Lattice Distortion and Magnetic Ground State of YTiO$_3$ and LaTiO$_3$

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Effects of lattice distortion on the magnetic ground state of YTiO$_3$ and LaTiO$_3$ are investigated on the basis of accurate tight-binding parametrization of the $t_{2g}$ electronic structure extracted from the local-density approximation. The complexity of these compounds is related with the fact that the $t_{2g}$-level splitting, caused by lattice distortions, is comparable with the energies of superexchange and spin-orbit interactions. Therefore, all these interactions are equally important and should be treated on an equal footing. The Hartree-Fock approximation fails to provide a coherent description simultaneously for YTiO$_3$ and LaTiO$_3$, and it is essential to go beyond.

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Among the large variety of transition-metal perovskite oxides, YTiO$_3$ (YTO) and LaTiO$_3$ (LTO) have received a particular attention. Both are regarded as prototypical examples of Mott-Hubbard insulators. It appears, however, that these, formally isoelectronic compounds (having one 3$d$ electron in the triply-degenerate $t_{2g}$ shell), exhibit very different magnetic properties: YTO is a ferromagnet, whereas LTO is a three-dimensional (G-type) antiferromagnet. Another puzzling feature is the nearly isotropic magnon spectrum, observed both in YTO and LTO despite a noticeable orthorhombic distortion.

Owing to the fractional population of the $t_{2g}$ manifold, the orbital degrees of freedom are expected to play a very important role and affect the magnetic properties. However, the theories proposed in this context crucially depend on several factors, and there are two points of view which are currently discussed in the literature. (i) The first one is based on the generalization of the superexchange (SE) theory of spin and orbital interactions between degenerate $t_{2g}$ levels. It starts with the spin-orbital SE model by Kugel and Khomskii (K&K) and exploits the idea of orbital fluctuations, which are inherent to this model. (ii) The spin and orbital structure is fully determined by lattice distortions, which lift the orbital degeneracy. The role of (relativistic) spin-orbit (SO) interaction has been also emphasized.

Therefore, there are two important questions, which can be clarified on the basis of electronic structure calculations. (i) What is the effect of the lattice distortion on the electronic structure of YTO and LTO? Particularly, how do the $t_{2g}$ levels split by this distortion? (ii) What is the hierarchy between the $t_{2g}$-level splitting, the SE interaction energy, and the SO coupling? The SE interaction in the bond $\mathbf{i}-\mathbf{j}$ is basically the kinetic energy gain, which is acquired by the $t_{2g}$ electron occupying the atomic orbital $|\mathbf{i}\rangle$ at the site $\mathbf{i}$ in the process of virtual hoppings into the subspace of unoccupied orbitals $\hat{P}_j$ at the (neighboring) site $\mathbf{j}$, and vice versa.

\[
\varepsilon_{\sigma\sigma'}^{\mathbf{i}\mathbf{j}} = -\frac{\alpha_{\mathbf{i}\mathbf{j}}^{\sigma\sigma'}}{\Delta E_{\sigma\sigma'}} \equiv -\frac{(\langle \mathbf{i}|\hat{P}_j|\mathbf{j}\rangle + (\mathbf{i} \leftrightarrow \mathbf{j}))}{\Delta E_{\sigma\sigma'}}. \tag{1}
\]

where $\sigma$ and $\sigma'$ are the spin states associated with the sites $\mathbf{i}$ and $\mathbf{j}$, respectively, and the transfer interactions $\hat{t}_{\mathbf{i}\mathbf{j}}$ are allowed only between orbitals with the same spin. For the nearest-neighbor interactions in the perovskite lattice, it is sufficient to consider two collinear configurations, $\sigma\sigma'=\uparrow\uparrow$ and $\uparrow\downarrow$, and select the ones which minimize the total energy gain $\varepsilon_T=\frac{1}{2}\sum_{\mathbf{i}\mathbf{j}}\varepsilon_{\mathbf{i}\mathbf{j}}^{\sigma\sigma'}$. In the case of the antiferromagnetic (AFM) alignment, $\sigma\sigma'=\uparrow\downarrow$, all orbitals with the spin $\uparrow$ at the site $\mathbf{j}$ are located in the unoccupied part of the spectrum and available for the hoppings. Therefore, $\hat{P}_j=1$ and $\alpha_{\mathbf{i}\mathbf{j}}^{\uparrow\downarrow}=(\langle \mathbf{i}|\hat{P}_j|\mathbf{j}\rangle + (\mathbf{i} \leftrightarrow \mathbf{j}))$. In the ferromagnetic (FM or F) case, $\sigma\sigma'=\uparrow\uparrow$, the occupied orbital $|\mathbf{j}\rangle$ should be excluded from the subspace $\hat{P}_j$. This yields $\hat{P}_j=1-|\mathbf{j}\rangle\langle \mathbf{j}|$ and $\alpha_{\mathbf{i}\mathbf{j}}^{\uparrow\uparrow}=\alpha_{\mathbf{i}\mathbf{j}}^{\uparrow\downarrow}-\Delta\alpha_{\mathbf{i}\mathbf{j}}$, where $\Delta\alpha_{\mathbf{i}\mathbf{j}}=2\langle \mathbf{i}|\hat{t}_{\mathbf{i}\mathbf{j}}|\mathbf{j}\rangle^2$. $\Delta E_{\sigma\sigma'}$ is the on-site Coulomb interaction between two 3$d$ electrons, which also depends on the spin state: $\Delta E_{\uparrow\uparrow}=U$ while $\Delta E_{\uparrow\downarrow}=U-J$, where $U$ is the Coulomb repulsion and $J$ is the intra-atomic exchange coupling. Because of this $J$, the “orthogonal” orbitals, which do not interact via the kinetic energy term, $(\langle \mathbf{i}|\hat{t}_{\mathbf{i}\mathbf{j}}|\mathbf{j}\rangle=0)$, tend to stabilize the FM structure. In the opposite limit $\Delta\alpha_{\mathbf{i}\mathbf{j}}\ll\alpha_{\mathbf{i}\mathbf{j}}^{\uparrow\downarrow}$, the FM alignment does not lead to any energy gain, and the coupling will be AFM.

The alternation of occupied orbitals at different atomic sites (the orbital ordering – OO) should be found variationally and minimize $\varepsilon_T$. This is the basic idea of the K&K theory. The orbital interactions have the same origin as the spin SE. Therefore, the energy gain associated with the OO is of the order of $\varepsilon_T \sim 1/U$, and there is a strong interplay between spin and orbital degrees of freedom. In the degenerate case, one can always find some orthogonal configuration of the occupied orbitals, which in the single-determinant Hartree-Fock (HF) approach corresponds to the FM ground state (GS). However, the HF solutions remain degenerate with respect to some number of orbital configurations. This degeneracy leaves a room for orbital fluctuations, which may alter the HF conclusion about the form of the magnetic GS.

An alternative mechanism of the OO is the lattice distortions, which lifts the orbital degeneracy and acts as an external field constraining the form of occupied orbitals in Eq. (1). Since the orbital degeneracy is lifted,
the HF approach may be justified. This mechanism is proportional to the electron-phonon coupling, and will dominate over the K&K SE mechanism in the large-U limit. Then, the OO does not depend on the magnetic state and the mapping onto the Heisenberg model yields the following expression for $J_{ij} = \frac{1}{2}(\epsilon_{ij}^{\uparrow \downarrow} - \epsilon_{ij}^{\uparrow \uparrow})$:

$$J_{ij} = \frac{\alpha_{ij}^{\uparrow \downarrow}}{2} \frac{J/U - \Delta \alpha_{ij}/\alpha_{ij}^{\uparrow \downarrow}}{U - J},$$

(2)

which can be both FM and AFM, depending on the ratio of $J/U$ and $\Delta \alpha_{ij}/\alpha_{ij}^{\uparrow \downarrow}$.

Let us consider the second scenario and assume that all relevant interactions can be described in the basis of some local $t_{2g}$ orbitals $|X\rangle$, $|Y\rangle$, and $|Z\rangle$, associated with the Ti sites. Then, the occupied orbital at the site 1 (see Fig. 1) can be searched in the form $|1\rangle = \sin \theta \cos \phi |X\rangle + \sin \theta \sin \phi |Y\rangle + \cos \theta |Z\rangle$, and the ones at the sites 2 and 3 are automatically generated from $|1\rangle$ using the symmetry operations of the $D_{1h}^{2}$ group (the $180^\circ$ rotations around the orthorhombic $a$ and $c$ axes, respectively). In principle, $\theta$ and $\phi$ are uniquely determined by the lattice distortion.

However, it is sometimes attempted to approach the problem from the opposite side and find $\theta$ and $\phi$ from the condition $J_{12} = J_{13}$, suggested by recent neutron scattering studies. In order to illustrate this idea, let us consider a simplified model and choose $|X\rangle$, $|Y\rangle$, and $|Z\rangle$ as $|yz\rangle$, $|zx\rangle$, and $|xy\rangle$, respectively, in the cubic coordinate frame shown in Fig. 1. The transfer interactions are parameterized according to Slater and Koster (S&K): i.e., the only nonvanishing matrix elements along $z$ are $t_{12}^{XX} = t_{13}^{YY} = t$, etc. Then, it is easy to verify that the condition $J_{12} = J_{13}$ leads to the following OO:

$|1\rangle = |2\rangle = \frac{1}{\sqrt{2}} (|xyz\rangle + |yoz\rangle + |zxy\rangle)$,

$|3\rangle = |4\rangle = \frac{1}{\sqrt{2}} (|xyz\rangle - |yoz\rangle - |zxy\rangle)$,

which does not depend on $J/U$. This is precisely the OO proposed in Ref. 17. It is compatible with the orthorhombic $D_{1h}^{2}$ symmetry, and corresponds to some local trigonal distortion, caused by either oxygen or La displacements.

This result, however, prompts several new questions. (i) The magnetic coupling is expected to be AFM for all reasonable values of $J/U$. Therefore, this would explain the experimental situation in LTO, but not in YTO. (ii) It is not clear whether this OO is compatible with the actual experimental distortion observed in LTO. Note that in the $D_{1h}^{2}$ group, only inversion centers coincide with the Ti sites. Therefore, the local $t_{2g}$-level splitting is controlled by 5 independent parameters, which may include both trigonal and Jahn-Teller modes. All distortions are formally equivalent, at least from the viewpoint of $D_{1h}^{2}$ symmetry, and $a$ priori there is no reason why the particular trigonal mode should dominate. In addition to the $t_{2g}$-level splitting, the crystal distortion may also affect the transfer interactions through the buckling of the Ti-O-Ti bonds. (iii) What are the roles of the K&K mechanism and the SO interaction? Are they totally quenched by the lattice distortion, as it was suggested in Refs. S&K? The situation should be carefully checked, and it is important to turn to first-principles calculations, which automatically include all these ingredients.

We use the linear-muffin-tin-orbital (LMTO) method and employ the tight-binding (TB) parametrization of the $t_{2g}$ bands, obtained in the local-density approximation (LDA) for the experimental crystal structures. The latter step is achieved through the downfolding procedure. A similar analysis has been undertaken in Ref. 17. (i) Each LMTO eigenvector is divided in two parts: $|t\rangle$, which is expanded over the local $t_{2g}$ orbitals $|X\rangle$, $|Y\rangle$, and $|Z\rangle$ at each Ti site, and $|r\rangle$, which is expanded over the rest of the basis functions. The corresponding secular equation, which holds for the LMTO Hamiltonian $\hat{H}$, is given by

$$\langle \hat{H}_{tt} - E |t\rangle + \langle \hat{H}_{tr} |r\rangle = 0,$$

(3)

$$\langle \hat{H}_{rt} |t\rangle + \langle \hat{H}_{rr} - E |r\rangle = 0.$$  

(4)

(ii) By eliminating $|r\rangle$ from Eq. 4 one obtains an effective $E$-dependent Hamiltonian: $\hat{H}_{tt}^{\text{eff}}(E) = \hat{H}_{tt} - \hat{H}_{tr}(\hat{H}_{rr} - E)^{-1}\hat{H}_{rt}$, where $|t\rangle$ obeys the condition $\langle t|\hat{S}|t\rangle = 1$ and $\hat{S}(E)^2 = 1 + \hat{R}_{tr}(\hat{H}_{rr} - E)^{-2}\hat{R}_{rt}$.

(iii) The TB parameters $\hat{t} = \|\hat{t}_{ij}\|$ are obtained after the orthonormalization of the vectors $|t\rangle \rightarrow \|\hat{t}_{ij}\|$: $\hat{t}(E) = \hat{S}^{-1/2}(E)\hat{R}_{tt}^{\text{eff}}(E)\hat{S}^{-1/2}(E)$.

(5)

Finally, $E$ is fixed to the center of the $t_{2g}$ band.

The choice of the local $t_{2g}$ orbitals is somewhat ambiguous. In our case we first calculated the site-diagonal elements of the density matrix in the basis of all Ti(3d) orbitals and taking into account the contributions of only the $t_{2g}$ bands shown in Fig. 2. This yields the $5 \times 5$ matrices at each Ti site. Then, we assign three most populated orbitals obtained after the diagonalization of these matrices to $|X\rangle$, $|Y\rangle$, and $|Z\rangle$.

The mapping onto the TB model is nearly perfect and well reproduces the behavior of LMTO bands (Fig. 2).
Then, the site-diagonal elements of \( t_{ij} \) describe the crystal-field (CF) splitting caused by lattice distortions, and the off-diagonal elements have a meaning of transfer interactions. Thus, we are ready to calculate the SE interactions in the strong coupling limit, assuming that the form of occupied orbitals is solely determined by \( t_{ij} \), and using these orbitals in subsequent calculations of \( \alpha_{ij}^{\uparrow\downarrow} \) and \( \Delta \alpha_{ij} \). The results are summarized in Table I.

(i) The CF splitting is larger in YTO, mainly due to the Jahn-Teller distortion\(^9\), which is reflected in the upward shift of one of the \( t_{2g} \) levels\(^{15}\). The CF splitting in LTO is not particularly strong (in fact it is considerably weaker than the model estimates presented in Refs.\(^7\,8\)). The inter-atomic interactions \( \alpha_{ij}^{\uparrow\downarrow} \) are larger in the less distorted LTO, that well correlates with the larger \( t_{2g} \) bandwidth (Fig. 2). (ii) Both compounds exhibit certain tendency to \( A \)-type antiferromagnetism, which is especially strong in YTO: since \( \Delta \alpha_{12} \sim 0 \) and \( \Delta \alpha_{13} \sim \alpha_{13}^{\uparrow\downarrow} \), the bonds 1-2 and 1-3 are expected to be FM and AFM, respectively, for all physical values of \( J/U \). Therefore, the crystal distortion alone cannot explain the FM GS of YTO.\(^{18}\) The situation is somewhat milder in LTO where the experimental G-type AFM ordering can be stabilized for \( J/U < \Delta \alpha_{12} / \alpha_{13}^{\uparrow\downarrow} \sim 0.37 \). However, even in this case the interatomic magnetic interactions are expected to be anisotropic. (iii) Realistic estimates for the on-site Coulomb interaction \( U \) in the \( t_{2g} \) band typically vary from 3.2 eV, suggested by constraint-LDA calculations and taking into account the empirical screening by the \( e_g \) electrons,\(^{10,20} \) to 4.4 eV suggested by photoemission studies.\(^{10,20} \) The intra-atomic exchange coupling can be estimated as \( J \sim 0.9 \text{ eV}. \) Therefore, \( \varepsilon_T \) can be as large as 10-40 meV per one Ti site. This value can be used as a rough estimate for the OO stabilization energy caused by SE interactions, which is \textit{comparable} with the CF splitting. Therefore, the K\&K mechanism remains robust even in the distorted perovskite compounds. As we will see below, it may help to explain the experimentally observed magnetic ground state in YTO (but not in LTO). (iv) The SO interaction at the Ti sites, \( \xi \approx 23 \text{ meV} \), is \textit{also comparable} with the CF splitting, and \textit{exceeds} the total energy difference between different magnetic states (Table II). Therefore, it is reasonable to expect essentially noncollinear magnetic GS with a considerable contribution of the orbital magnetic moments.\(^{21}\)

All these trends are clearly seen in HF calculations, in which the one-electron TB Hamiltonian for the \( t_{2g} \) bands was combined with the on-site Coulomb and exchange interactions extracted from the constraint-LDA calculations (unless it is specified otherwise) and (optionally) the SO interaction. The HF potential was treated in the rotationally-invariant form.\(^{22}\)

It is true that both in LTO and YTO, the OO is strongly constrained by the lattice distortion so that the visual change of the OO is not particularly strong in the row of FM, A-, C-, and G-type AFM states (Fig. 3). The basic question, however, is how this change is reflected in the change of other parameters. Our main concern is the behavior of inter-atomic magnetic interactions \( J_{ij} \). Since \( J_{ii} \) may depend on the magnetic state (through the change of the OO), Eq. 2 is no longer valid. Instead, we evaluate \( J_{ii} \) separately for different magnetic states using the second derivatives of the total energy with respect to the angles between spin magnetic moments.\(^{21}\) The results summarized in Table II clearly show that even tiny change of the OO may produce a dramatic change of \( J_{ii} \). In addition to the A-type AFM ordering, expected from the lattice distortion, the FM state (\( J_{12} > 0, J_{13} > 0 \)) can be stabilized by the K\&K mechanism both in YTO and LTO.\(^{22}\) Since \( J_{12} > 0 \), the G-type AFM state is unstable. In LTO it can be stabilized only for \( U \sim 4.5 \text{ eV} \) (which leads to \( J_{12} = -0.3 \) and \( J_{13} = -3.4 \text{ meV} \)). However, this \( U \) will also destroy the FM GS in YTO (\( J_{12} = -0.5 \) and \( J_{13} = -0.7 \text{ meV} \)). Thus, there is no such parameter \( U \) which would account for the experimental behavior of both YTO and LTO on the level of mean-field HF calculations. Contrary to the experimental finding,\(^{21} \) the magnetic interactions are strongly anisotropic.

The SO interaction gives rise to a noncollinear magnetic ordering.\(^{21} \) However, it does not solve the prob-
lens of the HF description. The magnetic GS realized in YTO is \(G_\alpha-G_\beta-C_\gamma\), which is consistent with the neutron-scattering data. Both spin (\(M_S\)) and orbital (\(M_L\)) magnetic moments have nonvanishing projections onto all three orthorhombic axis \(a\), \(b\), and \(c\), which are ordered according with the \(G\)-, \(A\)-, and \(F\)-type, respectively. The vectors themselves are given by (in \(\mu_B\): refered to the site 1): \(M_S=\begin{pmatrix} 0.05,0.83,0.34 \end{pmatrix}\) and \(M_L=\begin{pmatrix} -0.23,-0.33,0.03 \end{pmatrix}\). The relative weight of the \(F\) and \(A\) components in this structure is very sensitive to the value of \(U\). The \(F\) component will dominate for smaller \(U\), due to the enlarged K&K contribution to the OO: e.g. \(M_S=\begin{pmatrix} -0.07,-0.14,0.96 \end{pmatrix}\) and \(M_L=\begin{pmatrix} 0.17,0.14,-0.08 \end{pmatrix}\) for \(U=2.5\) eV. The magnetic GS obtained in LTO on the level of HF calculations is \(C_\alpha-F_\beta-A_\gamma\), which has large \(A\) component along the \(c\) direction: \(M_S=\begin{pmatrix} -0.13,0.18,0.89 \end{pmatrix}\) and \(M_L=\begin{pmatrix} -0.14,-0.07,-0.21 \end{pmatrix}\). The G-type AFM structure is totally excluded from \(C_\alpha-F_\beta-A_\gamma\). Therefore, there is a qualitative inconsistency between results of HF calculations and the experimental data for LTO. Formally, the problem can be resolved by using larger \(U=4.5\) eV, which enforces the strong-coupling limit (Table 1) and leads to the new magnetic GS: \(A_\alpha-G_\beta-C_\gamma\) with \(M_S=\begin{pmatrix} 0.31,0.88,0.14 \end{pmatrix}\) and \(M_L=\begin{pmatrix} -0.19,-0.23,0.04 \end{pmatrix}\). However, the same \(U\) would lead to the new magnetic GS also in YTO: \(C_\alpha-F_\beta-A_\gamma\) with \(M_S=\begin{pmatrix} 0.11,-0.19,0.72 \end{pmatrix}\) and \(M_L=\begin{pmatrix} 0.09,0.12,-0.09 \end{pmatrix}\), in disagreement with the experiment.

In summary, the lattice distortion alone does not provide a coherent explanation for the unusual magnetic properties of YTO and LTO. The complexity of these compounds is related with the fact that the CF splitting, the SE and SO interaction energies are of the same order of magnitude, and should be treated on an equal footing beyond the mean-field HF approximation.

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12. \(J\) is responsible for the first Hund rule. Interactions enforcing the second Hund rule are neglected in Eq. 11, but taken into account in HF calculations, discuss below.
13. \(\alpha_{12} = 2 - \sin^2 \theta\), \(\Delta \alpha_{12} = 2 (\cos^2 \theta + \frac{1}{2} \sin^2 \theta \sin 2\phi)^2\), \(\alpha_{13} = 2 \sin^2 \theta\), and \(\Delta \alpha_{13} = 2 \sin^4 \theta\), in units of \(t^2\).
14. The realistic parameters reveal a strong deviation from the S&K form, which holds for the cubic lattice, as well as the mixture between \(t_{2g}\) and \(e_g\) orbitals. All TB parameters are available at the request via e-mail.
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17. The TiO\(_6\) octahedron in YTO has two long and four short Ti-O bonds. Thus, the \(t_{2g}\) level interacting mainly with the short-distanced oxygen sites will be split off and shifted to the higher energies due to the Ti-O hybridization.
18. The behavior is qualitatively consistent with the OO shown in Fig. 1. The occupied orbitals are largely nonorthogonal along the \(c\) direction. This should lead to the AFM spin coupling. The nearly orthogonal occupied orbitals in the...
plane give rise to the FM coupling. The standard constraint-
LDA calculations yield $U \approx 8$ eV, which is too large.

Parameters reported in Ref. 10 have been recalculated as
$U = F^0$ and $J = (F^2 + F^4)/14$, in terms of Slater’s integrals.

The magnetic state is locally stable if the signs of $J_{ij}$ are
consistent with the form of this state.

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