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Electronic state of a photo-induced magnet of CoW cyanide studied by XANES

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Very recently, Hashimoto *et al.* found light-induced ferrimagnetism for a new type of transition metal cyanide $Cs_{0.8}Co_{1.1}W(CN)_8(3\text{-}CNpy)_{1.9}\cdot 2.1H_2O$ (3-CNpy = 3-cyanopyridine). It was suggested that the CoW cyanide undergoes the first-order spin transition at $T_{\downarrow c}$=152 K. On visible-light irradiation below 30 K, however, the material turns to a ferrimagnet. In the present study, we have investigated the electronic states of the high-temperature (HT) and low-temperature (LT) phases by means of XANES spectroscopy. Here, we have found x-ray induced transformation to the magnetized state at 30 K instead of visible-light irradiation.

Co *K*- and W *L*-edge XANES spectra of the CoW cyanide were taken with the conventional transmission mode at BL10B and 12C. The static XANES measurements were performed at BL 10B. The HT phase was examined at 300 K [sample (a)], while the LT phase was obtained at 130 K [sample (b)]. At BL12C, the x-ray induced phase transformation was examined at 30 K.

Figure 1 shows the Co *K*-edge XANES spectra of samples (a)-(c). Samples (a) and (b) exhibit the main peaks at ~7720 and ~7723 eV, respectively, implying that Co is in the divalent HS (high-spin) state at 300 K and in the trivalent LS (low-spin) state. Sample (c) shows a similar spectrum to sample (a), indicating that the x-ray induced trapped excited state consists of Co(II)HS, which contributes to induced ferrimagnetism. The factor analysis was similarly performed to obtain the Co(II) composition ratio of each sample. In Fig. 1, the spectrum of each component is plotted and the numerical Co(II)HS ratios are also given.

Figure 2 shows the W L_{III}-edge XANES spectra of samples (a) and (b), together with the reference spectra. The peak height of the white line is almost equal among the reference spectra, indicating that the peak height is not a good measure for the W valency. For reference spectra, however, a shoulder structure appears in the W(V) reference at ~10196 eV, while it does not in the W(IV) ones. The first derivative spectra are clearer to identify. It is reasonable to assign the shoulder to the singly occupied W 5*d* level since in the case of W(V), the most stable 5*d* orbital is singly occupied, while for W(IV) the 5*d* orbital is fully occupied. We find a similar shoulder structure appear in sample (a) while not in sample (b). This clearly indicates that W is pentavalent in the HT phase and is tetravalent in the LT one.

Combining the above Co *K*-edge XANES results, we can definitely conclude that at the spin transition a Co 3*d* electron is transferred to W 5*d*. The Co state is Co(II)HS (d^7, S=3/2) in the HT phase and is Co(III)LS (d^6, S=0) in the LT phase, while the W electronic states are LS in both the HT and LT phases (d^1, S=1/2 and d^2, S=0, respectively).

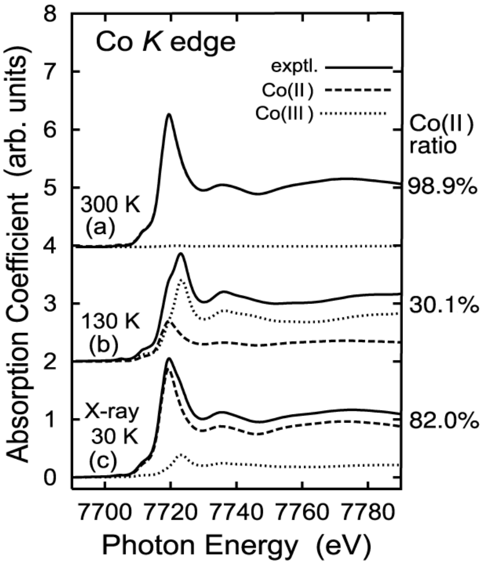

Fig. 1. Co *K*-edge XANES. Component spectra of Co(II) and Co(III) are also shown.

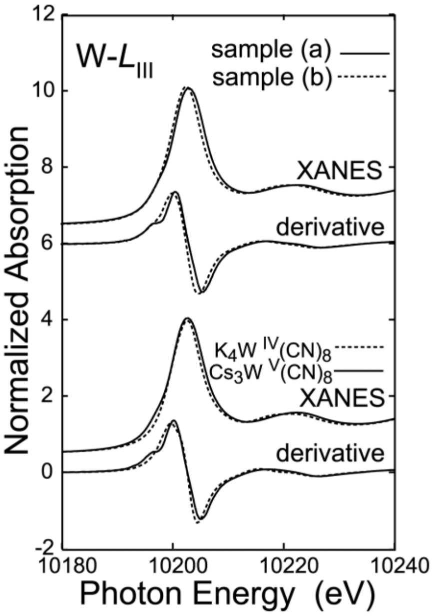

Fig. 2. W L_{III}-edge XANES and their derivatives.

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