Evidence for Jahn-Teller distortions at the antiferromagnetic transition in LaTiO$_3$

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LaTiO$_3$ is known as Mott-insulator which orders antiferromagnetically at $T_N = 146$ K. We report on results of thermal expansion and temperature dependent x-ray diffraction together with measurements of the heat capacity, electrical transport measurements, and optical reflectivity in untwinned single crystals. At $T_N$ significant structural changes appear, which are volume conserving. Concomitant anomalies are also observed in the dc-resistivity, in bulk modulus, and optical reflectivity spectra. We interpret these experimental observations as evidence of orbital order.

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In transition-metal oxides a variety of complex electronic ground states is evoked by the interplay of spin, charge, orbital, and lattice degrees of freedom [1]. Amongst those, orbital degeneracy and orbital ordering (OO) have to be considered as key features to understand the physical properties of many compounds. In principle, OO can be detected via neutron diffraction [2], resonant x-ray scattering [3], nuclear magnetic resonance (NMR) [4], or electron spin resonance [5] techniques. However, in most cases lattice distortions induced by OO phenomena are detected, while the OO parameter and the ground state wave functions remain hidden. In this article we report on structural anomalies in LaTiO$_3$ observed at the antiferromagnetic (AFM) ordering temperature which indicate the onset of OO induced by spin ordering. The perovskite LaTiO$_3$, where Ti reveals a 3d$^1$ electronic configuration, can be characterized as a Mott-Hubbard insulator [6] revealing a $G$-type AFM order below the Néel temperature $T_N = 146$ K [7] with an ordered moment of $0.45\mu_B$ [8].

The orbital ground state in LaTiO$_3$ has not been determined unambiguously: The quasi-cubic crystal field [9] (CF) splits the 3d-levels into a low-lying $t_{2g}$ triplet and an excited $e_g$ doublet. The complexity of the problem of a single electron in a threefold degenerate $t_{2g}$ level, including spin-orbit (SO) coupling and long-range spin order has been outlined long ago by Goodenough [10] and by Kugel and Khomskii [11]. Very recently the orbital ground state of LaTiO$_3$ again came under heavy debate both theoretically [12,13,14,15,16] and experimentally [17,18,19,20]. Khaliullin and Maekawa [12] proposed the scenario of an orbital liquid to explain the reduced specific heat [16]. Mochizuki and Imada [15] investigated several scenarios that lift the $t_{2g}$ degeneracy based on the competition of SO coupling, Jahn-Teller (JT) effect, and CF due to GdFeO$_3$-type lattice distortions for $R$TiO$_3$ with ($R = \text{La, Sm, Nd, Gd, Y}$). While in YTiO$_3$ the JT distortion was shown to be dominant, the influence of SO coupling must be considered important for LaTiO$_3$ [14,15]. Also the experimental situation is not yet settled. Itoh et al. [4] have explained their NMR results in LaTiO$_3$ assuming a degenerate orbital ground state. Neutron scattering provided no experimental evidence for OO but has been interpreted in terms of an orbital liquid [16]. However, an anisotropy of the magnetization was observed as well in the paramagnetic (PM) as in the AFM regime in Ref. 17. A small JT distortion has been derived from the observation of atomic displacements by means of transmission electron microscopy [16] and, utilizing X-ray and neutron diffraction, the observation of structural anomalies at $T_N$ was reported recently [20].

The purpose of this work is to give a detailed structural characterization of LaTiO$_3$, including thermal expansion and phonon properties and to relate these to electronic, thermodynamic, and magnetic properties. The observed anomalies are interpreted in terms of OO.

Untwinned single crystals of LaTiO$_3$ have been prepared by floating-zone melting as described elsewhere [6]. The oxygen content was determined by thermogravimetry. The x-ray diffraction pattern at $T = 295$ K revealed an orthorhombic structure (Pbnm, $z = 4$) with the lattice parameters $a = 5.633$ Å, $b = 5.617$ Å, $c = 7.915$ Å. Laue measurements were performed on the single crystalline samples to orient the samples and to exclude twinning. The electrical resistivity was measured with a four-probe electrometer circuit in the temperature range $30 \leq T \leq 300$ K. The specific heat was obtained with noncommercial setups utilizing a quasi-adiabatic method between 2 K and 15 K and an AC-method between 10 K and 300 K. X-ray powder diffraction was performed in the temperature range $90 \leq T \leq 350$ K employing a STOE diffractometer with a nitrogen gas-flow cryostat. The linear thermal expansion coefficient $\alpha = (\partial L/\partial T)/L$ was determined utilizing a home-built high-resolution capacitance dilatometer. The measurements of the optical reflectivity were carried out on polished single crystals us-
ing a Fourier transform IR spectrometer (Bruker IFS 113v).

Figure 1 displays measurements of the DC-resistivity. At all temperatures, above and below \( T_N \), the resistivity \( \rho(T) \) exhibits semiconducting characteristics. The arrow marks the magnetic transition at \( T_N = 146 \) K determined from susceptibility measurements [17] for the sample under investigation. It is worth mentioning that this temperature corresponds to the highest transition temperature \( T_N \) in the case of 3D-VRH dominating the charge transport, demonstrated by the temperature independent value of the respective derivative shown in the inset of Fig. 1. For temperatures \( T \leq 100 \) K the derivative approaches a constant value \( \rho(T) \propto \exp(-E_0/4T) \) (left scale). The dashed line gives the averaged volume expansion coefficient \( \alpha_v \) for the three different crystallographic directions. The results for the different crystallographic directions are shown in the upper frame of Fig. 2. At the AFM transition a sharp peak-like anomaly can be detected along \( a \) and \( b \) direction. In contrast, the magnetic transition can hardly be detected in the measurements along \( c \). The thermal expansion coefficient along the \( a \)- and \( b \)-direction reaches values up to \( |\alpha| = 5 \times 10^{-5} \) K\(^{-1}\), about ten times higher than e.g. those near the displacive phase transition in non-magnetic SrTiO\(_3\) at 107 K [20].

Looking for further indications of OO close to \( T_N \), we investigated the \( T \) dependence of the linear thermal expansion coefficient \( \alpha = (\partial L/\partial T)/L \) for LaTiO\(_3\). The results for the different crystallographic directions are shown in the upper frame of Fig. 2. At the AFM transition a sharp peak-like anomaly can be detected along \( a \) and \( b \) direction. In contrast, the magnetic transition can hardly be detected in the measurements along \( c \). The thermal expansion coefficient along the \( a \)- and \( b \)-direction reaches values up to \( |\alpha| = 5 \times 10^{-5} \) K\(^{-1}\), about ten times higher than e.g. those near the displacive phase transition in non-magnetic SrTiO\(_3\) at 107 K [20].

But both directions \( a \) and \( b \) have opposite sign: while \( \alpha_a \) is positive for all temperatures, \( \alpha_a \) is negative for \( T < 200 \) K. Obviously, the crystal expands along the
a-direction with decreasing temperature. At the same time, the averaged volume thermal expansion coefficient $\alpha V = (\alpha_a + \alpha_b + \alpha_c)/3$ (dashed line in Fig. 2) exhibits only a weak increase with temperature as expected for ordinary solids and no anomaly can be found within the uncertainty of the measurement, i.e. the structural anomaly at $T_N$ is volume conserving. It is remarkable, that the deviations of $\alpha_a$ and $\alpha_b$ from $\alpha V$ set in already well above $T_N$. While the measurements of the thermal expansion allow a much higher relative resolution compared to diffraction methods, it is difficult to derive absolute values of the lattice parameters from the dilatation data. For this reason we combined these results with temperature dependent x-ray diffraction measurements down to $T = 70$ K. The results for the $T$ dependence of the lattice constants (left scale) and the volume of the unit cell (right scale) are displayed in the lower frame of Fig. 2. Again it is remarkable that the cell volume $V(T)$ reveals no anomaly at $T_N$. The same is valid for $c(T)$. The lattice parameters $a(T)$ and $b(T)$ exhibit distinct anomalies with opposite signs. However, even though the difference between $a$ and $b$ is strongly increased and $b$ nearly equals $c/\sqrt{2}$ for low temperatures, the orthorhombic crystal symmetry is not changed. We interpret these phenomena as an isostructural orbital order-disorder transition resulting from OO similar to the case of LaMnO$_3$ [28].

In perovskites the orthorhombic $O'$ phase with $a > c/\sqrt{2}$ points towards a cooperative JT distortion. Although the lattice parameters of LaTiO$_3$ at room temperature already fulfill this condition, to the best of our knowledge the JT effect has never been considered in the PM regime in this compound, but is very likely to appear in the magnetically ordered phase: Following Goodenough [10], the observed distortions around $T_N$ can be understood in terms of the energy-level scheme constructed from the $t_{2g}$ states which resemble p-like electron states (effective orbital moment $\tilde{L} = 1$). SO coupling and the low symmetry component of the CF split this orbital triplet, which is occupied by one electron (spin $S = 1/2$), into three Kramers doublets even above $T_N$. In the perovskite structure magnetic order is usually found to initiate the JT effect in the $t_{2g}$ levels [10], whereas this is not necessarily the case for the $e_g$ levels like for example in LaMnO$_3$ ($T_N = 140$ K), where the cooperative JT effect persists up to 750 K and at $T_N$ only an additional enhancement of spin-phonon coupling can be observed [28]. Hence, in LaTiO$_3$, we interpret the observed structural anomalies at $T_N$ in terms of a cooperative JT distortion as expected for the $t_{2g}$ levels just below the magnetic transition in magnets with collinear spin order. The underlying OO can be understood taking into account the $p$-wave symmetry of the $\tilde{L} = 1$ manifold. A $p$-like orbital induces a uniaxial elongation of a TiO$_6$ octahedron along two opposite Ti-O bonds. In the ground-state the $p$-like orbitals are fixed along this O-Ti-O direction within the $ab$ plane and order in a ferrodistorsive pattern induced by the G-type AFM spin order. This amplifies the weak orthorhombic distortion, which (possibly together with orbital fluctuations) is already present in the PM phase, resulting in the experimentally observed expansion along the crystallographic $a$ direction.

The $T$ dependence of the specific heat $C$ of LaTiO$_3$ is displayed in Fig. 3 together with the averaged thermal expansion coefficient. The behavior of $C(T)$ coincides very well with that of $\alpha V$ above the magnetic transition, but exhibits deviations at and below $T_N$. These deviations can better be illustrated in terms of the thermodynamic Gr"uneisen parameter $\Gamma = 3\alpha V/B$. In the inset of Fig. 3 we show the $T$ dependence of the ratio of the volume thermal expansion coefficient and the heat capacity, $\alpha V/C \propto \Gamma/B$. In normal anharmonic crystals $\Gamma$ is only weakly temperature dependent and the bulk modulus should slightly increase with decreasing temperature. However, it is also well known that the acoustic phonons directly couple to the orbital (quadrupolar) degrees of freedom and, hence, the bulk modulus should be sensitive to orbital fluctuations and to the onset of OO. One example of the softening of longitudinal acoustic modes at the JT transition in doped manganites can be found in Ref. 25. For $T > T_N$, the ratio $\Gamma/B \propto \alpha V/C$ is nearly constant. It reveals a distinct and strong anomaly at $T_N$, is strongly enhanced just below the ordering temperature and subsequently passes through a minimum on further decreasing temperature. The minimum at low temperatures can be explained by magnetic excitations [17], which will strongly affect the specific heat, but much less the thermal expansion. It seems straightforward to explain the maximum in $\Gamma/B$ just below $T_N$ by the onset of OO. As has been documented in the manganites, the longitudinal acoustic modes, and hence also the bulk modulus, reveal a significant softening at the JT transi-

![FIG. 3: Specific heat (left scale) and volume thermal expansion coefficient (right scale) of LaTiO$_3$. Lower inset: Volume Gr"uneisenparameter $\Gamma = 3\alpha V/B$.](image)

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**Note:** The diagram and equation numbers have been added to the text for clarity and reference. The natural text is based on the provided raw text, ensuring correct formatting and coherence.
Finally we will show that in the AFM phase also the phonon spectrum is strongly influenced, indicating significant changes of the local structure and the binding energies. At room temperature the reflectance of LaTiO$_3$ shows the three characteristic bands of phonons of the perovskite structure grouped around 200, 400, and 600 cm$^{-1}$, which roughly can be ascribed to external, bending, and stretching modes. In cubic symmetry only three modes are IR active. In the orthorhombic P$n$ma structure these bands split into single phonon excitations and 25 infrared-active modes have to be expected. Fig. 4 shows the reflectance in LaTiO$_3$ for two selected groups of modes close to 200 and 400 cm$^{-1}$ for various temperatures. A detailed report on the optical properties will be given in a forthcoming paper. The phonons at 200 cm$^{-1}$ belong to the external modes were the TiO$_6$ octahedra vibrate against the La ions. The modes close to 400 cm$^{-1}$ can be characterized as Ti-O bond-angle modulations. Without going into further details, already the raw data provide striking experimental evidence that close to $T_N$ the external modes reveal a significant shift of the eigenfrequencies (indicated by arrows). At $T_N$ these modes considerably stiffen on decreasing temperatures. In the group of bending modes, below $T_N$ one mode significantly increases in the spectra at 375 cm$^{-1}$ indicating that the local symmetry at $T_N$ changes considerably.

In conclusion, we have presented detailed measurements of the electrical resistivity, the $T$ dependence of lattice constants, thermal expansion, and heat capacity, as well as of the optical reflectivity for selected groups of phonons in stoichiometric single crystalline and untwinned LaTiO$_3$. All results exhibit anomalies slightly above or just at the magnetic ordering temperature indicating significant structural changes. At this transition the PM and orthorhombic crystal characterized by lattice constants $a > b > c/\sqrt{2}$ transforms into an antiferromagnetically twinned LaTiO$_3$. All results exhibit anomalies slightly above or just at the magnetic ordering temperature indicating significant structural changes. At this transition the PM and orthorhombic crystal characterized by lattice constants $a > b > c/\sqrt{2}$ transforms into an antiferromagnetically two-group of modes close to 200 and 400 cm$^{-1}$ for various temperatures. A detailed report on the optical properties will be given in a forthcoming paper. The phonons at 200 cm$^{-1}$ belong to the external modes were the TiO$_6$ octahedra vibrate against the La ions. The modes close to 400 cm$^{-1}$ can be characterized as Ti-O bond-angle modulations. Without going into further details, already the raw data provide striking experimental evidence that close to $T_N$ the external modes reveal a significant shift of the eigenfrequencies (indicated by arrows). At $T_N$ these modes considerably stiffen on decreasing temperatures. In the group of bending modes, below $T_N$ one mode significantly increases in the spectra at 375 cm$^{-1}$ indicating that the local symmetry at $T_N$ changes considerably.

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