lattice deformation. The difference between 327-system with canting and 113-system without canting is understood in terms of the difference in the dimensionality of the crystal structure.

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Figure captions

Fig. 1. Phase diagram at zero temperature in the plane of the doping concentration ($x$) and the $AF$ interaction between $t_{2g}$ spins ($J_S$), without electron-lattice coupling ($g = 0$). Orbital shape is represented by $p$- (planer, orbital $F (0,0)$) and $n$- (not planer, orbital $G (100,-100)$ around $x = 0.1$ and orbital A $(-40,-40)$ around $x = 0.7$). The possibility of the spin canting are not taken into account ($\eta = 0, \pi$). Depicted arrow (a) ((b)) corresponds to the spin transition with fixed (increasing) $J_S$.

Fig. 2. The $x$-dependence of the optimized canting angle $\eta$ with $g = 0$.

Fig. 3. The phase diagram as a function of the doping concentration $x$ and the electron-lattice coupling $g$. $p$-spin A is always surrounded by the discontinous boundary with respect to $\eta$.

Fig. 4. $\eta$-dependence of the ground state energy calculated for a planer orbital ($\vec{T}$ points to the direction of $d_{x^2-y^2}$), which saddle point corresponds to the canting angle.

Fig. 5. The bonding/anti-bonding splitting of the band by the inter-layer hopping. The small (large) splitting case is depicted as (a) ((b)).

Fig. 6. Canting saddle point $\xi$ as a function of $J_S$ (for the case $\xi_c \leq 1$).

Fig. 7. Schematic sketch of the calculated phase diagram and the correspondence with the experiments.
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