

First electronic structure results with the ComIXS spectrometer

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High-storage-density magnetic devices require materials with a large magneto-resistance (MR) near room temperature. The recent discovery of “doped” manganites – $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ - (Ln = Lanthanoids; A = Alkali or Alkaline-Earth Metals) responds to this technological demand. For this reason an intense effort has been made to synthesize new “doped” manganites and to understand the origin of the unique properties shown by these intriguing materials [1].

In these mixed oxides the colossal magneto-resistance phenomena is accompanied by a wide range of exotic behavior such as magnetic ordering, metal-insulator transition, charge and orbital ordering. In addition, depending on temperature, pressure and “doping”, they exhibit a very rich phase diagram, including insulating antiferromagnetic, paramagnetic and metallic ferromagnetic phases [1].

The beautiful complexity of these phenomena arises from the interplay between several competing structural and electronic mechanisms, not fully understood, such as double exchange and cooperative Jahn-Teller distortions. In particular, ambiguities and missing information about the interplay between occupied and unoccupied states as well as controversies concerning the strength of the electronic correlations and the size of the band energy gap need to be addressed.

A powerful technique to investigate the elementary excitations in solids with elemental specificity is Resonant X-ray Emission (RXE) spectroscopy. In RXE an incident x-ray photon excites a core electron to the absorption threshold and the x-ray emission, resulting from the decay of the excited state, is energetically analyzed. In recent years

this spectroscopy has progressed significantly becoming an extremely effective tool to study low-energy neutral electronic transitions, charge transfer (CT) excitations, inter-band transitions and energy-band dispersion [2].

Here the study of $\text{La}_{1-x}\text{Na}_x\text{MnO}_3$ ($x = 0, 0.08$ and 0.15) compounds by RXE spectroscopy is reported. The samples were grown by radio-frequency magnetron sputtering [3]. In these manganites the J-T effect is less pronounced with respect to systems “doped” with divalent alkaline-earth ions (Ca and Sr) with same hole concentration because the tolerance factor is close to 1, hence the double exchange and the ferromagnetic pairing of the spins are favored [3].

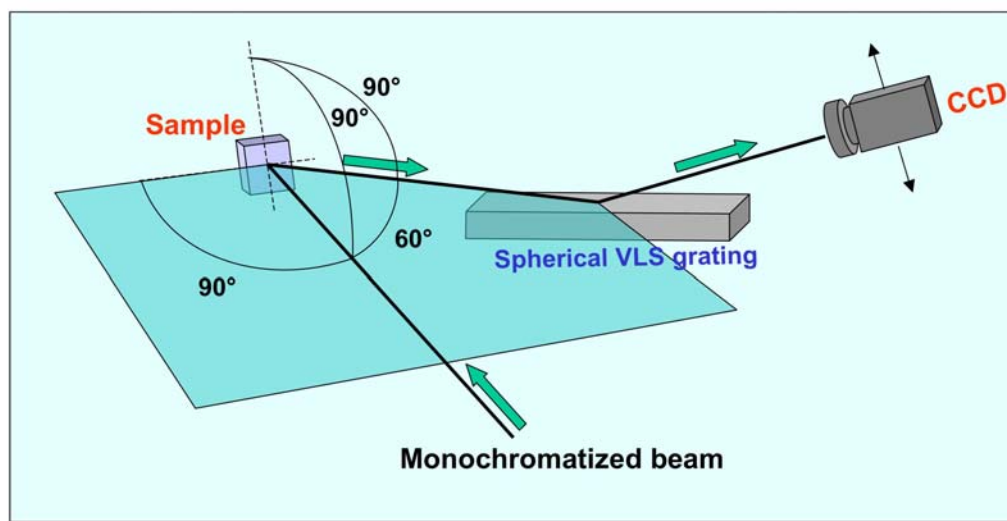


Fig.1. Experimental set-up and scattering geometry for RXE measurements at the BACH beamline.

The scattering geometry and the experimental set up are shown in Fig. 1. The spectra were collected with vertical polarization, *i.e.* the electric vector of the incident radiation perpendicular to the scattering plane (highlighted in Fig. 1). In this configuration the peak at zero energy loss, *i.e.* the elastic scattering, is visible in almost all the spectra, allowing an accurate calibration of the energy scale.

Fig. 2 (a) shows the RXE spectra obtained for the sample with $x= 0.08$ of Na “doping” at 300 K. The RXE raw data are plotted against an energy loss scale relative to the elastic peaks. The excitation energies are indicated with ticks in the x-ray absorption (XA) spectrum shown in the upper panel of Fig. 2.

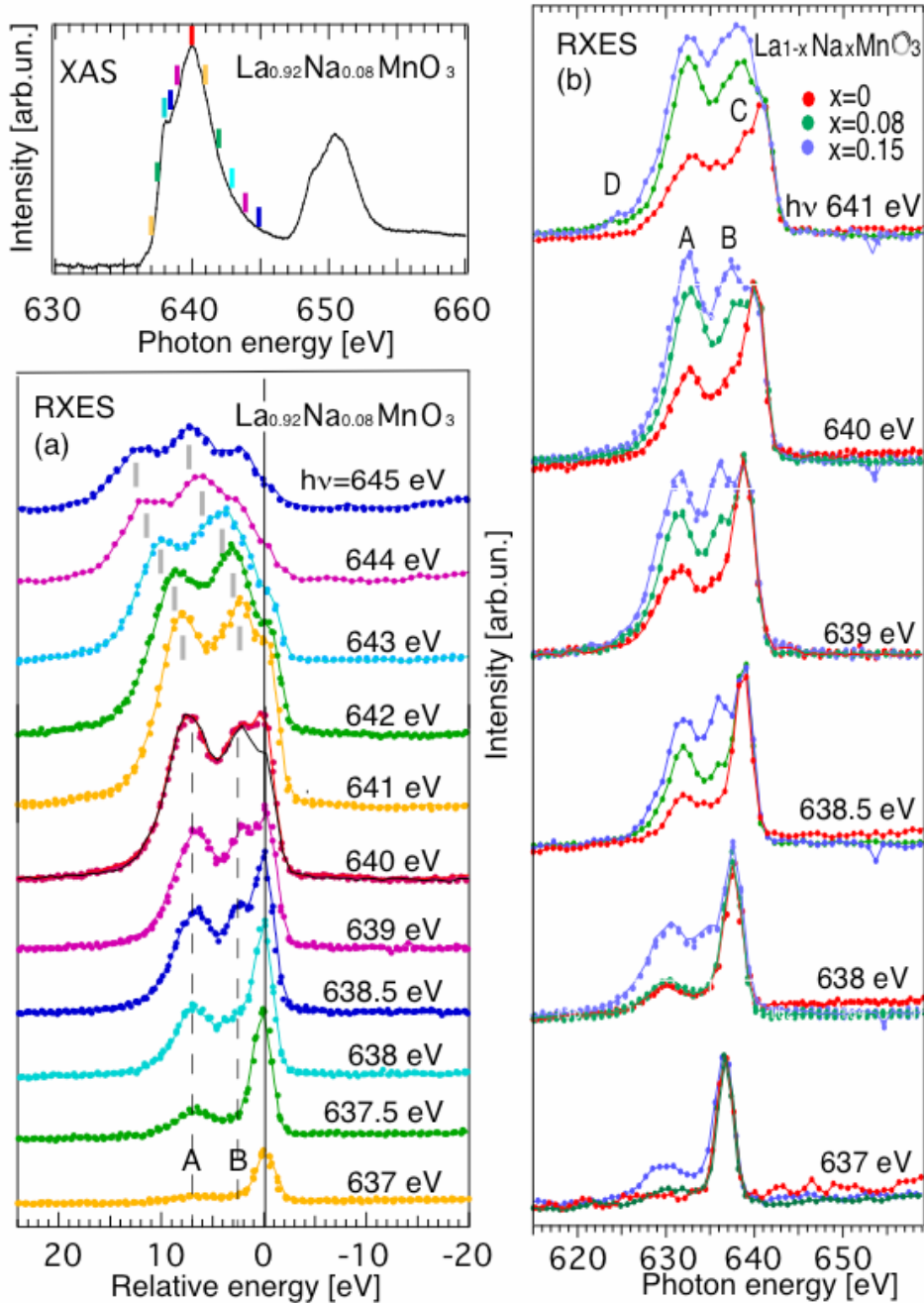


Fig.2. Top: Mn $L_{3,2}$ -edge XA spectrum of $\text{La}_{0.92}\text{Na}_{0.08}\text{MnO}_3$ at 300 K. Bottom: (a) RXE spectra measured with vertical polarization from the same $\text{La}_{0.92}\text{Na}_{0.08}\text{MnO}_3$ sample at different excitation energies across the Mn L_3 threshold at 300 K. One of the spectra recorded with horizontal polarization is shown (black full line, at 640 eV excitation energy). The RXE raw data are plotted against the transferred energy (curves are offset for clarity) and the excitation energies are indicated with ticks in the XA spectrum. (b) Variation of the Mn $3d \rightarrow 2p$ RXE spectra of $\text{La}_{1-x}\text{Na}_x\text{MnO}_3$ with the “doping” concentration ($x=0, 0.08$ and 0.15).

Resonant and non-resonant features can be easily identified. The non-resonant features appear at constant emission energy (hence, as dispersing peaks in the figure). These structures arise from ionization and subsequent normal x-ray emission, considered as a process in which excitation and emission are incoherent. The onset of Mn $2p_{3/2}$ ionization is located between 640 eV and 641 eV. Resonating inelastic loss features appear at constant energy, below the elastic peak. Two well-resolved inelastic emission peaks are observed between excitation energies 637 eV and 640 eV: structure A, at about 6.8 eV and structure B, at about 2.4 eV below the elastic peak. For the sake of comparison, some spectra were recorded with horizontal polarization, *i.e.* with the electric vector of the incident light in the scattering plane. In Fig. 2 (a), one of these spectra is displayed as a full black line at $h\nu = 640$ eV. In this scattering geometry the elastic peak is strongly suppressed. This helps to avoid possible ambiguities about the origin of the energy scale.

Fig. 2 (b) shows the “doping”-induced changes in the electronic structure of $\text{La}_{1-x}\text{Na}_x\text{MnO}_3$. The spectra are displayed on an emission energy scale and the data are normalized to the elastic peak.

The results of recent *ab-initio* partial DOS calculations for distorted orthorhombic LaMnO_3 derived from spin polarized density functional theory and the schematic diagram of the observed transitions are shown in Fig. 3 [4].

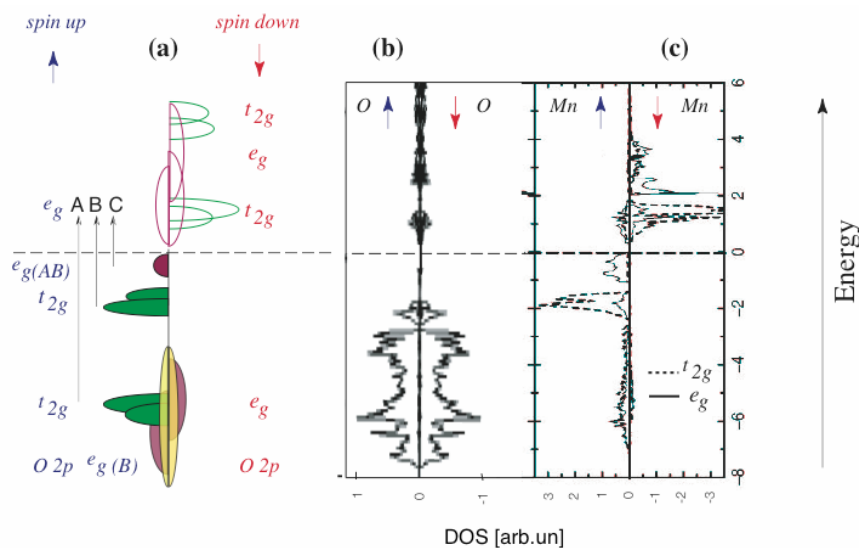


Fig.3. Mn 3d and O partial DOS for A-antiferromagnetic LaMnO_3 with orthorhombic GdFeO_3 structure obtained by full-potential linearized augmented plane-wave LSDA calculations. Adapted from ref. [4]

According to these calculations, the dominant contribution to the density of states (DOS) closer to the E_F is given by Mn $e_g\uparrow$ -like bands, split by a strong electron-phonon coupling of Jahn-Teller type. Mn t_{2g} electrons are well localized at -2 eV. Emission B [Fig. 2 (a)] can be associated with dd transitions from the occupied t_{2g} electrons to the $e_g\uparrow$ -like empty states. In contrast to optical spectroscopy, where dd transitions are dipole forbidden, the selection rule for RIXS are monopole or quadrupole, and hence dd transitions are allowed.

Peak B is significantly more intense in the “doped” samples. This effect can be explained considering the weaker hybridization of the t_{2g} and O $2p$ electrons due to a less pronounced structural distortion in the “doped” samples. However, the strong enhancement of peak B in the “doped” compounds can be rationalized with the higher density of empty $e_g\uparrow$ states in the lower part of the CB related to the presence of the Mn^{4+} ions. This interpretation is consistent with the band observed in optical conductivity measurements at 2.3 eV and associated with the presence of Mn^{4+} and/or O^- self-trapped holes in possible non-stoichiometric $LaMnO_3$ samples [5].

Both the Mn- t_{2g} - and $e_g\uparrow$ bonding bands, hybridized with O $2p$ states, give a broad contribution to the occupied DOS around 5-6 eV. Peak A in Fig. 2 (a) can be assigned to an electronic excitation from this band to the empty $e_g\uparrow$ band.

A weak shoulder (C) at about 2.0 eV below the elastic peak is observed in $LaMnO_3$ at $h\nu = 641$ eV. This peak is consistent with the reported optical gap of 1.3 eV [6] and it is tentatively assigned to the energy-gap transition between the highest occupied e_g bands to the unoccupied e_g majority bands.

Finally, a weak loss structure appears at around 17-17.5 eV [peak D in Fig. 2 (b)], however the origin of this feature require further investigations.

It is also interesting to compare the RXE spectra with optical conductivity measurements for alkali-“doped” and “undoped” $LaMnO_3$. Optical conductivity essentially also probes elementary excitations but without elemental selectivity and with different selection rules. The optical absorption spectra display several broad bands near 1.9-2.3, 4.6, 7, 9, 17 and 25 eV [6]. The features at about 4.6 eV, 9.0 eV and 25 eV are not detected in RXE spectra, for any “doping”. This observation leads to the conclusion that Mn ions are not directly involved in these transitions or these peaks could be Mn ion dipole transitions.

In conclusion, RXE spectra from “undoped” LaMnO₃ are in fair agreement with the theoretical predictions based on partial DOS calculations for distorted orthorhombic LaMnO₃ derived from spin polarized density functional theory. This agreement is used as a frame to interpret the RXE data for the “doped” materials. In particular it is possible to identify some resonant inelastic losses.

Furthermore, RXE experiments made it possible to observe a weak loss tentatively assigned to a gap excitation between e_g bands split by the Jahn-Teller electron-phonon coupling. A significant dependence on “doping” of the transition involving the t_{2g}-like states in the valence band was observed and explained.

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The resonant emission spectra were acquired exploiting the capabilities of the ComIXS fluorescence spectrometer [7]. The spectrometer, based on an innovative optical design, is mounted on the BACH beamline [8] at Elettra. The spectrometer exploits the small spot size, high flux and controllable polarization of BACH [<http://www.elettra.trieste.it/experiments/beamlines/bach/index.html>].

The small spot size of the radiation on the sample allows the direct detection of the dispersed photons emitted within a solid angle of about 30×10 mrad². The detector is a SX TE 1300/CCD PB/1 by Princeton Instruments. ComIXS is equipped with a variable line spacing (4800 l/mm of central groove density) spherical (VLS) grating, optimized in the 20-200 eV region. A second 19200 l/mm grating, optimized in the 150-1200 eV energy range, is currently undergoing commissioning. The measurements reported here (in the 630-660 eV energy range) were obtained with the fourth diffraction order of the low-energy grating. The energy bandwidth of the incident photon beam was set at 0.7 eV, which corresponds to high flux and a resolving power of ~950. The total resolution of the spectra, estimated from the elastic-peak FWHM, is 1.8 eV. A significantly better signal-to-noise ratio is expected with the installation of the high-energy grating.

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