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# Observation of π backbonding features appearing in Fe 2p X-ray absorption spectra and Fe 1s-4p-1s resonant X-ray emission spectra of RbMn[Fe(CN)$_6$]

**Yoshinori Kitajima[1], Yūsuke Nanba[2], Masayuki Tanaka[3], Yuji Koga[3], Akihiro Ueno[3], Kosuke Nakagawa[4], Hiroko Tokoro[4], Shin-ichi Ohkoshi[4], Toshiaki Iwazumi[3], Kozo Okada[2] and Yasuhito Isozumi[5]**

[1]Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization, 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan
[2]Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushima-naka, Kita-ku, Okayama 700-8530, Japan
[3]Department of Mathematical Sciences, School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Nakaku, Sakai, Osaka 599-8531, Japan
[4]Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan
[5]Radioisotope Research Center, Kyoto University, Yoshidakonoe-cho, Sakyo-ku, Kyoto 606-8501, Japan

E-mail: yoshinori.kitajima@kek.jp

**Abstract**. Satellite features by π backbonding (metal-to-ligand charge transfer) were observed in both Fe 2p (L$_{3,2}$-edge) X-ray absorption spectra and 1s-4p-1s resonant X-ray emission spectra for RbMn[Fe(CN)$_6$], which can be theoretically explained using common parameters. Fe L$_{3,2}$-edge and Mn L$_{3,2}$-edge X-ray absorption spectra for low temperature phase are also presented.

## 1. Introduction

Prussian blue analogues are potential candidates for novel magnetic devices. They exhibit the valence transition induced by temperature [1], photo-irradiation [2,3], pressure [3], and electric field [4]. For example, the valence states change from Fe(III)-Mn(II) to Fe(II)-Mn(III) and structural form from the cubic structure to the tetrahedral one accompanying the Jahn-Teller distortion of MnN$_6$ octahedrons with decreasing temperature in rubidium manganese hexacyanoferrate, RbMn[Fe(CN)$_6$]. That has been clearly shown by Fe K-edge and L$_{3,2}$-edge X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES) [5,6]. Hexacyano-compounds are composed of a 3-D network structure in which the transition-metal ions are strongly bridged by cyano groups [7]. One of the characteristics of the electronic states of cyanides is π backbonding (metal-to-ligand charge transfer, MLCT). Satellite peaks appearing in Fe L$_{3,2}$-edge XAS have been theoretically reproduced considering both the MLCT and electron correlation [8,9]. The importance of MLCT was confirmed both experimentally and theoretically for simpler model compounds [10,11] but further experiments have been desired for complex systems. To acquire more electronic information, we have adopted resonant X-ray emission

spectroscopy (RXES) around Fe K absorption edge for RbMn[Fe(CN)$_6$], together with the model compounds of K$_4$[Fe(CN)$_6$] and K$_3$[Fe(CN)$_6$] and also Fe and Mn L$_{3,2}$-edge XAS for low temperature phase.

## 2. Experimental

Fe L$_{3,2}$-edge XAS experiment was performed 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 (KEK-PF) [12]. Powder sample of Rb$_{0.94}$Mn[Fe(CN)$_6$]$_{0.98}$ 0.4H$_2$O was prepared by the method described elsewhere [1] and diffused on a carbon adhesive tape on a copper sample holder. The holder was set on a head of a closed-cycle He refrigerator and a heater was also set on the back side of the sample holder. 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 of model compounds were recorded by total electron yield. While the partial electron yield mode was adopted for temperature-controlled measurements using a microchannel plate (MCP) detector with applying a retarding voltage of -100 V to a mesh in front of the MCP. Although the light source is not an undulator but a bending magnet, sufficient photon flux with a reasonable energy resolution is available thanks to the stable top-up operation at 430 mA beam current of the PF 2.5-GeV storage ring and the MCP detector with a higher efficiency. The energy spread of the incident X-rays is estimated as less than 0.3 eV, which is much smaller than the previously reported spectra [6].

Fe 1s-4p-1s RXES experiment was conducted at BL-15B1 of KEK-PF, where the white synchrotron radiation beam from a bending magnet is monochromatized by a double-crystal Si(111) monochromator. Fe K-edge X-ray absorption spectra were measured by transmission method using powder samples spread over adhesive tapes. The emission spectra were recorded by a curved Ge(440) crystal monochromator installed in a vacuum chamber named "Escargot" spectrometer [13]. The analyzed X-rays were detected by a position-sensitive proportional counter using a charge division method. The overall experimental energy resolution was about 2.4 eV.

## 3. Results and Discussion

Figure 1 shows the Fe L$_{3,2}$-edge X-ray absorption spectra measured at 300 K (HT) and 40 K (LT) for RbMn[Fe(CN)$_6$] sample together with standard materials of K$_4$[Fe(CN)$_6$] 3H$_2$O and K$_3$[Fe(CN)$_6$]. HT spectrum is quite similar to that for K$_3$[Fe(CN)$_6$], where a distinct pre-edge peak A at around 706.3 eV is well known to be assigned to the transition of Fe(III) 2p - t$_{2g}$ [9,11] and is absent in the spectrum of K$_4$[Fe(CN)$_6$]. This peak was used as a reference for the energy calibration. With a configuration-interaction full-multiplet theory



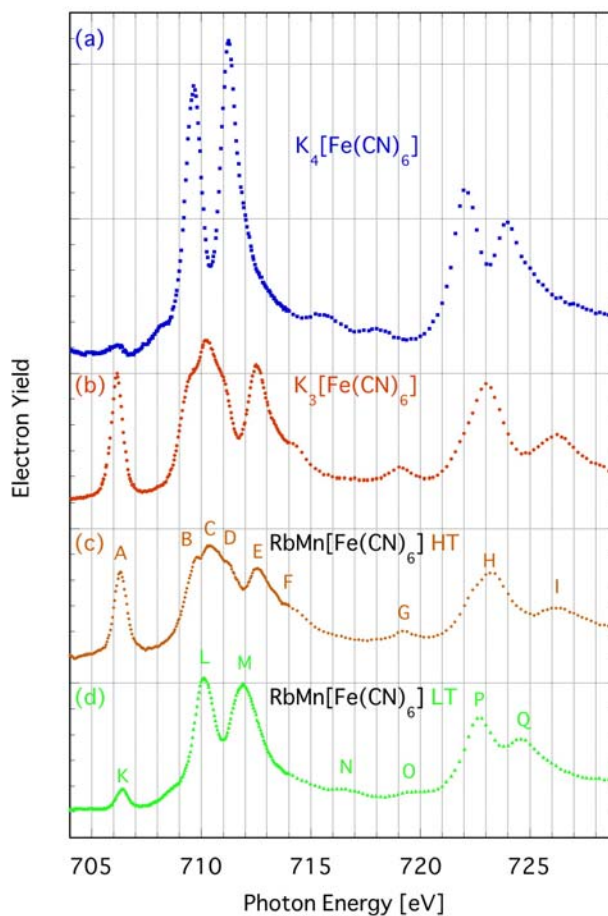**Figure 1.** Fe L$_{3,2}$-edge X-ray absorption spectra of (a) K$_4$[Fe(CN)$_6$], (b) K$_3$[Fe(CN)$_6$], (c) RbMn[Fe(CN)$_6$] measured at 300 K and (d) at 40 K.

for a $[Fe(CN)_6]^{3-}$ cluster model, satellite peaks E and I can be associated with the electron configuration of $d^4L(t_{2g})$ (MLCT). Detailed theoretical methods and discussion were described in Ref. 9.

Spectrum for LT phase (Fig. 1(d)) drastically changes from HT and shows some differences in peak position and intensity from $K_4[Fe(CN)_6]$ one, which means that the electronic state of Fe predominantly changes from +3 to +2, according with structural change through temperature-induced phase transition. Possibility of soft X-ray induced phase transition [6] cannot be eliminated completely but we believe that it is negligible because the intensity of the incident beam is much lower than the previous experiments. LT spectrum was also theoretically analyzed taking the crystal field of the tetragonal symmetry into account in detail in Ref. 9. The overall spectral features including satellite peak M were well reproduced by using $[Fe(CN)_6]^{4-}$ cluster model considering MLCT.

In addition, Mn $L_{3,2}$-edge X-ray absorption spectra for HT and LT phases were measured at the same time. HT spectrum (Fig. 2(a)) was again well reproduced theoretically using $[Mn(NC)_6]^{4-}$ cluster model including satellite peak U [9]. Backbonding is suppressed owing to the Hund's coupling in the Mn $L_{3,2}$-edge XAS. Analysis of LT spectrum is now in progress.

Figure 3 shows the results of 1s-4p-1s RXES with Fe K-edge XAS for $RbMn[Fe(CN)_6]$. The excitation energies of RXES shown by thick lines in the right panel are indicated by white arrows in the left one. Three Raman peaks (R1-R3) were observed. Raman peaks also appeared in theoretical calculation with the cluster model using the same parameters as in Fe $L_{3,2}$-edge XAS simulation such as charge transfer energy, Coulomb interaction, exchange interaction, hybridization interaction and crystal field splitting [8,9]. The observed Raman shift energies of 5.1 eV, 9.7 eV and 14.5 eV are close to those calculated for three features associated with $d^6\underline{L}(t_{2g})$, $d^4\underline{L}(t_{2g})$ and $d^6\underline{L}(e_g)$ CT transitions, respectively. Metal-to-ligand charge transfer (MLCT; $d^4\underline{L}(t_{2g})$ configuration) is also important for RXES.
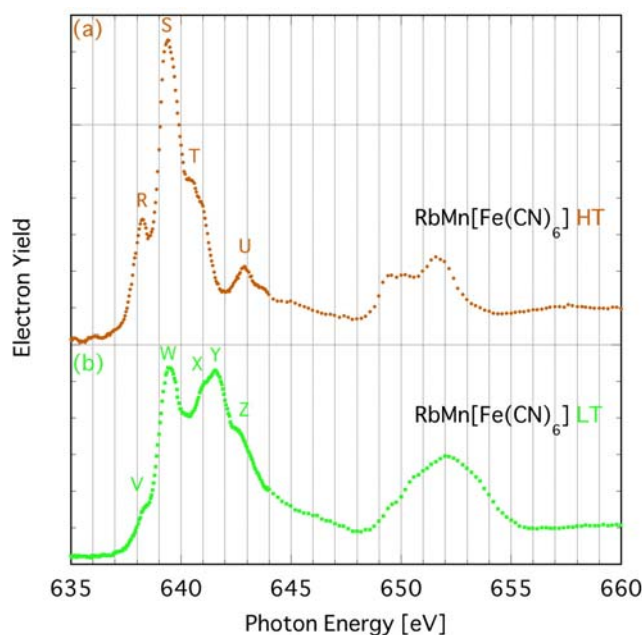


**Figure 2.** Mn $L_{3,2}$-edge X-ray absorption spectra of $RbMn[Fe(CN)_6]$ measured at (a) 300 K and (b) 40 K.



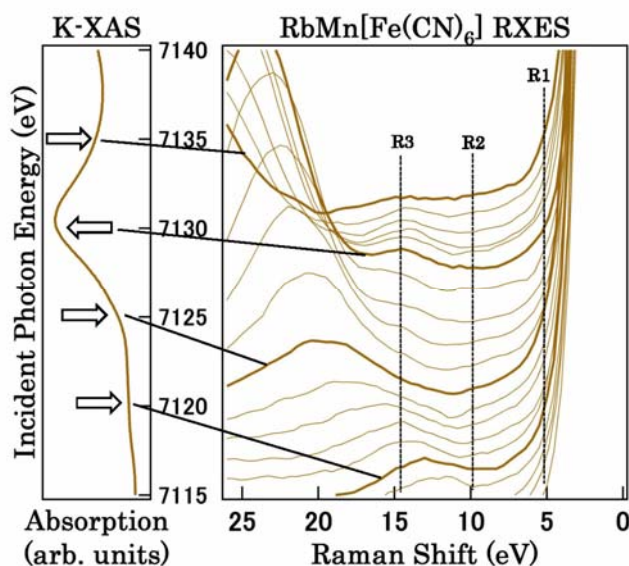**Figure 3.** (left) Fe K-edge X-ray absorption spectra and (right) Fe 1s-4p-1s resonant X-ray emission spectra of $RbMn[Fe(CN)_6]$ measured at 297 K. Three Raman peaks were observed at 5.1 eV, 9.7 eV and 14.5 eV.

These three Raman peaks were also observed at similar energies for reference compounds of $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$ (not shown).

## 4. Summary

Fe $L_{3,2}$-edge XAS and Fe 1s-4p-1s RXES were conducted for the $Rb_{0.94}Mn[Fe(CN)_6]_{0.98}$ $0.4H_2O$ powder sample. In all the spectra, $\pi$ backbonding (MLCT) features were observed and theoretically analyzed with a configuration-interaction full-multiplet theory for metal hexacyanide cluster model. Mn $L_{3,2}$-edge X-ray absorption spectra for HT and LT phases were also presented for further theoretical consideration.

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