

## Temperature-dependent core-level x-ray photoemission spectroscopy of the organic conductors $(\text{MeCl-DCNQI})_2\text{Cu}$ , $(\text{MeBr-DCNQI})_2\text{Cu}$ , and $(\text{DI-DCNQI})_2\text{Cu}$

O. Akaki, A. Chainani, and T. Takahashi

*Department of Physics, Tohoku University, Sendai 980-77, Japan*

Y. Kashimura and R. Kato

*Institute for Solid State Physics, The University of Tokyo, Tokyo 106, Japan*

(Received 17 July 1997; revised manuscript received 12 January 1998)

We study the quasi-one-dimensional (1D) organic conductors  $(\text{MeCl-DCNQI})_2\text{Cu}$ ,  $(\text{MeBr-DCNQI})_2\text{Cu}$ , and  $(\text{DI-DCNQI})_2\text{Cu}$  using x-ray photoemission spectroscopy. We observe negligible change of the Cu  $2p$  core-level spectra of  $(\text{DI-DCNQI})_2\text{Cu}$  and  $(\text{MeBr-DCNQI})_2\text{Cu}$  as a function of temperature, in the metallic phase. In contrast, Cu  $2p$  spectra of  $(\text{MeCl-DCNQI})_2\text{Cu}$ , which has a charge-density-wave/metal-insulator transition at 210 K exhibits clear changes across the transition. The spectral shape change occurring across the transition indicates charge transfer from Cu  $3d$  states to the 1-D DCNQI  $p\pi$  conduction band. A line-shape analysis shows that the average valence of Cu ions follows a systematic trend related to the tetrahedral angle  $\alpha$  between N-Cu-N, i.e., a more distorted tetrahedral angle corresponds to lesser charge transfer from the Cu ions to the  $p\pi$  band. The results also provide direct evidence for coupling of the electronic states involved in charge-ordering with the charge-density-wave formation. [S0163-1829(98)09719-7]

In charge-transfer compounds, electrons transferred from the donor to acceptor complex determine the electronic properties of the system. Recently, the quasi-one-dimensional (1D) organic salts containing  $R_1, R_2$ -DCNQI ( $R_1, R_2 = \text{CH}_3, \text{Cl}, \text{Br}, \text{I}$ , etc.; DCNQI =  $N, N'$ -dicyanoquinonediimine) molecules as an acceptor and metal ions (Li, Cu, Ag, etc.) as a donor have been studied extensively because of their interesting properties.<sup>1-7</sup> In the Cu-based systems, electrons are transferred from Cu atoms tetrahedrally coordinated to N-cyano groups of DCNQI molecules constituting the quasi-1D  $2p\pi$  lowest unoccupied molecular orbital (LUMO) band formed by stacking of DCNQI molecules along the  $c$  axis. Within this series of compounds,  $(\text{DMe-DCNQI})_2\text{Cu}$ , (with  $R_1 = R_2 = \text{methyl group, CH}_3$ ) remains metallic down to 50 mK. Such metallic compounds that do not show an electronic transition are classified as belonging to "group I." When pressure is applied on these compounds,<sup>2,3</sup> a halogen ion is substituted for a methyl group,<sup>4,5</sup> or deuterium is substituted for hydrogen,<sup>6,7</sup> they exhibit charge-density-wave/metal-insulator (CDW/ $M-I$ ) transitions. The transition is understood to be a mixed Peierls transition and Mott transition occurring on decreasing temperature,<sup>8</sup> with a three-fold CDW on the quasi-1D chain of DCNQI molecules.<sup>9</sup> Furthermore, the ratio of amount of  $\text{Cu}^+:\text{Cu}^{2+}$  is estimated to be 2:1, and the charge on Cu ions also orders along the quasi-1D direction<sup>10-12</sup> with the same period as the CDW, i.e.,  $(\cdots\text{Cu}^+-\text{Cu}^+-\text{Cu}^{2+}-\text{Cu}^+-\cdots)$ . This is also consistent with magnetic susceptibility studies that follow a Curie-Weiss law with a Curie constant corresponding to  $\frac{1}{3}$  mol of Cu atoms.<sup>10,11</sup> These systems belong to "group II." Compounds returning to a metallic phase (reentrant metal) below the  $M-I$  transition on further decreasing temperature<sup>13,14</sup> are classified as belonging to "group III." Thus, we can control transition temperatures by appropriately choosing  $R_1$  and  $R_2$  in these compounds, corresponding to "chemical pressure" by substitution, or by physical pressure.

In this work, we study the Cu  $2p$  core levels of  $(\text{DI-DCNQI})_2\text{Cu}$ ,  $(\text{MeCl-DCNQI})_2\text{Cu}$ , and  $(\text{MeBr-DCNQI})_2\text{Cu}$  using x-ray photoemission spectroscopy (XPS) as a function of temperature.  $(\text{DI-DCNQI})_2\text{Cu}$  belongs to group I and possesses the most stable metallic state among DCNQI-Cu salts. This is because of the experimental fact that the critical pressure  $P_c$  required for the  $M-I$  transition is the largest ( $\sim 15$  kbar) for  $(\text{DI-DCNQI})_2\text{Cu}$  among group-I compounds.<sup>3</sup> Also, anisotropy of electrical resistivity is about 3:1 (parallel:perpendicular to the 1D axis),<sup>3</sup> differing from 10:1 for  $(\text{DMe-DCNQI})_2\text{Cu}$ . In contrast,  $(\text{MeBr-DCNQI})_2\text{Cu}$  and  $(\text{MeCl-DCNQI})_2\text{Cu}$  have a CDW/ $M-I$  transition temperature,  $T_c = 160$  and 210 K, respectively,<sup>7</sup> and thus belong to group II. We observe temperature-dependent changes across the CDW/ $M-I$  transition in the Cu  $2p$  core-level spectra indicative of the charge transfer across the transition. From a line-shape analysis of the core-level spectra, we estimate the average valence of Cu ions. A systematic relation of the tetrahedral N-Cu-N angle to the transition temperature and the average Cu valence is obtained.

We synthesized polycrystalline samples in a glove box filled with nitrogen gas and directly connected to the photoemission spectrometer. As-prepared samples were washed in pure  $\text{CH}_3\text{CN}$ , mounted on a sample holder within the glove box, and transferred to the analysis chamber. The powder x-ray diffraction pattern of the sample synthesized as above is the same as that of a powdered single crystal and has been reported for the case of  $(\text{DMe-DCNQI})_2\text{Cu}$  earlier.<sup>15</sup> The XPS spectra were measured in a VG ESCALAB Mk II in the Institute for Molecular Science using an Al  $K\alpha$  ( $h\nu = 1486.6$  eV) source. The vacuum in the analysis chamber was  $\sim 8 \times 10^{-10}$  Torr, and the total energy resolution was 1.1 eV. The sample was cooled using flowing liquid  $\text{N}_2$ , down to 170 K, and the temperature was measured using a

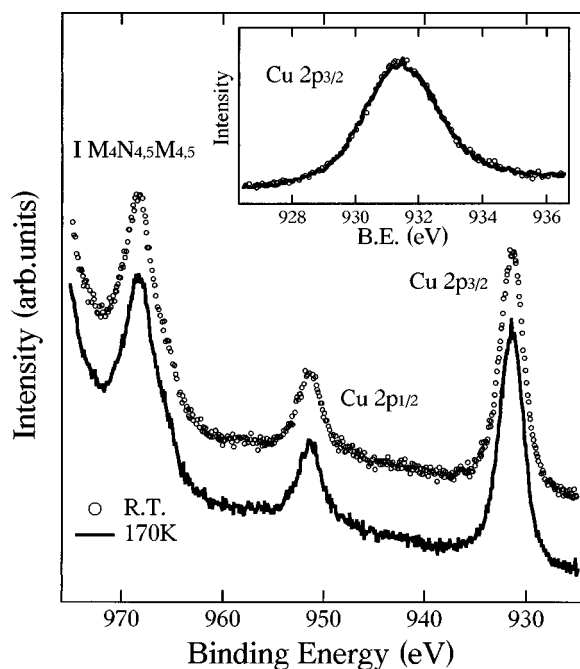


FIG. 1. Cu  $2p$  core-level spectra of  $(\text{DI-DCNQI})_2\text{Cu}$  at 300 K (circle) and at 170 K (solid line) obtained using Al  $K\alpha$  excitation. In the inset, Cu  $2p_{3/2}$  region is plotted on an expanded scale to show negligible change as a function of temperature.

calibrated thermocouple. Since the existence of the O  $1s$  signal is a good measure of the sample surface quality as is already known,<sup>16</sup> we monitored the sample quality by checking the same, and it was found to be negligible in every case.

Figure 1 shows the XPS spectra of the Cu  $2p$  core levels in  $(\text{DI-DCNQI})_2\text{Cu}$  measured at 300 and 170 K. Main peaks corresponding to the spin-orbit split core levels of Cu  $2p_{3/2}$  and Cu  $2p_{1/2}$  occur at the binding energy of about 931 and 951 eV, respectively, and the  $I M_4 N_{4.5} N_{4.5}$  Auger signals occur at a binding energy of about 968 eV. The Cu  $2p$  core-level spectral shapes are similar to that of  $(\text{DMe-DCNQI})_2\text{Cu}$  and  $(\text{MeBr-DCNQI})_2\text{Cu}$  reported in earlier studies,<sup>16–18</sup> except for the presence of the  $I M_4 N_{4.5} N_{4.5}$  Auger peak. It is known that the Cu  $2p_{3/2}$  main peak consists of Cu  $2p_{3/2}3d^{10}$  ( $\text{Cu}^+$ ) and Cu  $2p_{3/2}3d^{10}\bar{L}$  ( $\text{Cu}^{2+}$ ) final states, in which  $\bar{L}$  represents a ligand hole, and the satellite peak is made of Cu  $2p_{3/2}3d^9$  ( $\text{Cu}^{2+}$ ) final state.<sup>19,20</sup> In order to estimate the valence of Cu ions in  $(\text{DI-DCNQI})_2\text{Cu}$ , we do a line-shape analysis of the spectrum at 300 K and the results are shown in Fig. 2. The spectra are decomposed into a  $\text{Cu}^+$  peak,  $\text{Cu}^{2+}$  main peak, and the  $\text{Cu}^{2+}$  satellite peak for the spin-orbit split core levels. Each peak is a convolution of a Lorentzian due to lifetime broadening and a Gaussian due to the instrumental broadening. Following previous studies,<sup>16,18</sup> an additional plasmon loss satellite at 21.4 eV higher binding energy has been included, but is not shown here for clarity. The results indicate that the intensity ratio of  $\text{Cu}^+ : \text{Cu}^{2+} = 2 : 0.56$ , and the average valence of Cu ions is +1.22, i.e., about +3.66/3. This reduced average valence of Cu ions implies a much smaller charge transfer of electrons from Cu  $3d$  states to the  $2p\pi$  band of DCNQI molecules compared to all other DCNQI-Cu systems. Comparing the spectrum at 300 K with that obtained at 170 K, we observe negligible difference in

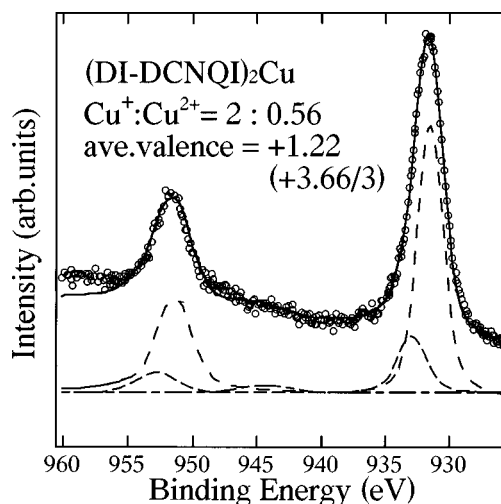


FIG. 2. Results of line-shape analysis of Cu  $2p$  core-level spectrum of  $(\text{DI-DCNQI})_2\text{Cu}$ . The spectrum (circle) is composed of a  $\text{Cu}^+$  component (dotted line) and two  $\text{Cu}^{2+}$  components for the main peak (dashed line) and satellite peak (dashed-dotted line).

the spectra as shown in the inset of Fig. 1, where the Cu  $2p_{3/2}$  region is plotted on an expanded scale. In  $(\text{DI-DCNQI})_2\text{Cu}$ , we thus conclude that negligible charge transfer occurs on decreasing temperature. This is in contrast to results on  $(\text{MeCl-DCNQI})_2\text{Cu}$  for which we observe clear spectral changes across the  $M-I$  transition at 210 K.

Figure 3 shows the XPS spectra of Cu  $2p$  core level of  $(\text{MeCl-DCNQI})_2\text{Cu}$  at 300 and 170 K, which is above and below the transition temperature of  $T_c = 210$  K, respectively. The spectrum obtained at 300 K is also superimposed on that of the 170 K spectrum so as to make it easy to observe the temperature-dependent spectral changes. We observe that at 170 K, the peak widths become broader only on the high binding-energy side and the intensity seems weaker for both Cu  $2p_{3/2}$  and Cu  $2p_{1/2}$  features. These changes are reversible and hence intrinsic, because a temperature cycling above the transition at 210 K resulted in reverting the low-temperature

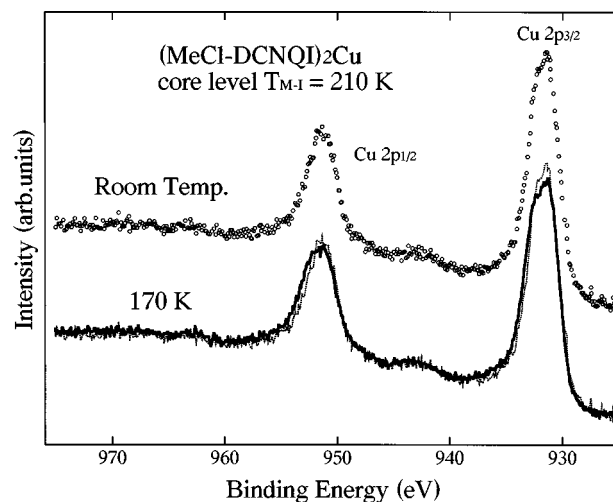


FIG. 3. Cu  $2p$  core-level spectra of  $(\text{MeCl-DCNQI})_2\text{Cu}$  at 300 K (circle) and at 170 K (dotted line) obtained using Al  $K\alpha$  excitation. The 300 K spectrum is superimposed on the 170 K spectrum as a solid line to show temperature-dependent spectral changes.

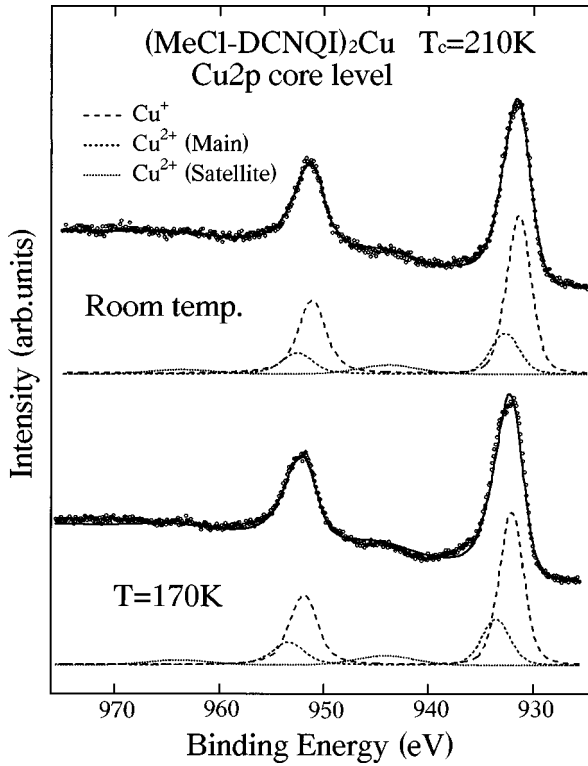


FIG. 4. Results of line-shape analysis of Cu  $2p$  core-level spectrum of (DI-DCNQI) $_2$ Cu at 300 and 170 K.

spectrum to the room-temperature spectrum. A line-shape analysis of Cu  $2p$  spectra as discussed above clarifies the changes across the transition temperature on a quantitative basis. Figure 4 show the fitting curves at 300 and 170 K, respectively. The line-shape analysis results show that the ratio of Cu ions is  $\text{Cu}^+ : \text{Cu}^{2+} = 2:0.9$  at 300 K and  $\text{Cu}^+ : \text{Cu}^{2+} = 2:1.0$  at 170 K, respectively, i.e., the average valence are  $+3.9/3$  and  $+4.0/3$ . It is to be noted that the fit for the low-temperature spectrum has slight discrepancies compared to the metallic-phase spectrum and we could not improve on the fit. The values of the average valence are reasonable, because the metallic phase at 300 K indicates a smaller valency than  $+4/3$ , consistent with an earlier study of (DMe-DCNQI) $_2$ Cu and (MeBr-DCNQI) $_2$ Cu.<sup>16</sup> Also, for the insulating phase at 170 K, a valence of  $+4/3$  is expected from an x-ray diffraction study,<sup>21</sup> which shows the existence of threefold superstructure along the  $c$  axis, and from the magnetic susceptibility<sup>11</sup> that follows the Curie-Weiss law with a Curie constant corresponding to  $1/3$  mol of  $\text{Cu}^{2+}$ .

In order to confirm that charge transfer occurs only across the transition, we have also studied the Cu  $2p$  XPS spectra of (MeBr-DCNQI) $_2$ Cu at 170 and 300 K. We do not observe any change in the spectra between 300 and 170 K, which is still above the transition temperature,  $T_c = 160$  K. The above results suggest that the  $\text{Cu}^+$  component in the spectrum at 300 K decreases, and simultaneously the  $\text{Cu}^{2+}$  component increases, only below the transition temperature. Thus, we infer that charge transfer from Cu ions to the  $p\pi$  conduction band made of DCNQI molecular chain occurs across the  $M-I$  transition. This charge transfer has been expected<sup>7,22,23</sup> within the following picture for the electronic states of DCNQI-Cu salts: in the crystal field of tetrahedrally coordi-

TABLE I. Transition temperature ( $T_{M-I}$ ), average valence of Cu ions, and angle between N-Cu-N ( $\alpha$ ) in four compounds with different  $R_1$  and  $R_2$ .

Compound	$T_{M-I}$ (K)	Average valence	$\alpha$ ( $^\circ$ )
(MeCl-DCNQI) $_2$ Cu	210	$+1.31 (+3.93/3)$	$126.2^a$
(MeBr-DCNQI) $_2$ Cu	160	$+1.32 (+3.95/3)^b$	$125.3^a$
(DMe-DCNQI) $_2$ Cu	Metallic	$+1.28 (+3.83/3)^b$	$124.5^a$
(DI-DCNQI) $_2$ Cu	Metallic	$+1.22 (+3.66/3)$	$122.3^c$

<sup>a</sup>From Ref. 22.

<sup>b</sup>From Ref. 16.

<sup>c</sup>From Ref. 3.

nated DCNQI molecules ( $T_d$  symmetry), the Cu  $3d$  electronic state is split into triply degenerate  $t_{2g}$  ( $d_{xy}$ ,  $d_{yz}$ , and  $d_{zx}$ ) and doubly degenerate  $e_g$  ( $d_z^2$  and  $d_{x^2-y^2}$ ). A distortion of the tetrahedron results in the  $t_{2g}$  state being further split with the  $d_{xy}$  state higher in energy level and the  $d_{yz}$  and  $d_{zx}$  states lower in energy. The degree of distortion is represented by the bond angle N-Cu-N ( $\alpha$ ). It has been reported that  $\alpha$  increases very slightly on decreasing temperature, and jumps at the transition temperature.<sup>7,22,23</sup> Owing to increasing  $\alpha$ , i.e., raising the  $d_{xy}$  state, the charge transfer from Cu ions to the  $p\pi$  band of DCNQI molecules increases on lowering the temperature. Therefore, the occupied  $d_{xy}$  state straddling the Fermi level interacts with the LUMO, forming mixed valent Cu ions. It is considered that such a charge transfer leads to the change of the XPS spectra of Cu  $2p$  core levels as in Fig. 3.

To corroborate this hypothesis, we list in Table I the average valence of four (DCNQI) $_2$ Cu salts to understand the systematics of charge transfer in these compounds. The average valence of (DI-DCNQI) $_2$ Cu is much smaller than the other compounds. It suggests that it is more difficult to have a  $M-I$  transition in a salt having the average valence farthest away from  $+4/3$ . Furthermore, the data of the tetrahedral angle  $\alpha$  between N-Cu-N at room temperature indicate a direct relation of the average valence with the angle  $\alpha$ , i.e., the average valence differs more from the value  $4/3$  for a more distorted tetrahedron.

A recent first-principles theoretical study<sup>24</sup> of the band structures of DCNQI systems supports our results. The  $p\pi-d$  hybridization in the DI salt is reduced in comparison with that in the DMe salt, since the energy difference between the bottom of LUMO and the top of  $d_{xy}$  for DI salt is larger than that for DMe salt. These changes lead to a decrease of charge transfer from the Cu  $d_{xy}$  orbital to the LUMO band, i.e., a decrease of the average valence of Cu atoms.

If the change of angle  $\alpha$  corresponds directly to the charge transfer of Cu  $3d$  electrons, it may seem contradictory that there is no temperature dependence of the XPS spectra in the metallic phase. This is because  $\alpha$  has a small temperature dependence in the metallic phase, and then the average valence should have temperature dependence. We consider the following two possibilities: Since it is known that the change in  $\alpha$  as a function of temperature in the metallic state is much smaller than the sudden change at the transition temperature,<sup>22,23</sup> it is possible that the instrument resolution is not enough to see the spectral changes, though there is a

small charge transfer due to temperature in the metallic phase. The other possibility is that, not only  $\alpha$ , but other parameters, affect the charge transfer. Although Table I shows that the value of  $\alpha$  is related to the amount of charge transfer, behavior of other parameters such as the electron-phonon coupling, may be different for changes in temperature compared to changes due to pressure. Then charge transfer may not have temperature dependence in the metallic state, i.e., there is actually no change in the core-level spectra of (DI-DCNQI)<sub>2</sub>Cu. It is not yet clear what is the real reason for negligible changes of the XPS spectra in the metallic phase and this needs further study.

In conclusion, x-ray photoemission spectroscopy of the quasi-one-dimensional organic conductors (DI-DCNQI)<sub>2</sub>Cu and (MeBr-DCNQI)<sub>2</sub>Cu shows negligible change of the Cu 2*p* core-level spectra as a function of temperature in the

metallic phase. In contrast, the Cu 2*p* spectra of (MeCl-DCNQI)<sub>2</sub>Cu, which has a CDW/*M-I* transition at 210 K, exhibits clear changes across the transition. The spectral shape change occurring across the transition indicates charge transfer from Cu 3*d* states to the 1D DCNQI *pπ* conduction band across the transition. A line-shape analysis shows a systematic dependence of the average valence of Cu ions to the tetrahedral N-Cu-N bond angle  $\alpha$ . The results provide direct evidence for a coupling of the electronic states involved in charge ordering with the CDW formation.

This work was supported by a Grant-in-Aid for Scientific Research on the priority area, Novel Electronic States in Molecular Conductors, from the Ministry of Education, Science and Culture of Japan.

- 
- <sup>1</sup>A. Aumüller *et al.*, *Angew. Chem. Int. Ed. Engl.* **25**, 740 (1986).  
<sup>2</sup>T. Mori *et al.*, *J. Phys. Soc. Jpn.* **56**, 3429 (1987).  
<sup>3</sup>Y. Kashimura *et al.*, *Solid State Commun.* **93**, 675 (1995).  
<sup>4</sup>T. Mori *et al.*, *Phys. Rev. B* **38**, 5913 (1988).  
<sup>5</sup>H. Kobayashi *et al.*, *Solid State Commun.* **65**, 1351 (1988).  
<sup>6</sup>S. Aonuma *et al.*, *Chem. Lett.* **1993**, 513.  
<sup>7</sup>R. Kato, S. Aonuma, and H. Sawa, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **284**, 183 (1996).  
<sup>8</sup>H. Fukuyama, *Physica B* **199&200**, 656 (1994).  
<sup>9</sup>A. Kobayashi *et al.* *Solid State Commun.* **64**, 45 (1987).  
<sup>10</sup>H. Kobayashi *et al.*, *Phys. Rev. B* **47**, 3500 (1993).  
<sup>11</sup>M. Tamura *et al.*, *J. Phys. Soc. Jpn.* **62**, 1470 (1993).  
<sup>12</sup>H.-P. Werner *et al.*, *Solid State Commun.* **65**, 809 (1988).  
<sup>13</sup>M. Tamura *et al.*, *J. Phys. Soc. Jpn.* **63**, 429 (1994).  
<sup>14</sup>H. Kobayashi *et al.*, *Solid State Commun.* **72**, 1 (1989).  
<sup>15</sup>A. Tanaka *et al.*, *Solid State Commun.* **93**, 1 (1995).  
<sup>16</sup>A. Tanaka *et al.*, *Phys. Rev. B* **52**, 7951 (1995).  
<sup>17</sup>I. H. Inoue *et al.*, *Physica C* **185-189**, 2691 (1991).  
<sup>18</sup>I. H. Inoue *et al.*, *Phys. Rev. B* **45**, 5828 (1992).  
<sup>19</sup>G. van der Laan *et al.*, *Phys. Rev. B* **23**, 4369 (1981).  
<sup>20</sup>J. Ghijsen *et al.*, *Phys. Rev. B* **38**, 11 322 (1988).  
<sup>21</sup>R. Moret, *Synth. Met.* **27**, 301 (1988).  
<sup>22</sup>R. Kato, H. Kobayashi, and A. Kobayashi, *J. Am. Chem. Soc.* **111**, 5224 (1989).  
<sup>23</sup>K. Sinzger *et al.*, *J. Am. Chem. Soc.* **115**, 7696 (1993).  
<sup>24</sup>T. Miyazaki and K. Terakura, *Phys. Rev. B* **54**, 10 452 (1996).