

Time-resolved XAFS spectroscopy for the electronic phases in cyano complexes

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Introduction

Prussian Blue-type transition metal cyanides $A_x\text{Co}[\text{Fe}(\text{CN})_6]_y\text{zH}_2\text{O}$ ($A=\text{K}, \text{Na}$) have a cyano-bridged network of Co and Fe ions. The cyanides can take two electronic configurations, that is, the low spin (LS) phase [$\text{Co}^{3+}(\text{t}_{2g}^6)\text{-Fe}^{2+}(\text{t}_{2g}^6)$] and the high spin (HS) phase [$\text{Co}^{2+}(\text{t}_{2g}^5\text{e}_g^2)\text{-Fe}^{3+}(\text{t}_{2g}^5)$]. The small- y cyanide often shows thermally- and/or photo-induced [1] phase transition from the LS phase to the HS phase. The large- y cyanide, e.g., $\text{Na}_{0.79}\text{Co}[\text{Fe}(\text{CN})_6]_{0.90}2.9\text{H}_2\text{O}$ (NCF90)[2], however, does not show the thermal phase transition. Recently, Kamioka et al.[3] reported a characteristic behavior in femtosecond time-resolve spectroscopy for the NCF90 film. The film remains in the LS phase for heating up to 500 K. They found that the photo-induced absorption band for LS Co^{2+} grew with a rise time of 13 ps. This spontaneous growth of the band implies the formation of a transient hidden phase with LS Co^{2+} , induced only by photo-excitation.

Experimental

We have investigated the photo-excited electronic states of the “hidden phase” in the NCF90 film by using of a time-resolved X-ray measurement system in the NW14A beamline[4]. Here the samples are excited by a Ti:Sapphire pulse laser in sync with the X-ray pulse from the PF-AR ring. The delay time between the pump laser pulse and the probe X-ray pulse is accurately controlled with the time-resolution of 100 ps. X-ray absorption spectra are obtained by normal XAFS techniques with the X-ray pulse at a delay time.

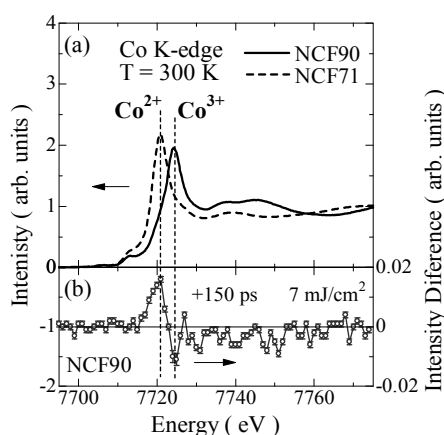


Fig.1 (a) XAFS spectra for NCF90 film (solid curve) and NCF71 film (broken curve) around the Co K-edge. (b) Difference spectrum at +150 ps for NCF90 film.

Results and Discussion

Figure 1(a) shows the X-ray absorption spectra around the Co K-edge in the NCF90 film and a small- y cyanide $\text{Na}_{0.15}\text{Co}[\text{Fe}(\text{CN})_6]_{0.71}3.8\text{H}_2\text{O}$ (NCF71) film at 300 K[5]. The latter is in the HS phase. The peak position of the NCF90 film is 7724 eV, while that of the NCF71 film is 7721 eV. The energy difference is mainly ascribed to the valence change of Co ion. Fig. 1(b) shows the difference spectrum at the delay time of +150 ps in the NCF90 film. The difference spectrum shows positive signal at 7721 eV and negative signal at 7724 eV, suggesting the photo-induced valence change from Co^{3+} to Co^{2+} . In order to obtain information for the spin state of Co^{2+} site, more elaborated experiments are in progress.

Figure 2 shows the time profile of the intensity difference at 7721 eV. The intensity difference steeply rises within the system time-resolution (solid curve in Fig.2), indicating a fast valence switch from Co^{3+} to Co^{2+} .

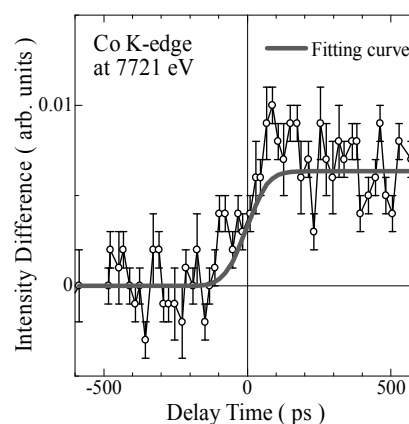


Fig.2 Time profile of the intensity difference at 7721 eV for NCF90 film. Solid curve represents a step function convoluted by the X-ray pulse shape.

References

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