

Orbital-Spin Structure and Lattice Coupling in $RTiO_3$ where $R = La, Pr, Nd, \text{ and } Sm$

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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 $R = Pr, Nd, \text{ and } Sm$ 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.

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Various spin and orbital phases and their phase transitions due to their interplay 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 [1]. Cuprate superconductors and manganites with colossal magnetoresistance belong to the TM oxides with $3d e_g$ bands at the Fermi level. Perovskite titanates $RTiO_3$ with R being a rare-earth ion belong to the same type but with $3d t_{2g}$ bands at the Fermi level and shows very different behavior. Particularly, while the above mother materials are commonly typical Mott insulators, $RTiO_3$ shows markedly rich and complicated behaviors possibly due to the above interplay.

The crystal structure of $RTiO_3$ is a pseudocubic perovskite with $GdFeO_3$ -type distortion and exhibits a magnetic phase transition as a function of this distortion [2,3]. The compounds of $R = Gd$ and Y with distortion showing the ferromagnetic (FM) ground state are relatively well understood [4,5]. In contrast, $LaTiO_3$ with relatively small distortion shows AFM(G) order (AFM coupling along all six Ti-O-Ti bonds) with T_N of ~ 130 K. The origin of this AFM(G) order has long been puzzling and controversial. The purpose of the present theoretical study is to solve this puzzle and offer an overall understanding of the interplay in these compounds.

In the perovskite TM compounds, the JT distortion often plays 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 JT distortion in $LaTiO_3$ has not been detected in contrast with the manganites and cuprates [6,7]. Therefore, in $LaTiO_3$, the crystal field of the O ions surrounding the Ti^{3+} ion has a cubic symmetry so that the degeneracy of t_{2g} orbitals is expected to survive. In fact, a number of papers have assumed this degeneracy as we describe below, and this is a source of controversies. Under this circumstance, the AFM(G) 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 electron transfers and by Hund's rule coupling [1,8].

Moreover, a recent neutron-scattering study shows a spin-wave spectrum well described by an isotropic spin-1/2 Heisenberg model with J of ~ 15.5 meV [9]. If the orbital moment is nonzero, the anisotropy appears through the LS interaction. Therefore, the isotropy indicates that the orbital moments are quenched.

Recently, a possible orbital liquid state with small orbital exchange was proposed by assuming the t_{2g} degeneracy and AFM(G) ordering [10]. However, in the titanates, spins and orbitals strongly couple to each other and both degrees of freedom should be determined self-consistently. Since a FM state with antiferro-orbital order was theoretically expected to be more stable in this system, the assumption for the AFM(G) order on this basis is hard to be justified, and the origin of the AFM(G) order is still puzzling.

On the other hand, a possibility of the trigonal (D_{3d}) distortion of the TiO_6 octahedra was also proposed for the origin of the AFM(G) [11]. In this distortion, the TiO_6 octahedron is contracted along the threefold direction, and the threefold-degenerate t_{2g} levels split into a non-degenerate lower a_{1g} level and twofold-degenerate higher e_g levels. Occupations of the a_{1g} orbitals well explain emergence of the AFM(G) and the isotropic spin-wave spectrum. However, this D_{3d} distortion has so far not been clearly detected.

In addition to the JT distortion, the $GdFeO_3$ -type distortion is another generic phenomenon in perovskites. However, it has been assumed mainly to control the bandwidth through the $M-O-M$ angle with M being a TM ion, while its direct effects on interplay of spins and orbitals have not been considered seriously. In fact, the generic $GdFeO_3$ -type distortion hardly distorts a unit TiO_6 octahedron so that it has been assumed that the t_{2g} degeneracy is retained. This is in fact the origin of the puzzles recognized in $LaTiO_3$. It is important to establish the precise estimate about the degree of orbital

degeneracy in the perovskites in the realistic experimental situation since this is the starting point of studies on orbital physics for perovskite compounds.

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 the R ions. This mechanism competes with that of JT distortion and LS interaction. We construct Hamiltonians for the crystal field of La ions in LaTiO_3 . Analyses of these Hamiltonians show that shifts of La ions due to the GdFeO_3 -type distortion turn out to generate a crystal field which is similar to the D_{3d} crystal field. As a result, the threefold-degenerate cubic- t_{2g} levels split into three non-degenerate 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 study the effects of the crystal field of the R ions in RTiO_3 with R being Pr, Nd, and Sm. Again experimentally observed orbital structure as well as the reduction of spin exchange are reproduced. We point out the importance of the GdFeO_3 -type distortion as a generic control mechanism of orbital-spin structure through generating the R crystal field in the perovskite compounds, which has been so far overlooked.

In the GdFeO_3 -type distortion, the R ions shift mainly along the $(1, 1, 0)$ axis or the b axis, and slightly along the $(1, -1, 0)$ axis or the a axis. There are two kinds of RO planes (plane 1 and plane 2) stacking alternately along the c axis. In plane 1, the R ions shift in the negative direction along the b axis while they shift in the positive direction in plane 2. Consequently, the crystal field from the R cations is distorted from a cubic symmetry. For sites 1 and 2, the distances between the Ti ion and the R ions located in the $\pm(1, 1, 1)$ directions decrease while those along the $\pm(1, 1, -1)$ directions increase [see Fig. 1(a)]. On the other hand, the distances along $\pm(1, 1, -1)$ directions decrease while those along $\pm(1, 1, 1)$ directions increase for sites 3 and 4. In Fig. 1(b), the stacking of each site is presented. The changes of the other Ti- R distances are rather small. Since the nominal valence of R ion is $3+$, we expect that the Ti $3d$ orbitals directed along the shorter Ti- R bonds are lowered in energy because of the attractive Coulomb interaction. Without any distortions of the TiO_6 octahedra, the crystal field of the ligand oxygens has a cubic symmetry. When we introduce the crystal field of the R ions (H_{R1}) as a perturbation, the threefold degeneracy of the cubic- t_{2g} levels splits. Here, for simplicity, we take H_{R1} by assuming that there exist point charges with $+3$ valence on each R ion. The Coulomb interaction between an electron on the Ti $3d$ orbital and a La^{3+} ion is given by using the dielectric constant ϵ_{TiR} as $v(\mathbf{r}) = -\sum_i (Z_R e^2 / \epsilon_{\text{TiR}} |\mathbf{R}_i - \mathbf{r}|)$, where \mathbf{R}_i expresses the coordinates of the i th R ion, and $Z_R (= +3)$ is the nominal valence of La^{3+} ion. We calcu-

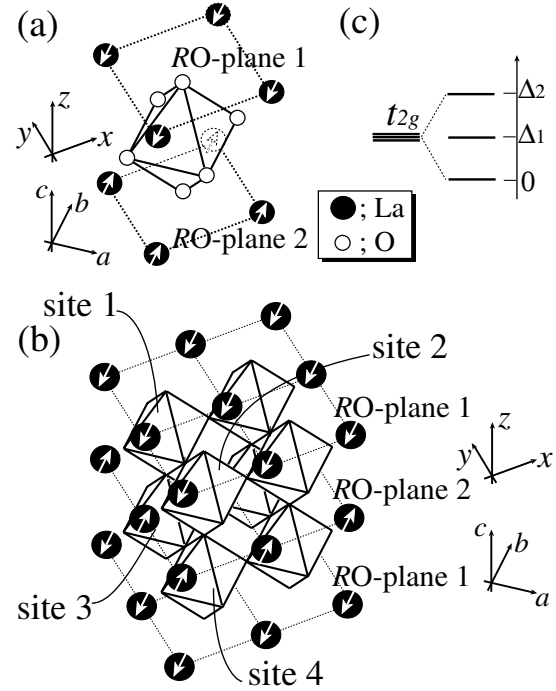


FIG. 1. (a) Displacements of the R ions around a TiO_6 octahedron (site 1) in the GdFeO_3 -type structure are presented by arrows (see text). Note that rotations of the octahedra due to the GdFeO_3 -type distortion are not presented. (b) Stacking of the TiO_6 octahedra as well as shifts of the R ions are presented. Note that Ti and O ions are not explicitly presented. (c) Energy-level structure in the crystal field of the R ions.

late the following matrix elements, $\langle m|v(\mathbf{r})|m'\rangle = \int d\mathbf{r} \varphi_{3d,m}^* v(\mathbf{r}) \varphi_{3d,m'}$ with $\varphi_{3d,m} = R_{3d,m}(r) Y_{2m}(\theta, \phi)$ by using experimentally measured coordinates of the La ions [6]. Here, the integer $m (= -2, \dots, 2)$ is the magnetic quantum number.

By diagonalizing H_{R1} , we can evaluate the $3d$ -level energies and their representations. The t_{2g} orbitals split into three isolated levels as shown in Fig. 1(c). The energy levels Δ_1 and Δ_2 are $0.77/\epsilon_{\text{TiLa}}$ eV and $1.58/\epsilon_{\text{TiLa}}$ eV, respectively. The representations of the lowest levels at each site can be specified by the linear combinations of xy , yz , and zx orbitals as $axy + cyz + bzx$, $axy + byz + czx$, $axy - cyz - bzx$, and $axy - byz - czx$, respectively, where $a^2 + b^2 + c^2 = 1$. The coefficients take $a = 0.60$, $b = 0.39$, and $c = 0.69$. 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 lowest orbitals in these D_{3d} crystal fields are $(1/\sqrt{3})(xy + yz + zx)$, $(1/\sqrt{3})(xy + yz + zx)$, $(1/\sqrt{3})(xy - yz - zx)$, and $(1/\sqrt{3})(xy - yz - zx)$, respectively. In the previous study [11], this trigonal-axes configuration was referred to as config. 3, and the D_{3d} crystal fields with config. 3 proved to strongly stabilize the AFM(G) structure. Here, we note that this orbital ordering is likely to induce the D_{3d} octahedral distortions with config. 3.

We next discuss the stability of the magnetic state in the crystal field of H_{R1} . For this purpose, we employ the effective spin-pseudospin Hamiltonian [4]: $H_{\text{eff}} = H_{\text{cry}} + H_{\text{st}}$. H_{cry} denotes the crystal field acting on the Ti t_{2g} orbitals. H_{st} is the spin-pseudospin term, in which the threefold t_{2g} orbitals are represented by the pseudo-spin-1 operator τ . 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 [12]. In this d - p model, the full degeneracies of the Ti $3d$ and O $2p$ orbitals as well as the on-site Coulomb and exchange interactions are taken into account [5]. The on-site Coulomb interactions are expressed using Kanamori parameters u , u' , j , and j' which satisfy the following relations [13,14]: $u = U + (20/9)j$, $u' = u - 2j$, and $j = j'$. Here, U gives the magnitude of the multiplet-averaged d - d Coulomb interaction. The charge-transfer energy Δ is defined using energies of the bare Ti $3d$ and O $2p$ orbitals ε_d^0 and ε_p as $\Delta = \varepsilon_d^0 + U - \varepsilon_p$. The parameters are estimated by the analyses of photoemission spectra and the first-principles calculations [15]. Substituting H_{R1} for H_{cry} , we calculate energies for several magnetic structures by applying the mean-field approximation. In Fig. 2, we plot the calculated energies as functions of Δ_1 ($= 0.77/\epsilon_{\text{TiR}}$). We tune the magnitude of Δ_1 by varying ϵ_{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, Δ_1 is much larger than $k_B T_N$ so that the orbital occupation is restricted to the lowest level. We estimate the spin-exchange constants for each Ti-Ti bond in the subspace of singly occupied lowest levels. The spin-exchange constant J is represented as $J = (E_{\uparrow\uparrow} - E_{\uparrow\downarrow})/2S^2$ with $E_{\uparrow\uparrow}$ and $E_{\uparrow\downarrow}$ being the energy gains of the Ti-Ti bond for $\uparrow\uparrow$ and $\uparrow\downarrow$ pairs, respectively. For LaTiO_3 , the values of J along the x -, y -, and z axes take as $J_x = 18.5$ meV, $J_y = 18.5$ meV, and $J_z = 19.7$ meV, respectively, which well reproduce the spin-wave spectrum with isotropic exchange constant of ~ 15.5 meV. We have confirmed that the values of J as well as the orbital

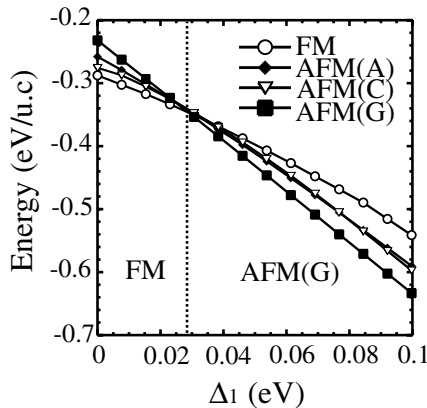


FIG. 2. Energies for several magnetic structures under the crystal field of H_{R1} are plotted as functions of Δ_1 .

wave functions obtained by the present calculations hardly change (within the accuracy of a few %) even if the further O and R ions are taken into account.

We further note that the crystal field of La ions 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 $3d$ orbitals and unoccupied orbitals on the La ions. We next examine the latter effects for LaTiO_3 . We construct the Hamiltonian for hybridization between the Ti $3d$ and La $5d$ orbitals (H_{R2}) by using the second-order perturbational expansion in terms of the transfers between these orbitals (t^{dd}). The expression of the matrix element of H_{R2} is $\langle m|H_{R2}|m'\rangle = -\sum_{i,\gamma} (t_{m;i\gamma}^{dd} t_{m';i\gamma}^{dd} / \Delta_{5d})$. Here, the indices m and m' run over the cubic- t_{2g} representations, xy , yz , and zx . The symbols i and γ are indices for the eight nearest-neighbor La ions and the fivefold La $5d$ orbitals, respectively. The symbol Δ_{5d} denotes the characteristic energy difference between the Ti t_{2g} and La $5d$ orbitals. The transfers t^{dd} are given in terms of Slater-Koster parameters $V_{dd\sigma}$, $V_{dd\pi}$, and $V_{dd\delta}$. 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 $V_{dd\sigma} = -1.04$ eV, $V_{dd\pi} = -0.56$ eV, and $V_{dd\delta} = 0$ eV for Ti-La bond length of 3.5 \AA , and $\Delta_{5d} = 3.6$ eV [16]. By diagonalizing thus obtained H_{R2} , we have evaluated the energy levels and their representations (see Table I). The threefold t_{2g} levels split into three nondegenerate levels similarly to that of H_{R1} . Since the lowest orbital 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 these two contributions. Considering the fact that AFM(G) state is stabilized in the region of $\Delta_1 > 0.03$ eV, and Δ_1 for H_{R2} is ~ 0.08 eV, the crystal field due to the hybridization (H_{R2}) alone turns out to stabilize the AFM(G) state strongly. In addition, Δ_1 is sufficiently larger than the LS coupling constant in Ti^{3+} ($\zeta_d = 0.018$ eV) [17]. Consequently, the crystal field of La ions dominates over the LS interaction, resulting in the quenched orbital moment. The reduction of the ordered moment is attributed to the itinerant fluctuation instead of the LS interaction near the metal-insulator phase boundary as discussed in the literature [11].

We have also studied the effects of the crystal field of the R ions in RTiO_3 with R being Pr, Nd, and Sm. Analyses of the crystal field Hamiltonian again reproduce the AFM(G) ground state in each compound.

TABLE I. Energy-level structures and representations of the lowest levels for levels for H_{R1} and H_{R2} .

	H_{R1}	H_{R2}	H_{R1}	H_{R2}
Δ_1 (eV) : $0.77/\epsilon_{\text{TiLa}}$		0.08	a : 0.60	0.62
Δ_2 (eV) : $1.58/\epsilon_{\text{TiLa}}$		0.14	b : 0.39	0.44
			c : 0.69	0.65

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 2 and 4 as the GdFeO₃-type distortion increases while at sites 1 and 3, the zx occupation decreases. As a result, the orbital structure in which sites 1, 2, 3, and 4 are occupied by $(1/\sqrt{2})(xy + yz)$, $(1/\sqrt{2})(xy + zx)$, $(1/\sqrt{2})(xy - yz)$, and $(1/\sqrt{2})(xy - zx)$, 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 YTiO₃ with a large JT distortion, which is consistent with recent RXS result [18]. It is interesting to note that, in our results, the character of the orbital symmetry in YTiO₃ is retained but quantitatively and continuously decreases toward the type of LaTiO₃ with decreasing GdFeO₃-type distortion. When the crystal field from O ions due to the JT distortion is superimposed, our calculation shows that the dominance is taken over by the JT mechanism at $R = \text{Sm}$. Through severe competition at $R = \text{Sm}$, the JT mechanism comes to control the orbital-spin structure at $R = \text{Gd}$ and Y . We note that since the JT mechanism is not taken into account, a recent puzzling finding of isotropic ferromagnetism in YTiO₃ [19] is not resolved in this study and is left for further study.

In summary, we have shown that in LaTiO₃ the t_{2g} degeneracy is eventually lifted by the R ions in the GdFeO₃-type structure, which generate a crystal field with nearly trigonal symmetry. We note that this distortion exists irrespective of the $3d$ electronic state [20] in contrast with the JT distortion. The lift of Ti $3d$ degeneracy occurs just as a consequence of the crystal field from R ions. In this sense, the mechanism proposed here is not a Jahn-Teller but a new mechanism, which is inherent and universal with GdFeO₃-type distortion. It has been shown that the lowest-orbital occupation in this crystal field stabilizes the AFM(G) state, and well explains the spin-wave spectrum of LaTiO₃ with (i) $J \sim 15.5$ meV, (ii) isotropic spin coupling, and (iii) quenched orbital moment. The orbital-spin structures for $R = \text{Pr}$, Nd , and Sm with relatively small JT distortions are also accounted for by the same mechanism. Here, we mention that since the magnitude of JT distortion is increased as the GdFeO₃-type distortion increases in the Ti systems, the competition between the crystal field from O ions and that from R ions comes about. In contrast with the dominance of La crystal field in LaTiO₃, the large JT distortion dominates over the R crystal field in YTiO₃ and GdTlO₃ although the GdFeO₃-type distortion is rather large. Actually, as observed by several experiments, the orbital structures in these compounds are well character-

ized by the JT distortion, which leads to a FM ground state. We emphasize that through generating the R crystal field, the GdFeO₃-type distortion has a universal relevance in determining the orbital-spin structure of the perovskite compounds in competition with the JT mechanism, which has been overlooked so far. Since the GdFeO₃-type distortion is a universal phenomenon, which is seen in a large number of perovskite compounds, this mechanism may also play important roles in other compounds of this type.

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Note added.—After the submission of this Letter, the D_{3d} distortions of the TiO₆ octahedra with config. 3 was actually reported in recent diffraction study [21]. In addition, the NMR spectrum for LaTiO₃ recently turned out to be well described by the present orbital ordering model [22]. These facts agree with the present predictions and support our theory.

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