XANES Analysis of Phthalocyanine Molecular Conductor

Kei Takahashi,† Takehis Konishi, and Takashi Fujikawa
Graduate School of Advanced Integration Science,
Chiba University, 1-33 Yayoi-cho, Inage, Chiba 263-8522, Japan

Noriaki Hanasaki
Department of Physics, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560-0043, Japan

Naomi Kawamura and Masaichiro Mizumaki
Japan Synchrotron Radiation Research Institute, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan

Masaki Matsuda
Department of Chemistry, Graduate School of Science and Technology,
Kumamoto University, Kurokami 2-39-1, Kumamoto 860-8555, Japan

Derrick Ethelbhart C. Yu, Toshio Naito, and Tamotsu Inabe
Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

Hiroyuki Tajima
Institute for Solid State Physics, University of Tokyo, Kashiwanoha, Kashiwa, Chiba 277-8581, Japan

(Received 28 December 2011; Accepted 14 March 2012; Published 14 April 2012)

The dicyano(phthalocyaninato)iron molecular conductor shows the Giant Magnetoresistance (GMR) effect. In order to investigate the effect of the molecular structure and charge on the X-ray absorption in the Fe(Pc)(CN)_2 molecule, we measured the Fe K-edge X-ray Absorption Near Edge Structure (XANES) spectra in the TPP[Fe(Pc)L_2](L=CN, Br, and Cl), DMDP[Fe(Pc)(CN)_2], and [(n-C_7H_15)_4N][Fe(Pc)(CN)_2]. In 7134-7152 eV, we found the clear difference in the XANES spectra between these Fe(Pc)(CN)_2 compounds. Our multiple scattering calculations indicate that the local structure of the iron and CN ligand, which tends to be changed by the nominal charge in the Pc ring, causes the spectral change.

Keywords: X-ray absorption spectroscopy; Electrical transport; NEXAFS

I. INTRODUCTION

The one-dimensional molecular conductor TPP[Fe(Pc)L_2](L=CN, Br, and Cl) show the Giant Magnetoresistance (GMR) at low temperature owing the strong intramolecular interaction between the local spin moment of Fe and π-electron of Pc ring [1–4]. Here, Pc and TPP denote phthalocyanine and tetr phenylphosphonium, respectively. Figure 1 shows the crystal structure of TPP[Fe(Pc)(CN)_2]. The crystal system is tetragonal and the space group is P4_2/n: a = b = 21.722, c = 7.448Å[3]. For the realization of the electron conduction, the HOMO of the Fe(Pc)(CN)_2 is partially oxidized, and the nominal charge of Pc ring is −1.5. The TPP[Fe(Pc)(CN)_2] undergoes the insulating state at low temperature, where the GMR effect is observed. For the understanding of this GMR effect, it is essential to clarify the ground state. The theoretical study predicts that the nearest-neighbor Coulomb interaction drives the charge-ordered state, in which there is the difference in the Pc molecular charge between the sites [5]. Thus, in order to detect the charge order by the X-ray diffraction, it is necessary to investigate the influence of the molecular structure and charge on the X-ray absorption spectra. The DMDP[Fe(Pc)(CN)_2] (DMDP=dimethyldiphenylphosphonium) and [(n-C_7H_15)_4N][Fe(Pc)(CN)_2] have the same Fe(Pc)(CN)_2 molecule as the TPP compound. In these two reference compounds, the Fe(Pc)(CN)_2 molecules are not oxidized, and the nominal charge of the Pc ring is −2. The comparison with other compounds helps clarify the influence of the molecular structure and charge. We measured X-ray Absorption Near Edge Structure (XANES) spectra and performed multiple scattering calculations.
The XANES theory used in this report is based on the short-range-order full multiple scattering theory proposed by Fujikawa et al. [6]. Later this theory was modified by a partitioning technique in order to reduce the computation time [7–10]. Here, we summarize the theoretical methods. The X-ray absorption intensity $\sigma$ from the core orbital $\phi_c(r)$ is expressed as

$$\sigma = -\frac{8}{3} \text{Im} \left\{ \sum_{m_c, l, l'} \left\langle l' | (\delta_l^A + \delta_l^B) | l \right\rangle \rho_c(l) \rho_c(l') G(L_l 10|LL') G(L_l 10|L') \times (t^{-1})^{A'AA'} |1 - X|^{-1}|LL' \right\},$$

where $G(LL'|L'')$ is Gaunt's integral and $\rho_c(l)$ is radial dipole integral between the radial part of $\phi_c(r)$ and the $l$-th partial wave of photoelectrons $R_l(r)$ at site A. The phase shift of the $l$-th partial wave at site A is represented by $\delta_l^A$. We introduce the matrix $X$ specified with site index $\alpha$ and angular momentum $L$ and so on; it is defined as

$$X^{\alpha \beta}_{LL'} = t_\alpha^l G_{LL'}(R_\alpha - R_\beta)(1 - \delta_{a\beta}),$$

where $t_\alpha^l$ represents the T-matrix at site $\alpha$ and $G_{LL'}$ represents the Green's function in an angular momentum representation and reflects the geometrical structure. The inverse matrix $(1 - X)^{-1}$ includes an infinite order of the full multiple scattering inside the cluster we are considering. The phase shift in $t_\alpha^l = -|\text{exp}(2\pi i \delta(l))| - 1|/2ik$ is one of the most important features and reflects the electronic structure of the surrounding atoms.

II. THEORY

Figure 2 shows the experimental result of Fe K-edge XANES spectra of TPP[Fe(Pc)(CN)$_2$]$_2$, DMDP[Fe(Pc)(CN)$_2$]$_2$, and [(n-C$_7$H$_{15}$)$_4$N][Fe(Pc)(CN)$_2$]. There is the difference in the spectra between three Fe(Pc)(CN)$_2$ compounds only in the energy region of 7134-7152 eV. The absorption in the TPP compounds, in which the nominal charge of Pc ring is $-1.5$, is higher than that in the DMDP and [(n-C$_7$H$_{15}$)$_4$N][Fe(Pc)(CN)$_2$] compounds, in which the charge is $-2$. To investigate the origin of the spectral difference, we carried out the multiple scattering calculation. The calculation model were constructed by using the crystal structure data measured by Matsuda et al. [3]. The electronic structure was calculated by Gaussian03 and Gaussian09(B3LYP/LanL2DZ) [11, 12]. In these three compounds, the molecular electronic structures such as the HOMO hardly differ from each other. The calculated XANES spectra are displayed in Fig. 3. The overall feature of the XANES spectra and three peaks above the Fe K-edge are reproduced by the double-crystal monochromator, and the transmitted beam by use of the ion chamber. To investigate the ligand effect, the Fe K-edge X-ray absorption measurements for TPP[Fe(Pc)Br$_2$]$_2$ and TPP[Fe(Pc)(Cl)$_2$]$_2$ were also performed at BL-39XU in SPring-8 with the transmission method. The transmitted beam was measured by SSD detector.

III. EXPERIMENTAL

The Fe K-edge X-ray absorption spectra in TPP[Fe(Pc)(CN)$_2$]$_2$, DMDP[Fe(Pc)(CN)$_2$]$_2$, and [(n-C$_7$H$_{15}$)$_4$N][Fe(Pc)(CN)$_2$] were measured in the energy range from 7.1 to 7.2 keV at BL-14B1 in SPring-8. The sample disks are prepared by pressing the mixture of the BN and the sample powder. The X-ray absorption coefficient of the samples is obtained by measuring the intensity of the incident X-ray beam, that is passed through the double-crystal monochromator, and the transmitted beam by use of the ion chamber.
TABLE I. Structure of the Fe atom and CN ligand in Fe(Pc)(CN)₂.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Bond length (Fe–C) (Å)</th>
<th>θ (deg.)</th>
<th>ϕ (deg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPP[Fe(Pc)(CN)₂]₂</td>
<td>1.981</td>
<td>99.07</td>
<td>174.94</td>
</tr>
<tr>
<td>DMDP[Fe(Pc)(CN)₂]</td>
<td>1.99</td>
<td>96.41</td>
<td>175.25</td>
</tr>
<tr>
<td>(n-C₇H₁₅)₄N[Fe(Pc)(CN)₂]</td>
<td>1.990</td>
<td>91.56</td>
<td>175.36</td>
</tr>
</tbody>
</table>

FIG. 3. Calculated Fe K-edge XANES spectra in the energy range between $E - E₀ = (a) 0$-100 eV and (b) 25-65 eV for TPP[Fe(Pc)(CN)₂]₂ (red), DMDP[Fe(Pc)(CN)₂] (blue), and [(n-C₇H₁₅)₄N][Fe(Pc)(CN)₂] (green). $E₀$ means the energy at the absorption edge.

FIG. 4. Molecular structures of (a) TPP[Fe(Pc)(CN)₂]₂, DMDP[Fe(Pc)(CN)₂], and (c) [(n-C₇H₁₅)₄N][Fe(Pc)(CN)₂].

In Table I, θ and ϕ are defined as $\theta = \angle \text{Fe–Pc–C}$ and $\phi = \angle \text{Fe–C–N}$, respectively. In [(n-C₇H₁₅)₄N][Fe(Pc)(CN)₂], the averaged Fe–C bond length is shown.

Owing to contact between the CN ligand and other molecules in the crystal, the CN ligand seems to be tilted from the direction perpendicular to the plane of the Pc ring, which θ and ϕ are 90 and 180 (deg.), respectively. There is small difference in the bond length of Fe–C between the Pc compounds, as well. The difference of the XANES spectra in 7314-7152 eV is ascribable to the angle of the CN ligand, the Fe–C bond length and Pc ring distortion. According to the structural study in other Fe(Pc)(CN)₂ compounds, the Fe–C bond length seems to change with the nominal charge of the Pc molecules. The spectra in this energy range can be considered as an indicator of the Pc molecular charge in Fe(Pc)(CN)₂. The detailed correlation between the XANES spectra and molecular charge will be left for the future study.

In order to investigate the axial ligand effect on the XANES spectra, we changed the CN ligand into Br and Cl. Through the GMR effect is also observed in the Br and Cl compounds, the amplitude of the GMR effect in these two compounds is smaller than that in the CN compound [4]. Figures 5 (a) and (b) display the experimental and calculated result in TPP[Fe(Pc)L₂]₂ ($L$=CN, Br, and Cl), respectively. The overall feature of our multiple scattering calculation has the similar incident-energy dependence to the experimental results, especially near edge region. The energy in the absorption edge and preedge, that contains the contribution of the 3d orbital, in $L$=Br and Cl is lower than that in $L$=CN, suggesting that the energy levels of next HOMOs, in which the local moments interacting with the conduction electron exists, in $L$=Br.
FIG. 5. (a) Experimental Fe K-edge XANES spectra with changing ligand at TPP[Fe(Pc)L₂]₂ molecules (L=CN, Br, Cl). (b) Calculated Fe K-edge XANES spectra of different axial ligands.

and Cl is lower than that in L=CN. As a possible origin of this energy shift, we consider the difference in the coordination power or the electron affinity between the ligands.

V. CONCLUSION

We reported the XANES spectra in the (phthalocyaninate)iron compounds. The XANES spectra show the difference in the region 7134-7152 eV. To analyze that difference, we performed the multiple scattering calculations, and revealed that the spectral difference is ascribable to the difference of the Fe(Pc)(CN)₂ molecular structure, that changes with the Pc molecular charge and stacking. We also investigated the ligand effect. The absorption edge energy is shifted by changing the CN ligand into Br and Cl, which is reproduced by multiple scattering calculations.

ACKNOWLEDGMENTS

This work was performed as an intercooperation of Global-COE program at Chiba University (Advanced School of Organic Electronics:G03 MEXT). I would like to thank T. Kaneko, M. H. Shang, Y. Ohori, M. Nagaosa, K. Hwang, and A. Koide for fruitful discussions and suggestions. The synchrotron radiation experiments were performed at the BL-30XU and BL-14B1 of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2008A1447 and 2010A3614).