

MAGNETIC AND THERMODYNAMIC PROPERTIES OF LaTiO_3 *

J. HEMBERGER, V. FRITSCH, H.-A. KRUG VON NIDDA, R. WEHN
F. LICHTENBERG, A. LOIDL

Elektronische Korrelation und Magnetismus, Institut für Physik
Universität Augsburg, 86135 Augsburg, Germany

AND M.V. EREMIN

Kazan State University, 420008 Kazan, Russia

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The orbital ground state of 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 LaTiO_3 is compared with that of orbitally ordered LaMnO_3 for temperatures around and below T_N . No indications for additional orbital contributions could be detected.

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1. Introduction

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 LaTiO_3 was found [1]. Because of the only weakly distorted TiO_6 octahedra in LaTiO_3 the crystal field acting on the 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 LaTiO_3 and to relate these to a possible orbital origin in comparison to LaMnO_3 .

All investigations were carried out using single crystals of 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 χ^{-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 K , both values beyond any physical interpretation. The observed behavior can be understood considering the spin-orbit coupling

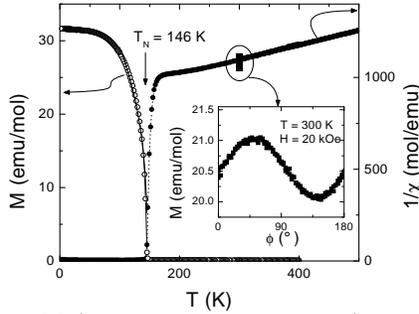


Fig. 1. DC magnetization M (left scale, open symbols) and inverse DC susceptibility $1/\chi$ (right scale, closed symbols) of LaTiO_3 in an external field of 100 Oe. The solid line below T_N is calculated as $M \propto (T_N - T)^\gamma$ with $\gamma = 0.34 \pm 0.1$. The inset gives the magnetization at $T = 300$ K in dependence of the angle ϕ 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 .

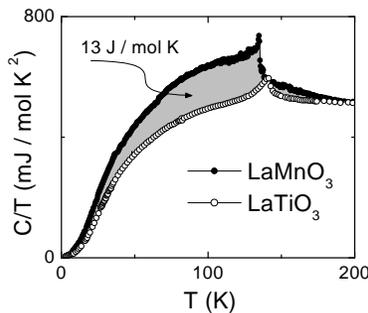


Fig. 2. Specific heat of LaMnO_3 (closed circles ●) and LaTiO_3 (open circles ○) represented as C/T vs T in a temperature range between 5 K and 200 K.

The specific heat of LaTiO_3 is displayed as C/T vs T in Fig. 2. For comparison the specific heat of single crystalline 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 LaTiO_3 . In the 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_{N} distinct anomalies show up in both compounds and for $T < T_{\text{N}}$, C/T of LaMnO_3 exceeds the heat capacity of 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_{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 $j = \frac{3}{2}$ (LaTiO_3) and $j = S = 2$ (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 LaTiO_3 with $S = \frac{1}{2}$. Hence, even considering only the spin states the heat capacity of LaMnO_3 is too large or that of LaTiO_3 is too small. Taking orbital contributions of 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 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_{N} on LaTiO_3 and in orbitally ordered 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 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_{N} cannot be ruled out [6]. From this the nature of the spin-orbital ground state in LaTiO_3 is still unclear and further investigations are needed.

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