First observation of soft X-ray induced phase transition of RbMn[Fe(CN)₆] studied by Fe L-edge X-ray absorption spectroscopy

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Abstract. Temperature-induced and photoinduced phase transition in a ferromagnet Rb₀.⁹₄Mn₀.⁹₈[Fe(CN)₆]₀.₄H₂O was studied by X-ray absorption spectroscopy at Fe L-edge. Compared with spectra of K₄[Fe(CN)₆] and K₃[Fe(CN)₆] as standards for Fe(II) and Fe(III), temperature-induced phase transition is clearly shown. At 43 K, phase transition induced by the soft X-rays was firstly observed.

1. Introduction

X-ray spectroscopy using synchrotron radiation is a powerful tool to study local electronic property and atomic structure because its elemental and chemical-state selectivity. X-ray absorption spectroscopy (XAS) is basically quite simple technique but both the electronic and atomic structures can be obtained from the near-edge region (X-ray absorption near edge structure; XANES) and extended X-ray absorption fine structure (EXAFS) analysis, respectively.

Concerning materials showing photoinduced phase transition, a lot of studies have been reported using X-ray absorption fine structure (XAFS) spectroscopy at the K-edge of 3d transition metals in hard X-ray region. However, XAFS in the soft X-ray region has not been applied for such materials to date. Using soft X-rays, we can obtain L-edge spectra that contain complementary information to the K-edge ones because the transition symmetry is different between those.

Here, we have applied Fe L-edge XAS to a Prussian blue analogue RbMn[Fe(CN)₆]. This material is well known to show the thermal phase transition of the magnetic susceptibility with a very wide hysteresis loop between 216 K and 298 K and also the photo-induced phase transition (PIPT) caused by visible light irradiation [1]. Fe and Mn K-edge XAS studies were already reported [2] which well showed the charge transfer from Fe(II)-Mn(III) to Fe(III)-Mn(II) in the phase transition from low-temperature (LT) phase to high-temperature (HT) phase.
2. Experimental
Sample preparation and magnetic susceptibility measurements using superconducting quantum interface device (SQUID) were conducted at the University of Tokyo by the method described elsewhere [1]. All the X-ray absorption measurements were performed in a high-vacuum chamber at a soft X-ray spectroscopy station BL-11A of the Photon Factory, a synchrotron radiation facility in the Institute of Materials Structure Science of the High Energy Accelerator Research Organization [3]. Powder sample was diffused on a carbon adhesive tape on a copper sample holder. A heater was set on the back side of the sample holder. The holder was attached on a head of a closed-cycle He refrigerator. The sample temperature was measured with a Si-diode thermometer set on the sample holder and controlled with a digital temperature controller.

X-ray absorption spectra were recorded by total electron yield using a microchannel plate detector, which is a typical alternative detection method in the soft X-ray region. A diode pumped solid state red laser (CW, 658 nm, maximum power of 30 mW) was employed as the excitation light for the PIPT.

3. Results and Discussion
The very wide hysteresis loop of the magnetic susceptibility was confirmed with the SQUID measurements as shown in figure 1 (top). Figure 1 (left) shows the X-ray absorption spectra at Fe L$_{3,2}$-edge region measured at 300 K (RT), 150 K, 43 K for the Rb$_{0.94}$Mn[Fe(CN)$_6$]$_{0.98}$ sample together with those of standard materials of K$_4$[Fe(CN)$_6$] and K$_6$[Fe(CN)$_6$]. A distinct pre-edge peak at around 707 eV in the spectrum of K$_6$[Fe(CN)$_6$] can be assigned to the transition of Fe 2p - t$_{2g}$ [4] and is absent in the spectrum of K$_4$[Fe(CN)$_6$]. In the spectrum at 300 K of Rb$_{0.94}$Mn[Fe(CN)$_6$]$_{0.98}$ sample, the pre-edge peak appears indicating the presence of the Fe(III) species. On the contrary, the peak almost disappears at 150 K and the spectrum becomes quite similar to that of K$_4$[Fe(CN)$_6$], indicating clearly that Fe is in the Fe(II) state in the low temperature (LT) phase. These results concerning the temperature-induced phase transition are consistent with those from hard X-ray experiments [2].

![Figure 1](image-url)

**Figure 1.** (top) Product of the molar magnetic susceptibility and the temperature versus the temperature plot obtained by SQUID measurements. (left) Fe L$_{3,2}$-edge X-ray absorption spectra of (a) K$_4$[Fe(CN)$_6$], (b) K$_6$[Fe(CN)$_6$] and Rb$_{0.94}$Mn[Fe(CN)$_6$]$_{0.98}$ 0.4H$_2$O measured at (c) 300 K, (d) 150 K, (e) 43 K under laser illumination and (f) without the laser.
Further lowering the temperature to 43 K, however, the pre-edge peak appears again. This disagrees with the results from the previous experiments by hard X-rays [5] where the spectra show no changes between 170 K and 25 K. Then we measured spectra at 43 K under the laser illumination for 10 minutes but the spectrum (figure 1(e)) does not change although PIPT should occur according to the previous experiments [1,2]. We suppose that even without the laser irradiation, a phase transition is induced by the soft X-rays at this temperature. This is the first observation of soft X-ray induced phase transition (SX-PIPT) of such materials.

Then, we have examined this new phenomenon rather in detail. There is a little difficulty that the probe X-rays are the pump light at the same time but we have found some properties of this SX-PIPT. Increase in the pre-edge peak intensity is seen only in the first few minutes in the present condition of the flux of $10^9$ photons/s monochromatized soft X-rays in about 0.5 mm$^2$ area. The spectrum does not change with further irradiation of much more intense soft X-rays of $10^{11}$ photons/s or the laser for a longer time such as one hour. No dependence on the photon energy in the range of 500-1000 eV is observed concerning the SX-PIPT. This means that the 2p-3d transitions of Fe or Mn seem to be no direct relation to the SX-PIPT. Soft X-ray induced phase is released; i.e., the pre-edge peak disappears by heating the sample up to 100-120 K. This temperature is almost the same as in the hard X-ray studies for the visible light induced phase [5].

The spectrum of the soft X-ray induced phase (figure 1(f)) can be reproduced by composition of the spectra of LT (figure 1(d)) and HT (figure 1(c)) phases. About 50% LT and 50% HT spectra well reproduce the present spectrum of the soft X-ray induced phase (figure 1(e)). It is unclear at present why the conversion ratio is as low as 50% even after a long time irradiation. We think that more detailed studies are necessary in a limited machine time to clarify the nature of this new phenomenon.

4. Summary
Thermal and photo-induced phase transition of the Rb$_{0.94}$Mn[Fe(CN)$_6$)$_{0.98}$ 0.4H$_2$O sample was studied by Fe L-edge soft X-ray absorption spectroscopy to show the feasibility of this method. Soft X-ray induced phase transition was firstly observed.

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