Origin of the orbital and spin orderings in rare-earth titanates

Julien Varignon,1 Mathieu N. Grisolia,1 Daniele Preziosi,1 Philippe Ghosez,2 and Manuel Bibes1

1Unité Mixte de Physique, CNRS, Thales, Université Paris Sud, Université Paris-Saclay, 91767, Palaiseau, France
2Theoretical Materials Physics, Q-MAT, CESAM, Université de Liège (B5), B-4000 Liège, Belgium

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Rare-earth titanates RTiO3 are Mott insulators displaying a rich physical behavior, featuring mostly orbital and spin orders in their ground state. The origin of their ferromagnetic to antiferromagnetic transition as a function of the size of the rare-earth however remains debated. Here we show on the basis of symmetry analysis and first-principles calculations that although rare-earth titanates are nominally Jahn-Teller active, the Jahn-Teller distortion is negligible and irrelevant for the description of the ground state properties. At the same time, we demonstrate that the combination of two antipolar motions produces an effective Jahn-Teller-like motion which is the key of the varying spin-orbital orders appearing in titanates. Thus, titanates are prototypical examples illustrating how a subtle interplay between several lattice distortions commonly appearing in perovskites can produce orbital orderings and insulating phases irrespective of proper Jahn-Teller motions.

ABO3 oxide perovskites, with partly filled d states on the B site, exhibit a rich physical behavior originating from the intimate coupling between structural, electronic (charge and orbital) and magnetic degrees of freedom [1]. Typical examples are the rare-earth vanadates R3+V3+O3 (3d2–t2g2 electronic configuration on V3+ ions) that exhibit two different spin and orbital orders yielding distinct symmetries for the ground state at low temperature [2–5]. With the electronic degeneracy of Ti3+ – 3d1–t2g configuration, – rare-earth titanates R3+Ti3+O3 are often expected to be another textbook example of such a subtle interplay between orbital and spin orders.

Rare-earth titanates are Mott insulators, which according to their small tolerance factor, adopt a common orthorhombic Pbnm structure characterized by large oxygen cage rotations [4–6], i.e. a−a−c+ antiferrodistortive motions in Glazer’s notations [7]. They also all undergo a magnetic phase transition to either a ferromagnetic (FM) ordering for small R = Lu-Gd+Y or a G-type antiferromagnetic (G-AFM) ordering for large R = Sm-La [6, 8, 9].

The nature of the very peculiar FM to G-AFM transition as a function of the rare-earth size is however puzzling and controversial [9]. On one hand, Ti3+ is nominally a Jahn-Teller (JT) active ion and the JT distortion is commonly proposed as a key ingredient to explain the transition [10, 11]. However, while such a distortion could be compatible with the ferromagnetic phase [12, 13], it cannot provide a satisfying explanation for the purely antiferromagnetic phase [10]. On the other hand, some other works have proposed that the JT distortion is neither responsible for the insulating phase of these materials nor for the observed orbital orders [14, 15].

Instead, Mochizuki et al. have suggested that specific orbital-ordering for the FM and AFM phases are triggered by the crystal field produced by the rare-earth [13, 16], with a potential competition with the JT distortion [11]. This latter model ultimately results in combinations of the three t2g orbits [9, 13, 16, 17], and now appears as a generic mechanism to yield the coupled spin-orbital orders in the ground state of 3d3 systems [14]. However, clear theoretical evidence of the individual role of each lattice distortions, including the ubiquitous oxygen cage rotations and/or rare-earths motions, is still missing.

In this manuscript, we revisit the nature of the orbital and spin orders in the ground state of rare-earth titanates on the basis of symmetry mode analysis and first-principles calculations. While the JT distortion appears rather negligible, we show that the combination of two specific antipolar distortions involving the rare-earth produces an effective JT motion tuning the spin-orbital properties of the low temperature phase.

We first performed a symmetry-adapted mode analysis (with AMPLIMODES [18, 19]) of some available experimental data in order to quantify the amplitude of distinct lattice distortions appearing in titanates. The results are summarized in Table I. As expected, all titanates develop strong antiferrodistortive motions – anti-phase Φ−xy (R4− irreps) and in-phase Φ+ (M5+ irreps) motions corresponding to a−a−c0 and a+ααc+ rotations respectively (see Figures 3a and d) – whose strengths are governed by steric effects. They also exhibit strong A X (X5− irreps) and A R (R4− irreps) distortions, involving antipolar motions of rare-earth and/or coplanar oxygens in the (ab)-plane as sketched in Figures 1b and c. These two modes also seem to be governed by steric effects, with a softening of their magnitude with increasing the rare-earth ionic radius albeit the R4− mode decreases more abruptly. Additionally, they also develop a Jahn-Teller (JT) distortion involving equatorial oxygen motions – two anions move inward, two outward – while apical oxygens are fixed (see Figure 1e).
This motion being in phase between consecutive planes along the $c$ axis, we label this JT mode as $Q^+_2$ ($M^+_5$ irreps) following Goodenough notation \[21\]. Surprisingly, this JT distortion is found very weak for all titanates, although it monotonously increases when going from $Y$ to La. JT distortions are well known to be smaller for $t_{2g}$ electrons than for $e_g$ electrons but they remain here one order of magnitude smaller than amplitudes appearing in the ground state of rare-earth vanadates \(V^{3+-t_{2g}}\) electronic degeneracy \[3\]. This analysis of experimental structures therefore provides strong support to the relatively small contribution of the JT distortion in titanates suggested by former studies \[15\].

In order to gain microscopic insights on the relationship between these distortions and spin-orbital orders, we performed first-principles calculations using Density Functional Theory (DFT) with the Vienna Ab-initio Simulation Package \[22, 23\]. We used the PBE functional revised for solids \[24\] in combination with effective Hubbard $U_{\text{eff}}$ corrections \[25\] of 2.5 eV on Ti 3$d$ levels and of 1 eV on the rare-earth 4$f$ levels in order to account for the electronic correlations (see supplementary materials \[26\] for a detailed discussion on the choice of these parameters). We used the Projector Augmented Waves (PAW) pseudopotentials \[25\] with the following valence electron configurations: $4s^23d^2$ (Ti), $2s^22p^4$ (O), $4s^24p^65s^25p^44f^0$ ($Y$), $5p^66s^25d^14f^0$ (La). An energy cut-off of 500 eV was used and we relaxed geometries until forces are lower than 1 meV/Å. A $6 \times 6 \times 4$ k-point grid was used to sample the Brillouin zone unless stated otherwise. We explored four different magnetic orderings during the calculations: ferromagnetic (FM), as well as A, C and G-type antiferromagnetic solutions with spins treated only at the collinear level. We focus in this study on YTiO$_3$ and LaTiO$_3$ appearing as model systems to understand the Ti 3$d$ electronic structure since they do not possess 4$f$ electrons.

Geometry optimizations for these two compounds yield a $Pbnm$ ground state associated with a FM and a G-type AFM solution for YTiO$_3$ and LaTiO$_3$ respectively, consistently with experiments. While the stability of the FM solution of YTiO$_3$ is rather large \((\Delta E = -18.5$ meV/f.u. between the FM and G-AFM solutions), the stability of the G-AFM over the FM solution in LaTiO$_3$ is small \((\Delta E = -3.4$ meV/f.u.) likely underlying a weakly stable AFM solution. The extracted amplitude of distortions of our ground states are reported in Table I and are compatible with experimental reports, therefore validating our optimizations (lattice parameters and atomic positions are given in supplementary material).

We then explored the origin of the orthorhombic structure by studying the energy potentials of the different lattice distortions. To that end, we have frozen some lattice motions in a hypothetical high-symmetry cubic structure \((Pm\bar{3}m)\) having the volume of the ground state structure. Note that the k-point mesh is increased to $12 \times 12 \times 8$ in order to enhance both accuracy and convergence of the wavefunction. Figure 2 reports the energy landscapes for YTiO$_3$ (blue squares) and LaTiO$_3$ (red circles) using a FM configuration \[27\] (energy potentials using a
G-type AFM configuration are reported in the supplementary material). As expected, the two oxygen cage rotations ($\Phi_{xy}$ and $\Phi_{xy}^\perp$ modes) present double well potentials associated with strong energy gains and produce the orthorhombic $Pbnm$ symmetry. The antipolar $A_X$ mode also develops a double well potential for $YTIO_3$ and $LaTiO_3$. The energy gain is larger for $YTIO_3$ albeit one order of magnitude smaller than that of the oxygen cage rotations. For both compounds, the antipolar $A_R$ mode is always associated with a single well energy potential, indicating that this mode is not intrinsically unstable and the driving force of the ground state. Importantly, the JT distortion behaves differently for the two compounds: we do observe single well potentials for $YTIO_3$ and $LaTiO_3$ but the minimum is shifted to non zero amplitude of the JT mode for $LaTiO_3$. It is worth noticing that we observe two distinct wells for $LaTiO_3$ depending on the sign of the lattice distortion. Therefore, it seems that in $LaTiO_3$, the JT distortion is able to produce an energy gain by favoring an orbital polarization. As inferred by the different behavior obtained for the two compounds, the ability of the JT distortion to produce energy gains seems to highly rely on the tolerance factor or the unit cell volume. We can check this hypothesis in our calculations by computing the energy potentials of $YTIO_3$ and $LaTiO_3$ by using the volume of the other compound (results are presented in the supplementary material). When using $YTIO_3$ volume, the JT potential for $LaTiO_3$ becomes a single well potential whose energy minimum is located at zero amplitude of the JT mode. On the other hand, under a volume expansion, the minimum of the JT potential of $YTIO_3$ is shifted to non zero amplitude similarly to $LaTiO_3$ ground state [30]. This striking result is in close agreement with the experimental observation of a strengthening of the JT distortion in any case. The latter appears in titanates. Although the two types of antipolar modes originate from secondary $Q_2$, $A_X$ and $A_R$ modes but are also the key to understand the different spin-orbital orders appearing in titanates. Although the two types of antipolar distortions ($A_X - X_5^-$ irreps – and $A_R - R_4^-$ irreps) have a distinct symmetry, their product belongs to the irreducible representation of the JT motion ($X_5^- \cdot R_4^- = M_4^+$) as inferred by the fourth term of Eq. 1. Consequently, 

\[ F \propto a \cdot \Phi_{xy} \cdot \Phi_{xy}^\perp \cdot A_X + b \cdot \Phi_{xy} \cdot \Phi_{xy}^\perp \cdot A_X \cdot Q_2^+ + c \cdot \Phi_{xy}^\perp \cdot A_X \cdot A_R + d \cdot A_X \cdot A_R \cdot Q_2^+ \]  

(1)

According to the first term, the condensation of the two rotations ($\Phi_{xy}^\perp$ and $\Phi_{xy}^\perp$ modes) automatically brings the antipolar $A_X$ motion in the system in order to lower the energy, irrespective of its stability/instability. Subsequently, the second term of equation 1 will force the appearance of the JT distortion in any case. The latter therefore has an improper origin, a mechanism already discussed in some other systems [3, 31, 32] and that explains its small amplitude for titanates with low tolerance factor. Finally, according to the third term in Eq. 1, the $A_R$ antipolar mode also appears as a consequence of the $\Phi_{xy}^\perp$ oxygen cage rotation and the $A_X$ antipolar motion.

These trilinear terms do not only explain the appearance of secondary $Q_2^+$, $A_X$ and $A_R$ modes but are also the key to understand the different spin-orbital orders appearing in titanates. Although the two types of antipolar distortions ($A_X - X_5^-$ irreps – and $A_R - R_4^-$ irreps) have a distinct symmetry, their product belongs to the irreducible representation of the JT motion ($X_5^- \cdot R_4^- = M_4^+$) as inferred by the fourth term of Eq. 1. Consequently,
In the search of the localization of this single Ti-d electron, we built the Maxi-Localized Wannier Functions (MLWFs) for the ground state of both materials using the Wannier90 software [40,42]. Firstly, we have followed the strategy discussed in reference [43]. We have initially projected the Kohn-Sham states onto three generic $t_{2g}$ orbitals per Ti sites in order to extract the initial gauge matrix for the localization procedure. The latter is then restricted to the occupied manifold in order to extract only occupied levels, albeit it is reduced to bands with dominant O and Ti characters. The optimization renders only one $t_{2g}$-like MLWFs per Ti site, and other MLWFs results in O-p states in the vicinity of Ti sites. It further confirms the occupancy of Ti 3d states by a single electron, whose localization renders the orbital-orderings depicted in Figure 5. These orbital-orderings are very similar to those reported on the basis of Dynamical Mean Field Theory calculations [13] as well as reference [44] for YTiO$_3$ and references [11] and [16] for LaTiO$_3$. However, the shape of the resulting $t_{2g}$ orbital on each Ti site can not be explained by a single electron lying in a particular $t_{2g}$ orbital [13]. We can deduce the different contributions of the $t_{2g}$ levels on the orbital ordering by using different set of bands for the localization procedure. To that end, we considered a total of 12 bands corresponding to dominantly Ti $t_{2g}$ contributions located around the Fermi level $E_F$, i.e. four bands below $E_F$, eight bands above $E_F$. We then integrate the density of states projected on the new $t_{2g}$-like WFs up to the Fermi level in order to extract their contribution to the orbital-ordering [45]. We end with very different contributions of the $t_{2g}$ states to the resulting orbital-ordering:

$$|\Psi_{YTiO_3}\rangle \propto 0.686 |d_{xy}\rangle + 0.728 (\alpha |d_{xz}\rangle + \beta |d_{yz}\rangle)$$ (2)

$$|\Psi_{LaTiO_3}\rangle \propto 0.565 |d_{xy}\rangle + 0.825 (\alpha |d_{xz}\rangle + \beta |d_{yz}\rangle)$$ (3)

where $\alpha$ and $\beta$ are coefficients describing the contribution of both $d_{xz}$ and $d_{yz}$ locally on each Ti sites ($\alpha^2 + \beta^2 = 1$). It then appears that going from R=Y to R=La, the orbital-ordering changes from a rather well balanced combination of the $d_{xy}$ and $(d_{xz}+d_{yz})$ orbitals to a dominant $(d_{xz}+d_{yz})$ character [13,14].

To gain insights on whether the contributions of the antipolar distortions and the existence of the effective JT mode drive the varying spin-orbital orders in titanates, we can track the evolution of the orbital-ordering upon condensing different lattice modes appearing in YTiO$_3$ in an ideal cubic phase having the ground state volume. Starting from a structure with the two oxygen cage rotations, we obtain an orbital ordering resembling that of YTiO$_3$ (see Figure 4.a) with a minimal $d_{xy}$ orbital contribution ($|\Psi\rangle \propto 0.360 |d_{xy}\rangle + 0.933 (\alpha |d_{xz}\rangle + \beta |d_{yz}\rangle$). On the one hand, adding the $A_X$ antipolar mode to the two rotations strongly suppresses the $d_{xy}$ character of the orbital-ordering, the latter almost vanishes ($|\Psi\rangle \propto 0.224 |d_{xy}\rangle + 0.975 (\alpha |d_{xz}\rangle + \beta |d_{yz}\rangle$), and therefore the orbital-order is very similar to that of LaTiO$_3$ (see Figure 4.b). On the other hand, adding the $A_R$
antipolar motion to the rotations completely switches the weight of the \(d_{xy}\) and \(d_{xz}/d_{yz}\) character (\(|\Psi\rangle \propto 0.706 |d_{xy}\rangle + 0.709 (\alpha |d_{xz}\rangle + \beta |d_{yz}\rangle\)) with an orbital ordering now resembling that of YTiO\(_3\) (see Figure 4(c)). Looking at the energy difference between FM and G-AFM solutions when condensing independently the two antipolar motions to the rotations, we observe that the \(A_R\) mode favors a FM ordering while the \(A_X\) mode strongly enhances the stability of G-AFM solution (see Figures 4(e) and 4(f)).

Therefore, starting from a structure with oxygen cage rotations and the sole \(A_X\) antipolar mode, all titanates should exhibit an antiferromagnetic ordering of the Ti\(^{3+}\) lattice (see Figure 4(g)). However, upon adding the \(A_R\) lattice distortion, the effective JT mode enters and is able to enhance the \(d_{xy}\) character of the orbital-ordering (\(|\Psi\rangle \propto 0.419 |d_{xy}\rangle + 0.908 (\alpha |d_{xz}\rangle + \beta |d_{yz}\rangle\)) and to stabilize the FM ordering over the G-AFM solution (see Figures 4(d) and 4(g)). We emphasize that the stability of the FM order versus the G-AFM order is strongly enhanced in comparison to the case of the sole condensation of \(A_R\) with the rotations, further proving the importance of the effective JT mode on the varying spin-orbital properties of titanates. Finally, we observe that the tetragonality \(c/\sqrt{2}a\) of the unit, scaling with the oxygen cage rotations amplitude, further increases the \(d_{xy}\) contribution to the orbital-order stabilizing the FM solution. It is worth to emphasize that we do observe that the \(Q^2_\perp\) mode has a rather marginal effect leaving the weight of the three \(t_{2g}\) orbitals on the orbital-ordering unchanged.

In conclusion, our first-principles simulations highlight the subtle interplay between structural, orbital and spin degrees of freedom in rare earth titanates. Most notably, we have shown that, in spite of the absence of sizable proper JT distortions, the oxygen rotations inherent to the \(Pbnm\) phase drive the appearance of two distinct antipolar rare-earth motions, which together correspond to an effective JT distortion. As the tolerance factor decreases, these antipolar motions increases together with the oxygen rotations and promote an orbital ordering similar to that which would be produced by proper JT motions and favors a FM spin order explaining the change of ground state from La to Y. The anti-polar motions being generic to any perovskite adopting a \(Pbnm\) structure, this study demonstrates that it is possible to achieve orbital orders and insulating phases in these materials irrespective of proper Jahn-Teller distortions.

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* julien.varignon@cnrs-thales.fr

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