

## Determination of the Orbital Moment and Crystal-Field Splitting in $\text{LaTiO}_3$

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Utilizing a sum rule in a spin-resolved photoelectron spectroscopic experiment with circularly polarized light, we show that the orbital moment in  $\text{LaTiO}_3$  is strongly reduced from its ionic value, both below and above the Néel temperature. Using Ti  $L_{2,3}$  x-ray absorption spectroscopy as a local probe, we found that the crystal-field splitting in the  $t_{2g}$  subshell is about 0.12–0.30 eV. This large splitting does not facilitate the formation of an orbital liquid.

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$\text{LaTiO}_3$  is an antiferromagnetic insulator with a pseudocubic perovskite crystal structure [1–3]. The Néel temperature varies between  $T_N = 130$  and 146 K, depending on the exact oxygen stoichiometry [3–5]. A reduced total moment of about 0.45–0.57  $\mu_B$  in the ordered state has been observed [3–5], which could imply the presence of an orbital angular momentum that is antiparallel to the spin momentum in the  $\text{Ti}^{3+} 3d^1$  ion [5,6]. In a recent Letter, however, Keimer *et al.* [7] have reported that the spin wave spectrum is nearly isotropic with a very small gap, and concluded that therefore the orbital moment must be quenched. To explain the reduced moment, they proposed the presence of strong orbital fluctuations in the system. This seems to be supported by the theoretical study of Khaliullin and Maekawa [8], who suggested that  $\text{LaTiO}_3$  is in an orbital liquid state. If true, this would in fact constitute a completely novel state of matter. By contrast, Cwik *et al.* [3], Mochizuki and Imada [9], as well as Pavarini *et al.* [10] estimated that small orthorhombic distortions present in  $\text{LaTiO}_3$  would produce a crystal-field (CF) splitting strong enough to lift the Ti  $3d t_{2g}$  orbital degeneracy. However, one of the latest theoretical papers finds a much smaller CF splitting, leaving open the possibility for an orbital liquid state [11].

In view of these controversies, it is highly desirable to have experimental tests which would allow to uniquely choose between different possibilities. On the experimental side, however, very little is known about the energetics of the  $\text{LaTiO}_3$  system. We have carried out spin-resolved photoemission (PES) experiments using circularly polar-

ized light, and by applying a sum rule we have determined unambiguously that the orbital moment is indeed strongly reduced from its ionic value in a wide temperature range. We have also performed temperature dependent Ti  $L_{2,3}$  x-ray absorption (XAS) measurements, and found from this local probe that the Ti  $3d t_{2g}$  orbitals are split by about 0.12–0.30 eV. Our results are consistent with the conclusion of Keimer *et al.* in that the orbital moment is very small. However, the sizable CF splitting does not provide conditions favorable for the realization of an orbital liquid.

Twinned single crystals of  $\text{LaTiO}_3$  with  $T_N = 146$  K have been grown by the traveling floating-zone method. The PES experiments were performed at the ID08 beam line of the European Synchrotron Radiation Facility in Grenoble. The photon energy was set to 700 eV, sufficiently high to ensure bulk sensitivity [12,13]. The degree of circular polarization was close to 100% and the spin detector had an efficiency (Sherman function) of 17%. The combined energy resolution for the measurements was 0.6 eV and the angle  $\theta$  between the Poynting vector of the light and the analyzer was  $60^\circ$ . The XAS measurements were carried out at the Dragon beam line of the NSRRC in Taiwan, with a photon energy resolution set at 0.15 eV for the Ti  $L_{2,3}$  edges ( $h\nu \approx 450\text{--}470$  eV). The spectra were recorded using the total electron yield method. Clean sample areas were obtained by cleaving the crystals inside the measuring chambers with a pressure of low  $10^{-10}$  mbar.

Figure 1 shows the spin-resolved photoemission spectra of the  $\text{LaTiO}_3$   $3d$  states in the valence band, taken with

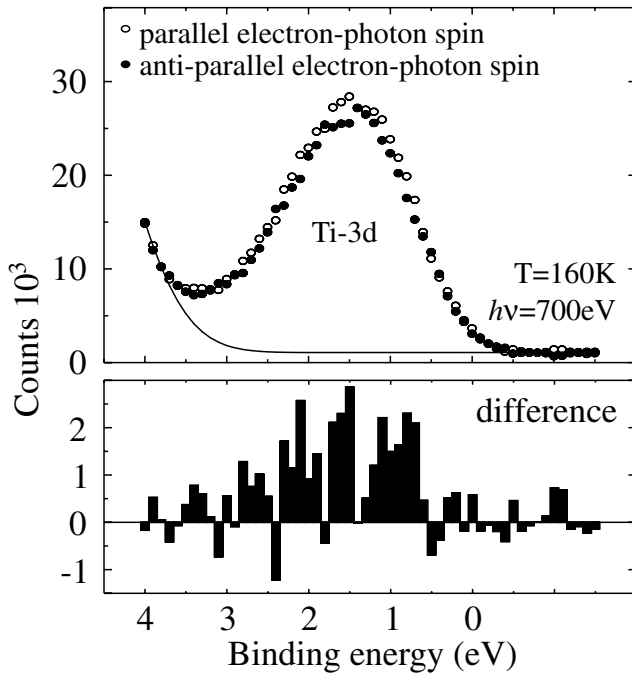


FIG. 1. Spin-resolved photoemission spectra of twinned LaTiO<sub>3</sub> single crystal taken with circularly polarized light.

circularly polarized light. The spectra are corrected for the spin detector efficiency. One can observe a small but reproducible difference between the spectra taken with the photon spin (given by the helicity of the light) parallel or antiparallel to the electron spin. The relevant quantity to be evaluated here is the integrated intensity of the difference spectrum ( $\int_{\text{dif}}$ ) relative to that of the integrated intensity of the sum spectrum ( $\int_{\text{sum}}$ ). This can be directly related to the expectation value of the spin-orbit operator ( $\mathbf{l} \cdot \mathbf{s}$ ) applied to the *initial* state, thanks to the sum rule developed by van der Laan and Thole [14]. For a randomly oriented sample [15], and for a  $3d$  system in which the final states are mainly of  $f$  character due to the high photon energies used [16], we obtain:

$$\frac{\int_{\text{dif}}}{\int_{\text{sum}}} = -\frac{1}{U(\theta)} \frac{\langle \sum_i \mathbf{l}_i \cdot \mathbf{s}_i \rangle}{3\langle n \rangle}, \quad (1)$$

where  $U(\theta) = [2 - \cos^2(\theta)]/[3 - 4\cos^2(\theta)]$  is a geometrical factor to account for the angle between the Poynting vector of the light and the outgoing photoelectron, the index  $i$  runs over the electrons in the  $3d$  shell, and  $\langle n \rangle$  is the number of  $3d$  electrons contributing to the spectra.

With  $\int_{\text{dif}} / \int_{\text{sum}} \approx 0.03$ ,  $\theta = 60^\circ$ , and  $\langle n \rangle \approx 0.8$  from our cluster calculations [16], we arrive at  $\langle \sum_i \mathbf{l}_i \cdot \mathbf{s}_i \rangle \approx -0.06$  (in units of  $\hbar^2$ ); see Fig. 2. This is, in absolute value, an order of magnitude smaller than the maximum possible value of  $-0.50$  for a  $3d^1 t_{2g}$  ion with  $s_z = 1/2$  and  $l_z = -1$  (in units of  $\hbar$ ). In fact, the  $-0.06$  value is so small that we can directly conclude that for this  $3d^1$  ion the orbital momentum is practically quenched. Figure 2 shows that

this is the case for a wide range of temperatures, both below and above  $T_N$ .

Having established that LaTiO<sub>3</sub> has a strongly reduced orbital moment, we now focus on the issue whether this is caused by strong orbital fluctuations [7,8] or rather by strong local CF effects as theoretically proposed [3,9,10]. To this end, we carry out temperature dependent x-ray absorption spectroscopy measurements at the Ti  $L_{2,3}$  ( $2p \rightarrow 3d$ ) edges. Here we make use of the fact that the  $2p$  core hole produced has a strong attractive Coulomb interaction with the  $3d$  electrons. This interaction is about 6 eV, and is more than 1 order of magnitude larger than the bandwidth of the  $3d t_{2g}$  states. The absorption process is therefore strongly excitonic, making the technique an ideal and extremely sensitive local probe [16–18].

The top panel of Fig. 3 shows the experimental Ti  $L_{2,3}$  XAS spectra for several temperatures below and above  $T_N$ . One can clearly observe that the spectra are temperature independent. In the subsequent sections we will discuss two aspects of the spectra that are relevant for the determination of the energetics and symmetry of the ground state and the lowest excited states of LaTiO<sub>3</sub>. The first is the detailed line shape of the spectra, and the second is their temperature insensitivity.

To start with the first aspect, we have performed simulations in order to obtain the best match with the experimental spectra, and by doing so, to determine the magnitude of the CF splitting in the  $t_{2g}$  levels. For this we have used the well-proven configuration interaction cluster model that includes the full atomic multiplet theory and the hybridization with the O  $2p$  ligands [16–18]. Curves (a) in left panel of Fig. 3 are the calculated isotropic spectra of a TiO<sub>6</sub> cluster with a noncubic crystal-field splitting of  $\Delta_{\text{CF}} = 230$  meV, as obtained, using a Wannier function projection procedure, from our local-density approximation (LDA) calculation [19] on the refined orthorhombic crystal structure [3]. One can see that

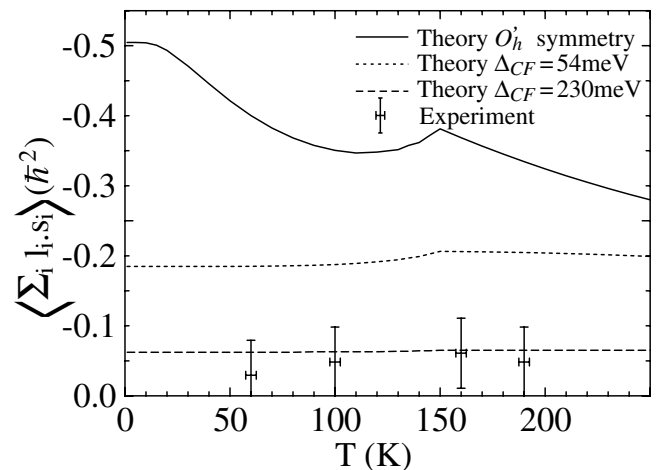


FIG. 2.  $\langle \sum_i \mathbf{l}_i \cdot \mathbf{s}_i \rangle$  values extracted from the spin-resolved circularly polarized photoemission data, together with theoretical predictions for various crystal-field parameters.

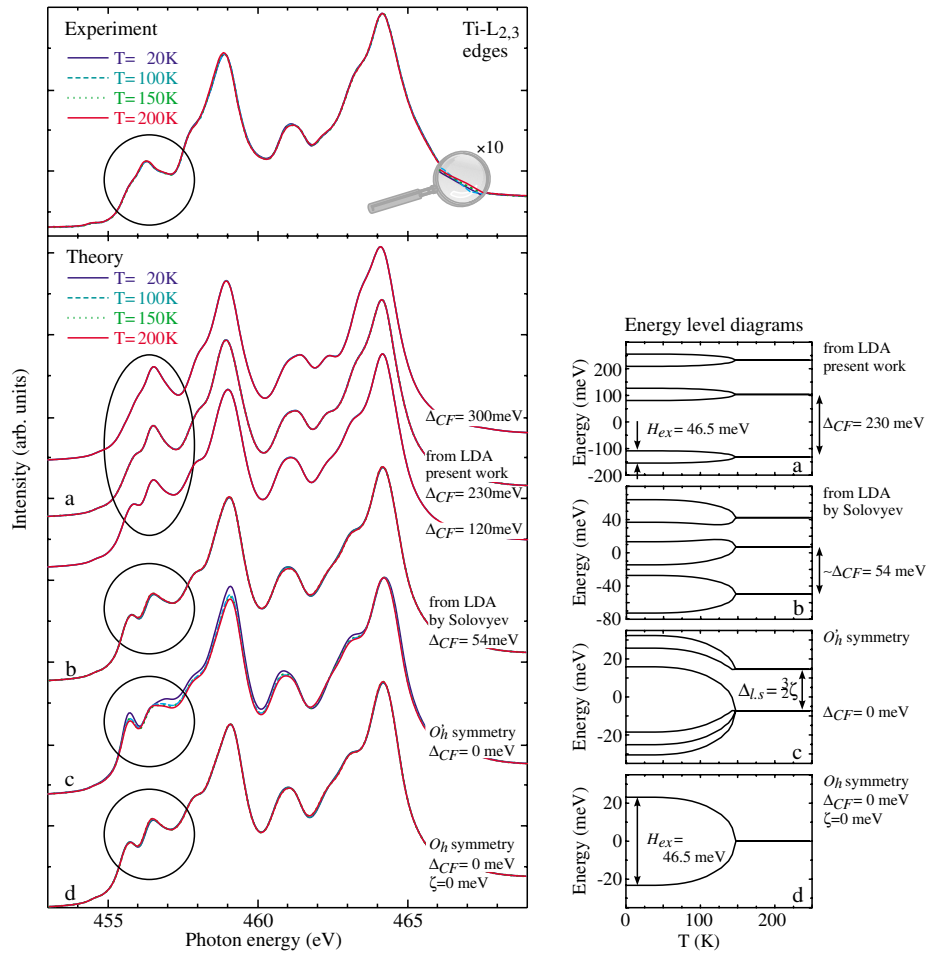


FIG. 3 (color online). Top panel: experimental Ti  $L_{2,3}$  XAS spectra taken from a twinned  $\text{LaTiO}_3$  single crystal at 20, 100, 150, and 200 K. Left panel: simulated isotropic spectra calculated for a  $\text{TiO}_6$  cluster at 20, 100, 150, and 200 K for several CF parameters. Right panel: corresponding energy level diagrams for the cluster in an exchange field of  $H_{ex} = 46.5$  meV (from Keimer *et al.* [7]) at  $T = 0$  K and vanishing at  $T_N = 146$  K. Four scenarios are presented: (a) noncubic symmetry with  $\Delta_{CF} = 230$  meV from our LDA calculation [19] and with  $\Delta_{CF} = 120$  and 300 meV, (b) noncubic symmetry with  $\Delta_{CF} = 54$  meV from Solovyev [11], (c)  $O'_h$ , and (d)  $O_h$  symmetry. The spin-orbit constant  $\zeta$  is 15.2 meV for (a), (b), and (c), and 0 for (d). Note the very different energy scales.

the experimental data are well reproduced. We have also carried out simulations with other  $\Delta_{CF}$  values, and found that  $\Delta_{CF}$  should be in the range of about 120 to 300 meV in order to maintain the good agreement. If we chose, for example,  $\Delta_{CF} = 54$  meV as proposed from the LDA calculations by Solovyev [11], we find that the simulated line shapes are less satisfactory: curves (b) show deviations from the experimental spectra, especially in the encircled region. More important is that the situation without CF splitting, i.e., in  $O'_h$  symmetry as shown by curves (c), definitely does not agree with the experiment. Also the case as depicted by curves (d), in which the spin-orbit interaction in  $O_h$  symmetry is artificially switched off as to obtain fully degenerate  $t_{2g}$  levels, which was the starting point of the treatment of Khaliullin and Maekawa [8], does not agree with the measurement. From the line shape analysis we can thus firmly conclude that the crystal-field splitting in  $\text{LaTiO}_3$  is quite appreciable.

The second aspect of the Ti  $L_{2,3}$  XAS spectra is their temperature insensitivity. This may look like a trivial observation, but actually it is not. For a  $3d$  system with an open  $t_{2g}$  shell, one usually expects to see an appreciable temperature dependence in the isotropic spectrum: for instance, in Fig. 4 we depict the Co  $L_2$  XAS spectra of polycrystalline CoO, and indeed, we do see a strong temperature dependence. The reason for this behavior is that for a system with an unquenched orbital moment like CoO, the ground state and the lowest excited states are split in energy by the spin-orbit interaction and are separated in energy by an amount of the order of the spin-orbit coupling [20]. Since the final states that can be reached from the ground state and from the lowest excited states are very different, the spectrum will change with temperature depending on how much each of the initial states is thermally populated. In Fig. 4 we have also simulated the CoO spectra using a  $\text{CoO}_6$  cluster model, and clearly the tem-

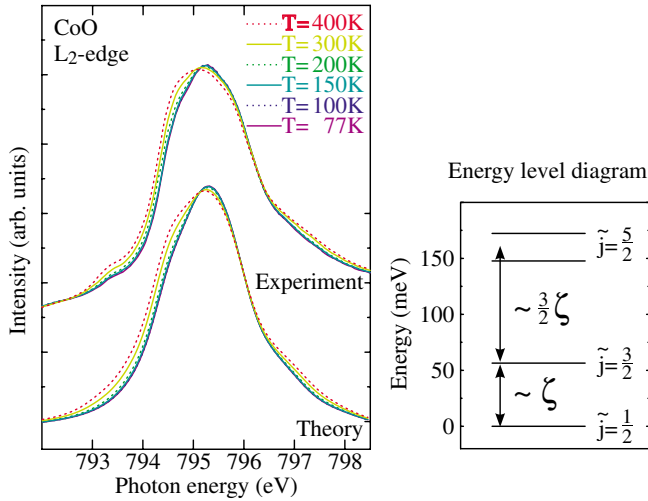


FIG. 4 (color online). Experimental temperature dependent Co  $L_2$  XAS spectra of polycrystalline CoO, together with the simulated isotropic spectra and corresponding energy level diagram.

perature dependence is reproduced. In the left panel of Fig. 3, we have calculated the  $\text{LaTiO}_3$  spectra assuming a perfect  $O'_h$  local symmetry, and the resulting curves (c) show indeed also a strong temperature dependence. However, the fact that experimentally the  $\text{LaTiO}_3$  spectra are temperature independent indicates directly that the spin-orbit interaction is inactive in  $\text{LaTiO}_3$ . Indeed, simulations carried out for CF splittings much larger than the spin-orbit interaction, e.g., curves (a) and (b) in Fig. 3, are not temperature sensitive. The experimentally observed temperature insensitivity is therefore fully consistent with the very small orbital moment found from the spin-resolved photoemission measurements. We would like to note that the XAS simulations were carried out including, for completeness, the presence of an exchange field as depicted in the right panel of Fig. 3, although this had a negligible influence on the isotropic spectra.

Returning to the spin-resolved photoemission data, we are able to reproduce the very low  $\langle \sum_i \mathbf{l}_i \cdot \mathbf{s}_i \rangle$  of about  $-0.06$  if we use  $\Delta_{\text{CF}}$  values in the range of 120 and 300 meV. In Fig. 2 we show the results calculated for the  $\Delta_{\text{CF}} = 230$  meV as found from our LDA. The corresponding extracted orbital moment is  $L_z = -0.06$ . The  $\Delta_{\text{CF}} = 54$  meV value as proposed by Solovyev [11], however, clearly gives a  $\langle \sum_i \mathbf{l}_i \cdot \mathbf{s}_i \rangle$  value that deviates substantially from the experimental one. The orbital moment in this scenario is quite large:  $L_z = -0.24$ . It is almost superfluous to note that the calculation with  $\Delta_{\text{CF}} = 0$  meV, i.e., in perfect  $O'_h$  symmetry, gives results that are in strong disagreement with the experiment.

To conclude, we have observed that the orbital moment in  $\text{LaTiO}_3$  is strongly reduced from its ionic value, supporting the analysis from the neutron experiment by Keimer *et al.* [7]. Our experiments have also revealed the presence of noncubic crystal fields sufficiently strong to

split the Ti  $t_{2g}$  levels by about 0.12–0.30 eV, confirming several of the theoretical estimates [3,9,10,19]. Such a large crystal-field splitting provides a strong tendency for the Ti 3d orbitals to be spatially locked; i.e., the quadrupole moment measured at 1.5 K by NMR [21] should also persist at the more relevant higher temperatures, making the formation of an orbital liquid in  $\text{LaTiO}_3$  rather unfavorable.

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- [1] D. A. MacLean, H.-N. Ng, and J. E. Greedan, *J. Solid State Chem.* **30**, 35 (1979).
- [2] M. Eitel and J. E. Greedan, *J. Less-Common Met.* **116**, 95 (1986).
- [3] M. Cwik *et al.*, *Phys. Rev. B* **68**, 060401 (2003).
- [4] J. P. Goral and J. E. Greedan, *J. Magn. Magn. Mater.* **37**, 315 (1983).
- [5] G. I. Meijer *et al.*, *Phys. Rev. B* **59**, 11832 (1999).
- [6] T. Mizokawa and A. Fujimori, *Phys. Rev. B* **54**, 5368 (1996).
- [7] B. Keimer *et al.*, *Phys. Rev. Lett.* **85**, 3946 (2000).
- [8] G. Khaliullin and S. Maekawa, *Phys. Rev. Lett.* **85**, 3950 (2000).
- [9] M. Mochizuki and M. Imada, *Phys. Rev. Lett.* **91**, 167203 (2003).
- [10] E. Pavarini *et al.*, *Phys. Rev. Lett.* **92**, 176403 (2004).
- [11] I. V. Solovyev, *Phys. Rev. B* **69**, 134403 (2004).
- [12] E. Weschke *et al.*, *Phys. Rev. B* **44**, 8304 (1991).
- [13] A. Sekiyama *et al.*, *Nature (London)* **403**, 396 (2000).
- [14] G. van der Laan and B. T. Thole, *Phys. Rev. B* **48**, 210 (1993).
- [15] G. Ghiringhelli *et al.*, *Phys. Rev. B* **66**, 075101 (2002).
- [16] A. Tanaka and T. Jo, *J. Phys. Soc. Jpn.* **63**, 2788 (1994);  $p$ -final states contribute about 4% to the signal when 450 eV photons are used, and much less for the actual 700 eV photons;  $\text{TiO}_6$  cluster with  $\Delta = 4.0$ ,  $U_{\text{dd}} = 4.0$ ,  $pd\sigma = -2.22$ ,  $10Dq = 1.0$ ,  $T_{\text{pp}} = 0.5$ ,  $U_{\text{dc}} = 6.0$ , all values in eV. Here we assume that the weak spin signal of the Ti 3d inside the overwhelming O 2p band is negligible. We have verified using the  $\text{TiO}_6$  cluster that this signal amounts to less than  $\approx -0.02$  for  $\langle \sum_i \mathbf{l}_i \cdot \mathbf{s}_i \rangle$ , which is, in absolute terms, indeed very small and also well within the experimental error of  $\pm 0.05$ .
- [17] See review by F. M. F. de Groot, *J. Electron Spectrosc. Relat. Phenom.* **67**, 529 (1994).
- [18] See review in the Theo Thole Memorial Issue, *J. Electron Spectrosc. Relat. Phenom.* **86**, 1 (1997).
- [19] S. V. Streltsov *et al.* (to be published).
- [20] F. M. F. de Groot *et al.*, *J. Phys. Condens. Matter* **5**, 2277 (1993).
- [21] T. Kiyama and M. Itoh, *Phys. Rev. Lett.* **91**, 167202 (2003).