Local structure of a photo-induced magnet of CoW cyanide studied by EXAFS

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Very recently, Hashimoto *et al.* found light-induced ferrimagnetism for a new type of transition metal cyanide $Cs_{0.8}Co_{1.1}W(CN)_8(3\text{-CNpy})_{1.9}$ $2.1H_2O$ (3-CNpy = 3-cyanopyridine). Following the XANES work in this Activity Report, we have investigated the local structures of the high-temperature (HT), low-temperature (LT) and x-ray-induced magnetized phases of this material by means of EXAFS spectroscopy.

Co *K*- and W *L*-edge EXAFS spectra were taken with the conventional transmission mode at BL10B and 12C. The static EXAFS measurements were performed at BL 10B for the HT phase at 300 K [sample (a)] and 30 K [sample (a')] and the LT phase at 130 K [sample (b)]. Sample (a'), the trapped HT phase, was obtained by quick cooling of sample (a). At BL12C, W L_{III}-edge EXAFS of the x-ray induced phase transformation was examined at 30 K [sample (c)].

The EXAFS analysis was carried out in well-established procedures using the analysis code EXAFSH. Figure 1 shows Fourier transforms of the Co *K*-edge EXAFS functions $k^3\chi(k)$. The employed Δk ranges in the Fourier transforms were around 3-16 Å. Several complicated peaks are also observed; those around 1-2 Å and 4.3-5.4 Å ranges are ascribed to the Co-N and Co-W shells, respectively. Those are significantly dependent on the samples, indicating noticeable structural difference around Co between the HT and LT phases. The features appearing in the 2-4 Å range are more complicated; there should exist the contributions not only from the C atoms of the NC^- ligands but also from the C atoms of the 3-CNpy molecules. In the W L_{III}-edge EXAFS (not shown), three dominant contributions that are attributed to the W-C, W-N, and W-Co shells are clearly detected.

In order to obtain structural information, the curve-fitting analysis was performed. Theoretical standards evaluated by using the FEFF6 assuming $W(CN)_8Co_4$ for W EXAFS and $Co(NC)_4(3\text{-CNpy})_2W_4$ for Co EXAFS. The obtained interatomic distances are tabulated in Table 1. The W-C and W-N distances are found to be almost equal for all the samples. On the other hand, it is clearly found that the Co(II)-N distance is noticeably different from the Co(III)-N one by as much as ~0.17 Å. Correspondingly, the Co(II)-W and Co(III)-W distances are deviated from each other. Judging from the distances the alignment of -W-C-N-Co- is confirmed to be almost linear as in the case of rock-salt type Prussian blue analogues such as CoFe cyanides. This is reasonable because of the π bonding nature between metal cations and CN^- ligands. A model structure is schematically shown in Fig. 2.

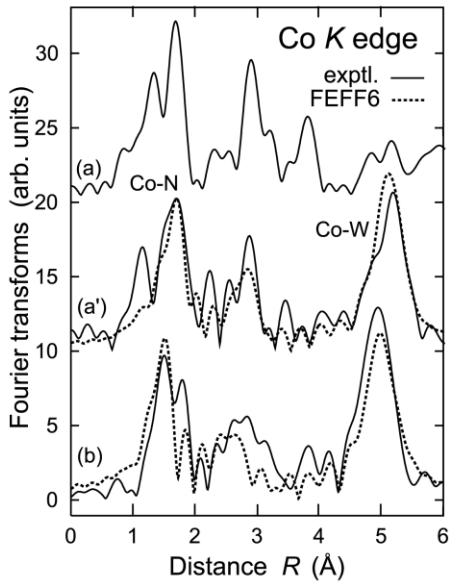

Fig. 1. Fourier transforms of Co *K*-edge EXAFS.

Table 1. Interatomic distances (Å) determined by EXAFS.

Sample	(a)	(a')	(b)	(c)
Co^{II} ratio	98.9%	85.0%	30.1%	82.0%
W-C	2.161(10)	2.152(9)	2.161(10)	2.158(7)
W-N	3.318(8)	3.314(8)	3.319(8)	3.306(14)
$W\text{-}Co^{II}$	5.35(2)	5.37(1)	5.36(3)	5.39(2)
$W\text{-}Co^{III}$		5.22(6)	5.18(2)	5.24(7)
Co^{II}-N	2.072(13)	2.072(12)	2.117(25)	
Co^{III}-N			1.911(13)	
Co^{II}-W		5.37(2)	5.43(6)	
Co^{III}-W		5.14(3)	5.16(2)	

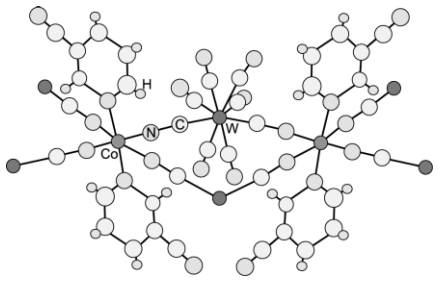

Fig. 2. Model structure of the CoW cyanide.

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