Photoinduced phase transition of $RbMnFe(CN)_6$ studied by XANES

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Introduction

Recently Ohkoshi et al. discovered a photoinduced (PI) phase transition in a Prussian-blue analogue of $RbMnFe(CN)_6$. $RbMnFe(CN)_6$ exhibits the magnetic phase transition at T_c=12 K, below which the material shows spontaneous magnetization. Upon visible-light irradiation (650 nm), the spontaneous magnetization is quenched completely, and some minutes after turning off the light the magnetization is recovered abruptly.

In the present study, we have investigated the electronic state in the PI phase of $RbMnFe(CN)_6$ by measuring Mn, Fe and Rb *K*-edge XANES.

Experimental

The Mn, Fe and Rb *K*-edge XANES spectra were recorded with a transmission or fluorescence-yield mode at BL12C at the temperatures of 300 K for the high-temperature (HT) phase and 30 K for the low-temperature (LT) and PI phases. The PI phase was obtained by irradiating the visible light (532 nm, Nd:YAG laser) at 30 K and the fluorescence-yield spectra were taken under irradiation.

Results and discussion

Figure 1 shows the preedge region of the Fe *K*-edge XANES. The sample in the dark gives a single absorption band indicated by an arrow in the 1*s* 3*d* transition. This band is split into two components when irradiated by the lights. The occurrence of the phase transition is clearly identified. The splitting is ascribed to the crystal-field splitting associated with the presence of the hole in the $3dt_{2g}$ level. These findings imply that Fe is in the low-spin (LS) trivalent (d^5) and LS divalent (d^6) states in the LT and PI phases, respectively. The PI phase seems identical to the HT one consisting of LS trivalent (d^5) Fe.

Figure 2 shows the preedge region of the Mn *K*-edge XANES. Although the spectral features in the 1*s* 3*d* transition regions is less clear, the spectrum in the dark gives double peaks, which is merged to a single peak under light irradiation. The spectrum of the PI phase is again similar to the HT one. By comparing the spectra in Fig. 2, we can conclude that the PI phase consists of high-spin (HS) divalent (d^5) Mn as in the case of the HT phase, while the LT phase gives high-spin trivalent (d^4) Mn.

Although the overall features of the Mn *K*-edge XANES are found to change drastically between the LT and PI phases and to be similar between the PI and HT phases, this cannot be shown due to the limitation of the report and will be given elsewhere. As a consequence, upon light irradiation, the charge-transfer tautomeric photoinduced transition takes place and the electronic state turns from Fe(II)LS-Mn(III)HS to Fe(III)LS-Mn(II)HS. The PI phase is identical to the HT phase.

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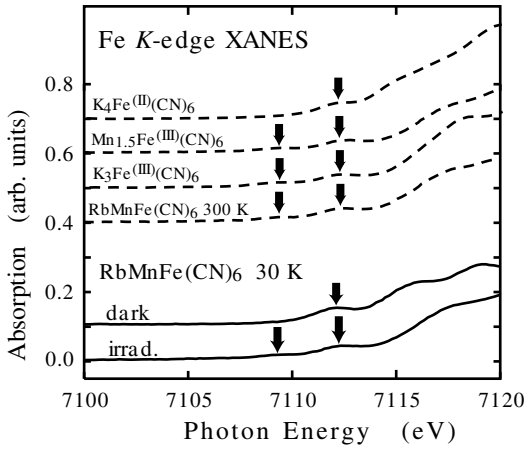

Fig. 1 Preedge region of the Fe *K*-edge XANES of the LT (dark) and PI (irrad.) phases, together with those of the HT phase (300 K) and other reference materials.

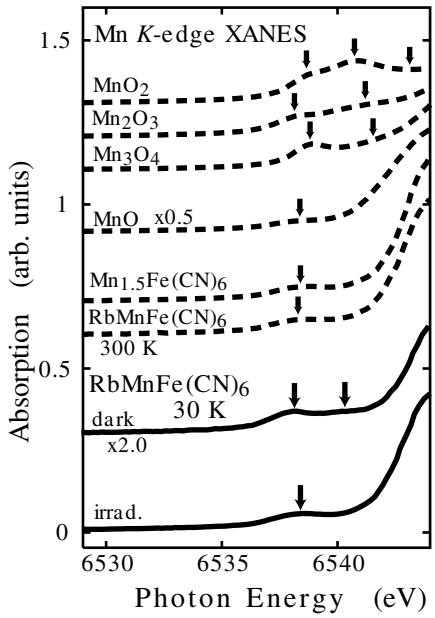

Fig. 2 Preedge region of the Mn *K*-edge XANES of the LT (dark) and PI (irrad.) phases, together with those of the HT phase (300 K) and other reference materials.