X-Ray Induced Magnetic Phase Transition in CoW Cyanide Probed by XMCD

Hitoshi Osawa[1], Naomi Kawamura[1], Tomoyuki Matsuda[2,3], Youich Arimoto[3], Hitoko Tokoro[2,4], Kazuhito Hashimoto[3], and Shin-ichi Ohkoshi[2,3]

[1] *JASRI /SPring-8, 1-1-1 Kouto, Sayo, Hyogo, 679-1598, Japan*
[2] *Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*
[3] *Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*
[4] *Department of physics, School of Science, University of Tokyo 7-3-1 Hongo, Bunkyo-ku, Tokyo, 113-0033, Japan*

Abstract. The X-ray induced magnetic phase transition of $Cs_{0.8}Co_{1.3}[W(CN)_6](3\text{-cyanopyridine})_{1.9}$ $2.1H_2O$ has been observed using X-ray absorption near edge structure (XANES) and X-ray magnetic circular dichroism (XMCD). The Co K- and W $L_{2,3}$-edge XANES measurements show that charge transfer between Co and W and spin crossover of Co were induced by X-ray irradiation. A conspicuous magnetic diachronic signal was observed at the Co and W edges in the X-ray induced phase, and the XMCD signals of Co and W indicate that the magnetic moment of each magnetic ions is parallel to the applied magnetic field. Therefore, the magnetization of the X-ray induced phase of this material is deduced to be the ferromagnetism.

Keywords: Prussian blue analog, Photo-induced phase transition, Photo-magnet, XMCD
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INTRODUCTION

Over the past few years, photo-induced phase transitions have been extensively studied in a variety of systems, e.g., photo-magnets, spin-crossover complexes, and charge transfer complexes [1-5]. In addition, not only phase transitions induced by visible or UV light irradiation but also by X-ray irradiation has been discovered in some materials [6,7]. Recently, Yokoyama *et al*. discovered an X-ray induced phase transition of $Cs_{0.8}Co_{1.1}(3\text{-CNpy})_{1.9}[W(CN)_8]2.1H_2O$, here after referred to as CoW cyanide [6]. They observed the X-ray induced phase transition of this material using Co K- and W $L_{2,3}$ edge X-ray absorption near edge structure (XANES) spectroscopy at 30 K, and reported that the electric and spin state of the Co and W ions changes from Co^{3+}(low-spin (LS), S=0) and W^{4+}(LS,S=0) for the low temperature (LT) phase to Co^{2+}(high-spin(HS), S=3/2) and W^{5+}(LS, S=1/2) by the X-ray irradiation. This variation in Co and W valence and spin states was same as the thermal transition in this material.

A similar transition is induced by visible light irradiation in some analogous compounds, and it has been reported that the photo-induced magnetic phase transition by visible light irradiation shows the transition from nonmagnetic- to ferromagnetic phases [8,9]. It is also expected that the X-ray induced phase shows ferromagnetism, however, the magnetic observation has not yet been carried out. Since X-ray induced phase is relaxed to LT phase above 100 K, it is very difficult to move the sample to devices such as SQUID while maintaining the X-ray induced phase.

In this study, we report experimentally determined magnetism of the x-ray induced phase using Co K- and W $L_{2,3}$- edge X-ray magnetic circular dichroism (XMCD). The understanding of the magnetic interaction between metallic ions is the essence of a design for a molecular magnet.

EXPERIMENTS

XANES and XMCD measurements at the Co K- and W $L_{2,3}$ absorption edge were performed at the undurator beamline (BL39XU) at SPring-8. A Si(111) rotated-inclined double-crystal was employed as the monochromator, and the higher-order harmonics were cut using flat Pt coated mirror [10]. A diamond phase

retarder was used in the Laue geometry with the (220) reflection plane in order to produce circularly polarized X-rays having plus or minus helicities in the A.C. mode with a frequency of 40 Hz by using a piezo oscillator [11]. The degree of circular polarization was estimated to be 0.9 in the energy range used, as determined by polarization analysis. A transition mode was employed to record the XANES and XMCD spectra. The intensity of incident and transmitted X-ray were measured by the ionization chambers filled with pure N_2 gas. CoW cyanide powder mixed with APIEZON L grease was used for the measurements, and the samples were made in thickness suitable for XANES observation. The external magnetic field was applied parallel (or anti-parallel) to the direction of the incident X-rays using a split-type superconducting magnet.

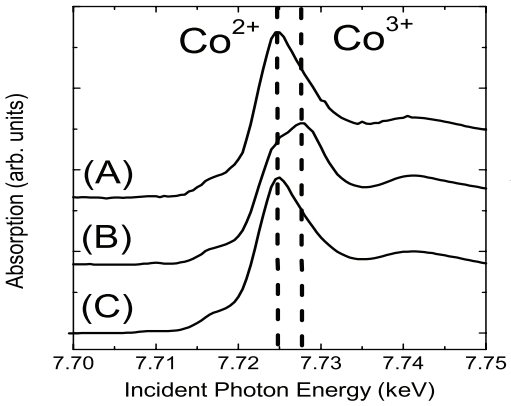

FIGURE 1. Experimental Co K-edge XANES spectra of HT(A), LT(B), and X-ray induced(C) phases. The white line energy of Co^{2+} and Co^{3+} states was indicated by dotted lines, respectively.

RESULTS AND DISCUSSION

The X-ray induced phase transition observed using Co K-edge XANES is shown in figure 1. The HT phase (A) was observed at 300 K, and the LT phase (B) at 120 K where the X-ray induced phase transition was not observed. Comparing the HT and LT phases, a drastic change in the XANES spectra was observed. The white line of the LT phase was shifted to higher energy by 3.1 eV compared to the HT phase, indicating that the Co valence state is changed from Co^{2+}(HS, S=3/2) to Co^{3+}(LS, S=0) during the thermal phase transition. The X-ray induced phase (C) was observed after X-ray irradiation for 2 hours at 5 K. The XANES profile of the X-ray induced phase is similar to the HT phase (A). This shows that the valence and spin states of Co changes from Co^{3+}(LS, S=0) to Co^{2+}(HS, S=3/2) due to the charge transfer from tungsten induced by X-ray irradiation. Therefore, the

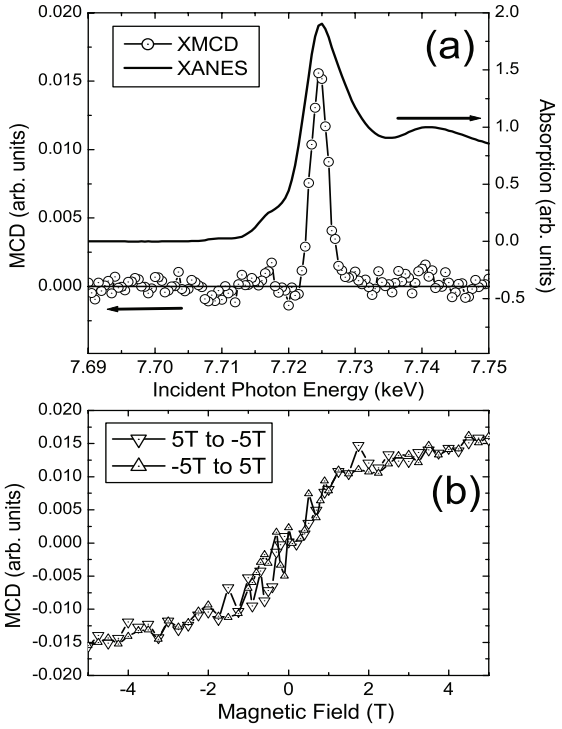

FIGURE 2. (a) Co K-edge XANES (line) and XMCD (circle + line) spectra of X-ray induced phase at 5 K with applied magnetic field of 5 T. (b) Magnetic field dependence of the Co K-edge XMCD signal for X-ray induced phase. The upper (downer) triangle was measured during increasing (decreasing) external magnetic field.

valence state of W changes from W^{4+}(S=0) to W^{5+}(S=1/2). This variation of the valence state by the X-ray induced phase transition is in agreement with the previous report by Ref 6.

Figure 2(a) shows the Co K-edge XMCD and the polarization averaged XANES spectra of the X-ray induced phase of CoW cyanide at 5 K under a magnetic field of 5 T. A positive XMCD signal with a peak at 7.723 keV, the white line of Co-K XANES was observed. The positive single structure in the Co K-edge XMCD spectrum of CoW cyanide was different from that observed in pure Co metal. However, it was similar to the Co K-edge XMCD spectra of $CoFe_2O_4$ which has the same Co valence and spin state of Co^{2+} (HS: S=3/2)[12]. Furthermore, the Co K-edge XMCD shape and direction of CoW cyanide is the same as the Co K-edge XMCD observed in the photo-induced phase of CoFe cyanide, which shows spontaneous magnetization and the Co^{2+} (HS: S=3/2) state [13]. Therefore, the magnetic moment of Co^{2+} in the X-ray induced phase is parallel to the direction of the applied magnetic field. Figure 2(b) shows the magnetic field dependence of the Co K-edge XMCD for the X-ray induced phase at 5 K. The XMCD signal intensity was measured with the

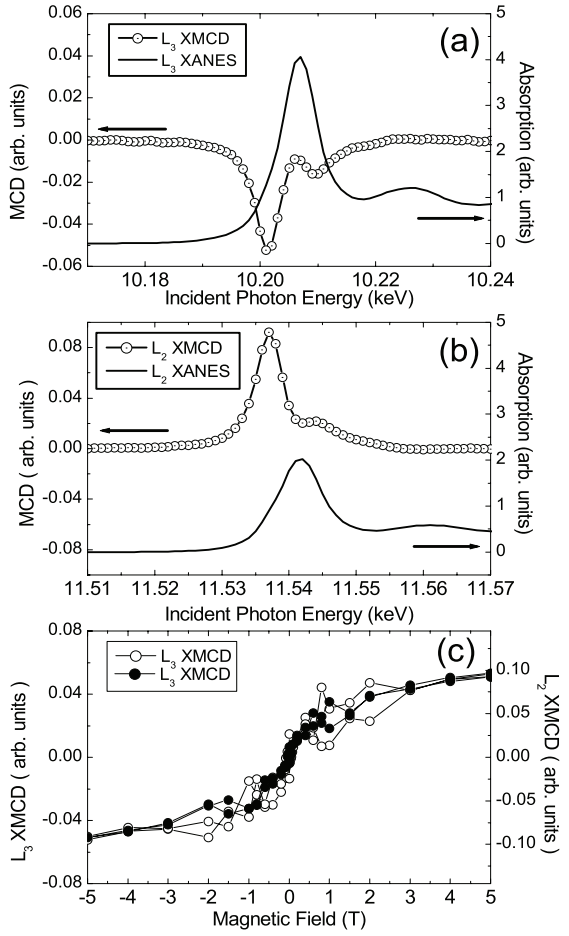

FIGURE 3. (a) and (b) W $L_{3,2}$ -edge XANES (line) and XMCD (circle + line) spectra of X-ray induced phase at 5 K with applied magnetic field of 5 T. (C) Magnetic field dependence of the W L_3 (○) and L_2 (●) -edge XMCD signal for X-ray induced phase. The L_2-edge XMCD signal is plotted with positive and negative are reversed.

incident energy fixed at 7.723 keV where the maximum XMCD signal was observed. The XMCD signal increases sharply up to 1 T. Above 1 T it increases in linearly with magnetic fields, and it is not saturated even at 5 T.

The XANES and XMCD spectrum at the W $L_{2,3}$ edge of the X-ray induced phase was also observed, and are shown in Figures 3 (a) and (b). These spectra were recorded at 5 K under the magnetic field of 5 T. The XMCD spectra exhibit the clear magnetic dichroic effect, indicating the polarization of the 5d state in tungsten. It is also suggested that the transition from W^{4+}(S=0), which does not have a spin moment, to W^{5+}(S=1/2) by the X-ray irradiation. The sign of the XMCD spectra was negative at the L_3 edge and positive at the L_2 edge, showing that the magnetization of the tungsten is parallel to the magnetic field. The XMCD spectra at the L_2- and L_3- edges have a similar structure, and the satellites are observed on the higher energy side. The magnetic field dependence of the W $L_{2,3}$- edge XMCD signal intensity is plotted in figure 3 (c), which was observed at the energy of maximum XMCD effect for both edges. The XMCD curve obtained at both edges show analogous shapes. They show the steep increases up to 1 T followed by the steady rise with saturation still not reached at 5 T. This result resembles the magnetic field dependence of Co^{2+}, and suggests the existence of a magnetic interaction between W^{5+} and Co^{2+} ions. Moreover, the above results confirm that the Co^{2+} and W^{5+} ions couple ferromagnetically, and that they are parallel to the applied magnetic field.

CONCLUSION

The X-ray induced magnetic phase transition of $Cs_{0.8}Co_{1.1}(3\text{-}CNpy)_{1.9}[W(CN)_8]2.1H_2O$ has been observed using XANES and XMCD spectroscopy. The XANES measurements show that X-ray irradiation of the LT phase at 5 K induces charge transfer between the metallic ions and spin crossover in cobalt. The X-ray induced phase has been characterized as ferromagnetic based on the XMCD measurements results at the Co K- and W $L_{2,3}$- absorption edges.

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