Monografia de FI089 - Técnicas de Luz Síncrotron

"Resonant Inelastic X-ray Scattering - RIXS"

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I. INTRODUCTION

The purpose of this work is to give an introductory survey on orbital excitations on electronic systems in condensed matter physics that have been recently investigated by resonant inelastic X-ray scattering (RIXS). RIXS is a spectroscopy technique used to investigate electronic structure of materials, which differentiate the energy, as well as the direction of scattered photons. This enables us to probe local and collective electron behavior, which makes RIXS a very powerful tool for investigating the electronic dynamics and phonon/electronic excitations. RIXS is a low-yield technique, the probability of a inelastic event to happen is much less probable than an elastic event (about 1000 times less probable). That presents a challenge in RIXS experiments, but since around 2000, third-generation synchrotron facilities have enabled the development of new photon-demanding experimental techniques.

Inelastic X-ray scattering (IXS) may be classified in two regimes, resonant and nonresonant. In nonresonant inelastic X-ray scattering (NIXS), the experiment is performed with incident photon energies far from the absorption edge energies of the elements that constitute the sample. NIXS sometimes suffers from a low count rate because its scattering intensity is proportional to the electron charge correlation function, and this restricts the study of charge excitations on materials with light elements [1]. Nevertheless, it has a unique capability of measuring higher multipole transitions, which are usually forbidden in conventional optical absorption. For instance, Isaacs *et al.* measured the NIXS spectra of $V_{1.978}Cr_{0.022}O_3$ across the metal–insulator transition and found features related to plasmonlike excitations and a low energy shoulder, which is consistent with the opening up of a Hubbard gap [2]. In addition, Larson *et al.* succeeded in observing strong dipole forbidden d-d excitations NiO and CoO via large-q NIXS measurements [3]. The first part will present the work of Schlappa *et al.* published on Nature on 2012 entitled *Spin-orbital separation in the quasi-one-dimensional Mott insulator* Sr_2CuO_3 [4]. Theoretically, an electron can be described in terms of three quasi-particles: a spinon, carrying the electron's spin; a holon (or chargon), carrying its charge; and an orbiton (coined as such in Ref. [5]), carrying its orbital degree of freedom. The separation of the electron into independent quasi-particles that carry either spin or charge (spin-charge separation) was first observed 22 years ago [6]. Since then, a long and difficult search for further fractionalization of the electron took place. Schlappa *et al.* reported in his work the first unambiguous observation of the separation of the orbital degree of freedom using RIXS on the one-dimensional Mott insulator Sr_2CuO_3 .

Then we will discuss the work of Ulrich *et al.* entitled Orbital excitations in $YTiO_3$ and $LaTiO_3$ probed by resonant inelastic soft x-ray scattering published in 2008 [7]. Motivated by previous Raman spectroscopy results, which indicates the presence of orbital excitations in these compounds [8], they performed RIXS experiments at the $L_{2,3}$ edge of the Mott insulators $LaTiO_3$ and $YTiO_3$ using excitation energy close to the one of the t_{2g} and e_g energy levels. They were able to identify an inelastic peak about 250 meV away from the elastic peak as being an orbital excitation. Moreover, they were able to estimate the crystal split energy separation between the t_{2g} and e_g energy levels due to another broad inelastic peak in the RIXS spectra.

Lastly, we will present the article Polarization-analyzed resonant inelastic x-ray scattering of the orbital excitations in $KCuF_3$ published by Ishii *et al.* in 2011 [9]. There reported a Cu K edge XAS/RIXS study of the orbital excitations in the orbital-ordered compound $KCuF_3$. By symmetry arguments and polarization-analyzed RIXS, they were able to assign different features in the RIXS spectra to different types of orbital excitations within the material. Furthermore, they were able to estimate the Jahn-Teller splitting between the two e_g orbitals, which is about 1 eV.

II. SPIN–ORBITAL SEPARATION IN Sr₂CuO₃

Decades ago, theoretical calculations predicted that the electronic excitations break up is a fundamental property of one-dimensional systems (See Ref. [10] for a review on the subject). This was latter confirmed by angle-resolved photo-emission spectroscopy experiments, which showed the separation of the electron spin to its charge (spin-charge separation) [6, 11, 12]. Fig. 1 (b) illustrate the spin-charge separation, the electron hole propagates to the right (holon), and this induces a spin wave (spinon) to move left. To search for the further electron fractionalization, Schlappa *et al.* used high-resolution RIXS at the Cu L₃ to investigate excitations related to the orbital degree of freedom on Cu ions of single crystal Sr₂CuO₃ samples. They performed the experiments at the ADRESS beamline of the Swiss Light Source at the Paul Scherrer Institut [13, 14]. The scattering angle was fixed at either $2\Theta = 90^{\circ}$ or 130° and the incident light was chosen to to have polarization parallel to the scattering plane (π orientation), because they observed this yielded the maximum cross-section for the Cu $2p^{6}3d^{9} \rightarrow 2p^{5}3d^{10}$ transition. The sample was cooled below the antiferomagnetic magnetic transition by a helium-flow cryostat to 14K during the measurements.

 Sr_2CuO_3 is a quasi-one dimensional orbital ordered Mott insulator. The Cu^{2+} ion has 9 valence electrons in its 3d orbital, hence the 3d orbital has one hole. Fig. 1 (e) depicts the hole ordering in the 3d orbitals, where the ground state is the $3d_{x^2-y^2}$. Fig. 1 (f) shows the 3d orbitals, the higher it is positioned, higher the energy of its energy state. Fig. 1 (a) illustrate the spin-orbital separation, the electron is promoted to a higher orbital and this "electron promotion" propagates to the right (orbiton), and, just like in the spin-charge separation, this induces a spinon moving left.

Fig. 1 (d) shows the RIXS intensity map of the dispersing spin and orbital excitations. There we can see three collective orbital excitations from the ground state orbital $3d_{x^2-y^2}$ to the orbitals with xy, xz/yz and $3z^2 - r^2$ symmetry (d-d excitations are further discussed in this text when we present the work of Ishii *et al.*). The orbital assignment in was done based on *ab initio* quantum chemistry cluster calculations [15]. The excitations are also clearly seen in Fig. 1 (c), which shows the RIXS map as a function of photon excitation energy and energy transfer. The RIXS map has an intensity maximum (marking the L₃ edge resonance), and Fig. 1 (g) shows the RIXS spectrum at this maximum intensity energy, which is just a cross-section cut of the RIXS map at this energy value. The excitations are indicated. Moreover, the spin and orbital excitations dispersion (see Fig. 1 (d)) are indicative of their collective nature. Note that periodicity π of the orbiton dispersion (see Fig. 1 (d)) indicates that the orbiton is liberated from the spinon.



FIG. 1. Illustrative schematic of the a) spin-orbital separation and b) spin-charge separation, in a one dimensional structure generated as a consequence of a RIXS process and angle-resolved photoemission spectroscopy process, respectively. c) RIXS intensity map of Sr_2CuO_3 in log scale as a function of photon excitation energy (left axis) and energy transfer (bottom axis). The black curve shows the total fluorescence yield (TFY) of the XAS spectrum. d) RIXS intensity map of the dispersing spin and orbital excitations in Sr_2CuO_3 as functions of photon momentum transfer along the chains. Data obtained with $2\Theta = 130^{\circ}$. e) Illustrative schematic of the type of orbital hole ordering at the one dimension magnetic chains of Sr_2CuO_3 . f) shows the 3d orbitals, the higher it is positioned, higher the energy of its energy state. g) RIXS spectrum measured at the maximum intensity energy of the copper L_3 edge resonance (dashed line in (c)). Figure modified from Ref. [4]

III. ORBITAL EXCITATIONS IN YTiO₃ AND LaTiO₃

 $YTiO_3$ and $LaTiO_3$ are insulating titanates that have only one valence electron on the Ti^{3+} ions. Despite their similar lattice structures, $LaTiO_3$ orders antiferromagnetically at $T_N = 150$ K and $YTiO_3$ orders ferromagnetically at $T_C = 30$ K. This difference is attributed to the large number of quantum ground states available to the one Ti^{3+} valence electron at the degenerated t_{2g} energy level. The specific ground state of these titanates have recently been

a focus of intense debate and several theoretical scenarios have emerged. Some approaches defend a static ground state where subtle lattice distortions remove the degeneracy of the t_{2g} energy level [16–19]. However, some magnetic properties of these materials are difficult to reconcile with a static scenario. On the other hand, some researches defend an orbit liquid behavior in this titanates [20–22]. Moreover, Raman scattering for both compounds presents a pronounced broad peak about 235 eV [8]. This may be associated with an orbital excitation which roots for a dynamic scenario. A investigation of this orbital excitation have the potential to discriminate between these conflicting scenarios.

Ulrich measured the XAS and RIXS spectra at room temperature of $YTiO_3$ and $LaTiO_3$ across the L_2 and L_3 absorption edges of Ti at the soft x-ray beamline ID08 of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. At this beamline, the insertion device are two APPLE II type undulators, which allows full polarization control of the beam. Fig. 2 (a) show the XAS spectra taken in total electron yield of $YTiO_3$ and the Ti^{4+} reference SrTiO₃. By the comparison with the reference compound, we note $YTiO_3$ has spurious peaks associated to Ti⁴⁺. These are attributed to the long exposure of samples to air after cleaving. The assignment of relevant features was done based on polarized soft X-ray linear dichroism [23]. The incident photon energy selected for the RIXS experiment was the one that matches the low energy e_g (Fig. 2 (b)) and t_{2g} (Fig. 2 (c)). Fig. 2 (c) show the data taken at the Ti^{4+} peak of $YTiO_3$ and $LaTiO_3$ at 459.8 eV and the spectrum of $SrTiO_3$ excited at 457.6 eV for comparison. The polarization used was parallel to the scattering plane (π orientation), because, although vertical polarization also leads to similar spectrum, the horizontal polarization in the geometry used diminish the elastic peak, due to elementary selection rules for elastic scattering. Both the $YTiO_3$ and $LaTiO_3$ RIXS spectra show an excitation about 0.25 eV away from the elastic peak which agrees with optical Raman spectra [8]. RIXS is an element specific technique, and allows a direct and unambiguous association of the observed excitation with the Ti d orbitals. For completeness, note that the e_g RIXS spectra (Fig. 2 (b)) exhibit a strong inelastic feature at 2.0–3.0 eV. As this feature does not appear in the spectra for t_{2g} , this can be attributed to dd intrasite transitions from the partially occupied t_{2g} to the unoccupied e_g energy level. By that we can infer the crystal field split between the $e_{\rm g}$ and $t_{\rm 2g}$ energy level (the fit gives that 10Dq is about 2.2 eV). Also this features is very broad compared to other features, displaying the band character of the 3d energy levels in solid crystals.



FIG. 2. a) XAS spectra of YTiO₃ and SrTiO₃ across the L₂ and L₃ edges of Ti. The assignment of relevant features was done based on Ref [23]. b) The RIXS spectra of LaTiO₃ and YTiO₃ excited at 458.9 eV, first e_g peak in the XAS absorption spectrum in (a). b) The RIXS spectra of LaTiO₃ and YTiO₃ excited at 456.2 eV, first t_{2g} peak in the XAS absorption spectrum in (a). b) The RIXS spectra of LaTiO₃ and YTiO₃ and YTiO₃ excited at 456.2 eV, first t_{2g} peak in the XAS absorption spectrum in (a). In c) the YTiO₃ and LaTiO₃ spectra is shown at the Ti⁴⁺ peak at 459.8 eV and the SrTiO₃ spectrum excited at 457.6 eV for comparison. Figure modified from Ref. [7]

IV. POLARIZATION-ANALYZED RIXS OF THE ORBITAL EXCITATIONS IN $KCuF_3$

 $KCuF_3$ is an orbital-ordered Mott insulator that presents one-dimensional magnetic properties, with antiferromagnetic ordering along the c axis. This originates from the strong super exchange interaction between the Cu^{2+} e_g orbitals [24]. A direct observation of the electrons dynamics between the e_g orbitals in this compound was required to understand better the microscopic interaction between the e_g orbitals, and probe possible orbital excitations.

Ishii *et al.* reported a Cu K edge RIXS study of the orbital excitations in this compound. RIXS was the technique chosen in this case, because of its element specificity, then one can probe the excitations on the magnetic Cu^{2+} ions of KCuF₃. Moreover, a momentum resolution is required to the complete understanding of the elementary orbital excitation (orbiton). On the other hand, the observation of this kind of excitation (depending on the orbital degree of freedom between 3d orbitals) is problematic, since intra-atomic d-d (orbital) excitations are forbidden within the dipole approximation. Moreover, due to the different symmetry existing between the different 3d orbitals, the polarization study is essential in this experiment, because one can use it to assign the excitations displayed in the RIXS spectra to its respective orbital excitation.

Ishii *et al.* measured the XAS and RIXS spectra at room temperature of KCuF₃ across the Cu K absorption edge at BL11XU beamline at *Super Photon ring-8 GeV* (SPring-8), Japan. Incident X-ray is monochromatized by a double crystal Si(111) monochromator and a secondary Si(400) channel-cut monochromator and scattered X-ray is analyzed in energy by spherically bent Ge(733) or Ge(800) crystals. Fig. 3 (a) show the XAS spectrum of the Cu K edge, and Fig. 3 (b) show the RIXS spectrum across a large energy loss energy range. The incident photon energy for the RIXS measurements was fixed at 8994 eV (see arrow position in Fig. 3 (a)), because this is the energy they verified where the intensity of the 1.2 eV excitation was maximum (note small peak about 1.2 eV in Fig. 3 (b)). Cu²⁺ has 9 valence electrons in its 3d orbital, hence the 3d orbital has one hole (same as the Sr₂CuO₃ case presented at the beginning of this work). The 3d orbitals are ordered in such a way that the hole is in the orbitals $3d_{z^2-x^2}$ and $3d_{y^2-z^2}$, interchanging on adjacent Cu sites. This is indicated in the inset on Fig. [9] (b).

The incident photon polarization lies in the scattering plane (π polarization) and, the scattering angle (2 θ) was chosen to be as close as possible to 90°, in order reduce elastic scattering. Note in Fig. 3 (c-f), that there are two excitations right next to the elastic peak, one at 1 eV and another one at 1.2 eV. The former is enhanced in $\pi \to \pi'$ polarization, mainly on the experimental geometry presented on 3 (c). By symmetry arguments (which we will not reproduce here for the sake of simplicity), this is compatible to a excitation between eg orbitals (which the author calls a "eg excitation"). This type of excitation is possible because the Janh-Teller active tetragonal crystal field splits the eg energy levels into the $3d_{g^2-x^2}$ and $3d_{y^2-z^2}$ orbitals. We may conclude that the Jahn-Teller splitting between the two eg orbitals is about 1 eV, this value agrees with with recent optical absorption study [25]. The other excitation at 1.2 eV may be associated to the transition of an electron from the t_{2g} orbital to an eg orbital (the author calls it a " t_{2g} excitation"). This excitation is clearly seen in all spectra. After the assignment of the features, the author study them as a function of the results, but it worthy mention the main result, which is that the



FIG. 3. a) XAS spectrum of polycrystalline KCuF₃. The arrow indicates the incident photon energy used at the RIXS experiments. b) RIXS spectrum of single crystal KCuF₃. The inset shows the orbital order pattern representation in the hole picture. c-f) Polarization-analyzed RIXS spectra. Polarization conditions are indicated in the legend and corresponding experimental geometries are shown in insets. Figure modified from Ref. [9]

splitting between the two e_g orbitals does not depend on the value of the moment and that the excitation was nearly dispersionless (within their experimental resolution).

V. FINAL REMARKS

In this work presented three recent articles that used RIXS to investigate electronic dynamics in systems of interest. The work of Schlappa *et al.* is particularly import because it was the first unambiguous observation of the separation of the electrons orbital degree of freedom. The work of Ulrich *et al.* was chosen because it displays the application of RIXS to elucidate some orbital excitations previously suggested by Raman spectroscopy. The last work, from Ishii *et al.*, shows how powerful Polarization-analyzed RIXS can be on extracting information on the orbitals involved in the excitations. As we have shown,

RIXS is a powerful technique to probe collective electronic excitations, these are commonly found in systems in which the electrons are strongly correlated. The search for collective electronic excitations is critical, as it helps us understand better the physical behavior of electrons condensed matter systems. For instance, Kim *et al.* used RIXS to investigate magnetic excitations on Sr_2IrO_4 and established relevant links to cuprate superconductors [30]. Moreover, important theoretical advances are being made in the field of electronic excitations, as an example we may cite the work of Wohlfeld *et al.*, which studied the microscopic origin of spin-orbital separation in Sr_2CuO_3 [31], the same compound from Schlappa *et al.* [4]. Besides, Wohlfeld *et al.* have made some very general statements about the coupling of orbital excitations to spin Fluctuations in Mott insulators [32]. In addition, many other systems of great scientific value (not cited in this work) have been investigated by RIXS for orbital excitations and worth mention here, for example $Sr_2CuO_2Cl_2$ [26], LaMnO₃ [27], vanadates [28], and Li₂CuO₂ [29].

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