

# MAGNETIC AND THERMODYNAMIC PROPERTIES OF $\text{LaTiO}_3$ \*

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The orbital ground state of  $\text{LaTiO}_3$  is still under debate. Recent letters [B. Keimer, *et al.*, *Phys. Rev. Lett.* **85**, 3946 (2000) and G. Khaliullin, S. Maekawa, *Phys. Rev. Lett.* **85**, 3950 (2000)] discuss a scenario of a locally disordered orbital liquid and provide theoretical predictions about orbital contributions to the specific heat. We present magnetic measurements together with results for the heat capacity. In the magnetic susceptibility a distinct anisotropy can be found, not only in the magnetically ordered regime but also well above. The paramagnetic susceptibility cannot be evaluated in terms of a Curie-Weiss type behavior and seems to be determined by a small crystal-field splitting and spin-orbit coupling. In addition the heat capacity of  $\text{LaTiO}_3$  is compared with that of orbitally ordered  $\text{LaMnO}_3$  for temperatures around and below  $T_N$ . No indications for additional orbital contributions could be detected.

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## 1. Introduction

$\text{LaTiO}_3$  is an antiferromagnetic  $3d^1$  Mott-Hubbard-Insulator with a Néel-temperature  $T_N = 146$  K. The system can roughly be characterized as a pseudo-cubic perovskite, with degenerate  $t_{2g}$ -orbitals. According to the Goodenough-Kanamori rules one expects local ferro-type orbital correlations in a spin-Néel state, but no evidence of orbital order in  $\text{LaTiO}_3$  was found [1]. Because of the only weakly distorted  $\text{TiO}_6$  octahedra in  $\text{LaTiO}_3$  the crystal field acting on the  $\text{Ti}^{3+}$  ions ( $\text{Ti}^{3+}: 3d^1$ ) is nearly cubic, resulting

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in a threefold degenerate  $t_{2g}$  band. In recent letters it was proposed that the system could be described assuming a disordered orbital liquid ground state, where the orbital degrees of freedom are interacting via magnons and which is dominated by fluctuations [2]. Below the opening of an orbital gap, also a linear term in the specific heat is predicted [2]. The purpose of this work is to characterize the electronic and thermodynamic properties of  $\text{LaTiO}_3$  and to relate these to a possible orbital origin in comparison to  $\text{LaMnO}_3$ .

All investigations were carried out using single crystals of  $\text{LaTiO}_3$ , which were prepared by floating-zone melting as described elsewhere [3]. The X-ray diffraction pattern at room temperature reveals an (almost pseudo cubic) orthorhombic structure ( $Pbnm$ ) with the lattice parameters  $a = 5.633 \text{ \AA}$ ,  $b = 5.617 \text{ \AA}$ ,  $c = 7.915 \text{ \AA}$ , which is comparable to results reported in literature (*e.g.* Ref. [4]). The magnetization measurements were performed with a commercial SQUID-system between 1.8 K and 500 K. No geometric demagnetization effects had to be considered due to the small absolute value of the ferromagnetic magnetization (see below). The specific heat has been measured with noncommercial setups utilizing a quasi-adiabatic method between 2 K and 15 K and an AC-method between 10 K and 200 K.

## 2. Results and discussion

In Fig. 1 we present measurements of the DC susceptibility up to  $T = 500 \text{ K}$ . The magnetic phase transition into a (canted) antiferromagnet takes place at  $T_N = 146 \text{ K}$ . This corresponds to the highest reported transition temperatures and thus denotes the quality of the samples, as already smallest deviations in the stoichiometry lower  $T_N$  drastically [3]. The small ferromagnetic component can be explained by the antisymmetric Dzyaloshinsky–Moriya (DM) interaction due to the buckling of the oxygen octahedra and lies in the order of  $0.01\mu_B$ /formula unit [4,5]. The antiferromagnetic component was determined to be  $\approx 0.45\mu_B$  by neutron diffraction experiments [1]. The onset of the spontaneous magnetization can be described using a critical exponent of  $\gamma = 0.34 \pm 0.01$  as it is typical for experimentally observed magnetic second order phase-transitions. In the magnetically ordered phase a clear anisotropy can be detected [5]. Nevertheless, it is astonishing that already well above  $T_N$  the susceptibility is anisotropic (see inset of Fig. 1). In addition it is notable that the small but distinct slope of the inverse paramagnetic susceptibility can be described neither by a Curie–Weiss type behavior nor by a constant Pauli-contribution (which would be difficult to motivate in an insulator anyway). A parameterization of  $\chi^{-1}$  in terms of a Curie–Weiss law would lead to an effective moment of  $3.2 \mu_B$  and a Curie–Weiss temperature of  $-1100 \text{ K}$ , both values beyond any physical interpretation. The observed behavior can be understood considering the spin-orbit coupling

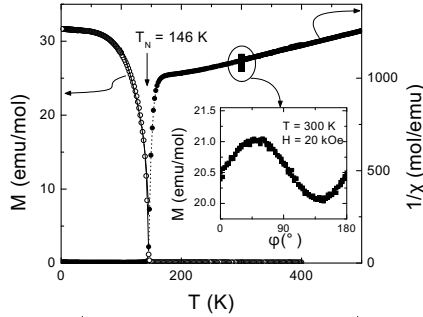


Fig. 1. DC magnetization  $M$  (left scale, open symbols) and inverse DC susceptibility  $1/\chi$  (right scale, closed symbols) of  $\text{LaTiO}_3$  in an external field of 100 Oe. The solid line below  $T_N$  is calculated as  $M \propto (T_N - T)^\gamma$  with  $\gamma = 0.34 \pm 0.1$ . The inset gives the magnetization at  $T = 300$  K in dependence of the angle  $\phi$  between the  $b, c$ -plane and the magnetic field ( $H = 20$  kOe).

and the local axial crystal field [5]. Expecting a spin-orbit splitting value of  $\Delta \approx 300$  K, the susceptibility is dominated by a van Vleck contribution. The effective  $g$ -value for the pure quadruplet  $j = 3/2$  is zero, but becomes sizable and anisotropic due to the axial crystal field [5]. The resulting complex orbital configuration generates the observed paramagnetic behavior. Nevertheless, it remains unclear how the orbital ground state is influenced by the onset of magnetic order. To elucidate this question and to find a possible evidence for the postulated opening of an orbital gap [2], caloric measurements were performed for temperatures around and below  $T_N$ .

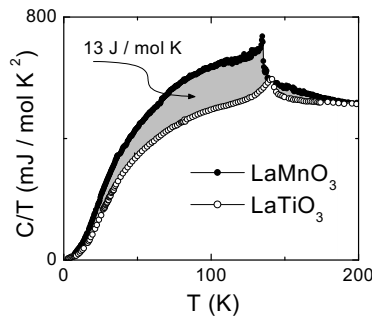


Fig. 2. Specific heat of  $\text{LaMnO}_3$  (closed circles ●) and  $\text{LaTiO}_3$  (open circles ○) represented as  $C/T$  vs  $T$  in a temperature range between 5 K and 200 K.

The specific heat of  $\text{LaTiO}_3$  is displayed as  $C/T$  vs  $T$  in Fig. 2. For comparison the specific heat of single crystalline  $\text{LaMnO}_3$  is shown. This system is also an antiferromagnetic insulator ( $T_N = 140$  K) and also shows the orthorhombic  $O'$  structure, where the slight distortion from cubic symmetry results from a buckling of the oxygen octahedra, but here with a value

for  $c/\sqrt{2}a < 1$  smaller than in  $\text{LaTiO}_3$ . In the  $\text{LaMnO}_3$  ( $\text{Mn}^{3+}: 3d^4$ ) the  $e_g$  band is occupied by one electron, the degeneracy is lifted by the Jahn–Teller effect ( $T_{\text{JT}} = 800$  K), and the orbitals are ordered. At high temperatures ( $T > T_{\text{N}}$ ) the heat capacities almost coincide signaling similar phonon contributions. Close to  $T_{\text{N}}$  distinct anomalies show up in both compounds and for  $T < T_{\text{N}}$ ,  $C/T$  of  $\text{LaMnO}_3$  exceeds the heat capacity of  $\text{LaTiO}_3$  significantly. Electronic (spin and orbital) entropy obviously determines this behavior. At low temperatures linear contributions to the specific heat are found, which can be addressed to magnons in both compounds [5]. The magnetic entropy which is hidden at temperatures below  $T_{\text{N}}$  should be of the order  $\ln(2j + 1)$ . The area between the two curves shown in Fig. 2 sums up to approximately  $\Delta S \approx 13$  J/mol K. With  $j = \frac{3}{2}$  ( $\text{LaTiO}_3$ ) and  $j = S = 2$  ( $\text{LaMnO}_3$ ) the calculated difference is 1.9 J/mol K and becomes 7.8 J/mol K, if we use the spin-only value of  $\text{LaTiO}_3$  with  $S = \frac{1}{2}$ . Hence, even considering only the spin states the heat capacity of  $\text{LaMnO}_3$  is too large or that of  $\text{LaTiO}_3$  is too small. Taking orbital contributions of  $\text{LaTiO}_3$  into account would further reduce the calculated difference in electronic entropy, contrary to the experimental observation.

In conclusion, we examined the magnetic and caloric properties of  $\text{LaTiO}_3$  as well in the paramagnetic and antiferromagnetic regime. The anisotropic van Vleck type behavior of the susceptibility can be explained by means of spin-orbit splitting and small crystal-fields, suggesting a complex orbital ground state. The comparison of the additional contributions to the specific heat below  $T_{\text{N}}$  on  $\text{LaTiO}_3$  and in orbitally ordered  $\text{LaMnO}_3$  suggests the absence of orbital contributions, such as *e.g.* the opening of an orbital gap. In addition even the magnetic entropy in  $\text{LaTiO}_3$  seems to be rather small, compared with naive assumptions. Nevertheless there are indications from preliminary measurements of the thermal expansion and the temperature dependent x-ray diffraction, that even orbital order at  $T_{\text{N}}$  cannot be ruled out [6]. From this the nature of the spin-orbital ground state in  $\text{LaTiO}_3$  is still unclear and further investigations are needed.

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