Origin of G-type Antiferromagnetism and Orbital-Spin Structures in LaTiO$_3$

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The possibility of the $D_{3d}$ distortion of TiO$_6$ octahedra is examined theoretically in order to understand the origin of the G-type antiferromagnetism (AFM(G)) and experimentally observed puzzling properties of LaTiO$_3$. By utilizing an effective spin and pseudospin Hamiltonian with the strong Coulomb repulsion, it is shown that AFM(G) state is stabilized through the lift of the $t_{2g}$-orbital degeneracy accompanied by a tiny $D_{3d}$-distortion. The estimated spin-exchange interaction is in agreement with that obtained by the neutron scattering. Moreover, the level-splitting energy due to the distortion can be considerably larger than the spin-orbit interaction even when the distortion becomes smaller than the detectable limit under the available experimental resolution. This suggests that the orbital momentum is fully quenched and the relativistic spin-orbit interaction is not effective in this system, in agreement with recent neutron-scattering experiment.

KEYWORDS: LaTiO$_3$, GdFeO$_3$-type distortion, $D_{3d}$-crystal field, orbital ordering, second-order perturbation theory, G-type antiferromagnetism

§1. Introduction

Perovskite-type Ti oxide $RTiO_3$ have recently attracted much interest because of the rich magnetic and orbital phases caused by an interplay of spin and orbital degrees of freedom. In these compounds, Ti$^{3+}$ has a $3d^1$ configuration, and one of the threefold $t_{2g}$-orbitals is occupied at each transition-metal site. The crystal structure is a pseudocubic perovskite with GdFeO$_3$-type distortion in which the TiO$_6$ octahedra forming the perovskite lattice tilt alternatingly. The unit cell contains four TiO$_6$-octahedra, as shown in Fig. 1. With a smaller ionic radius of the $R$ ion, the distortion increases with the decrease in the Ti-O-Ti
bond angle from 180°. The bond angle can be controlled by use of the solid-solution systems 
La$_{1-y}$Y$_y$TiO$_3$ or in RTiO$_3$, by varying the $R$ ions.

Recently, the magnetic phase diagrams have been investigated intensively in the plane of
temperature and the magnitude of the distortion.\textsuperscript{2-5} In particular, LaTiO$_3$ exhibits a G-type
AFM (AFM(G)) ground state with magnetic moment of 0.45 $\mu_B$,\textsuperscript{4} and the Néel temperature ($T_N$) takes about 130 K. With increasing the GdFeO$_3$-type distortion, $T_N$ decreases rapidly
and is suppressed to almost zero, subsequently a ferromagnetic (FM) ordering appears. In Y-
rich systems and in YTiO$_3$ in which the GdFeO$_3$-type distortion is relatively large, the system
shows a FM ground state accompanied by a large Jahn-Teller (JT) distortion. Recently, the
AFM-FM phase transition with the second-order-like behavior has been understood from
the strong two-dimensionality in the spin-coupling realized near the transition point.\textsuperscript{6,7} However, the origin and nature of AFM(G) state in the end compounds LaTiO$_3$ remains
unresolved.

Recent model Hartree-Fock study predicts the AFM(G) state with the spin-orbit ground
state in the absence of static JT distortion.\textsuperscript{8,9} However, in contrast to the prediction from the
spin-orbit ground state, recent neutron-scattering study shows the spin-wave spectrum well
described by an isotropic spin-1/2 Heisenberg model with a nearest-neighbor superexchange
constant $J \sim 15.5$ meV.\textsuperscript{11} This also suggests the absence of unquenched orbital moments.
When the orbital degeneracy remains, a FM spin structure with antiferro-orbital ordering
in which the neighboring orbitals are orthogonal to each other is eventually expected in
the presence of the transfers and the Coulomb-exchange interaction. Indeed, recent weak
coupling study shows that in the cubic-crystal field in the absence of the static JT distortion,
a FM state, out of which two states $\frac{1}{\sqrt{2}}(yz + izx) \uparrow$ and $xy \uparrow$ are alternating is favored both
by the spin-orbit interaction and by the spin-orbital superexchange interaction.\textsuperscript{10} However,
no evidence for the orbital ordering is found in a resonant x-ray scattering study.\textsuperscript{11}

Recently, a possible orbital liquid state was proposed on the basis of small exchange inter-
action in the orbital sector in the AFM(G) state.\textsuperscript{12} However, in a system with strong orbital
fluctuations, the spin and orbital degrees of freedom strongly couple, and both degrees of freedom can not be determined independently to each other. In this circumstance, the origin of AFM(G) state in LaTiO$_3$ is to be clarified in a self-consistent manner.

In this letter, in order to understand the above properties of AFM(G) state in LaTiO$_3$, we propose that the puzzle is solved if we assume the existence of a small $D_{3d}$-crystal field. If the $D_{3d}$ distortion exists, TiO$_6$-octahedron is contracted along the threefold direction as shown in Fig. 2. As a result, threefold degenerate $t_{2g}$-levels split into non-degenerate lower $a_{1g}$-level ($\varphi_1$) and twofold-degenerate higher $e_g$-levels ($\varphi_2, \varphi_3$). In the distortion with $[1,1,1]$-trigonal axis, the $a_{1g}$ representation is $\frac{1}{\sqrt{3}}(xy + yz + zx)$ and the $e_g$ representations are $\frac{1}{\sqrt{6}}(2xy - yz - zx)$ and $\frac{1}{\sqrt{2}}(yz - zx)$. Since the lowest level has no degeneracy, this distortion significantly and sensitively lowers the energy of the electron system in $t_{2g}$ configuration. Though the $d$-type JT distortion is stabilized in YTiO$_3$ or in the compounds with large GdFeO$_3$-type distortion due to the effects of covalency between O 2$p$ and unoccupied $d$-orbitals on the $R$-site cations, $^{13)}$ LaTiO$_3$ with small GdFeO$_3$-type distortion turns out to be unstable to the $D_{3d}$ distortion. The magnitude of the distortion can be denoted by the $D_{3d}$-distortion angle $\omega$ (see Fig. 2). By utilizing the effective spin and pseudospin Hamiltonian in the strong Coulomb repulsion, we solve the self-consistent Hartree-Fock equation and show that the emergence of the AFM(G) state and the following features in LaTiO$_3$ are well explained by the effects of $D_{3d}$ distortion even when $\omega$ is as small as 1$^\circ$:

- $T_N \sim 130$ K, $J \sim 15.5$ meV,
- magnetic moment of 0.45 $\mu_B$,
- no detectable JT distortion,
- no evidence for orbital ordering in the resonant x-ray scattering.

We analyze why the orbital ordering has not been detected so far, and propose experimental ways for testing the validity of our proposal.
§2. Formalism

We start with the multiband $d$-$p$ model in which the full degeneracies of Ti $3d$ and O $2p$ orbitals as well as the on-site Coulomb and exchange interactions are taken into account. The nearest-neighbor $d$-$p$ and $p$-$p$ transfers are given in terms of Slater-Koster parameters $V_{pd\sigma}, V_{pds\sigma}, V_{pp\pi}$ and $V_{pp\sigma}$. The on-site Coulomb interactions are expressed using Kanamori parameters, $u, u', j$ and $j'$ which satisfy the following relations: $u = U + \frac{20}{9}j$, $u' = u - 2j$ and $j = j'$. Here, $U$ gives the magnitude of the multiplet-averaged $d$-$d$ Coulomb interaction.

The charge-transfer energy $\Delta$, which describes the energy difference between occupied O $2p$ and unoccupied Ti $3d$ levels, is defined by using $U$ and energies of the bare Ti $3d$ and O $2p$ orbitals $\varepsilon_0^d$ and $\varepsilon_p$ as $\Delta = \varepsilon_0^d + U - \varepsilon_p$, since the characteristic unoccupied $3d$ level energy on the singly occupied Ti site is $\varepsilon_0^d + U$. The values of the parameters are estimated by the cluster-model analyses of valence-band and transition-metal $2p$ core-level photoemission spectra and the analyses of the first-principle band calculations. We take the values of these parameters as $\Delta = 5.5$ eV, $U = 4.0$ eV, $V_{pd\sigma} = -2.4$ eV, $V_{pds\sigma} = 1.3$ eV, $V_{pp\pi} = 0.52$ eV, $V_{pp\sigma} = -0.11$ eV and $j = 0.46$ eV throughout the present calculation. The effects of the GdFeO$_3$-type distortion are considered through the transfer integrals which is defined by using the Slater-Koster’s parameters. In the present calculations, we simulate the GdFeO$_3$-type distortion by rotating the TiO$_6$ octahedra by angle $+14.1^\circ$ and $-14.1^\circ$ around the [1,1,1] and [-1,-1,1] axes. As a result, the Ti-O-Ti bond angle takes $\sim 157^\circ$. The effects of the $D_{3d}$ distortion are also considered. We integrate out the O $2p$ orbital degrees of freedom in the path-integral formalism to arrive at the effective multiband Hubbard model which includes only Ti $3d$ orbital degrees of freedom. Starting with thus obtained multiband Hubbard Hamiltonian, we can derive an effective Hamiltonian in the low-energy region on the subspace of states with singly occupied $t_{2g}$ orbitals at each transition-metal site by utilizing a second-order perturbation theory. The states of $3d$ electrons localized at the transition-metal sites can be represented by two quantum numbers, the $z$-component of the spin $S_z$ and the type of the occupied orbitals. The threefold degeneracy of $t_{2g}$-orbitals at each site can be described by a pseudospin with the spin-1 operator $\tau$. We follow an approach similar to the Kugel-Khomskii formulation. We express the $3d$ electron operators in terms of $S$ and $\tau$ to arrive at the effective spin and pseudospin Hamiltonian: $H_{\text{eff}} = H_{\text{cry}} + H_{t_{2g}} + H_{e_g}$. The first term $H_{\text{cry}}$ denotes the effects of $D_{3d}$-crystal field. This term is obtained from the zeroth-order perturbational processes. The second term $H_{t_{2g}}$ is obtained from the second-order perturbational processes whose intermediate states contain only $t_{2g}$-orbital degrees of freedom. The third term $H_{e_g}$ is obtained from the second-order perturbational processes whose intermediate states contain $e_g$-orbital degrees of freedom. We neglect the relativistic spin-orbit coupling in the model and discuss this issue later.
§3. Results

There are four trigonal-axes in the TiO$_6$ octahedron, namely, [1,1,1], [1,1,-1], [1,-1,1] and [1,-1,-1] with respect to the $x$, $y$ and $z$ axes. At this stage, there are several possibilities for configurations of the trigonal axes at sites 1, 2, 3, and 4. The spin-couplings between the neighboring sites depend on the configuration. There are five configurations which lower the AFM(G) spin structure in energy as shown in Table I. In this letter, we examine the AFM(G) state with a trigonal-axes configuration in which [1,1,1]-axis is chosen at every sites (config. 1), and we show that a considerably small $D_{3d}$-distortion does strongly stabilize the AFM(G) state and the experimentally observed properties are well explained when we assume the distortion. It is an interesting problem to study which configuration has the lowest energy, which would require an entirely separate work and is left for future discussion. In the $D_{3d}$ distortion with config. 1, the lowest level is $1/\sqrt{3}(xy + yz + zx)$ at every sites. In Fig. 3, we plot the energies of several magnetic structures with config.1 as functions of $D_{3d}$-distortion angle $\omega$. In the region of $\omega > 1^\circ$, the AFM(G) state is strongly stabilized relative to other structures. This may indeed drive the $D_{3d}$ distortion even in the cost of lattice energy. Since the lattice elastic-energy is not accounted in Fig. 3, the real energy minimum including the elastic-energy cost should be in the range $0^\circ < \omega < 8^\circ$. In Fig. 4, we plot the $t_{2g}$-level-splitting energy due to the $D_{3d}$-crystal field ($\Delta_{D_{3d}}$) as a function of $\omega$. In the region of $\omega > 1^\circ$, the value of $\Delta_{D_{3d}}$ is sufficiently larger than the coupling constant of the relativistic spin-orbit interaction in Ti$^{3+}$ ion ($\xi_d = 0.018$ eV), though this distortion angle $\omega > 1^\circ$ is substantially smaller than the tilting angle of GdFeO$_3$-type distortion. In fact, it is not surprising if such small $D_{3d}$ distortion has not been detected so far.

When the level-splitting energy is sufficiently large as compared to the characteristic energy of the spin-orbital exchange interaction, the orbital occupation at each site is restricted to
Table I. Trigonal-axes configurations which lower the AFM(G) spin structure in energy.

|          | site 1       | site 2       | site 3       | site 4       |
|----------|--------------|--------------|--------------|--------------|
| config.1 | [1,1,1]      | [1,1,1]      | [1,1,1]      | [1,1,1]      |
|          | $\varphi_1$ | $\frac{1}{\sqrt{3}}(xy + yz + zx)$ | $\frac{1}{\sqrt{3}}(xy + yz + zx)$ | $\frac{1}{\sqrt{3}}(xy + yz + zx)$ |
| config.2 | [1,-1,1]     | [1,-1,1]     | [1,-1,1]     | [1,-1,1]     |
|          | $\varphi_1$ | $\frac{1}{\sqrt{3}}(-xy - yz + zx)$ | $\frac{1}{\sqrt{3}}(-xy - yz + zx)$ | $\frac{1}{\sqrt{3}}(-xy - yz + zx)$ |
| config.3 | [1,1,-1]     | [1,1,-1]     | [1,1,-1]     | [1,1,-1]     |
|          | $\varphi_1$ | $\frac{1}{\sqrt{3}}(xy + yz + zx)$ | $\frac{1}{\sqrt{3}}(xy + yz + zx)$ | $\frac{1}{\sqrt{3}}(xy + yz - zx)$ |
| config.4 | [1,1,-1]     | [1,1,-1]     | [1,1,-1]     | [1,1,-1]     |
|          | $\varphi_1$ | $\frac{1}{\sqrt{3}}(xy - yz - zx)$ | $\frac{1}{\sqrt{3}}(xy - yz - zx)$ | $\frac{1}{\sqrt{3}}(xy + yz + zx)$ |
| config.5 | [1,-1,1]     | [1,-1,1]     | [1,-1,1]     | [1,-1,1]     |
|          | $\varphi_1$ | $\frac{1}{\sqrt{3}}(-xy - yz + zx)$ | $\frac{1}{\sqrt{3}}(-xy - yz + zx)$ | $\frac{1}{\sqrt{3}}(-xy + yz + zx)$ |

Fig. 4. Level-splitting energy due to the $D_{3d}$-crystal field ($\Delta_{D_{3d}}$) as a function of the $D_{3d}$-distortion angle.
\( \phi_3 = \frac{1}{\sqrt{3}}(-yz+zx) \)
\( \phi_2 = \frac{1}{\sqrt{6}}(-2xy+yz+zx) \)
\( \phi_1 = \frac{1}{\sqrt{2}}(xy+yz+zx) \)

Fig. 5. Characteristic transfers which contribute to the spin-exchange interaction.

\[
J_{\text{Heis}}^{ab}, J_{\text{Heis}}^{c} = \frac{4}{u} t_{2}^{2} - 2 \frac{(t_{2}^{2} + t_{3}^{2})j}{(u' + \Delta D_{3d})^{2}} - 2 \frac{(t_{2}^{2} + t_{3}^{2})j}{(u' + \Delta D_{3d})^{2}}.
\] (1)

In Fig. 6, the values of \( J_{\text{Heis}}^{ab} \) and \( J_{\text{Heis}}^{c} \) are plotted as functions of \( \omega \). Both \( J_{\text{Heis}}^{ab} \) and \( J_{\text{Heis}}^{c} \) take approximately 0.015-0.022 eV, and they are in agreement with the value obtained by the neutron scattering experiment of \( \sim 15.5 \) meV. In LaTiO\(_3\), the magnetic moment takes 0.45 \( \mu_{B} \), which is reduced from the spin-only moment. Recent optical measurement shows that LaTiO\(_3\) has a considerably small optical gap of \( \sim 0.1 \) eV in the vicinity of the metal-insulator phase boundary with strong itinerant character. Therefore, in this system, we expect that
some amount of orbital and spin fluctuations remain. The reduction of the magnetic moment may easily be attributed to these fluctuations. We note that in this context, the calculated \( J_{\text{Heis}}^{ab} \) and \( J_{\text{Heis}}^c \) in the localized limit seem rather small at first sight. To elucidate this issue, we have examined how the values of \( J_{\text{Heis}}^{ab} \) and \( J_{\text{Heis}}^c \) change within the error bars of the parameters estimated from the analyses of photoemission spectra. In LaTiO\(_3\) with strong itinerant character, we can expect that the Coulomb and exchange interactions are rather small. We calculate the values in the case of \( U = 3.0 \) eV, \( j = 0.50 \) eV and \( \Delta = 5.0 \) eV and in the case of \( U = 3.0 \) eV, \( j = 0.40 \) eV and \( \Delta = 5.0 \) eV. The values take \( \sim 0.03 \) eV, which are larger than the previous estimate (see Inset of Fig. 6). Considering these variations and uncertainties, we conclude that the calculated \( J_{\text{Heis}}^{ab} \) and \( J_{\text{Heis}}^c \) in the localized limit are in qualitative agreement with the experimentally obtained \( J \) in the presence of itinerant charge fluctuations.

Here, a question arises: why has the orbital ordering caused by the occupation of the lowest level in the \( D_{3d} \) distortion not been detected experimentally so far? Detection of the orbital ordering by the resonant x-ray scattering is based on the splitting of the Ti 4\( p \) levels induced by the orbital ordering of the Ti 3\( d \) states. When the Ti 3\( d \) orbitals are ordered in the \( D_{3d} \) distortion, the Coulomb interaction between Ti 4\( p \) and occupied 3\( d \) orbitals, \( U_{4p-3d} \) and the interaction between Ti 4\( p \) and ligand O 2\( p \) orbitals, \( U_{4p-2p} \) make opposite contributions. Among the threefold Ti 4\( p \) orbitals, the orbital directed along the trigonal axis has higher energy due to \( U_{4p-3d} \). On the contrary, along this axis, \( U_{4p-2p} \) is weakened so that the crystal field works to lower the Ti 4\( p \) orbital. In addition, the weakened hybridizations between the Ti 4\( p \) and O 2\( p \) orbitals might lower the Ti 4\( p \) orbital. This cancellation may lead to the absence of detectable orbital ordering in the resonant x-ray scattering in LaTiO\(_3\).\(^{11} \) The orbital ordering accompanied by the \( D_{3d} \) distortion would be more easily detected in the AFM(G) compounds with relatively large optical gap and small charge fluctuations: PrTiO\(_3\) and NdTiO\(_3\).

In summary, in order to interpret the experimentally observed properties of AFM(G) state in LaTiO\(_3\), we have examined the effects of possible \( D_{3d} \)-crystal field as a candidate for their origin. In the presence of the \( D_{3d} \)-crystal field, threefold cubic-\( t_{2g} \)-levels are split into non-degenerate \( a_{1g} \)- and twofold-degenerate \( e_g \)-levels. Since the lowest level has no degeneracy, this distortion strongly lowers the energy of the electron system in \( t_{2g}^{1} \) configuration. Moreover, the calculated \( D_{3d} \)-splitting energy \( \Delta_{D_{3d}} \) suggests that the \( D_{3d} \)-splitting dominates over the relativistic spin-orbit interaction in the region of \( D_{3d} \)-distortion angle \( \omega > 1^\circ \). The calculated spin-exchange constant is in agreement with that obtained experimentally. Finally, our proposal for the small \( D_{3d} \) distortion should in principle be observed by the displacement of O ions if the experimental resolution is sufficient.
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