Orbital-Spin Structure and Coupling to Lattice in \( R \)TiO\(_3\) with \( R = \)La,Pr,Nd and Sm

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The origin of the G-type antiferromagnetism (AFM(G)) and puzzling properties of RTiO\(_3\) with \( R = \)La are studied. We clarify that the crystal field from La caused by the GdFeO\(_3\)-type distortion lifts the \( t_{2g} \) degeneracy at Ti 3d orbitals. The lift stabilizes the AFM(G) with spin-exchange constant in agreement with neutron scattering results. The orbital-spin structures for \( R = \)Pr, Nd and Sm are also consistent with experiments. We propose that the GdFeO\(_3\)-type distortion has a universal mechanism of controlling orbital-spin structure competing with the Jahn-Teller (JT) mechanism.

Recently, a possible orbital liquid state was proposed by assuming the G-type antiferromagnetism on the basis of resultant small exchange interaction in the orbital sector. However, the origin of the AFM(G) state in LaTiO\(_3\) is still puzzling when the orbital is disordered. On the other hand, the possibility of the \( D_{3d} \) distortion of the TiO\(_6\) octahedra was also proposed for the origin of the AFM(G). In this distortion, the TiO\(_6\) octahedron is contracted along the threefold direction, and the threefold-degenerate \( t_{2g} \)-levels split into a nondegenerate lower \( a_{1g} \)-level and twofold-degenerate higher \( e_g \)-levels. The lift of the \( t_{2g} \) levels with the occupation of the lowest \( a_{1g} \)-orbital well explains the emergence of the AFM(G) and the isotropic spin-wave spectrum. However, this \( D_{3d} \) distortion has so far not been detected.

In addition to the JT distortion, the GdFeO\(_3\)-type lattice distortion is another generic phenomenon in perovskites. It has been assumed mainly to control the bandwidth through the \( M-O-M \) angle with \( M \) being TM ions, while its direct effects on interplay of spins and orbitals have not been considered seriously.

In this letter, by taking a particular example of LaTiO\(_3\), we clarify that the generic GdFeO\(_3\)-type distortion actually generates a new mechanism for control of orbital-spin low-energy structure through lift of the orbital degeneracy by crystal fields of \( R \) ions. This mechanism competes with that of the JT distortions and LS interactions. By utilizing the experimentally obtained coordination parameters, we construct the Hamiltonian for the crystal field of La cations in LaTiO\(_3\). The analyses of the obtained Hamiltonian show that the shifts of La cations due to the GdFeO\(_3\)-type distortion turn out to generate the crystal field which is similar to the \( D_{3d} \)-crystal-field. As a result, the threefold degeneracy of the cubic-\( t_{2g} \)-levels splits into three nondegenerate levels. The calculations of the energies and the spin-exchange constant well explain the emergence and the properties of the AFM(G) state in LaTiO\(_3\). In addition, we also

Rich magnetic and orbital phases, their phase transitions and interplays have attracted much interest in strongly correlated electron systems, particularly in transition metal (TM) oxides. Coupling to lattice further enriches the interplay through lattice distortions, dynamical phonons and cooperative effects such as JT distortions. Cuprate superconductors and manganese perovskite compounds with colossal magnetoresistance have not been detected in contrast to the manganites and relativistic spin-orbit (LS) interaction and by the spin-orbital superexchange interaction. Moreover, a 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 \( J \approx 15.5 \) meV. If the orbital moment is nonzero, the anisotropy appears through the LS interaction. Therefore, the isotropy indicates that the orbital moments are quenched.

In perovskite TM compounds, the JT distortions often play crucial roles in determining low-energy electronic states. However, with early TM ions, the JT coupling is considerably weaker than that in the late-3d compounds. Actually, the distortion of the TiO\(_6\) octahedra in LaTiO\(_3\) has not been detected in contrast to the manganites and cuprates. Therefore, in LaTiO\(_3\), the crystal field of O ions surrounding the Ti\(^{3+}\) ion has a cubic symmetry so that the degeneracy of the \( t_{2g} \) level survives. Under this circumstance, the AFM(G) ground state is surprising and controversial since in the orbitally degenerate system, we expect that a FM state with antiferro-orbital ordering is stabilized both by transfers and the Coulomb exchange interaction. Indeed, a recent weak coupling study shows that a FM state, out of which two states \( (yz + izx)/\sqrt{2} \uparrow \) and \( xy \uparrow \) are alternating is favored both by the relativistic spin-orbit (LS) interaction and by the spin-orbital superexchange interaction.
The distortions of the R cations along the b-axis due to the GdFeO$_3$-type distortion are presented in RO-plane 1, they distort in the positive direction while in RO-plane 2, they distort in the negative direction. In the case of site 1, the distances between the Ti ion and R ions located in the $\pm (1, 1, 1)$-directions are decreased. As a result, the La ions generate the crystal field which is similar to the $D_{3d}$-crystal field with $[1, 1, 1]$-trigonal axis (see text). The distortions of the O ions along the c-axis are induced by the tilting of the octahedron are also presented. (c) The energy-level structure in the crystal field due to the R cations. The threefold degeneracy of the cubic-$t_{2g}$ levels split into three nondegenerate levels.

The Cu ions generate the crystal field with $\phi_3$ 0.6945. This orbital structure forms the basis from which the oxygen has a cubic symmetry. When we introduce the crystal field of R cations ($H_{RI}$) as a perturbation, the threefold degeneracy of the cubic-$t_{2g}$-levels split. Here, for simplicity, we take $H_{RI}$ by assuming that there exist the point charges with +3 valence on each R cation. The Coulomb interaction between an electron on a Ti 3d orbital and a La$^{3+}$ ion is given by using the dielectric constant $\varepsilon_TIR$ as,

$$v(r) = -\frac{Z_re^2}{\varepsilon_TIR|R_i - r|},$$

where $R_i$ expresses the coordinates of the $i$-th R ion, and $Z_R(=+3)$ is the nominal valence of La$^{3+}$. We calculate the following matrix elements,

$$\langle m'|v(r)|m \rangle = \int d\varphi^*_{3d,m}v(r)\varphi_{3d,m}$$

with

$$\varphi_{3d,m} = R_{3d}(r)Y_{2m}(\theta, \phi).$$

Here, the integer $m=(-2, ..., 2)$ is the magnetic quantum number. The coordinates of the La ions are calculated by using the positional parameters and the cell constants obtained by the x-ray diffraction study. After transforming the basis from $m$ to the $t_{2g}$ representations, we obtain the Hamiltonian $H_{RI}$ with $xy$, $yz$, and $zx$-basis. These representations are defined in the coordinates with $x$, $y$, and $z$-axes attached to each TiO$\_6$ octahedron.

By diagonalizing the obtained $H_{RI}$, we can evaluate the 3d-level energies and their representations. The threefold degeneracy of the $t_{2g}$ orbitals is split into three isolated levels as shown in Fig. (c). The energy levels $\Delta_1$ and $\Delta_2$ are 0.7685/\varepsilon_{TLa} eV and 1.5849/\varepsilon_{TLa} eV, respectively. The representations of the lowest levels at each site can be specified by the linear combination of $xy$, $yz$, and $zx$ orbitals as $axy - byz - czx$, $axy - cyz - bxz$, $axy + byz + czx$, and $axy + cyz + bxz$, respectively, where $a^2 + b^2 + c^2 = 1$. Here, we note that there exists a mirror plane vertical to the c-axis, and the orbital structure has the same symmetry as the orthohombic GdFeO$_3$-type distortion. The coefficients take the values, $a=0.6046$, $b=0.3900$, and $c=0.6945$. This orbital structure is similar to that in the $D_{3d}$-crystal-fields with $[1, 1, 1]$- $[1, 1, -1]$- $[1, 1, 1]$- and $[1, 1, 1]$-trigonal axes at sites 1, 2, 3 and 4, respectively. The representations of the lowest levels in these $D_{3d}$-crystal-fields are $\frac{1}{\sqrt{3}}(xy - yz - zx)$, $\frac{1}{\sqrt{3}}(xy - yz - zx)$, $\frac{1}{\sqrt{3}}(xy + yz + zx)$, and $\frac{1}{\sqrt{3}}(xy + yz + zx)$,
respectively. In the previous study [13], this configuration was referred to as config. 4, and it was shown that the $D_{3d}$-crystal-field with this trigonal-axes configuration strongly stabilizes the AFM(G) spin structure.

We next discuss the stability of the magnetic state in the crystal field of $H_{R1}$. For this purpose, we employ the effective spin and pseudospin Hamiltonian [6]:

$$H_{\text{eff}} = H_{\text{cry}} + H_{\tau}.$$  

The first term $H_{\text{cry}}$ denotes the crystal field on the Ti $t_{2g}$ orbitals. The second term $H_{\tau}$ is the spin and pseudospin term, in which the threefold $t_{2g}$ orbital degrees of freedom are represented by the pseudo-spin-1 operator $\tau$. This effective Hamiltonian is derived from the multiband $d$-$p$ model in the insulating limit by following an approach similar to the Kugel-Khomskii formulation [14, 15]. In this $d$-$p$ model, the full degeneracies of Ti 3$d$ and O 2$p$ orbitals as well as the on-site Coulomb and exchange interactions are taken into account [7]. The on-site Coulomb interactions are expressed using Kanamori parameters $u, u', j$ and $j'$ which satisfy the following relations [16, 17]: $u = U + 2j$, $u' = u - 2j$ 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 2$p$ and unoccupied Ti 3$d$ levels, is defined using $U$ and the energies of the bare Ti 3$d$ and O 2$p$ orbitals $\epsilon_{O}^{p}$ and $\epsilon_{p}$ as $\Delta = \epsilon_{O}^{p} + U - \epsilon_{p}$, since the characteristic unoccupied 3$d$ level energy on the singly occupied Ti site is $\epsilon_{O}^{p} + U$. The values of the parameters are estimated by the cluster-model analyses of valence-band and transition-metal 2$p$ core-level photoemission spectra and the analyses of the first-principles band calculations [18, 19]. We take the values of these parameters as $\Delta = 5.5$ eV, $U = 4.0$ eV, $V_{pd\tau} = -2.4$ eV, $V_{p\tau\tau} = 1.3$ eV, $V_{pp\tau} = 0.52$ eV, $V_{pp\tau} = -0.11$ eV and $j = 0.46$ eV. The effects of the GdFeO$_3$-type distortion are considered through the transfer integrals which are defined using Slater-Koster parameters [20]. Substituting the $H_{\text{cry}}$ term with $H_{R1}$, we calculate the energies for several magnetic structures by applying the Hartree-Fock approximation. In Fig. 2 we plot the calculated energies as functions of the magnitude of $\Delta_{1}$ ($=0.7685/\varepsilon_{\text{TiR}}$). We tune the magnitude of $\Delta_{1}$ by varying $\varepsilon_{\text{TiR}}$. In the region of $\Delta_{1} >0.03$ eV, the AFM(G) state is strongly stabilized relative to the other structures. In this region, $\Delta_{1}$ is much larger than $k_{B}T_{N}$ so that the orbital occupation is restricted to the lowest level irrespective of the spin structure. We can estimate the magnitudes of the spin-exchange interactions for each Ti-Ti bond in the subspace of singly-occupied lowest levels. The spin-exchange constant $J$ can be represented as $J = (E_{\uparrow\downarrow} - E_{\downarrow\uparrow})/2S^{2}$ with $E_{\uparrow\downarrow}$ and $E_{\downarrow\uparrow}$ being the energy gains of the Ti-Ti bond for $\uparrow\downarrow$- and $\downarrow\uparrow$-pairs, respectively. For LaTiO$_3$, the values of $J$ along the $x$-, $y$- and $z$-axes take as $J_{x}=18.45$ meV, $J_{y}=18.45$ meV and $J_{z}=19.71$ meV, respectively. They are in agreement with the value obtained by the neutron scattering experiment of $\sim 15.5$ meV, and are consistent with the spin-wave spectrum well described by the isotropic Heisenberg model.

We further note that the crystal field of the La cations has two origins. One is the Coulomb potential from charged La ions as we have studied above, and the other is the hybridization between the Ti 3$d$ orbitals and unoccupied orbitals on the La cations. We next estimate the effect of the crystal field due to the latter origin for LaTiO$_3$. We construct the Hamiltonian for hybridization between Ti 3$d$ and La 5$d$ orbitals ($H_{R2}$) by using the second-order perturbational expansion in terms of the transfers between Ti 3$d$ and La 5$d$ orbitals ($t_{dd}$). The expression of the matrix element of $H_{R2}$ is

$$\langle m|H_{R2}|m' \rangle = -\sum_{i,\gamma}^{t_{dd}} \frac{t_{dd}}{\Delta_{5d}}$$  \(4\)

Here, the indices $m$ and $m'$ run over the cubic-$t_{2g}$-representations, $xy$, $yz$ and $zx$. The symbols $i$ and $\gamma$ are indices for the eight nearest-neighbor La ions and the fivefold La 5$d$ orbitals, respectively. The symbol $\Delta_{5d}$ denotes the characteristic energy-difference between Ti 3$d$ and La 5$d$ orbitals. The transfers $t_{dd}$ are given in terms of Slater-Koster parameters $V_{d\tau\tau}$, $V_{d\tau\tau}$ and $V_{dd\tau}$. It is assumed that these parameters are proportional to $d^{-5}$ with $d$ being the Ti-La bond length. On the basis of the analyses of LDA band structure, we fix these parameters as $V_{dd\tau} = -1.04$ eV, $V_{d\tau\tau} = 0.56$ eV and $V_{dd\tau} = 0$ eV for Ti-La bond length of 3.5 Å, and $\Delta_{5d} = 3.6$ eV [21]. By diagonalizing thus obtained $H_{R2}$, we have evaluated the energy-levels and their representations (see Table II). In the obtained energy-level structure, the threefold $t_{2g}$-levels split into three nondegenerate levels, which is similar to that of $H_{R1}$. Since the representation of the lowest level of $H_{R2}$ is also similar to that of $H_{R1}$, the level splitting of $H_{R1}+H_{R2}$ is well expressed by the sum of the two contributions. Considering the fact that AFM(G) state is stabilized in the region of $\Delta_{1} >0.03$ eV, and
TABLE I: The energy-level structures and the representations of the lowest levels for $H_{R1}$ and $H_{R2}$.

|   | $H_{R1}$ | $H_{R2}$ | $H_{R1}$ | $H_{R2}$ |
|---|----------|----------|----------|----------|
| $\Delta_1$ (eV) | 0.7685/$\varepsilon_{TiLa}$ | 0.0849 | a | 0.6046 | 0.6233 |
| $\Delta_2$ (eV) | 1.5849/$\varepsilon_{TiLa}$ | 0.1443 | b | 0.3900 | 0.4385 |
| c | 0.6945 | 0.6474 |

$\Delta_1$ for $H_{R2}$ is $\sim 0.085$ eV, the crystal field due to the hybridization between Ti 3d and La 5d orbitals ($H_{R2}$) alone turns out to stabilize the AFM(G) spin structure strongly. In addition, the value of $\Delta_1$ is sufficiently large as compared with the coupling constant of the LS interaction in Ti$^{3+}$ ($\zeta_{a}=0.018$ eV) \[22\]. Consequently, the crystal field of La cations dominates over the LS interaction, resulting in the quenched orbital moment. The reduction of the ordered magnetic moment is attributed to the itinerant fluctuation instead of the LS interaction near the metal-insulator phase boundary as discussed in the literature \[12\].

We have also studied the effects of the crystal field of R ions in RTiO$_3$ with R being Pr, Nd and Sm. The analyses of the crystal field Hamiltonian again reproduces the AFM(G) ground state in each compound. Moreover, the gradual decrease of the spin-exchange constant $J$ as R goes from La, Pr, Nd to Sm is reproduced (for example $J$ shows 20\% reduction at Nd from La), which is consistent with the gradual decrease of $T_N$ of these compounds. The orbital states show that the occupation of the $yz$ orbital decreases at sites 1 and 3 as the GdFeO$_3$-type distortion increases while at sites 2 and 4, the $zx$-occupation decreases. As a result, the orbital structure in which sites 1, 2, 3 and 4 are occupied by $\frac{1}{\sqrt{2}}(xy-zx)$, $\frac{1}{\sqrt{2}}(xy-yz)$, $\frac{1}{\sqrt{2}}(xy+zx)$ and $\frac{1}{\sqrt{2}}(xy+yz)$, respectively is progressively stabilized. For example, for Sm, the coefficients take $a=0.63$, $b=0.73$ and $c=0.24$ even without the JT distortion. It has the similar symmetry as that realized in YTiO$_3$ with a large JT distortion, which is consistent with recent RXS study \[23\]. It is interesting to note that, in our results, the character of the orbital symmetry in YTiO$_3$ is retained but quantitatively and continuously decreases toward the type of LaTiO$_3$ with the decreasing GdFeO$_3$-type distortion. When the crystal field from O ion due to the JT distortion is superimposed, our calculation shows that the dominance is taken over by the JT mechanism at $R=Sm$. Through severe competition at $R=Sm$, the Jahn-Teller mechanism comes to control the orbital-spin structure at $R=Gd$ and Y.

In summary, in order to elucidate the origin of the AFM(G) state in RTiO$_3$ with $R=Ti$, we have examined the crystal field of La cations by considering the experimentally observed distortion of the La ions. The crystal field Hamiltonian is constructed by using the experimental position parameters. Based on this Hamiltonian, we have shown that the distortion of the La ions caused by the GdFeO$_3$-type distortion generate the crystal field with lower symmetry, which is similar to the $D_{3d}$ crystal field. Then the threefold degenerate cubic-$t_{2g}$-levels split into three isolated levels. The energies and the spin-exchange constant calculated by the effective Hamiltonian show that the lowest-level occupations in this crystal field stabilize the AFM(G) state, and account for the spin-wave spectrum for LaTiO$_3$ with (1) $J \sim 15.5$ meV, (2) isotropic spin-coupling, and (3) quenched orbital moment. The orbital-spin structure for $R=Pr$, Nd and Sm is also accounted for by the same mechanism. GdFeO$_3$-type distortion has a universal relevance in determining the orbital-spin structure of perovskite compounds in competition with the JT mechanism.

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