Orbital ordering and multiferroics
Nenert, Gwilherm

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2007

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
Chapter 3

Orbital Ordering in RTiO$_3$

3.1 Introduction

The transition metal perovskite oxides ABO$_3$ with partially filled d-orbitals have been intensively investigated in order to understand the nature of their electronic states. In cases where the partially occupied orbitals are degenerate, the degeneracy is usually lifted and long-range ordering of the occupied orbitals occurs below a transition temperature. However, the local degeneracy may already be lifted above $T_C$. Such ordering is accompanied by a coherent Jahn-Teller (JT) distortion, which often results in a change of crystal symmetry. The most widely studied of such systems is La$_{1-x}$A$_x$MnO$_3$ series (A = Ca, Sr, Ba), where the JT effect due to degeneracy of the $e_g$ orbitals, is known to play an important role in the mechanism of the colossal magnetoresistance phenomenon, emerging in these materials upon doping [1]. Of more recent interest is the quantum effect in the orbital ordering dominated by electron correlations. With respect to $e_g$ systems, $t_{2g}$ systems have a larger degeneracy and weaker coupling to the lattice.

Here, we report on the rare-earth titanates RTiO$_3$, which belong to the $t_{2g}$ degenerate systems. RTiO$_3$ has an orthorhombically distorted perovskite structure (space group: $Pbnm$) (see figure 3.1). The RTiO$_3$ system is fascinating and has generated a tremendous amount of work. The debate focuses on the possible interactions lifting the threefold degeneracy of the $t_{2g}$ orbitals in the ground state. The TiO$_6$ octahedra in LaTiO$_3$ exhibit small GdFeO$_3$ related distortions [2]. One would expect, at first sight, quadruply degenerate single-ion ground states, represented by fictitious angular momentum due to spin-orbit (SO) interaction, with unquenched orbital moment. This scenario is consistent with the observed reduced magnetic moment [3]. However, Keimer et al. suggested that the SO interaction is not dominant in this system, because they observed an isotropic spin-wave dispersion [4]. They therefore proposed a model of strongly fluctuating orbital states [4, 5], followed by a calculation of the orbital excitations [6].
On the other hand, Mochizuki and Imada have successfully explained the physical properties of LaTiO$_3$ by an orbital state expressed approximately as $\frac{1}{\sqrt{3}} \times (d_{xy} + d_{yz} + d_{zx})$[7]. Subsequently, corresponding distortions of the TiO$_6$ octahedra have been reported from detailed structural data [8] with a $T_{OO}$ (temperature of orbital ordering)~$T_N$. The orbital state in RTiO$_3$ with R = La-Nd proposed by Mochizuki and Imada can result from a crystal field and is supported by NMR experiments [9]. The reduced moment of Ti$^{3+}$ and the different arguments given to explain this unexpected observation [4, 5, 6, 10, 11] motivated us to perform further experiments in comparison with known orbital ordered and disordered systems.

We have investigated two compounds of the RTiO$_3$ family, LaTiO$_3$ and YTiO$_3$ looking for possible lowering of symmetry due to orbital ordering. Several studies have concluded that YTiO$_3$ exhibits an orbital ordering from both experimental [12, 13] and theoretical results [10, 13]. We expect that the orbital ordering pattern is reflected in the crystal structure, as for orbital ordered systems like RMnO$_3$, RVO$_3$ and ACuX$_3$ (A = alkali, X = halogen) [14, 15, 5]. Here, the orbital ordering resulting from a cooperative JT effect, gives rise to a lowering of the symmetry expressed by the JT theorem [17].

This lowering of the symmetry in the JT active systems is often the signature of the orbital ordering. We can also observe a pseudo-JT effect which would give rise to a distortion of the octahedra but without change of symmetry as in orthorhombic RMnO$_3$ [14, 18]. We discuss our results in the light of already proposed theories and the GdFeO$_3$ distortion type that is present in the RTiO$_3$ family.
3.2 Experimental

Single-crystal samples of RTiO$_3$ have been synthesized in one step by direct reaction of Ti metal (99.9%, metal basis), R$_2$O$_3$ (99.99%) and TiO$_2$ (99.9%, metal basis) by the floating zone technique using a four-mirror furnace in a flow of 5% H$_2$/95% Ar gas. The oxide starting materials were predried overnight at 1000°C before use. The magnetic properties of RTiO$_3$ are very sensitive to the content of oxygen [19]. The high quality of the YTiO$_3$ and LaTiO$_3$ crystals is evidenced by narrow diffraction peaks (FWHM = 0.0087±0.00031) and the values of the magnetic transition temperatures of T$_C$$\sim$30 K and T$_N$$\sim$145 K respectively. Powder diffraction was performed on beamline ID31 at ESRF. We used a X-ray energy of 40 keV and a step size of 0.003° in 2θ. The temperature was controlled with a liquid-helium-cooled cryostat with spinning quartz capillary. Data sets were collected at 5K, 100K and 295K for YTiO$_3$ and at 5K, 100K, 175K and 295K for LaTiO$_3$. The data were analyzed by the Rietveld method implemented in the GSAS software package [20]. The background levels of the X-ray diffraction profiles were modelled using a simple linear interpolation of the seventh kind (in GSAS nomenclature) with 12 and 24 parameters, for LaTiO$_3$ and YTiO$_3$ respectively. The peak shape of the profiles was described by a convolution of a pseudo-Voigt function with an instrumental asymmetry (peak profile function 4 in GSAS). The data have been corrected for both compounds by taking into account the anomalous scattering factors (f’ and f”). The values of these factors were derived by using the program Fprime [21].

3.3 Results

3.3.1 Refinements

We obtain a good refinement for both compounds YTiO$_3$ and LaTiO$_3$ in the $P$bnm symmetry as illustrated in figure 3.2. The good refinements are confirmed by the good statistics that we obtained $R_{wp}$ = 6.05% and $R_p$ = 4.99% for LaTiO$_3$ and $R_{wp}$ = 7.72% and $R_p$ = 6.43% for YTiO$_3$ at 5K. We did not observe any signature of a possible splitting of reflections which could be the signature of a lowering of the $P$bnm symmetry.
Figure 3.2: Comparison of the fit of the recorded pattern of LaTiO$_3$ (bottom) and of YTiO$_3$ (top) at 5K. Similar quality of the refinements is obtained at all the measured temperatures for both compounds. The squares represent the observed pattern, the triangles represent the calculated pattern and the straight line represents the difference between both.

We observe as a function of temperature in LaTiO$_3$ between 5K and 295K that while the $b$ and $c$ cell parameters increase by 0.482% and 0.187% respectively, the $a$ cell parameter contracts by 0.161% resulting in an increase of the volume (cf. figure 3.3). As reported by Cwik et al. [8], one can see that this temperature effect on the cell parameters is particularly pronounced around the magnetic transition temperature. This can be interpreted either as a pure magnetostrictive effect or as a mixture of the strictions due to the magnetic ordering and a possible orbital ordering. This issue will be discussed in the next section.
3.3. Results

Figure 3.3: *Comparison of the cell parameters of LaTiO$_3$ and of LaVO$_3$ extracted from [22] versus temperature.*

In figure 3.4, we present the evolution of the cell parameters versus temperature of YTiO$_3$. One can see that the temperature dependence of YTiO$_3$ is different than in the case of LaTiO$_3$. Indeed while the cell parameter $b$ is increasing versus temperature in LaTiO$_3$, it is decreasing in YTiO$_3$ by 0.064% around the magnetic ordering temperature between 5K and 100K ($T_C=30K$). The other cell parameters $a$ and $c$ are increasing by 0.0802% and 0.0113%, respectively. One of the other main differences between YTiO$_3$ and LaTiO$_3$ is the cell parameters variations versus temperature. This difference is very significant since there is about one order of magnitude of difference between LaTiO$_3$ and YTiO$_3$. This difference in the variation of the cell parameters can be explained by the difference in the strength of the magnetic exchange between LaTiO$_3$ and YTiO$_3$. 
Chapter 3. Orbital Ordering in RTiO₃

Figure 3.4: Evolution of the cell parameters of YTiO₃ as a function of temperature.

In tables 3.1 and 3.2, we present the results of the refinements of both compounds LaTiO₃ and YTiO₃ at all temperatures in the Pbnnm setting. Although these compounds do not present any obvious monoclinic distortion at any temperature, they still may present orbital ordering with conservation of the Pbnnm symmetry as in the case of the orthorhombic RMnO₃ [14, 18]. We will discuss the possible ordering in section 4.8.

Table 3.1: Results of the synchrotron powder diffraction study at different temperatures of LaTiO₃ using Pbnnm symmetry. Lattice constants are given in Å and thermal parameters in Å² at different temperatures.
3.3. Results

<table>
<thead>
<tr>
<th>Sample</th>
<th>5K</th>
<th>100K</th>
<th>295K</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>5.52140(1)</td>
<td>5.52347(1)</td>
<td>5.52341(1)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>5.69676(1)</td>
<td>5.69312(1)</td>
<td>5.68529(1)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>2.027(2)</td>
<td>2.027(2)</td>
<td>2.031(2)</td>
</tr>
<tr>
<td>Ti-O</td>
<td>2.0208(9)</td>
<td>2.072(2)</td>
<td>2.073(2)</td>
</tr>
<tr>
<td>Y</td>
<td>0.9770(7)</td>
<td>0.97804(7)</td>
<td>0.97913(8)</td>
</tr>
<tr>
<td>x</td>
<td>0.074(26)</td>
<td>0.07429(6)</td>
<td>0.07311(6)</td>
</tr>
<tr>
<td>y</td>
<td>0.4565(5)</td>
<td>0.4571(5)</td>
<td>0.4572(5)</td>
</tr>
<tr>
<td>z</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>O1</td>
<td>0.6903(4)</td>
<td>0.6903(4)</td>
<td>0.6901(4)</td>
</tr>
<tr>
<td>x</td>
<td>0.3076(4)</td>
<td>0.3080(4)</td>
<td>0.3086(6)</td>
</tr>
<tr>
<td>y</td>
<td>0.0577(3)</td>
<td>0.0580(3)</td>
<td>0.0586(3)</td>
</tr>
<tr>
<td>z</td>
<td>0.0544(7)</td>
<td>0.0460(7)</td>
<td>0.00716(9)</td>
</tr>
<tr>
<td>Ti</td>
<td>0.0031(1)</td>
<td>0.0043(1)</td>
<td>0.0059(1)</td>
</tr>
<tr>
<td>O1</td>
<td>0.0049(6)</td>
<td>0.0051(6)</td>
<td>0.0053(6)</td>
</tr>
<tr>
<td>O2</td>
<td>0.0063(4)</td>
<td>0.0069(5)</td>
<td>0.0100(5)</td>
</tr>
</tbody>
</table>

Table 3.2: Results of the synchrotron powder diffraction study at different temperatures of YTiO₃ using Pbnm symmetry. Lattice constants are given in Å and thermal parameters in Å² at different temperatures.

3.3.2 Asymmetric peak shape below $T_N$

Despite of the good refinements done with $P$bnm symmetry, we observe some asymmetry in some reflections during the refinements on LaTiO₃. We remind the reader that a pseudo-Voigt peak profile function convoluted to an instrumental asymmetry has been used to describe the peak shape. But in addition to this instrumental asymmetry, we observe for LaTiO₃ an extra asymmetry of experimental (sample) origin. This asymmetry starts to develop under $T_N$. This asymmetry is characterized by a tail on the left side of (hkl) reflections having a high value of h (see figure 3.5). On the contrary for reflections having a high value of k, the tail starts to develop on the right side (see figure 3.6). However, no asymmetry could be observe on the reflections having a high l value irrespective of the temperature.

![Figure 3.5: Refinement of LaTiO₃ in Pbnm setting. An asymmetry (left tail) is observed under $T_N$ of the (400) reflection ($T=5K$, left panel) which is not present above $T_N$ ($T=175K$, right panel).](image)

The asymmetries in the peak shape observed in the refinements of LaTiO₃
are not present for the refinements done on YTiO$_3$. The main difference between these two compounds is the type of magnetic ordering. While LaTiO$_3$ orders antiferromagnetically under $T_N \approx 145$K, YTiO$_3$ orders ferromagnetically with a magnetic moment along the $c$ axis ($Pbnm$ setting) below $T_C \approx 30$K. The experimental asymmetry follows the trends in lattice parameters through $T_N$. The response of the lattice below $T_N$ is different in different parts of the sample. There is a continuous range of lattice parameters. This asymmetry could result from the magnetostriction which would involve new strain components giving rise to this asymmetry. YTiO$_3$ presents a different magnetic ordering and thus one can expect a different behavior than in LaTiO$_3$. However further and more thorough investigations are necessary in order to clarify the origin of this asymmetry in LaTiO$_3$.

![Figure 3.6: Refinement of LaTiO$_3$ in Pbnm setting. An asymmetry (right tail) is observed under $T_N$ of the (131) reflection ($T=5$K, left panel) which is not present above $T_N$ ($T=175$K, right panel).](image)

3.4 Discussion

3.4.1 Possible structural signature of Orbital Ordering

*LaTiO$_3$*

One should notice that the anomaly in the cell parameters in LaTiO$_3$ is much smaller than in the related compound LaVO$_3$ (which is also a $t_{2g}$ system with $T_N \sim 140$K) where the $a$, $b$ and $c$ cell parameters change by a factor of 2.1, 2.6 and 16.7 times more than in LaTiO$_3$, respectively, between 100 K and 150 K [22] (see figure 3.3).

The orbital ordering is often probed structurally by an anisotropy in the metal-oxygens bond distances (M-O) resulting from a particular distortion mode. In the $Pbnm$ space-group, the symmetry already allows a differentiation in the different M-O bonds since only the inversion center remains compared to the $O_h$ symmetry. In figure 3.7, we show the evolution versus temperature of the different Ti-O bond distances. $O_1$ is the apical oxygen.
while O$_{21}$ and O$_{22}$ form the basal plane of the octahedra. As stated already, we see that we have 3 different bond distances. As a function of temperature, one of the basal plane Ti-O distance (Ti-O$_{22}$) and Ti-O$_{1}$ increase continuously while the bond distance Ti-O$_{21}$ decreases. Around T$\approx$225K, we observe that Ti-O$_{1}\approx$Ti-O$_{21}$. We notice that our results are significantly different than the ones of Cwik et al. [8]. They found that one of the basal plane Ti-O is independent of temperature. The other Ti-O bond distance belonging to the basal plane is almost temperature independent. This is in contradiction with our results where we observe that one is contracting while the other one is expanding. Moreover we can notice that it is unexpected to have no variations in bond length over almost 300K.

In order to investigate the possible structural signature of any orbital ordering, we compare our data with another $t_{2g}$ system which is not orbital ordered: LaCrO$_3$ ($P$bnm symmetry; Cr$^{3+}$, $t_{2g}$, e$_g^0$). At room temperature, the M-O bond distances are 1.957Å, 1.930Å and 2.009Å [23]. In LaCrO$_3$, as in LaTiO$_3$, the variations in bond length M-O in the basal plane versus temperature are similar [24]. Moreover the distortion scheme is strictly similar. While M-O$_{1}$ and M-O$_{22}$ increase with temperature, M-O$_{21}$ decreases. Thus we believe that the temperature behavior of LaTiO$_3$ is simply the typical temperature behavior for a $t_{2g}$ populated system having $P$bnm symmetry. Moreover, recent spin-resolved photoelectron spectroscopy experiment claims the absence of orbital ordering in LaTiO$_3$ [25]. Thus, from these simple structural parameters, LaTiO$_3$ does not present any structural signature of a possible Jahn-Teller ordered state below its Néel temperature.

Figure 3.7: Evolution of the Ti-O bond distances in LaTiO$_3$ versus temperature in the Pbnm setting.
$YTiO_3$

Since the critical temperatures of both studied compounds have a factor 5 of difference (145K versus 30K), we think that the difference of exchange striction can be explained by the difference of the magnitude of the magnetic dipole. As in LaTiO$_3$, we present in figure 3.8 the temperature behavior of the Ti-O bond distances. As in LaTiO$_3$ due to the $P$bnm symmetry, we observe 3 different bond distances. However, on the contrary of LaTiO$_3$, we notice that one of the basal plane Ti-O distance is significantly larger than the two others. This has been one of the reasons for which several works reported orbital ordering in YTiO$_3$. This differentiation in the bond distances is also present at room temperature suggesting that the orbital order exists already at room temperature. This is very surprising. Indeed since the $t_{2g}$ orbitals are much less coupled to the lattice and due to the higher degeneracy, the orbital ordered/disordered transition is expecting to take place at much lower temperature than in the $e_g$ system. It is consistent with the study of orbital ordering in RVO$_3$ where the transition temperatures are well below room temperature [15, 26]. Thus we would expect the same for titanates.

As stated already the orbital ordering is reflected in the asymmetry of the distribution of the bond distances. It is effectively what is observed for YTiO$_3$. However, it is not sufficient. If there is an orbital ordered state, the anisotropy of the bond distances disappears or at least is reduced versus temperature. And it is not what we observe in figure 3.8. We see that the difference between the 2 short bonds and the long Ti-O bond remains constant as a function of temperature. This indicates that the existence of 2 short and 1 long bond distances is not related to a possible orbital order. This has been already observed in YCoO$_3$ which presents similar structural properties ($P$bnm symmetry, 2 long and 1 short M-O bond distances). A study from room temperature until 1000K demonstrated that the difference between the short and the long bond distances was more or less constant between room temperature and 1000K [27]. Thus, we can say that the structural features of YTiO$_3$ can not be ascribed to an orbital ordered state.
3.4. Discussion

3.4.2 GdFeO$_3$ distortion versus Orbital Ordering

About the in-plane distortion

Cwik and collaborators have investigated using neutron powder diffraction, the distortions of the octahedra network of LaTiO$_3$. Making a comparative study with other rare-earths, they observed a strong variation in the basal plane edge lengths for the large rare-earths. They use the parameter $r_{O_2-O_2}=(O_2-O_2\text{long}/O_2-O_2\text{short})$ to quantify this distortion. Contrary to the large rare-earths, the variation of the Ti-O distances for small rare-earth was found to be large with small distortion of the basal plane of the octahedron. The two distinct deformations of the octahedron were interpreted as two different orbital ordering schemes. Following the approach taken by Cwik et al., we have investigated the variations in the Ti-O distances as well of the basal plane edges defined respectively by $r_{O_2-O_2}$ and $r_{M-O}=(M-O\text{long}/M-O\text{short})$. We plot in figure 3.9 the basal plane edge lengths of LaTiO$_3$ and YTiO$_3$ as obtained from our refinements. We observe as Cwik et al. that the difference between the two basal plane edges is significantly smaller in YTiO$_3$ compared to LaTiO$_3$. 

Figure 3.8: Evolution of the Ti-O bond distances in YTiO$_3$ versus temperature in the Pbnm setting.
Figure 3.9: Distortion of the basal plane of octahedron TiO$_6$ in RTiO$_3$ as a function of temperature.

The existence of a difference between the M-O distances and O-O distances of the basal plane is directly related to the pseudo-cubic structure adopted by the RTiO$_3$ family. To investigate the structural signature of orbital ordering in RTiO$_3$, we compare the available data on RTiO$_3$ with a very well known non orbital ordered system RFeO$_3$. This family presents like the RTiO$_3$ a pseudo-cubic structure (space-group Pbnm) but no orbital ordering. We plot in figure 3.10 the r$_{O_2-O_2}$ parameter and the r$_{M-O}$ parameter in figure 3.11 of the RFeO$_3$ and RTiO$_3$ families. For this purpose, we use the different reported structures in the literature [2, 28].
3.4. Discussion

As noticed by Cwik et al., we observe a change in the trend of both parameters \( r_{O_2-O_2} \) and \( r_{M-O} \) around an ionic radius corresponding to Sm. However, this trend is also present in the RFeO\(_3\) system. For the \( r_{O_2-O_2} \) parameter, we see that the value of the parameter and the trend is very similar between the RTiO\(_3\) and RFeO\(_3\) systems. Concerning the \( r_{M-O} \) parameter, the trend is also similar between the RTiO\(_3\) and RFeO\(_3\) systems. The difference in the value of \( r_{M-O} \) parameter is decreasing when increasing the size of the rare-earth to finally vanish for the bigger rare-earth. We conclude that the two distinct deformations (\( r_{O_2-O_2} \) and \( r_{M-O} \)) are determined by the rare-earth ionic radius variation. These deformations are intrinsic to the pseudo-cubic structure of the RTiO\(_3\) system. Consequently, the deformations observed in RTiO\(_3\) can not be ascribed to an orbital ordering scheme.

Figure 3.10: Comparison of the distortion of the basal plane of MO\(_6\) octahedron between the RFeO\(_3\) and RTiO\(_3\). We use the same parameter \( r_{O_2-O_2} = O_2\)-O\(_2\)long/O\(_2\)-O\(_2\)short as Cwik [8]. We use structural parameters reported in literature for comparison [2, 28].
Trigonal Distortion

Starting from the ideal cubic perovskite ABO₃, which has the space-group Pm\( \bar{3} \)m, it is possible to derive the space-groups of the distorted perovskites (hettotypes). These hettotypes are produced by tilts of the octahedra and limited to multiplication by 2 in any direction of the unit-cell. Based on the different possible tilting of the octahedra, Glazer identified 23 tilt systems [29] which have been reduced to 15 recently by Howard and Stokes [30]. Mochizuki et al. claimed that a crystal field having the symmetry D₃d (trigonal distortion) was sufficient to lift the degeneracy of the t\(_{2g}\) orbitals [7]. The resulting orbital state can be expressed approximately as \( \frac{1}{\sqrt{3}} \times (d_{xy} + d_{yz} + d_{zx}) \) which has been confirmed experimentally by NMR experiment [9]. The authors claimed that the shift of La ions creates a crystal field having a trigonal symmetry. In this picture, the crystal field due to the eight nearest La ions gives a nearly equidistant splitting scheme between the three t\(_{2g}\) orbitals which is only a first approximation. This has been pointed out by Schmitz et al. [31]. By taking into account the exchange Hamiltonian, Schmitz et al. have been able to describe better the origin of the magnetic ordering and to complete the model proposed by Mochizuki et al.
The difference in the distortion between the model elaborated by Mochizuki et al. and the one of Schmitz et al. has been ascribed to the Jahn-Teller effect present in LaTiO$_3$. However one can show that a crystal field of D$_{3d}$ symmetry on the transition metal ion site (Wyckoff position a) will not give the space-group Pnma (other setting of Pbnm) starting from Pm$\overline{3}$m, even through the corner shared octahedra network. Indeed, Howard and Stokes have shown that the distortion which gives the space-group Pnma starting from Pm$\overline{3}$m belongs to the six-dimensional reducible representation $M^{3+} \oplus R^{4+}$; the direct sum of $M^{3+}$ and $R^{4+}$ [30]. The distortions due to the IR $M^{3+}$ are along 2-fold axis parallel to the (100) direction of Pm$\overline{3}$m. The ones due to the irreducible representation IR $R^{4+}$ are along the 2-fold axis parallel to the (011) direction. Both distortions due to the different irreducible representations have the $E_u$ symmetry. The distortion along the (100) direction due to IR $M^{3+}$ lowers the symmetry from $O_h$ to $C_{2v}$. The distortion due to $R^{4+}$ along the (011) direction lowers also to $C_{2v}$. The simultaneous distortions of the two irreducible representations lower the symmetry finally to $C_s$. Consequently, we can see that the crystal field resulting from the lanthanum ion shift does not have a trigonal symmetry which would correspond to a distortion along one of the three fold axes of the $O_h$ symmetry. Consequently, one can see that the hypothesis of having a D$_{3d}$ distortion type is incorrect and it will not reduce the local symmetry of Ti to $C_s$ starting from $O_h$. However, if we consider the correct distortion pattern, one can reach the correct local symmetry of Ti. The $C_s$ crystal field does not require any nearly equidistant splitting scheme between the three $t_{2g}$ orbitals. On the other hand, if one applies a trigonal distortion on the Ti site to the Pm$\overline{3}$m symmetry, it will give rise to a trigonal distortion on the

Figure 3.12: D$_{3d}$ type distortion responsible for the lifting of the degeneracy of the $t_{2g}$ orbitals in RTiO$_3$ according to the scenario proposed by Mochizuki et al. [7].
transition metal site through the corner shared octahedra network. This trigonal distortion will lower the symmetry to $R\overline{3}c$ (n°167) due to the IR $R^{4+}$ alone [30]. However, $R\overline{3}c$ is not the symmetry adopted by the RTiO$_3$ family. In other words, the $P$$\overline{n}$ma symmetry of RTiO$_3$ is not due to the Jahn-Teller effect but due to rigid-unit modes which are characterized by a tilting of the oxygen octahedra rather than other effects.

### 3.4.3 A reduced magnetic moment

RTiO$_3$ and LaTiO$_3$ in particular have attracted attention when an ordered magnetic moment of $0.45\mu_B$ was reported [3]. This experimental value is surprisingly small for a single electron with quenched orbital moment, for which one would have expected $1\mu_B$. Cwik et al. were the first to notice that quantum fluctuations could explain about 15% of reduction of the magnetic moment [8, 32]. Later Schmitz et al. mention that this moment could be further reduced by about 14% due to on-site spin-orbit coupling leading to an overall estimate of $0.72\mu_B$ [31]. Completing the model proposed by Mochizuki et al. and including a Jahn-Teller distortion, they claimed that LaTiO$_3$ was orbital ordered. In addition, they could reproduce the NMR measurement of Kiyama [9]. However, it is well known that the magnetic moment is strongly correlated to the stoichiometry of the sample [19]. Cwik et al. reported an experimental magnetic moment of $0.57\mu_B$ which is significantly higher than the $0.45\mu_B$ reported by Meijer et al. [3, 8]. Moreover, the reported 10% error on the measurement is not negligible [8]. In addition, it is very well known that covalency can reduce the magnetic moment due to spin transfer to the ligands of a given ion. This was already observed by Alperin in NiO [33]. The form factors for neutron are also altered by covalent effects. For instance, in LaCrO$_3$ it was reported that the spin transfer is about 5% [34]. Consequently, if one takes into account all the possible effects (crystal field, spin-orbit, quantum fluctuations, covalency) and the experimental errors, one can easily find a fair agreement between experimental and theoretical values for the magnetic moment without considering any orbital ordering. This conclusion is supported by the calculations of Radwanski and Ropka on YTiO$_3$ [35]. Using a single-ion picture and taking into account the low symmetry of the crystal they are able to reproduce the value of the magnetic moment and its characteristics without involving any orbital ordering.

### 3.5 Conclusions

We have investigated with high resolution X-ray diffraction the possible presence of a lowering of symmetry in LaTiO$_3$ and YTiO$_3$ resulting from an
allowed Jahn-Teller type of distortion. We show that at any temperature, the best model is given using the Pbnm space-group. Based on symmetry arguments and by comparing to very-well known non Jahn-Teller active systems, we provided evidence that the structures of LaTiO$_3$ and YTiO$_3$ do not exhibit any signature of orbital ordering. This supports the interpretation of Keimer et al. and of Haverkort et al. [4, 25] and contradicts the recent calculations by Schmitz et al. [31]. This work demonstrates the importance of symmetry when considering possible distortion patterns of a compound.

References


