Determination of the orbital moment and crystal field splitting in 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 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.

LaTiO$_3$ is an antiferromagnetic insulator with a pseudocubic perovskite crystal structure. The Néel temperature varies between $T_N = 130$ and 146 K, depending on the exact oxygen stoichiometry. A reduced total moment of about 0.45-0.57 $\mu_B$ in the ordered state has been observed, which could imply the presence of an orbital angular momentum that is antiparallel to the spin momentum in the Ti$^{3+}$ $3d^1$ ion. In a recent Letter, however, Keimer et al. 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 Khalifullin and Maekawa, who suggested that 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., Mochizuki and Imada, as well as Pavarini et al., estimated that small orthorhombic distortions present in 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.

The objective of our work is to establish via an independent experimental method whether or not the orbital moment in LaTiO$_3$ is quenched, and if so, whether the explanation for the properties of LaTiO$_3$ should be searched in the proposed orbital liquid picture or rather in terms of a large local CF splitting. In other words, the magnitude of the CF splitting has to be determined. We have carried out spin-resolved photoemission (PES) experiments using circularly polarized 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 LaTiO$_3$ with $T_N = 146$ K have been grown by the traveling floating-zone method. The PES experiments were performed at the ID08 beamline of the ESRF in Grenoble. The photon energy was set to 700 eV, sufficiently high to ensure bulk sensitivity. 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°. The XAS measurements were carried out at the Dragon beamline of the NSRRC in Taiwan, with a photon energy resolution set at 0.15 eV for the Ti $L_{2,3}$ edges ($h\nu \approx 450 - 470$ 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.

Fig. 1 shows the spin-resolved photoemission spectra of the LaTiO$_3$ $3d$ states in the valence band, taken with 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 \( \langle \sum_i I_i \cdot s_i \rangle \). This can be directly related to the expectation value of the spin-orbit operator \( \langle \mathbf{L} \cdot \mathbf{s} \rangle \) applied to the initial state, thanks to the sum rule developed by van der Laan and Thole \[14\]. For a 3d system in which the final states are mainly of f character due to the high photon energies used, and for a randomly oriented sample, we obtain \[15\]:

\[
\frac{I_{\text{dif}}}{I_{\text{sum}}} = -U(\theta) \frac{\langle \sum_i I_i \cdot s_i \rangle}{3\langle n \rangle} \tag{1}
\]

where \( U(\theta) = (3-4\cos^2(\theta))/(2-\cos^2(\theta)) \) 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 \( I_{\text{dif}}/I_{\text{sum}} \approx 0.03 \), \( \theta = 60^\circ \), and \( \langle n \rangle \approx 0.8 \) from our cluster calculations \[16\], we arrive at \( \langle \sum_i I_i \cdot s_i \rangle \approx -0.06 \) (in units of \( h^2 \)), 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 \( h \)). 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. Fig. 2 shows that this is the case for a wide range of temperatures, both below and above \( T_N \).

Having established that LaTiO\(_3\) has a strongly reduced orbital moment, we now focus on the issue whether this is caused by strong orbital fluctuations \[4\] or rather by strong local CF effects as theoretically proposed \[3, 9, 10\]. To this end, we carry out temperature dependent XAS measurements at the Ti \( L_{2,3} \) (2\( p \) \( \rightarrow \) 3\( d \)) edges. Here we make use of the fact that the 2\( p \) core hole produced has a strong attractive Coulomb interaction with the 3d electrons. This interaction is about 6 eV, and is more than one order of magnitude larger than the band width of the 3d \( t_{2g} \) states. The absorption process is therefore strongly excitonic, making the technique an ideal and extremely sensitive local probe \[10, 17, 18\].

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\(_3\). 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 \( t_{2g} \) states. 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 2\( p \) ligands \[16, 17, 18\]. Curves (a) in left panel of Fig. 3 are the calculated isotropic spectra of a TiO\(_6\) cluster with a non-cubic crystal field splitting of \( \Delta_{CF} = 230 \) meV, as obtained, using a Wannier function projection procedure, from our LDA calculation \[16\] on the refined orthorhombic crystal structure \[3\]. One can see that the experimental data are well reproduced. We have also carried out simulations with
FIG. 3: (Color online) Top panel: experimental Ti $L_{2,3}$ XAS spectra taken from a twinned LaTiO$_3$ single crystal at 20, 100, 150 and 200 K. Left panel: simulated isotropic spectra calculated for a 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 $H_{\text{ex}} = 46.5$ meV (from Keimer et al. [7]) at $T = 0$ K and vanishing at $T_N = 146$ K. Four scenarios are presented: (a) non-cubic symmetry with $\Delta_{\text{CF}} = 230$ meV from our LDA calculation [19], (b) non-cubic symmetry with $\Delta_{\text{CF}} = 54$ 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.

other $\Delta_{\text{CF}}$ values, and found that $\Delta_{\text{CF}}$ should be in the range of about 120 to 300 meV in order to maintain the good agreement. If we chose, for example, $\Delta_{\text{CF}} = 54$ 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 LaTiO$_3$ is quite appreciable.

The second aspect of the Ti $L_{2,3}$ XAS spectra is their
 Returning to the spin-resolved photoemission data, we are able to reproduce the very low \( \langle \sum_i l_i \cdot s_i \rangle \) 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 \( \Delta_{\text{CF}} = 230 \text{ meV} \) as found from our LDA. The corresponding extracted orbital moment is \( L_z = -0.06 \). The \( \Delta_{\text{CF}} = 54 \text{ meV} \) value as proposed by Solovyev [11], however, clearly gives a \( \langle \sum_i l_i \cdot s_i \rangle \) 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 \( \Delta_{\text{CF}} = 0 \text{ meV} \), 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 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 non-cubic crystal fields sufficiently strong to split the Ti \( t_{2g} \) levels by about 0.12-0.30 eV, confirming several of the theoretical estimates [4-6, 10-12]. 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 LaTiO\(_3\) rather unfavorable.

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(1994); TiO$_6$ cluster with $\Delta=4.0$, $U_{dd}=4.0$, $pd\sigma=-2.22$, $10Dq=1.0$, $T_{pp}=0.5$, $U_{dc}=6.0$, 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 TiO$_6$ cluster that this signal amounts to less than $\approx -0.02$ for $\langle \sum_i l_i \cdot s_i \rangle$, which is, in absolute terms, indeed very small and also well within the experimental error of $\pm 0.05$.

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