Local structures of $RbMnFe(CN)_6$ studied by EXAFS: The photoinduced phase and the high- and low-temperature phases

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Introduction

A Prussian-blue analogue of $RbMnFe(CN)_6$ shows a thermally induced first-order phase transition at T_c =231 K and T_c =304 K [1] and a photoinduced phase transition at very low temperature. Especially, below T_c=12 K, spontaneous magnetization is quenched rapidly by the visible-light irradiation.

In the present study, we have investigated the local structures in the low-temperature (LT), high-temperature (HT) and photo-induced (PI) phases of $RbMnFe(CN)_6$ by measuring Mn, Fe and Rb *K*-edge EXAFS.

Experimental

The Mn, Fe and Rb K-edge EXAFS spectra were recorded with a transmission or fluorescence-yield mode at BL12C at the temperatures of 300 K for the HT phase and 30 K for the 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

Figures 1 and 2 shows the Fourier transforms of Fe and Mn *K*-edge EXAFS, respectively, taken with the fluorescence-yield mode. In principle, three peaks are seen in both figures. In Fig. 1, the peaks at 1.5, 2.6 and 4.6-4.8 Å are ascribed to the Fe-C, Fe-N and Fe-Mn shells, respectively. Similarly, the Mn-N, Mn-C and Mn-Fe shells can be found in Fig. 2. Since the present material shows a NaCl-type framework, higher-nearest neighbor shells are enhanced due to the multiple-scattering focusing effect.

The curve-fitting analysis was performed assuming the collinear configuration of the –Fe-C-N-Mn- chain. The Fe-C distances were obtained as 1.914 0.003, 1.897 0.004 and 1.93 0.02 Å for the HT, LT and PI phases, respectively. The presence of the octahedral $Fe(CN)_6$ unit is clearly confirmed. These results indicate that Fe is in the divalent state in the LT phase and is in the trivalent state in the RT and PI phases.

Two kinds of the Mn-N distances of ~1.96 and ~2.21 Å were found in all the phases. The coordination number for each shell changes drastically, depending on the phases. The longer Mn-N bonds are dominated in the HT and PI phases, while both contributions are clearly seen in the LT phase. In the HT and PI phases, an octahedral $Mn(NC)_6$ unit is most probable with divalent high-spin d^5 Mn and with the longer Mn-N distance of ~2.21 Å. A small contribution from the shorter Mn-N bond in the HT and PI phases might be caused by the coexistence of the LT phase, this being confirmed by XANES.

In the LT phase, it is concluded that the $Mn(NC)_6$ unit is Jahn-Teller distorted, leading to four shorter and two longer Mn-N bonds. This is typical in trivalent high-spin Mn and the tetragonal distortion observed by powder x-ray diffraction is explained by the present findings. Moreover, the Mn-Fe and Fe-Mn distances agree excellently with those estimated from the lattice constants of the HT and LT phases. From the Rb *K*-edge EXAFS, Rb is found to locate at the center of the cubic framework.

The local structures of all the phases were successfully determined and the PI phase is found to be structurally identical to the HT phase.

References

[1] S. Ohkoshi et al., J. Phys. Chem. 106, 2423 (2002).

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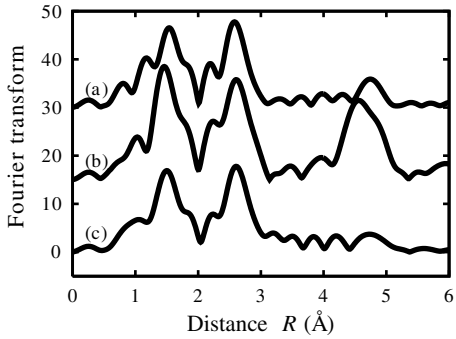

Fig. 1 Fourier transforms of Fe *K*-edge EXAFS of (a) the HT phase, (b) the LT phase and (c) the PI phase.

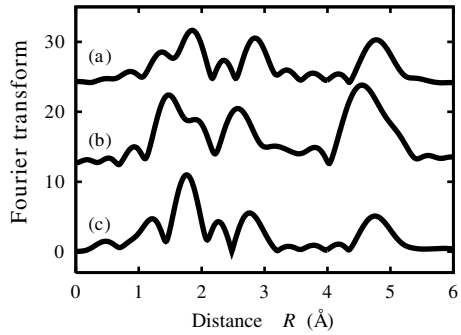

Fig. 2 Fourier transforms of Mn *K*-edge EXAFS of (a) the HT phase, (b) the LT phase and (c) the PI phase.