	Experiment title: RIXS in novel CoO_2 layer-based superconductor	**Experiment number**: HE-1683
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Report:

We report here on the investigation of the electronic properties of a novel Co-based superconductor by resonant inelastic x-ray scattering (RIXS). The experiment was carried out at ID16 on single crystals of both parent Na_xCoO_2 (NCO) and hydrated $Na_xCoO_2 \cdot yH_2O$ (NCOH) samples (x=0.35,y=1.3) where superconductivity was reported [1]. Both samples crystallize in the hexagonal structure. They consist of alternating Na and CoO_2 planes stacked along the c axis. The NCOH structure differs from NCO by the presence of ice-like sheet, sandwiching the Na planes, which inflates the unit cell along the c direction. In both samples, the CoO_2 planes are composed by edge-sharing Co-O octahedrons positioned on a triangular lattice. The crystal quality of NCO, retrieved after dehydration of NCOH under vacuum, was checked by angular-dispersive x-ray diffraction on ID-15 at 88 keV. Typical diffraction pattern is shown on figure 1(b). Sharp spots and 6-fold symmetry indicate good crystallinity of the sample, although twining is not excluded. The c axis is found perpendicular to the sample surface. As a matter of fact, the samples easily cleaved in the direction perpendicular to the c axis, as we observed looking under the microscope (see figure 1, panel (a)).

The samples were aligned in the beam prior to measurements in order to either keep the momentum transfer q or the incident polarization parallel to the c axis, depending on whether reflection geometry or transmission mode was chosen. The Co-K edge obtained in total fluorescence yield (TFY) is illustrated in panel (c) of figure 1 for NCO. The spectrum exhibits a pronounced pre-edge feature reflecting strongly hybridized 3d states, followed by an intense 4p-like white line. The RIXS spectra were measured close to the recombination (elastic) peak in both hydrated and non-hydrated-sample at various incident energy E_1 across the Co K-edge. Resolution was estimated to ~1 eV from the FWHM of the elastic peak. Figure 1, panel (d) illustrates the results obtained in NCO as function of transferred energy $\Delta E = E_1 - E_2$. A clear-cut excitation builds up around $\Delta E = 10$ eV (CT label in figure 1) as the incident energy approaches the white line, in good agreement with preliminary results obtained at Spring-8 on powder sample [2]. Simultaneously, the valence band fluorescence (VB label in figure 1(d)) grows on the high transferred energy side, leading to a steeply rising

background (see green spectrum measured at 7.719 keV in the pre-edge region). Note that on the transfer energy scale, the valence band fluorescence shows a dispersive behavior as a function of incident energy. Its center of mass is pushed away from the elastic peak as E_1 increases and progressively reveals the inelastic feature. We repeated similar measurements in the hydrated sample. To prevent dehydration of NCOH under vacuum, the measurements were done at 100 K using the ID-16 cooling head. The sample was first glued on a copper piece, and dipped into liquid nitrogen prior to mounting. The sample was then installed on the pre-cooled cold head under a flow of gaseous nitrogen. No difference in the excitation spectrum with NCO could be observed. There was also the possibility that the tail of the elastic peak could mask low energy excitations. Therefore, we measured high resolution RIXS spectra by inserting a Si(440) channel cut after the Si(111) pre-monochromator. An excellent resolution of 0.3 eV could be achieved, but no other inelastic features showed up.
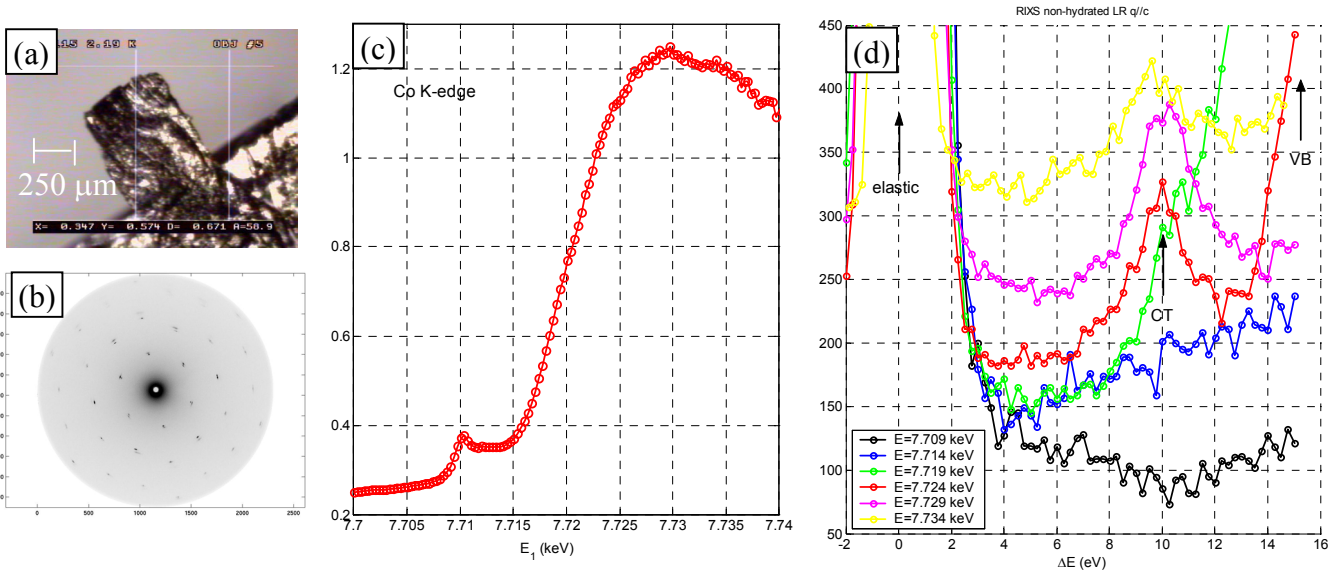

Figure 1 : *Panel (a) Snapshot of the NCOH sample under the microscope prior to loading ; Panel (b) : angular dispersive diffraction pattern in NCO measured at 88.6 keV on ID-15. Panel (c) : Typical absorption spectrum at the Co-K edge in NCO measured at ambient temperature. Panel (d) RIXS spectra as function of transfer energy measured at increasing incident energy from bottom to top. CT and VB stem for charge transfer excitation and valence band emission respectively.*

We associate the 10 eV feature to a charge transfer (CT) excitation from the oxygen ligand to the Co atom. The CT peak does not show any dispersion with q but decrease in intensity, as the scattering angle gets closer to 90°. This dipolar-like behavior is rather surprising for excitations involving 3d states, which would rather call for a quadrupolar character. So-called "constant final state" RIXS scans, measured by keeping a constant transfer-energy of 10 eV as the incident energy is swept across the edge, confirmed that the 10 eV feature only resonates in the white line region and not in the pre-edge region. Furthermore, the energy of the CT excitation is about twice higher than comparable CT excitation observed in simple transition metal oxides like CoO or NiO. We tentatively assign the 10 eV feature in NCO and NCOH to a double CT excitation of a $3d^n \rightarrow 3d^{n+2}\underline{L}^2$ type, in which two electrons from the ligand oxygen are involved. Complementary analysis is on the way to define the precise nature of the observed excitations. Finally, we were able to unravel the Co-spin state configuration of Co in both NCO and NCOH by measuring the Kβ emission line in the fluorescence regime. In both cases, the absence of a satellite structure definitively points to a low-spin state.

[1] K. Takada et al., Nature 422, 53 (2003)
[2] H. Ishii et al., Private Comm.