Raman study of the charge transferred metastable state leading to the photoinduced magnetic phase transition in rubidium manganese hexacyanoferrate

Ryo Fukaya¹, Kenji Ohki¹, Makoto Nakajima¹, Hiroko Tokoro²,³, Snin-ichi Ohkoshi², and Tohru Suemoto¹

¹Institute for Solid State Physics, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan
²Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan
³PRESTO, JST, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

Abstract

The photoinduced charge transfer process in Rb₀.₉₄Mn[Fe(CN)₆]₀.₉₈·₀.₂H₂O was investigated by observing the pair valence states of adjacent metal ions by Raman spectroscopy near the high-temperature end of the hysteresis loop. After prolonged irradiation at the ligand-to-metal charge transfer band, the Fe³⁺-CN-Mn²⁺ pair valence state corresponding to the high-temperature phase was completely depleted, and the Fe²⁺-CN-Mn³⁺ pair corresponding to the low-temperature phase appeared. In addition, peaks ascribable to Fe²⁺-CN-Mn²⁺ and Fe³⁺-CN-Mn³⁺ pair valence states were found.

Keywords: rubidium manganese hexacyanoferrate, photoinduced phase transition, charge transfer, Raman spectroscopy.

PACS numbers: 64.60.-I, 78.30.-j
1. Introduction

Optical control of the material properties by light irradiation has attracted a great deal of attention as optical physics and chemistry. The photoinduced phase transition (PIPT) is observed in cyano-bridged metal complexes showing the novel optical functionalities, such as photoinduced magnetization and pole inversion [1-5]. Among these complexes, rubidium manganese hexacyanoferrate, whose formula is Rb$_x$Mn[Fe(CN)$_6$]$_y$·$n$H$_2$O, have been attracting interests because of showing a photinduced valence and structural changes by the charge transfer (CT) transition [6-8]. The compound is constructed with Mn and Fe ions bridged by CN$^-$ ions in three-dimensional network, and shows a thermal phase transition between Fe$^{III}$ ($S=1/2$)-CN-Mn$^{II}$ ($S=5/2$) in high-temperature (HT) phase and Fe$^{II}$ ($S=0$)-CN-Mn$^{III}$ ($S=2$) in low-temperature (LT) phase [9]. Here the Fe has a low-spin state and the Mn has a high-spin state in both phases. The thermal phase transition accompanies the electron transfer from Mn$^{II}$ to Fe$^{III}$, the Jahn-Teller distorted Mn$^{III}$ ion site, and the structural transformation from cubic in HT phase to tetragonal in LT phase. Some interesting functionalities in Rb$_x$Mn[Fe(CN)$_6$]$_y$·$n$H$_2$O series, such as a magnetization-induced second harmonic generation, a pressure-induced magnetic pole inversion, and ferroelectric ferromagnetism, can be realized [10-12]. Recently, reversible photomagnetization has been observed by light irradiation at 410 or 532 nm [13]. These phenomena related to multistability are important for observing the PIPT.

To understand the PIPT mechanism in this material, we have to investigate not only the magnetization but also the valence states of the transition metals. The phase transition in rubidium manganese hexacyanoferrate is triggered by a valence change following the metal to metal or CN$^-$ ligand to the adjacent metal CT transition. Since the frequency of
the CN stretching mode is sensitive to the valence states of the adjacent metal ions, we can obtain information about the pair valence distribution of the Fe and Mn ions bridged by the CN⁻ ions by observing the Raman or infrared (IR) absorption spectra. We can discriminate not only the fraction of the valence state of Fe or Mn, but also four possible pairs of the valence states: Fe⁺⁺-CN-Mn⁺⁺, Fe⁺⁺-CN-Mn⁺⁺⁺, Fe⁺⁺⁺-CN-Mn⁺⁺, and Fe⁺⁺⁺-CN-Mn⁺⁺⁺. Thus, the CN vibration spectroscopy is an effective method for investigating the PIPT in cyano-bridged metal complexes.

In rubidium manganese hexacyanoferrate, PIPT starting from the LT phase has been observed [5, 13]. In this work, we report the photoinduced valence changes leading to the phase transition starting from HT phase near the high-temperature end of the hysteresis loop, observed by Raman spectroscopy. We observed all pair valence states, including not observed in IR absorption spectra, expected from the photoinduced CT process.

2. Experimental setup

The sample used was the Rb₀.₉₄Mn[Fe(CN)₆]₀.₉₈·₀.₂H₂O powder dispersed in liquid paraffine. The transition temperature of magnetic susceptibility at lower and higher sides end of the hysteresis loop were 230 K (=T₁/₂: HT → LT phase) and 300 K (=T₁/₂: LT → HT phase), respectively. The IR spectra were measured using a FT-IR spectrometry system. The Raman measurements were carried out using the second harmonics (395 nm) of 790 nm light from a mode-locked Ti:sapphire laser (repetition rate: 82 MHz, pulse width: ~1.5 ps, energy resolution: ~15 cm⁻¹) or 488.0 nm light from a CW Ar-ion laser. The former was in resonance with the ligand-to-metal CT (LMCT) band from CN⁻ to Fe⁺⁺⁺, and the latter was not in resonance [14, 15]. The excitation density was ~10⁻³.
W/cm² and the spot size was ~100 μm for each excitation source. The Raman spectra were taken with a triple grating monochromator equipped with a liquid-nitrogen-cooled CCD. The spectral resolutions measured under 395 and 488.0 nm excitation were ~15 and 14 cm⁻¹, respectively.

3. Results and discussion

The measured IR spectrum is shown in the inset of Fig. 1, where peaks are observed at 2072 and 2152 cm⁻¹. In the previous report on the IR absorption spectra by Tokoro et al., the CN stretching modes due to Fe²⁺-CN-Mn²⁺ and Fe³⁺-CN-Mn²⁺ in the HT phase have been observed at 2073 and 2153 cm⁻¹, respectively, which are in good agreement with the present measurement [16]. These peaks have been observed also in Raman spectra under 532 nm excitation [17]. The Fe²⁺-CN-Mn²⁺ peak was rather weak and shifted to 2080 cm⁻¹, while the Fe³⁺-CN-Mn²⁺ peak split into 2156 and 2165 cm⁻¹ [17]. The Raman spectrum measured under 488.0 nm excitation is shown in Fig. 1 (solid line), where we can see a pronounced peak at 2159 cm⁻¹, which is unambiguously assigned to Fe³⁺-CN-Mn²⁺ by comparing it with the IR spectrum. The splitting of the Fe³⁺-CN-Mn²⁺ peak is not observed in our measurement, because the energy resolution is insufficient. However, the frequency is close to the average of the separate two peaks (2160.5 cm⁻¹) and the split component is seen as a shoulder at high-energy side.

The peak around 2072 cm⁻¹ (inset of Fig. 1) corresponding to Fe²⁺-CN-Mn²⁺ is scarcely seen in our Raman spectrum. This may be ascribed to a small Raman cross-section and the composition of our sample close to stoichiometry. Comparing IR and
Raman spectra, we can see that the CN stretching modes observed in Raman spectra tend to appear at higher frequencies.

The dotted curve in Fig. 1 shows the Raman spectrum taken under 488 nm excitation after irradiated for 7.5 min by 395 nm light, which is in resonance with the LMCT band. The spectral shape was changed dramatically, i.e., the peak due to Fe$^{III}$-CN-Mn$^{II}$ pair valence state corresponding to the HT phase decreases and three new peaks appear at 2083, 2126, and 2238 cm$^{-1}$. The Fe$^{II}$-CN-Mn$^{II}$ peak has been observed at 2073 cm$^{-1}$ in the IR spectrum and around 2080 cm$^{-1}$ in the 532 nm excited Raman spectra [16, 17]. Therefore, the peak at 2083 cm$^{-1}$ observed in our measurement is assigned to Fe$^{II}$-CN-Mn$^{II}$.

For detailed investigation of Raman spectral change by 395 nm light irradiation, we measured Raman spectra under 395 nm excitation. Figure 2 shows the irradiation time dependence of Raman spectrum under 395 nm excitation. Immediately after irradiation (at 1.5 min), a strong peak at 2159 cm$^{-1}$ due to Fe$^{III}$-CN-Mn$^{II}$ dominates the spectrum. On the other hand, when the irradiation time elapses, the intensity of this peak decreases and simultaneously the intensities of the peaks at 2083 and 2126 cm$^{-1}$ increase. The former peak is assigned to Fe$^{II}$-CN-Mn$^{II}$, as already discussed in Fig. 1. Hence, this behavior indicates the decreasing of Fe$^{III}$ ions and the increasing of Fe$^{II}$ ions. Moreover, a very strong peak appears at 2238 cm$^{-1}$. The positions of the photoinduced Raman peaks are determined from the spectrum at 51 min as 2083, 2126, and 2238 cm$^{-1}$. All the intermediate Raman spectra can be expressed by superposing these four components, as can be seen from an example shown in Fig. 3. Here double Lorentzian fitting is used for the peak at 2238 cm$^{-1}$ because a shoulder structure is seen at the higher-energy side.
In the following we discuss the origin of the new peaks at 2126 and 2238 cm$^{-1}$. In the LT phase, a broad IR band due to Fe$^{II}$-CN-Mn$^{III}$ spreading from 2080 to 2140 cm$^{-1}$ (centered around 2110 cm$^{-1}$) has been observed [17]. As the frequency of the new Raman peak at 2126 cm$^{-1}$ is close to 2100 cm$^{-1}$, this peak is assigned to Fe$^{II}$-CN-Mn$^{II}$, although the frequency is slightly higher. The reason for this discrepancy is speculated as follows. First, as already discussed, Raman peaks appear at frequency slightly higher than those of IR peaks. Second, in the case of the reported IR spectra for LT phase, the Fe$^{II}$-CN-Mn$^{III}$ units reside in the LT phase domain. Thus, the lattice is considerably distorted due to the Jahn-Teller effect resulting in lowering of the CN vibration frequency. However, in the case of LT-like phase created by LMCT band excitation in HT phase, the Fe$^{II}$-CN-Mn$^{III}$ units are embedded in the framework of the HT phase lattice. Hence, the peaks due to CN vibration frequency are expected to be slightly higher because the lattice is not fully adjusted to Jahn-Teller distortion. In fact, the CN stretching frequency tends to shift gradually to low frequency during irradiation in our measurements. This is because increasing of the number of Fe$^{II}$-CN-Mn$^{III}$ enhances the lattice distortion and lower the frequency approaching to the value in LT phase. This mechanism will explain the high frequency shift of the Fe$^{II}$-CN-Mn$^{III}$ peak.

These experimental results indicate that the photoinduced CT from Mn$^{II}$ to Fe$^{III}$ takes place by LMCT band excitation, i.e., the electron transfer from Mn$^{II}$ to CN$^{-}$ occurs after the CN$^{-}$ to Fe$^{III}$ electron transfer, as shown in Fig. 4(left). When one electron transfers from Mn$^{II}$ to Fe$^{III}$ in the perfect HT phase lattice, two kinds of pair valence states, i.e. five Fe$^{II}$-CN-Mn$^{II}$ and five Fe$^{III}$-CN-Mn$^{III}$, are produced besides Fe$^{II}$-CN-Mn$^{III}$ as shown in Fig. 4 (right). Certainly, the Raman peak due to Fe$^{II}$-CN-Mn$^{II}$ appears after 395 nm
irradiation. Similarly, the Raman peak due to Fe\textsuperscript{III}-CN-Mn\textsuperscript{III} should appear after LMCT excitation. The typical frequency of the CN stretching mode for the valence combination of II-II and II-III ions falls between approximately 2000 and 2200 cm\textsuperscript{-1}. In addition, the peak due to the valence state with a larger valence number of Fe or Mn trend to appear at high frequency. Therefore, the new Raman peak at 2238 cm\textsuperscript{-1} is interpreted as that of the Fe\textsuperscript{III}-CN-Mn\textsuperscript{III}, although this peak has not been observed in IR spectroscopy.

When the CT from Mn\textsuperscript{II} to Fe\textsuperscript{III} takes place, two N-Mn\textsuperscript{III}-N bond distances increase and four bond distances decrease by Jahn-Teller distortion of Mn\textsuperscript{III} ion sites [18, 19]. Hence, the CN stretching frequency in the pair valence state containing the Mn\textsuperscript{III} ion splits into two. Thus, the double Lorentzian fitting used for the peak at 2238 cm\textsuperscript{-1} due to Fe\textsuperscript{III}-CN-Mn\textsuperscript{III}, as shown in Fig. 2, can be understood. Although, the peak due to Fe\textsuperscript{II}-CN-Mn\textsuperscript{III} is expected to split similarly, no splitting is found probably because the splitting width is smaller than the bandwidth. Consequently, the Raman spectra under 395 nm excitation can be interpreted in terms of four kinds of pair valence states expected from inter-metallic CT process.

It is interesting to note that the system is not converted to pure LT phase and that appreciable amount of irregular pair valence states (Fe\textsuperscript{II}-CN-Mn\textsuperscript{II} and Fe\textsuperscript{III}-CN-Mn\textsuperscript{III}) remain, even after complete disappearance of HT phase. This situation is contrasted with the production of the LT phase by cooling the sample; in this case almost all valence states are converted to Fe\textsuperscript{II}-CN-Mn\textsuperscript{III}. This difference is attributed to the localized nature of the CT process in photo-excitation. In the case of thermal process, CT and Jahn-Teller distortion will occur simultaneously over several unit cells, a domain of LT phase will be created and the irregular pair valence states will be expelled. However, as the
photoinduced CT process occurs at random on the individual metal sites and no cooperative effect is working at this excitation density, the irregular pair valence states are conserved. In the mixed valence metastable state, a Fe$^{\text{III}}$ and Mn$^{\text{II}}$ ions, not contribute to the CT transition, may be enclosed with the pure LT phase valence state.

**Conclusions**

The photoinduced CT from Fe$^{\text{III}}$-CN-Mn$^{\text{II}}$ to Fe$^{\text{II}}$-CN-Mn$^{\text{III}}$ by excitation at the LMCT band in the HT phase was observed in rubidium manganese hexacyanoferrate by Raman spectroscopy. The measured Raman spectra were interpreted in terms of four kinds of pair valence states, i.e. Fe$^{\text{III}}$-CN-Mn$^{\text{III}}$, Fe$^{\text{III}}$-CN-Mn$^{\text{II}}$, Fe$^{\text{II}}$-CN-Mn$^{\text{III}}$, and Fe$^{\text{II}}$-CN-Mn$^{\text{II}}$, expected to be created by the inter-metallic CT process from Mn$^{\text{II}}$ to Fe$^{\text{III}}$. After prolonged irradiation, the Fe$^{\text{III}}$-CN-Mn$^{\text{II}}$ pair valence state corresponding to the HT phase was completely depleted and the LT-like phase containing the Fe$^{\text{II}}$-CN-Mn$^{\text{III}}$ pair valence state corresponding to the pure-LT phase was locally created by the photoinduced CT process.

**Acknowledgments**

This work has been support by a Grant-in-Aid for Scientific Research (B) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

**References**

1. O. Sato, T. Iyoda, A. Fujishima, and K. Hashimoto, Science, 272 (1996) 704.
2. S. Ohkoshi, S. Yorozu, O. Sato, T. Iyoda, A. Fujishima, and K. Hashimoto, Appl. Phys. Lett., 70 (1997) 1040.
3. S. Ohkoshi, N. Machida, Z. J. Zhong, and K. Hashimoto, Synth. Met., 122 (2001) 523.
4. T. Yokoyama, K. Okamoto, T. Ohta, S. Ohkoshi, and K. Hashimoto, Phys. Rev. B, 65 (2002) 64438.
5. H. Tokoro, S. Ohkoshi, and K. Hashimoto, Appl. Phys. Lett., 82 (2003) 1245.
6. H. Tokoro, T. Matsuda, K. Hashimoto, and S. Ohkoshi, J. Appl. Phys., 97 (2005) 10M508.
7. H. Tokoro, K. Hashimoto, and S. Ohkoshi, J. Mag. Mag. Mater. 310 (2007) 1422.
8. S. Margadonna, K. Prassides, and A. N. Fitch, Angew. Chem. Int. Ed., 43 (2004) 6316.
9. H. Tokoro, S. Ohkoshi, T. Matsuda, and K. Hashimoto, Inorg. Chem., 43 (2004) 5231.
10. S. Ohkoshi, H. Tokoro, T. Matsuda, H. Takahashi, H. Irie, and K. Hashimoto, Angew. Chem. Int. Ed., 46 (2007) 3238.
11. T. Nuida, T. Matsuda, H. Tokoro, S. Sakurai, K. Hashimoto, and S. Ohkoshi, J. Am. Chem. Soc., 127 (2005) 11604.
12. L. Egan, K. Kamenev, D. Papanikolaou, Y. Takabayashi, and S. Margadonna, J. Am. Chem. Soc., 128 (2006) 6034.
13. H. Tokoro, T. Matsuda, T. Nuida, Y. Moritomo, K. Ohoyama, E. D. L. Dangui, K. Boukhedaden, and S. Ohkoshi, Chem. Mater., 20 (2008) 423.
14. P. N. Schatz, A. J. McCaffery, W. Su˜etaka, G. N. Henning, and A. B. Stephens, J. Chem. Phys., 45 (1966) 722.
15. S. Ohkoshi, T. Nuida, T. Matsuda, H. Tokoro, and K. Hashimoto, J. Mater. Chem., 15 (2005) 3291.

16. H. Tokoro, S. Miyashita, K. Hashimoto, and S. Ohkoshi, Phys. Rev. B, 73 (2006) 172415.

17. E. J. M. Vertelman, E. Maccallini, D. Gournis, P. Rudolf, T. Bakas, J. Luzon, R. Broer, A. Pugzlys, T. T. A. Lummen, P. H. M. van Loosdrecht, and P. J. van Koningsbruggen, Chem. Mater. 18 (2006) 1951.

18. S. Ohkoshi, H. Tokoro, M. Utsunomiya, M. Mizuno, M. Abe, and K. Hashimoto, J. Phys. Chem. B, 106 (2002) 2423.

19. Y. Moritomo, K. Kato, A. Kuriki, M. Takata, M. Sakata, H. Tokoro, S. Ohkoshi, and K. Hashimoto, J. Phys. Soc. Jpn., 71 (2002) 2078.
Figure captions

1. Raman spectra under 488 nm excitation at room temperature. Solid and dotted lines are the Raman spectra before and after 395 nm light irradiation, respectively. Inset: IR spectrum at room temperature.

2. Irradiation time dependence of Raman spectra under 395 nm excitation after irradiation for 1.5, 4.5, 7.5, 33, and 51 min at room temperature. The guidelines correspond, in order increasing of Raman shift, to the Fe$^{II}$-CN-Mn$^{II}$, Fe$^{II}$-CN-Mn$^{III}$, Fe$^{III}$-CN-Mn$^{II}$, and Fe$^{III}$-CN-Mn$^{III}$.

3. Raman spectrum under 395 nm excitation after irradiation for 7.5 min at room temperature. Solid and dotted lines are the experimental data and the Lorentzian curves included in the multi-Lorentzian fitting, respectively.

4. Illustration of the Fe-CN-Mn pair valence states before (left) and after (right) CT transition in HT phase. Large dark and light gray circles are Fe and Mn atms, respectively. Roman numerals inside circles are valence numbers. Small dark and light gray circles are C and N atms, respectively. In the right figure, the part enclosed by a dotted oval indicates the Fe$^{II}$-CN-Mn$^{III}$ pair valence state created by electron transfer. Five Fe$^{III}$-CN-Mn$^{III}$ and one Fe$^{II}$-CN-Mn$^{III}$ are produced. In this figure, the Mn$^{II}$ ion is surrounded by six Fe$^{III}$ ions. Similarly, the Fe$^{III}$ ion surrounded by six Mn$^{II}$ ions exists in HT phase. In this case, five Fe$^{II}$-CN-Mn$^{II}$ are produced.
R. Fukaya et al., Fig. 1
R. Fukaya et al., Fig. 2
R. Fukaya et al., Fig. 3
R. Fukaya et al., Fig. 4