Determination of the Crystal Field Splitting and the Orbital Moment in $LaTiO_3$

From a combined experimental and theoretical study on the Ti-$L_{2,3}$ x-ray absorption spectroscopy of $LaTiO_3$, we found that the crystal field splitting in the t_{2g} subshell is about 120-300 meV. This splitting is large enough to quench the orbital moment and, at the same time, to lock the orbitals spatially thereby disproving the claims for an orbital liquid behavior of this material.

$LaTiO_3$ is an antiferromagnetic insulator with a pseudocubic perovskite crystal structure. The Néel temperature varies from 130 K to 146 K, depending on the exact oxygen stoichiometry. A reduced total moment of about 0.45-0.57 $_B$ 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. However, Keimer *et al.* have reported that the spin wave spectrum is nearly isotropic with a very small gap, and concluded that the orbital moment must be quenched. To explain the reduced moment, it was proposed that there are strong orbital fluctuations in this system. This seems to be supported by a recent theoretical study of Khaliullin and Maekawa, who suggested that $LaTiO_3$ is in an orbital liquid state based on the cubic crystal field. If true, this would in fact constitute a completely novel state of matter. By contrast, an orthorhombic distortion was found by neutron-diffraction experiments, which would produce a crystal field (CF) splitting strong enough to lift the Ti *3d* t_{2g} orbital degeneracy. One of the latest LDA calculations, however, finds a much smaller t_{2g} splitting, 54 meV, leaving open the possibility for an orbital liquid state.

From our 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 in a wide temperature range. This point is in agreement with results from the spin wave spectrum. The question is, however, whether this reduced orbital moment is caused by strong orbital fluctuations in an orbital liquid state or rather by strong local CF distortion effects. To this end, we have carried out temperature dependent XAS measurements at the Ti $L_{2,3}$ ($2p \rightarrow 3d$) edges. Here we make use of the fact that the *2p* core hole 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 bandwidth of the *3d* t_{2g} states. The absorption process is therefore strongly excitonic, making the technique an ideal local probe.

The top panel of Fig. 1 shows the experimental Ti-$L_{2,3}$ XAS spectra of $LaTiO_3$ for several temperatures below and above T_N. One can clearly observe that the spectra are temperature independent. There are two aspects of the spectra 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} levels. A well-proven configuration interaction cluster model that includes the full atomic multiplet theory and the hybridization with the O *2p* ligands is used. Curves (a) of Fig. 1(top) are the calculated isotropic spectra of a TiO_6 cluster with a non-cubic crystal field splitting of Δ_{CF} (t_{2g}) = 230 meV as obtained from our LDA calculation. One can see that the experimental data are well reproduced. We have also carried out simulations with other $\Delta_{CF}(t_{2g})$ values, and found that $\Delta_{CF}(t_{2g})$ should be in the range of about 120 to 300 meV in order to maintain the good agreement as shown in Fig. 1. If we choose, for example, $\Delta_{CF}(t_{2g})$ = 54 meV as proposed from the LDA calculations by Solovyev, 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, the starting point of the orbital liquid state, does not agree with the measurement. From the line shape analysis we can thus firmly conclude that the crystal field distortion in $LaTiO_3$ 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 appreciable temperature dependence in the isotropic spectrum. For instance, in Fig. 2 we depict the Co L_2 XAS spectra of polycrystalline

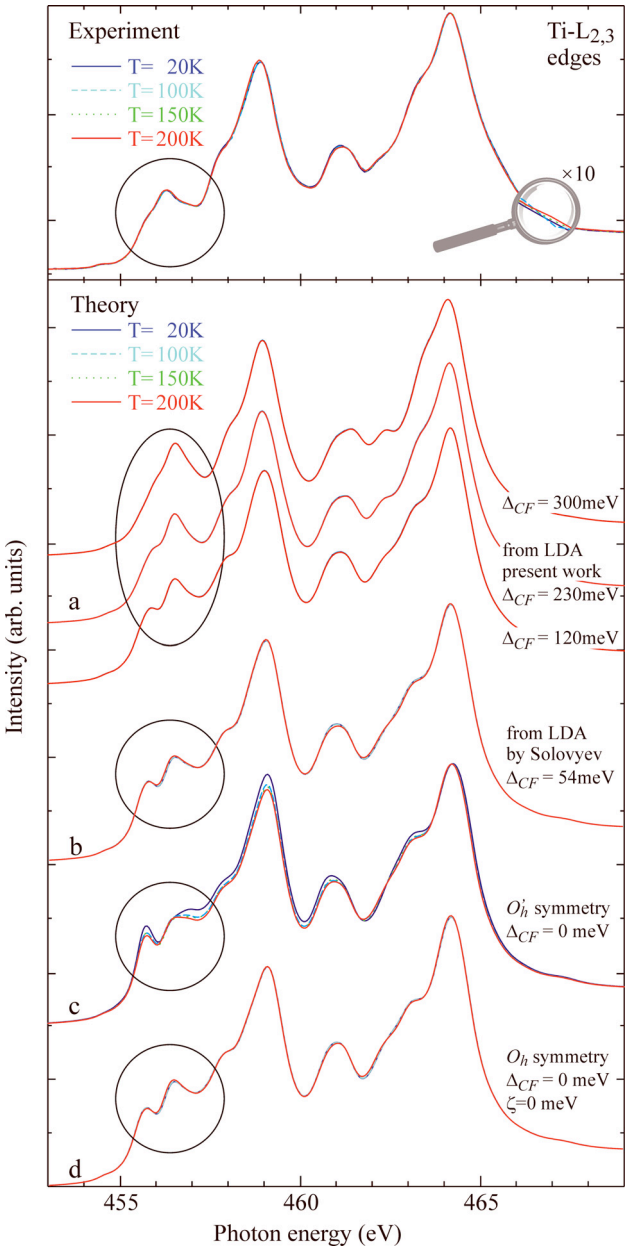

Fig. 1: Experimental (top) and theoretical T-$L_{2,3}$ XAS spectra of $LaTiO_3$ taken at 20, 100, 150, and 200 K for several CF parameters: (a) noncubic symmetry with $\Delta_{CF}(t_{2g})$ = 230 meV from our LDA calculation and with $\Delta_{CF}(t_{2g})$ = 120, and 300 meV, (b) $\Delta_{CF}(t_{2g})$ = 54 meV from Solovyev, (c) O_h' and (d) O_h symmetry. The spin-orbital constant ξ is 15.2 meV for (a), (b), and (c), and 0 for (d).

CoO, and indeed, we do see a strong temperature dependence. The reason for this behaviour is that for a system with an unquenched orbital moment like CoO, the ground state and the lowest excited states are split in energy due to the spin-orbit interaction by an amount of the order of the spin-orbit coupling, a number not much larger than k_BT_{room}. 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. 2 we have also simulated the CoO spectra using a CoO_6 cluster model and clearly the temperature dependence is reproduced. In Fig. 1, we have also calculated the $LaTiO_3$ spectra assuming a perfect O_h' local symmetry and the resulting curves (c) show indeed a strong temperature dependence. However, the fact that experimentally the $LaTiO_3$ spectra are temperature independent indicates directly that the spin-orbit interaction is inactive in $LaTiO_3$. Indeed, simulations carried out for CF splitting Δ_{CF} (t_{2g}) much larger than the spin-orbit interaction, e.g., curves (a) and (b) in Fig. 1, are not temperature sensitive. Using CF splitting Δ_{CF} (t_{2g}) in the range of about 120 to 300 meV we obtained an orbital moment L_Z = -0.06 $_B$, fully consistent with our spin-resolved photoemission measurements. In contrast, the $\Delta_{CF}(t_{2g})$ = 54 meV value as proposed by LDA calculation of Solovyev gives a quite large orbital moment: L_z = -0.24 $_B$. It is almost superfluous to note that the calculation with Δ_{CF} (t_{2g}) = 0 meV, i.e., with perfect O_h' symmetry, gives results that are in strong disagreement.

To conclude, our experiments have revealed the presence of non-cubic crystal fields sufficiently strong to split the Ti t_{2g} levels by about 120-300 meV. Such a large crystal field splitting provides a strong tendency for the Ti *3d* orbitals to be spatially locked. It is therefore rather unlikely that $LaTiO_3$ is an orbital liquid.

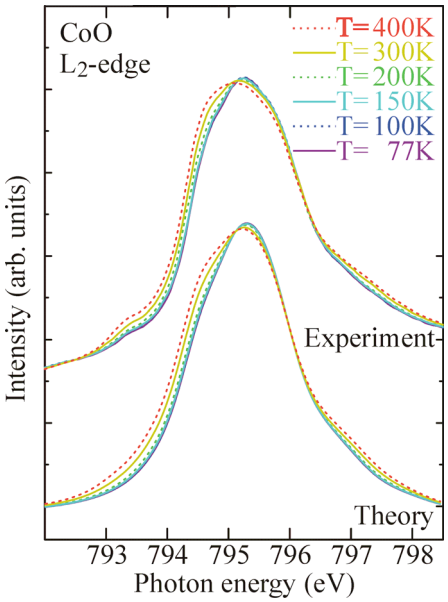

Fig. 2: Experimental temperature dependent Co L_2 XAS spectra of polycrystalline CoO, together with the simulated isotropic spectra and corresponding energy level diagram.

BEAMLINE
11A1 Dragon beamline

EXPERIMENTAL STATION
XAS chamber of the Universität zu Köln, Germany

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PUBLICATIONS

- Z. Hu, H. Wu, M. W. Haverkort, H. H. Hsieh, H.-J. Lin, T. Lorenz, J. Baier, A. Reichl, I. Bonn, C. Felser, A. Tanaka, C. T. Chen, and L. H. Tjeng, Phys. Rev. Lett. **92**, 207402 (2004).
- M.W. Haverkort, S. I. Csiszar, Z. Hu, S. Altieri, A. Tanaka, H.H. Hsieh, H.-J. Lin, C. T. Chen, T. Hibma, and L. H. Tjeng. Phys. Rev. B Rapid communications, **69**, 020408 (2004).
- M. W. Haverkort, Z. Hu, A. Tanaka, G. Ghiringhelli, R. Roth, M. Cwik, T. Lorenz, C. Schüßler-Langeheine, S. V. Stretsov, A. S. Mylnikova, V. I. Anisimov, C. de Nadai, N. B. Brookes, H. H. Hsieh, H.-J. Lin, C. T. Chen, T. Mizokawa, Y. Taguchi, Y. Tokura, D. I. Khomskii and L. H. Tjeng, Phys. Rev. Lett., **94**, 056401 (2005).

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