Observation of X-ray-induced phase transition phenomenon of cesium manganese hexacyanoferrate

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Abstract. Cesium manganese hexacyanoferrate is an interesting material which exhibits the phase transition with the magnetic susceptibility variation under the effect of external stimuli; such as temperature and visible light irradiation. This phase transition attributes the charge transfer between ions in the Fe-CN-Mn bond. Recently, we observed the phase transition by X-ray irradiation below 80 K. The X-ray absorption spectrum of the low-temperature (LT) phase approached toward that of the high-temperature (HT) phase. The spectrum variation by X-ray irradiation attributes the charge transfer from Fe\textsuperscript{II} to Mn\textsuperscript{III}.

1. Introduction

Prussian blue analogues compounds are molecular-based materials with a 3-D network structure which are strongly bridged by cyano groups and exhibit interesting properties with unusual electric and magnetic properties by a temperature variation \cite{1-4} and visible light irradiation \cite{5-8}. Especially, many investigations about the phase transition phenomenon of rubidium manganese hexacyanoferrate have been reported. Tokoro \textit{et al.} \cite{7, 8} observed that rubidium manganese hexacyanoferrate exhibited the phase transition with a magnetic susceptibility variation by a temperature variation and visible light irradiation. Matsuda \textit{et al.} \cite{4} also observed the temperature-induced phase transition of cesium manganese hexacyanoferrate. They indicated the charge transfer between Fe\textsuperscript{III}-CN-Mn\textsuperscript{II} for the high-temperature (HT) phase and Fe\textsuperscript{II}-CN-Mn\textsuperscript{III} for the low-temperature (LT) phase. In these years, the structural variation by X-ray irradiation of rubidium manganese hexacyanoferrate was reported \cite{9}. The phase transition by X-ray irradiation is remarkable and reports are few. Cesium manganese hexacyanoferrate is also expected to exhibit the phase transition by X-ray irradiation because the structure of cesium manganese hexacyanoferrate is very similar to that of rubidium manganese hexacyanoferrate. Recently, we discovered the X-ray-induced phase transition phenomenon of cesium manganese hexacyanoferrate, and introduce it in this paper.
2. Experimental

Cesium manganese hexacyanoferrate was prepared by reacting an aqueous solution of \( \text{MnCl}_2 \) (0.025 mol dm\(^{-3}\)) and \( \text{CsCl} \) (0.5 mol dm\(^{-3}\)) with a mixed aqueous solution of \( \text{K}_3[\text{Fe(CN)}_6] \) (0.025 mol dm\(^{-3}\)) and \( \text{CsCl} \) (0.5 mol dm\(^{-3}\)) at room temperature. The precipitate was filtered and dried, yielding a powdered sample. The formula of the prepared sample was introduced as \( \text{Cs}_{1.54}\text{Mn}^{\text{II}}_{1.0}\text{Fe}^{\text{II}}_{0.5}\text{Fe}^{\text{III}}_{0.46}[\text{CN}]_6 \) for the HT phase and \( \text{Cs}_{1.54}\text{Mn}^{\text{II}}_{0.5}\text{Mn}^{\text{III}}_{0.46}\text{Fe}^{\text{II}}_{1.0}[\text{CN}]_6 \) for the LT phase in ref. [10].

The X-ray absorption experiments were conducted because the absorption coefficient around the absorption edge is sensitive to the phase transition [1, 6, 10]. The X-ray data were obtained using a transmission geometry at the beamline 9A of Photon Factory in Institute of Materials Structure Science, Japan. The \( \text{Si}(111) \) monochromator and focusing mirrors were employed. The sample was diluted with \( \text{BN} \) and pressed to prepare a disk. The temperature was controlled by using a helium refrigerator. The cooling and heating speeds were 3 K/min. During the cooling and heating processes, the X-ray absorption coefficient at the Mn K-edge main peak was captured.

3. Results and Discussion

Figure 1 shows the X-ray absorption coefficient as a function of temperature at the Mn-K edge main peak (6552.2 eV). The magnetic susceptibility curve measured by using a superconducting quantum interference device magnetometer is also shown in Fig. 1. The hysteresis loop of the temperature-induced phase transition was appeared above 150 K in both profiles. The upper and lower levels of the hysteresis loop indicate the HT and LT phases, respectively. There is slightly the disagreement between the two loops. It is caused by the small difference of the thermal sensor position, the thermal conduction of the sample holder, and so on between two kinds of experiments. With further cooling, the behaviour of the profile is more intriguing. In the magnetic curve, \( \chi_T \) increased as the temperature decreased below 100 K. This phenomenon corresponds to the spontaneous magnetization, and the ferromagnetic interaction between \( \text{Mn}^{\text{II}} \) and \( \text{Mn}^{\text{III}} \) is operated in the applied field direction [4]. In the absorption profile, the small loop was observed below 80 K. The loop indicates the evidence of the phase transition by X-ray irradiation. In order to obtain the additional evidence and develop the understanding of the phenomenon, we conducted the X-ray absorption spectroscopy at 25 K with varying the incident X-ray intensities. Figure 2 shows the Mn K-edge absorption spectra with the incident X-ray intensities of \( 5.5 \times 10^{11} \), \( 1.8 \times 10^{11} \), \( 5.9 \times 10^{10} \), \( 1.9 \times 10^{10} \), and \( 6.0 \times 10^9 \) photons/sec. As references, the spectra of the HT (at 290 K) and LT (at 150 K) phases are described in Fig. 2. The spectra depended on the incident X-ray intensity; the spectrum of the LT phase approached toward that of the HT phase as the incident X-ray intensity increased. This trend is the powerful evidence of the X-ray-induced phase transition.

Margadonna et al. [9] observed the lattice constant variation by X-ray irradiation of rubidium manganese hexacyanoferrate from the X-ray diffraction pattern. The lattice constant decreased with the temperature variation; the lattice distorted. At 10 K, the lattice constant increasing was provoked by X-ray irradiation; the distorted lattice was relaxed. They suggested that the lattice relaxation was...
caused by the charge transfer from Fe^{II} to Mn^{III}. In cesium manganese hexacyanoferrate, the lattice constant decreased as the temperature reduced [4]. This gives the prediction that the lattice constant increasing of cesium manganese hexacyanoferrate by X-ray irradiation advances like the phenomenon of rubidium manganese hexacyanoferrate. However, there are differences between cesium manganese hexacyanoferrate and rubidium manganese hexacyanoferrate. The X-ray-induced phase transition of rubidium manganese hexacyanoferrate seems to develop at any temperature and is the slow reaction; the lattice constant variation was in minutes scale [9]. On the other hand, the phase transition of cesium manganese hexacyanoferrate was observed below 80 K and induced in a moment (we confirmed the absorption variation by the X-ray shutter operation). These are the specific behaviours of cesium manganese hexacyanoferrate. Such differences attribute the production principle of the X-ray-induced phase transition, but the details are unclear in the present.

4. Summary

In this work, we obtained the evidence of the X-ray-induced phase transition of cesium manganese hexacyanoferrate. The phase transition developed below 80 K and depended on the incident X-ray intensity. The lattice constant increasing may be provoked by X-ray irradiation and relates to the charge transfer from Fe^{II} to Mn^{III} in the Fe-CN-Mn bond.

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