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Orbital excitations in $YTiO_3$ and $LaTiO_3$ probed by resonant inelastic soft x-ray scattering

C. Ulrich,[1] G. Ghiringhelli,[2] A. Piazzalunga,[3] L. Braicovich,[3] N. B. Brookes,[4] H. Roth,[5] T. Lorenz,[5] and B. Keimer[1]
[1]*Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany*
[2]*CNR/INFM COHERENTIA and Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy*
[3]*CNR/INFM and Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy*
[4]*European Synchrotron Radiation Facility, Boîte Postale 220, 38043 Grenoble, France*
[5]*II. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany*
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We have performed resonant inelastic x-ray scattering (RIXS) experiments at the $L_{2/3}$ edge $(2p \rightarrow 3d)$ of the Mott insulators $LaTiO_3$ and $YTiO_3$. Pronounced electronic excitations are observed at an energy of ~0.25 eV in both materials. These modes had been assigned to orbital excitations based on prior optical Raman scattering experiments. The present RIXS experiment strongly supports the Ti $3d$ orbital character of the excitations and confirms the great potential of high resolution soft x-ray RIXS as a probe of electronic excitations in complex materials.

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Inelastic x-ray scattering (IXS) has recently developed into a powerful tool to study the lattice and charge dynamics of complex materials.[1] This method holds several unique advantages over alternative experimental methods. For instance, specimens with dimensions in the micrometer range are sufficient to investigate phonon dispersion relations by IXS, whereas neutron scattering experiments typically require much larger sample volumes. Further, while optical spectroscopy is restricted to the center of the Brillouin zone, IXS experiments (by virtue of the larger photon momenta) are capable of probing the charge dynamics over an extended range of wave vectors.

An additional advantage lies in the ability to tune the photon energy to absorption resonances of specific elements in compounds. In resonant inelastic x-ray scattering (RIXS), the contributions of different elements to the scattering cross section can be discriminated, and information about valence states can be directly obtained. RIXS has proven particularly useful as a probe of the charge dynamics of transition metal oxides (TMOs) with strongly correlated electrons. In particular, the dispersion relations of interband transitions (with characteristic energies of several eV) in cuprates,[2–7] nickelates,[8] and manganites[9] were determined with photons tuned to the K absorption edges of the constituent transition metal ions. The spectra of local crystal field excitations were studied by working at the M or L edges in the same class of compounds.[10–13] As the ordering and dynamics of the orbital degree of freedom of the electrons play a key role in the electronic properties of TMOs, there has also been a large-scale effort to observe collective shape oscillations of the valence orbitals, termed orbitons. Spectroscopic data on orbitons can bring incisive information about the interaction between orbitals on neighboring lattice sites. The observation of such excitations (which have characteristic energies of several tenths of an eV) by Raman scattering with visible light has been reported in several TMOs,[14–16] but some of the results have been quite controversial.[17,18] Attempts to observe orbitons by IXS, on the other hand, have been unsuccessful mainly due to insufficient signal intensity.[19]

$LaTiO_3$ and $YTiO_3$ are isostructural members of a family of insulating titanates whose orbital state has recently been the focus of intense investigation. Since $LaTiO_3$ is an antiferromagnet and $YTiO_3$ is a ferromagnet, the Goodenough-Kanamori rules imply different orbital ordering patterns for the two compounds. This expectation is confirmed by a variety of electronic structure calculations.[20–23] However, since some key aspects of the microscopic magnetic dynamics are inconsistent with the rigid orbital state postulated by these calculations,[24,25] an alternative theoretical approach has invoked liquidlike orbital correlations.[26,27] The charge distribution around the Ti^{3+} ions in theories stipulating complete orbital order is much more anisotropic than in those incorporating strong orbital quantum fluctuations. This leads to similarly divergent predictions for the spatial anisotropy of the orbiton dispersion relations.[27,28] Moreover, the orbiton line shape is expected to be dominated by coupling to phonons in the former, and to spin excitations in the latter scenario. An experimental probe of orbitons, therefore, has the potential to discriminate between these competing scenarios. Recent optical Raman scattering[16] and infrared spectroscopy[29] experiments have revealed unusual low-energy excitations of both compounds. These excitations were identified as orbitons by excluding other possible origins such as magnon, multiphonon, and defect scattering.

Here, we report the observation of electronic excitations in $LaTiO_3$ and $YTiO_3$ by high resolution RIXS measured across the L_2 and L_3 absorption edges of Ti, at energies that match those determined in the optical Raman experiments. As the element-specific and strongly resonantly enhanced RIXS method offers a direct access to the Ti t_{2g} valence orbitals, these data directly confirm the $3d$ electronic nature of the observed excitations and indicate different perspectives for RIXS as a probe of low-energy electronic excitations in transition metal oxides.

High-quality single crystals of $LaTiO_3$ and $YTiO_3$ were grown by the floating-zone technique. Details of the growth procedure have been described elsewhere.[30] X-ray absorption spectroscopy (XAS) and RIXS measurements were performed at the soft x-ray beamline ID08 of the European Synchrotron Radiation Facility in Grenoble, France. $LaTiO_3$ and $YTiO_3$ samples freshly cleaved in air, together with a (100) oriented $SrTiO_3$ crystal as reference, were mounted into the

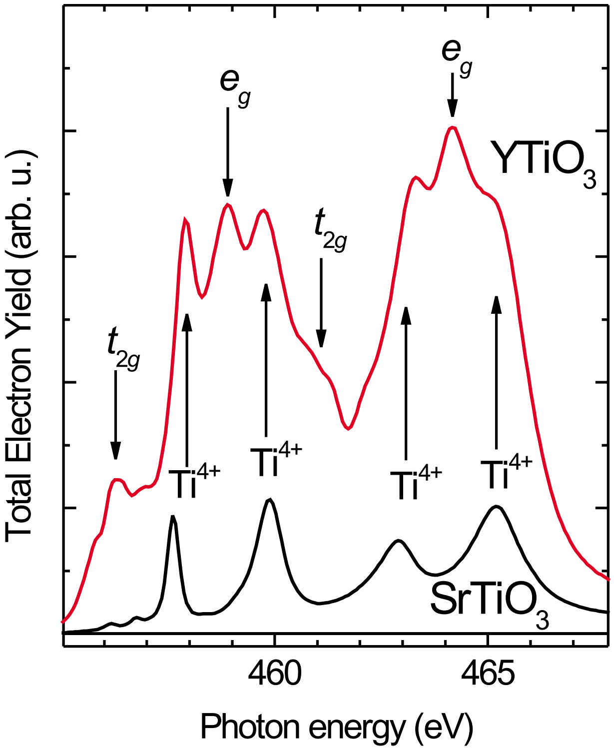

FIG. 1. (Color online) XAS spectra of $YTiO_3$ and $SrTiO_3$ across the L_2 and L_3 edges of Ti (lower- and higher-energy multiplets, respectively). The assignments of relevant absorption features of Ti^{3+} in $YTiO_3$ are reproduced from Ref. 36. The additional contributions from Ti^{4+} are determined from comparison with $SrTiO_3$.

high-vacuum chamber ($P = 10^{-8}$ mbar) of the spectrometer. The two APPLE II type undulators allowed full polarization control, such that the linearly polarized photons had electric field vectors perpendicular or parallel to the horizontal scattering plane (vertical and horizontal configurations, respectively). The incident beam was monochromatized by the PoLIFEMo grating monochromator.[31] The spectral distribution of the scattered beam was measured using the AXES spectrometer, which is based on a variable line density spherical grating and a Peltier cooled charge coupled device detector.[32,33] All spectra were collected at room temperature. The XAS spectra were measured *in situ* in total electron yield using the same instrumental linewidth adopted for RIXS. The incident beam had a full width at half maximum of 150 meV (theoretically estimated), and the combined energy width of the RIXS spectra was 270 meV (directly obtained from the elastic peak). In order to minimize the self-absorption effects in RIXS, the beam was incident 20° away from the sample surface and the scattered beam was along the surface normal, with a 110° scattering angle. The spectra shown here are sums of partial spectra, each accumulated for 15 min for a total of 6 h.

The XAS spectra were taken in total electron yield mode to select the excitation energies during the RIXS measurements (Fig. 1). The data are in good agreement with XAS spectra on $LaTiO_3$ (Refs. 34 and 35) and $YTiO_3$,[36] except for additional contributions from Ti^{4+} that were identified based on reference measurements on $SrTiO_3$. The Ti^{4+} features can be attributed to the exposure of samples to air after cleaving. The prolonged exposure to the very intense x-ray beam led to a slow increase of those features, both in $YTiO_3$ and in $LaTiO_3$.[36,37] The XAS signal is extremely surface sensitive due to the short electron escape depth (a few tens of angstroms). RIXS, on the other hand, probes ~1000 Å below the surface, so that the Ti^{4+} signal is probably negligible. Moreover, the RIXS signal of Ti^{4+} is zero between 0 eV (elastic peak) and 4 eV (onset of the charge transfer excitations) because the $3d^0$ electronic configuration of Ti^{4+} does not give rise to *dd* excitations.[38] Thus, the RIXS spectra of Figs. 2 and 3 are genuinely representative of the Ti^{3+} electronic excitations in $YTiO_3$ and $LaTiO_3$. For a direct comparison, we show here the spectra measured on $SrTiO_3$ (where Ti is in the 4+ valence state) as well.

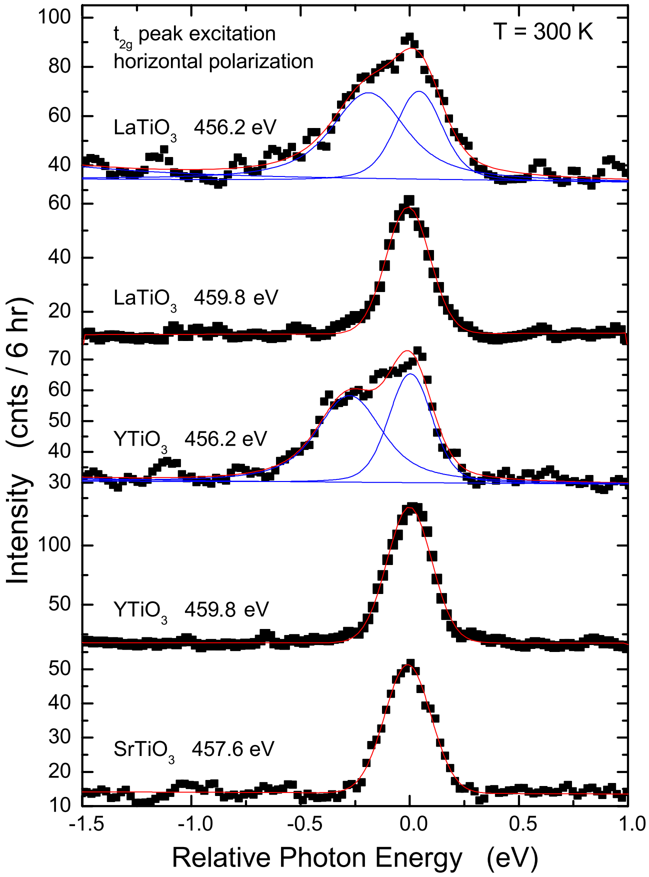

FIG. 2. (Color online) RIXS spectra of $LaTiO_3$ and $YTiO_3$ excited at 456.2 eV, t_{2g} peak in the absorption spectrum of Fig. 1. For comparison, the data taken at the extraneous Ti^{4+} peak of $YTiO_3$ and $LaTiO_3$ at 459.8 eV and the spectrum of $SrTiO_3$ excited at 457.6 eV are also shown. All spectra were taken at room temperature. The lines are the results of fits as described in the text.

For the RIXS experiments, we chose the incident energies of 456.2 and 458.9 eV corresponding to the two main absorption peaks at the L_3 edge of Ti^{3+}. These two energies are associated with transitions of a Ti $2p$ core electron into the partially occupied t_{2g} orbital manifold and into the completely empty e_g states, respectively,[34] as indicated in Fig. 1. The experimental data for horizontal beam polarization are

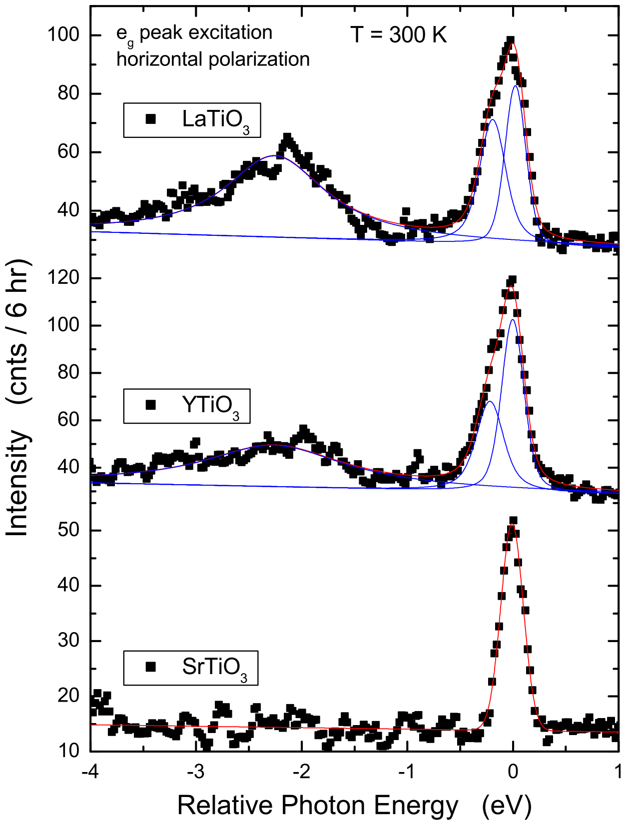

FIG. 3. (Color online) RIXS spectra of $LaTiO_3$ and $YTiO_3$ excited at 458.9 eV, e_g peak in the absorption spectrum of Fig. 1. For comparison, the spectrum of $SrTiO_3$ excited at 457.6 eV is also shown. All spectra were taken at room temperature. The lines are the results of fits as described in the text.

shown in Figs. 2 and 3 for the e_g and t_{2g} excitations energies, respectively. In both samples and at both photon energies, the RIXS spectra show pronounced peaks ~250 meV away from the elastic peak. The same measurements made with vertical polarization of the incident beam gave very similar results: the elastic peak becomes stronger due to elementary selection rules for elastic scattering, but the inelastic features can be found at the same energies and with comparable intensities. The detection of a characteristic energy loss in Ti L_3 RIXS unambiguously indicates the existence of $3d$ electronic excitations around 250 meV in both $YTiO_3$ and $LaTiO_3$.

For a detailed analysis of the spectra, we have assumed a Lorentzian line shape for the inelastic peak. The convolution of a Lorentzian profile with the Gaussian spectrometer resolution can be modeled using the Voigt line shape. Fits to Voigt profiles (solid lines in Figs. 2 and 3) yielded excitation energies of 0.23 ± 0.03 eV and 0.26 ± 0.04 eV for $LaTiO_3$ and $YTiO_3$, respectively. To within the experimental error, both the peak energies and the intrinsic peak widths (0.23 ± 0.05 eV and 0.22 ± 0.05 eV) are in excellent agreement with the optical Raman data of Ref. 16.

The experiment was repeated for a total of seven incident photon energies, but for only two it was possible to accumulate sufficient statistics (6 h each spectrum). The pronounced inelastic peak around 0.25 eV is better visible with 456.2 eV excitation, but it is present also at 458.9 eV. Spectra taken with photons of energy 458.9 eV, corresponding to transitions into the e_g levels (Fig. 3), also exhibit strong inelastic features at 2.0–3.0 eV for both $LaTiO_3$ and $YTiO_3$. The 2.0–3.0 eV peaks can be attributed to dd intrasite transitions from the singly occupied t_{2g} to the unoccupied e_g states. The energy of this transition corresponds to the cubic crystal field splitting, commonly denoted as $10Dq$. We note here that by definition, $10Dq=E(e_g)-E(t_{2g})$ in the single occupation configuration. Our RIXS spectra provide a direct measurement of $10Dq \simeq 2.2$ eV, in agreement with the results of Ref. 34, whereas other authors give smaller values from 0.5 to 1.5 eV.[35,36] It must, however, be noted that the value of $10Dq$ can change considerably from one model to another, depending on the way the hybridization is taken into account.[13] Neither spectra taken with photon energies at the extraneous Ti^{4+} $L_{2,3}$ absorption edges marked in Fig. 1 nor reference spectra taken on $SrTiO_3$ (Figs. 2 and 3) show the inelastic peaks at 0.25 and 2.5 eV. This confirms that the inelastic features we identified are intrinsic to Ti^{3+} and are unaffected by surface oxidation and beam damage.

In summary, we have used high-resolution resonant inelastic x-ray scattering to detect orbital excitations in $LaTiO_3$ and $YTiO_3$ at energies around 250 meV. RIXS holds two unique advantages over optical Raman spectroscopy experiments[14–16] that had previously detected such excitations. First, while one has to draw upon indirect (and sometimes highly controversial[17,18]) arguments in the interpretation of optical Raman data, the element specificity of RIXS allows a direct and unambiguous association of the observed excitation modes with the Ti d orbitals. Second, RIXS has the potential to test detailed, quantitative predictions of theoretical models. In particular, the peak shape, polarization dependence, and k-space dispersion of orbital excitations calculated in the framework of localized crystal field models can be compared to nonlocal models that predict dispersive orbitons over at least part of the Brillouin zone. RIXS experiments can also discriminate between different orbital ordering patterns by virtue of their distinct orbiton dispersion relations.[27,28] Measurements with better energy resolution and variable scattering angle required to test such predictions have thus far been precluded by instrumental constraints, but will become possible at the next generation of RIXS instruments currently under construction at synchrotron sources worldwide.[39]

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