Crystal and magnetic structure of LaTiO₃: evidence for non-degenerate t₂g-orbitals

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LaTiO₃ has been studied already in the seventies and was thought to be a text book example of a Mott-insulator with antiferromagnetic order [1]. Ti is in its three-valent state with a single electron in the t₂g-orbitals of the 3d-shell. The titanate is hence an electron analog to the cuprates with a single hole in the 3d-shell. The physics of the orbital degree of freedom has recently reattracted attention to this material [2, 3].

The ordered moment in LaTiO₃ amounts to 0.46 μB which is much smaller than the value of 1μB expected for a single electron with quenched orbital moment. Quantum fluctuations can explain only about 15% reduction in the 3D-case. A straight-forward explanation could be given in terms of spin-orbit coupling, as an unquenched orbital moment would align antiparallel to the spin-moment in the titanate. However, in a recent neutron scattering experiment the magnon spin gap was observed at 3.3 meV, and it was argued that the strong interaction of an orbital moment with the crystal lattice implies a much larger value for the spin gap 2. An orbital contribution to the ordered moment in LaTiO₃ was hence excluded. On the basis of standard theories, however, even the G-type antiferromagnetic ordering in LaTiO₃ may not be explained without a spin-orbit coupling. Instead one expects ferromagnetism related with the orbital degeneracy. Under the assumption of a specific structural distortion, Moshizuki and Imada recently presented a successful model for the antiferromagnetic order in LaTiO₃ [4]. However, there is no experimental evidence for such a distortion. The puzzling magnetic properties of LaTiO₃ led Khalufullin and Maekawa to suggest a novel theoretical description for RETiO₃ based on the idea of an orbital liquid. They were able to explain many of the magnetic characteristics of LaTiO₃ [5], but the presumed orbital fluctuations have not been observed [6]. Therefore, magnetism in LaTiO₃ still remains an open issue.

We have reanalyzed the crystal and magnetic structure of LaTiO₃ by x-ray and by neutron diffraction samples with almost perfect stoichiometry. First, we find a clear structural anomaly near the Néel-ordering and, second, the shape of the octahedra in this compound is not ideal but distorted. From these observations we conclude that LaTiO₃ has to be considered as a soft Jahn-Teller system thereby explaining many of its unusual magnetic properties.

Samples of LaTiO₃ were prepared following the standard solid state reaction; however the last process was performed in a floating zone image furnace. This procedure gave large single crystals with small mosaic spread. Since twinning would induce severe problems in any single crystal diffraction experiment, we crushed parts of these single crystals in order to perform powder diffraction studies. Special care was attracted to the stoichiometry of these samples. LaTiO₃ has the tendency to incorporate La and Ti vacancies which are frequently denoted by an excess of oxygen in the formula LaTiO₃+δ. By adjusting the ratio of Ti⁺ and Ti⁺ in the starting materials one may vary the final oxygen content of the samples. Stoichiometry was verified by thermogravimetric analyzes and by determining the Néel-temperature in a SQUID magnetometer. For the stoichiometric sample studied here we obtain T_N=146 K, amongst the highest values reported so far for LaTiO₃. The temperature dependence of the lattice parameters was determined on a Siemens D5000 x-ray diffractometer using Cu-Kα radiation. Powder neutron diffraction experiments were performed at the Orphée-reactor in Saclay, using the high-resolution diffractometer 3T.2 (λ=0.12Å) and the high-flux diffractometer G4.1 (λ=0.24Å).

At room temperature, LaTiO₃ exhibits the crystal structure of GdFeO₃-type (space group Pbnm), see Fig. 1. This structure arises from the ideal perovskite (space group Pm3m) by tilting the TiO₆-octahedron around a [110]_L-axis (the subscript c denotes the notation with re-
TABLE I: Results of the neutron high resolution powder diffraction studies at different temperatures, the two right columns present data from references [12] and [11] respectively. Lattice constants are given in Å and thermal parameters in Å$^2$.

|        | a (Å) | b (Å) | c (Å) | $\alpha$ (°) | $\beta$ (°) | $\gamma$ (°) | $U_{11}$ (Å$^2$) | $U_{22}$ (Å$^2$) | $U_{33}$ (Å$^2$) | $\Theta$ (°) | $\Phi$ (°) |
|--------|-------|-------|-------|-------------|-------------|-------------|-----------------|-----------------|----------------|-------------|------------|
| LaTiO$_3$, $T_N = 150\, K$ | 5.6336(1) | 5.6353(1) | 5.6435(1) | 90.0 | 90.0 | 90.0 | 0.0052(2) | 0.0052(2) | 0.0052(2) | 12.85(5) | 9.53(1) |
| LaTiO$_3$ | 5.6156(1) | 5.6021(1) | 5.5885(1) | 90.0 | 90.0 | 90.0 | 0.0052(2) | 0.0052(2) | 0.0052(2) | 12.86(5) | 9.60(1) |
| YTiO$_3$ | 5.6071(1) | 5.6071(1) | 5.6071(1) | 90.0 | 90.0 | 90.0 | 0.0052(2) | 0.0052(2) | 0.0052(2) | 12.86(5) | 9.60(1) |

FIG. 1: Crystal structure of LaTiO$_3$ in space group Pbnm, O2 denotes the oxygen in the $a$, $b$-planes O1 the apical-one. The left part shows four octahedra connected in the $a$, $b$-plane, the right part a pair of neighboring octahedra along $c$.

spect to the cubic perovskite lattice) followed by a rotation around the c-axis (or [001]$_c$ axis). One may note that while tilt distortions are opposite for any neighboring pair of octahedra, octahedra neighboring along the c-axis rotate in the same sense.

Fig. 2 shows the temperature dependence of the orthorhombic lattice parameters and that of the crystal volume. There are clear anisotropic anomalies near the antiferromagnetic ordering. Upon passing into the ordered state the lattice elongates along $a$ and shrinks along $b$, whereas for the $c$-direction and for the lattice volume no anomalous changes can be resolved. Anomalies in the thermal expansion have also been observed independently in a capacitance dilatometer experiment [10].

The anomalous temperature dependence of the $a$ and $b$ lattice parameters is not restricted to a temperature range close to $T_N$, see Fig. 3. In particular the $a$-parameter which is almost constant between 200-500 K deviates from a normal thermal expansion over a large temperature interval. Here, it is instructive to analyze the orthorhombic splitting. The lattice in Pbnm results from that of an ideal cubic perovskite (denoted by subscript c) by setting $a = \sqrt{2}a_c$, $b = \sqrt{2}a_c$ and $c = 2a_c$. Considering a rigid tilt of the ideal octahedron one obtains the non-equalities $c = \frac{b-a}{2}$ due to the rotation and the tilt and $a \neq b$ due to the tilt distortion only. However, tilting of an ideal octahedron around the $b$-axis would lead to $b > a$, whereas LaTiO$_3$ exhibits just the opposite behavior below about 650 K. The sign of the orthorhombic distortion, $\epsilon = \frac{b-a}{a+b}$, already indicates that the octahedron shape in LaTiO$_3$ is not ideal.

We have determined the crystal structure on our almost stoichiometric sample using high resolution neutron diffraction. The results are given in table 1. The splitting in the Ti-O-bond distances is small though not negligible. There is, however, a large splitting in the O2-O2 edge lengths of the octahedron basal plane, which has escaped previous attention. At 8 K the edges along $a$ and $b$ differ by about 4%. This distortion is comparable in
its strength to that observed for the Ti-O-bond distances in YTiO₃ which is considered as being orbitally ordered [1]. In LaTiO₃, the octahedron elongation perpendicular to the tilt axis over-compensates the shortening of a through a rigid tilt. The negative sign of the orthorhombic strain in LaTiO₃ is hence caused by the elongation of the octahedron along a. Interestingly, this effect is found to be strengthened at the antiferromagnetic transition; the behavior of the O₂-O₂ bond distances accounts for the anisotropic anomalies: an elongation along a and a shrinking along b. Comparing our new results with those of ref. [11, 12] one recognizes that the splitting in Ti-O-bond lengths, the splitting in the O₂-O₂ edges as well as the anomalies near $T_N$ are less pronounced in the samples of ref. [11, 12]. Non-stoichiometry seems to significantly reduce the long-range distortion of the TiO₆-octahedron. This was confirmed by our own studies on samples with excess oxygen which revealed a continuous reduction of the orthorhombic strain and the anomalies around $T_N$.

Meijer et al. performed neutron diffraction studies on single crystals in order to determine the magnetic structure [3]. According to the symmetry of the GdFeO₃ structure [13] a G-type antiferromagnetic order may be associated with a weak ferromagnetic moment. However, Meijer et al. could not distinguish between the following two configurations due to twinning: either a G-type moment along a and ferromagnetism along c or a G-type moment along c and ferromagnetism along a. Using the high flux diffractometer data we get evidence that the ordered antiferromagnetic moment points along the a-direction, see Fig. 4, although some underlying weak nuclear reflection complicates the analysis. Constraining the crystal structure to the high resolution results given in Table I, we find a low temperature ordered moment of 0.57(5) $\mu_B$ slightly higher than previous studies.

The crystal structure within the RETiO₃ series is determined through the ionic radius of the RE. A smaller radius implies increasing tilt and rotation distortions. In Fig. 5a) we plot the orthorhombic splitting against the square of the tilt angle. There is a clear deviation from the proportionality expected in Landau-theory [14], which we attribute to the anomalous stretching of the octahedron basal plane. Without this anomalous elongation one would expect an orthorhombic splitting in LaTiO₃ three times larger and of positive sign. The anomalous octahedron elongation at the magnetic ordering is, therefore, about an order of magnitude smaller than the total deformation in LaTiO₃, see Fig. 3 and table I. In Fig. 5b) we compare the octahedron deformation in LaTiO₃ with that seen in the RETiO₃-series using the data of MacLean et al. [11]. In LaTiO₃ we find a small variation in the Ti-O-bond distances, described by $r_{TiO} = \frac{T_i-O_{short}}{T_i-O_{long}}$, but a strong variation in the basal plane edge lengths described by $r_{O2-O2} = \frac{O2-O2_{long}}{O2-O2_{short}}$. In contrast, in YTiO₃ the variation in the Ti-O-distances is strong and that in the O₂-O₂-lengths is small, as it was recently confirmed [12]. Fig. 5b) shows that these distortions change continuously in the RETiO₃ series. The two distinct deformations of the octahedra imply different orbital ordering schemes. The variation of the Ti-O-distances arises from the shift of an O₂-site towards a Ti-site; in consequence, the distance to the opposite Ti is elongated and antiferroorbital-type ordering results which has been directly observed in YTiO₃ [10]. In contrast the elongation of the basal planes along a in LaTiO₃ implies ferro-orbital-type ordering. Following Goodenough-Kanamori rules these orderings imply fer-
romagnetic and antiferromagnetic coupling, respectively. Most interestingly, the cross-over between the two types of structural deformation coincides with the cross-over from antiferromagnetic to ferromagnetic ordering in the RETiO\(_3\)-compounds. With decreasing RE ionic radius NdTiO\(_3\) and SmTiO\(_3\) exhibit still antiferromagnetic order with small \(T_N\), whereas GdTiO\(_3\) is ferromagnetically ordered. A similar magnetic crossover is seen in the La\(_1-\gamma\)Y\(_2\)TiO\(_3\)-series. This coincidence between the structural and magnetic crossovers clearly documents the relevance of the octahedron deformation for the magnetism in RETiO\(_3\).

In the following we analyze the effect of the octahedron basal plane elongation on the \(t_{2g}\)-energy levels. Qualitatively one may argue, that the octahedron elongation splits the degenerate \(xz\) and \(yz\)-levels into \(\sqrt{2}(xz + yz)\) and \(\frac{1}{\sqrt{2}}(xz - yz)\). In the notation used here the orbital coordinates refer to the cubic perovskite lattice, i.e. \(x, y, z\) are parallel to the Ti-O-bonds. We have calculated the \(t_{2g}\)-level splitting within a full Madelung-sum point charge model taking into account the second order covalent contribution. Using the experimentally determined crystal structure, we obtain a sizeable splitting: one level is about 0.24eV below the two others which remain almost degenerate. The crystal field splitting is about one order of magnitude stronger than the spin orbit coupling, and we have to conclude that the \(t_{2g}\)-orbitals are not degenerate in LaTiO\(_3\); but the splitting is not sufficient to completely quench the orbital moment. The occupied orbital can be constructed as a linear combination of the three standard \(t_{2g}\)-orbitals: 

\[
0.77(\frac{1}{\sqrt{2}}xz + yz) \pm 0.636(xy). 
\]

The admixture of the \(xy\)-orbital to \(\frac{1}{\sqrt{2}}xz + yz\) alternates in its sign along the \(c\)-axis and is constant in the \(a, b\)-plane. The occupied orbital is oriented in the orthorhombic \(b, c\)-plane and has almost the shape of the usual \(3z^2 - r^2\) orbital pointing near the cubic [111], direction \(22\) (56° angle with the \(c\)-axis compared to 54.7° for the [111]-direction), see Fig. 5c). The lowered orbital points to the center of one of the octahedron triangles-faces which are formed by two O2’s and one O1. It is interesting to note that the O2-O1 distances of this triangle are elongated compared to the average. This means that the TiO\(_6\)-octahedron is compressed along the direction of the occupied orbital. Since the occupied orbital is not oriented along one of the bonds the resulting antiferromagnetic exchange is not expected to be very anisotropic. Assuming the calculated orbital splitting and quantum fluctuations we obtain an ordered moment of 0.72 \(\mu_B\). The ordered moment will be further reduced as covalence will diminish the level splitting, admix orbital contributions and transfer a part of the spin to the oxygen-sites which are not active in the G-type antiferromagnetic ordering. Similar to the proposal by Moshizuki and Imada, we may hence explain most of the magnetic properties of LaTiO\(_3\) basing on the structural distortion observed in the almost stoichimetric compound. The distortion assumed in reference has not the same geometry as the one we find but is comparable in magnitude.

Since LaTiO\(_3\) exhibits intermediate strong \(t_{2g}\)-level splitting, the orbital occupancy, the admixture of an orbital moment and the resulting antiferromagnetic exchange interaction depend sensitively on the crystal structure. On one side the system may gain magnetic energy in the ordered phase either by an enhancement of the magnetic interaction parameter or via spin-orbit coupling. On the other side there will be a loss of elastic energy associated with the additional structural distortion. In the ordered state there should be a trend to increase the orbital ordering in agreement with experiment; according to our calculation the level splitting is enhanced by 6% between 155 and 8 K.

In summary we have found a sizeable deformation of the TiO\(_6\)-octahedron in LaTiO\(_3\) which causes a relevant splitting in the \(t_{2g}\)-levels (about 0.24eV).

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[1] M. Imada et al., Rev. Mod. Phys. 70, 1039 (1998).
[2] B. Keimer et al., Phys. Rev. Lett. 85, 3946 (2000).
[3] G. Kahlullin and S. Maekawa, Phys. Rev. Lett. 85, 3950 (2000).
[4] G. I. Meijer et al., Phys. Rev. B 59, 11832 (1999).
[5] T. Mizokawa and A. Fujimori, Phys. Rev. B 54, 5368 (1996).
[6] T. Mizokawa et al., Phys. Rev. B 60, 7309 (1999).
[7] Moshizuki and Imada, J. Phys. Soc. Jpn. 70, 2872 (2001).
[8] V. Fritsch et al., Phys. Rev. B 65, 212405 (2002).
[9] F. Lichtenberg et al., Z. Phys. B 82, 211 (1991).
[10] D. Bruns and B. Büchner, private communication.
[11] D. A. MacLean et al., J. Solid State Chem. 30, 35 (1979).
[12] M. Eitel and J. E. Greedan, J. Less-Common Met. 116, 95 (1986).
[13] E.F. Bertaut, Magnetism III, p. 149, Ed. Rado and Suhl, Academic Press 1963.
[14] A.D. Bruce and R.A. Cowley, Structural Phase Transitions, Taylor and Francis, London (1981).
[15] J.R. Heester et al., Acta Cryst. B53, 739 (1997).
[16] J. Akimitsu et al., J. Phys. Soc. Jpn. 70, 3475 (2001).
[17] Caution has to be taken concerning the stoichiometry of the compounds studied in [11]; also, the early magnetic study did not observe the antiferromagnetism in NdTiO\(_3\) and SmTiO\(_3\), structural data on these samples indicate a smoother crossover.
[18] J.E. Greedan, J. Less Common Metals 111, 335 (1985).
[19] G. Amow et al., J. Sol. State Chem. 121, 443 (1996).
[20] G. Amow et al., J. Sol. State Chem. 141, 262 (1998).
[21] Y. Okimoto et al., Phys. Rev. B 51, 9581 (1995).
[22] In a rotated coordinate system the orbital can be described by \(3z^2 - (1.1x^2 + 0.9y^2 + 0.8z^2)\).