Electronic Structure and Charge Disproportionation of Co in Na_xCoO_2 Superconducting Compounds

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We report on resonant x-ray emission spectroscopy (RXES) at the Co–K edge in novel cobaltate compounds: Na0.7CoO2 (NCO) and Na0.35CoO2.yH2O (NCOH). The experiment was carried out on beamline BL12XU at Spring-8. We used single crystals of NCO and NCOH supplied by Prof. Sasaki's group at Tohoku University. To retain hydration in NCOH (and simultaneously prevent NCO from absorbing humidity), both samples were mounted in a close-cycle cryostat operated at 20 K. The beamline RIXS spectrometer was equipped by a Si(531) analyzer and a Rontec X-flash detector provided by our group at SOLEIL, which can handle much higher countrate than the beamline Si-diode.

We focused on the Co-Kalpha emission lines measured in resonant conditions at the Co K-edge. The absorption spectra were measured (Fig. 1) in partial fluorescence yield mode. Typical countrate at the maximum of the emission line was 500 000 cps.

RXES results for NCOH are summarized in the attached figure (Fig. 2). The RXES spectra are shown as a contour plot as a function of the incident energy (E1) and transfer energy (E1-E2). In this plane, fluorescence like spectra disperse along the diagonal while resonant structures show up at constant transfer energy and are vertical. The two main diagonals are related to Kalpha-1 and Kalpha-2 fluorescence lines. They are split in energy by the spin-orbit interaction acting on the 2p core-hole in the RXES final states. The broad structures emerging at low incident energy (bottom right on the figure) are associated to transition to virtual states usually spread in energy.

Our main objective was to clarify the Co valent state in these compounds, and discuss the effects of hydration. RXES spectroscopy is a powerful tool to unravel different valent states of a given atomic species with considerably more details than conventional spectroscopy such as XAS or photoemission. RXES was already successfully applied to series of mixed-valent rare-earth compounds [1]. Theoretical analysis of the RXES at the K-edge of transition metal further provides information about the electronic states close to the Fermi energy as recently demonstrated in cuprates [2].

A similar method is envisaged in NCO and NCOH. The mid-zone between the two fluorescence components (figure centre) is mostly appropriate to carry out such an analysis. Calculations are underway.

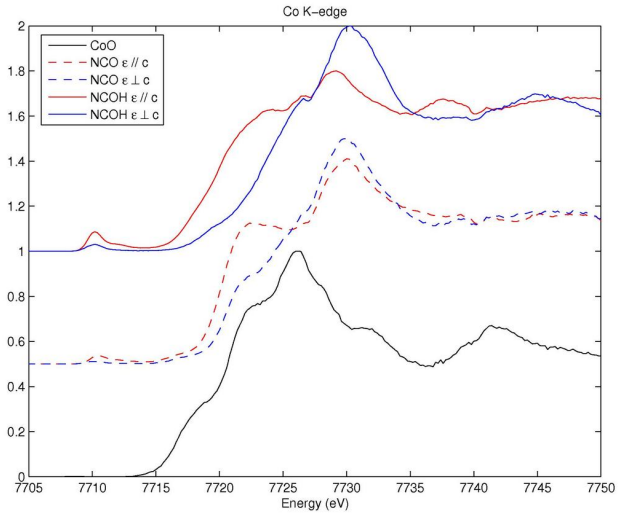

Figure 1. RXES of Co-Kalpha emission lines.

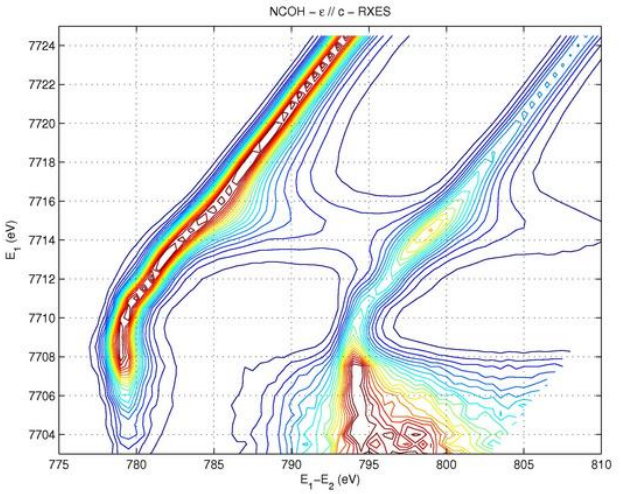

Figure 2. RXES intensity cotour plot for NCOH.

References:
[1] I. Jarrige et al., Phys. Rev. B, 72, 075122 (2005)
[2] A. Shukla et al., cond-mat/0506650