Observation of anisotropy in the electronic states of $N,N'$-dicyanoquinonediimine-Cu salt by x-ray-absorption spectroscopy

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We have studied the unoccupied electronic states of an organic quasi-one-dimensional conductor partially deuterated (DMe-DNCQI-$d_1$)$_2$Cu, where DMe is (CH$_3$)$_2$ and DNCQI denotes $N,N'$-dicyanoquinonediimine, by linearly polarized x-ray-absorption spectroscopy in the metallic and insulating phases. The N 1s spectra have clearly shown a strong anisotropy in the lowest unoccupied molecular orbital band, indicating the onedimensional character of the $p\pi$ conduction band. From the Cu 2p spectra, we have confirmed the mixed valence state of Cu. The polarization dependence of the Cu 2p spectra suggests a significant mixture of $d_{xy}$ and $d_{xy}$ character into the predominant $d_{xy}$ character for the Cu 3d holes. The Cu 2p spectra show a slight difference between the metallic and insulating phases, indicating that the occupation of the Cu 3d orbitals increases in going from the insulating to the metallic phase. [S0163-1829(97)09339-9]

I. INTRODUCTION

Low-dimensional conductors have fascinated researchers because they exhibit various interesting phenomena such as metal-insulator transition (MIT), charge-density waves (CDW), spin-density waves (SDW), and superconductivity. Effects of electron correlation and/or electron-phonon interaction are thought to be important to understand these phenomena in the low-dimensional electron systems. A series of organic conductors ($R_1,R_2$-DNCQI)$_2$Cu ($R_1,R_2$-DNCQI = 2,5-disubstituted $N,N'$-dicyanoquinonediimine, Fig. 1) have unique electronic properties that are derived from the one-dimensional (1D) $p\pi$ chains of the DNCQI molecules and the Cu 3d orbitals connecting the $p\pi$ chains. Because of the bridging Cu 3d orbitals, they are not simple 1D conductors but have weak three dimensionality. The 1D chains run along the crystallographic c axis and, as shown in Figs. 2, the Cu ion is coordinated to the N atoms of the cyano groups in the DNCQI molecules in a $D_{2d}$ distorted tetrahedral way. Some deuterated (DMe-DNCQI-$d_1$)$_2$Cu ($R_1,R_2$-DNCQI = 2,5-disubstituted $N,N'$-dicyanoquinonediimine) undergo a metal-to-insulator transition with decreasing temperature, and show antiferromagnetic ordering at lower temperatures ($\leq 10$ K). Other deuterated (DMe-DNCQI-$d_2$)$_2$Cu ($R_1,R_2$-DNCQI = 2,5-disubstituted $N,N'$-dicyanoquinonediimine) undergo a metal-to-insulator transition with decreasing temperature, and show antiferromagnetic ordering at lower temperatures ($\leq 10$ K). Some deuterated (DMe-DNCQI-$d_2$)$_2$Cu ($R_1,R_2$-DNCQI = 2,5-disubstituted $N,N'$-dicyanoquinonediimine) undergo a metal-to-insulator transition with decreasing temperature, and show antiferromagnetic ordering at lower temperatures ($\leq 10$ K). Some deuterated (DMe-DNCQI-$d_2$)$_2$Cu ($R_1,R_2$-DNCQI = 2,5-disubstituted $N,N'$-dicyanoquinonediimine) undergo a metal-to-insulator transition with decreasing temperature, and show antiferromagnetic ordering at lower temperatures ($\leq 10$ K).

II. EXPERIMENT

Single crystals of the DNCQI-Cu salt were prepared by the diffusion method. These samples were black thin needles with lengths of 1.5–3 mm and cross-section diameters of 0.4–1 mm. X-ray-absorption measurements were made at the soft x-ray undulator beam line BL-2B of Photon Factory, National Laboratory for High Energy Physics. We recorded the XAS spectra in the total electron yield mode at room temperature, where the DNCQI-Cu salt is in the metallic phase, and at $\sim 30$ K, where it is in the insulating phase.
A schematic view of the experimental setup for the XAS measurements is shown in Fig. 3. The angle $\theta$ between the electric field $E$ of the incident light and the $c$ axis of the samples was varied by rotating the sample. The spectra were measured at $\theta = 0^\circ \pm 5^\circ$, $E \parallel c$, and $60^\circ \pm 2^\circ$, $E \perp c$. The spectra were obtained from properly normalized $\theta = 0^\circ$ and $\theta = 60^\circ$ spectra through

$$I_{\theta=60^\circ}(\omega) = \frac{1}{2} I_{\perp}(\omega) + \frac{1}{2} I_{\parallel}(\omega),$$

where $I_{\theta=60^\circ}(\omega)$ and $I_{\parallel}(\omega)$ are the spectra measured at $\theta = 60^\circ$ and $0^\circ$, respectively. $I_{\perp}(\omega)$ deduced by this procedure may contain at most 5% mixture of $I_{\parallel}(\omega)$ because of errors in $\theta$. The base pressure in the spectrometer was $\sim 4 \times 10^{-10}$ Torr. In order to obtain clean surfaces, the samples were cleaved in situ at each measuring temperature. We confirmed that the spectra did not change for several hours after cleaving. The energy resolution was $\sim 0.1$ and $\sim 0.5$ eV for the N 1$s$ and Cu 2$p$ XAS spectra, respectively. The photon energies and the resolution were calibrated using the O 1$s$ absorption peak of TiO$_2$ at 530.7 eV (Ref. 16) and the Cu 2$p$ threshold of a copper plate at 932.5 eV. 17

III. RESULTS AND DISCUSSION

A. N 1$s$ XAS spectra

In Fig. 4, we show linearly polarized N 1$s$ XAS spectra of (DMe-DCNQI-d$_7$)$_2$Cu. The N 1$s$ spectra have been normalized at $\sim 415$ eV, where there is no pronounced structure nor polarization dependence. Sharp peaks at 399 and 401 eV and broad structures at 404, 408, and 413 eV are observed in all the spectra. The N 1$s$ x-ray photoemission (XPS) spectrum of undeuterated (DMe-DCNQI)$_2$Cu was reported by Inoue et al., where the N 1$s$ peak was 399.5 eV. Thus the peak at 399 eV of the XAS spectra is attributed to a transition from the N 1$s$ core level to the lowest unoccupied molecular orbital (LUMO) conduction band. The difference in the peak energies between the XAS and XPS spectra probably originates from the attractive interaction between the core hole and the excited electron in the XAS final state. Previously, a N 1$s$ XAS spectrum of undeuterated (DMe-DCNQI)$_2$Cu was reported by Schmeißer et al. 18 but their spectrum is quite different from ours. The 399-eV peak is not seen in their spectrum. The origin of the discrepancy is not clear because they have not described how they cleaned and characterized the sample surfaces.

A band-structure calculation has been made for (DMe-DCNQI)$_2$Cu in the metallic phase using the local density

FIG. 1. (a) Structure of the DMe-DCNQI-d$_7$ molecule. (b) Crystal structure of (DMe-DCNQI)$_2$Cu projected on the ab plane. (c) Face-to-face stacking of DMe-DCNQI molecules.

FIG. 2. (a) Coordination geometry of Cu in the DCNQI-Cu salt. (b) Schematic energy diagrams of the Cu 3$d$ levels in the DCNQI-Cu salt.

FIG. 3. Schematic view of the experimental setup for the linearly polarized XAS measurement.
approximation (LDA) by Miyazaki et al.\textsuperscript{19,20} We have simulated the XAS spectrum using the appropriately broadened density of states (DOS) above $E_F$ as shown in Fig. 5. Because the N 2p partial DOS has not been calculated, we have used the total DOS. The simulated spectrum is in good agreement with the E||c spectra. Previously, we reported high-resolution photoemission (PES) spectra of this compound.\textsuperscript{21} In that study, we pointed out that the same LDA calculation does not reproduce the PES spectra near $E_F$, and concluded that the discrepancy between the PES spectra and the LDA calculation originates from the Tomonaga-Luttinger liquid behavior\textsuperscript{22} due to their 1D character and strong electron correlation. This seems to be contrary to the good agreement between the LDA calculation and the XAS E||c spectra. The reason is unclear at present, but we may speculate the origin as follows: the PES spectra directly yield the single-particle spectral function (apart from matrix element effects and surface effects), and therefore the PES spectra near $E_F$ are strongly influenced by electron correlation, which can modify the PES spectra from those based on the band-structure calculation. On the other hand, the XAS spectra do not exactly give the single-particle spectral function because of the presence of the core hole in the final state. Since the total electric charge of the system is conserved in the XAS process, XAS spectra would more faithfully reflect the DOS of the N-electron ground state given by the LDA band-structure calculations rather than PES spectra. PES spectra reflect the DOS of the (N−1)-electron final states, where the total charge increases by +e compared to the N-electron ground state. We also note that the energy scale of the comparison between the LDA calculation and the XAS spectra (∼5 eV) is ten times as large as that between the LDA and PES spectra (∼0.5 eV).

There is little difference between the N 1s spectra in the metallic phase and those in the insulating phase as shown in Fig. 4. (Such a small difference could originate from a possible misalignment of the angle $\theta$.) We may conclude that the unoccupied electronic structure around the N atoms of the DCNQI-Cu salt does not change at the MIT appreciably on the energy scale probed with the present energy resolution. Between the E||c and E⊥c spectra, there are differences in the intensities of the peaks. The peak at 399 eV and the broad structure at 404 eV are significantly reduced in the E⊥c spectra compared with those in the E||c spectra although they do not completely vanish as shown in Fig. 5. If the polarized spectra reflect only the local symmetry of the atomic orbital on each N atom, such a strong polarization dependence would not be expected since the DCNQI $p\pi$ bands mainly consist of the 2$p_z$ orbitals of C and N of the DCNQI molecule, whose plane makes an angle of ±(40−50)° with the c axis as shown in Fig. 1(c). Therefore, we conclude that the strong polarization dependence reflects the anisotropy of the extended band states derived from the 2$p_z$ orbitals strongly overlapping along the c axis. According to the LDA calculation, the lowest unoccupied conduction band is the 1D $p\pi$ band dispersing along the c axis, and the dispersion perpendicular to the c axis is very weak.\textsuperscript{19} We therefore conclude that the strong polarization dependence of the 399-eV peak reflects the quasi-1D character of the conduction band. We note that in the E⊥c spectra the intensity of the 399-eV peak is strongly suppressed but is still 20±5% of that in the E||c spectra, which is much larger than what could originate from the possible misalignment of the angle $\theta$.

Contrary to the peak at 399 eV, the peak at 401 eV shows no strong polarization dependence. The height of the 401-eV peak in the E||c spectra is almost same as that in the E⊥c spectra although the width of the peak in the E⊥c spectra is a little narrower. According to the LDA calculation, this peak corresponds to the second LUMO band. The band is also derived from the $p\pi$ orbitals of the DCNQI molecules but has a quite weak dispersion along any direction because the overlap between the orbitals is very small.\textsuperscript{20} Therefore we consider that the $p\pi$ electrons in this band are localized and the polarized XAS spectra reflect the local symmetry of the $p_z$ atomic orbitals, which make an angle of ±(40−50)° with the c axis [Fig. 1(c)], and do not show appreciable difference between the E||c and E⊥c spectra.
B. Cu $2p$ XAS spectra

Figure 6 shows linearly polarized Cu $2p$ XAS spectra of the DCNQI-Cu salt. There are peaks at 931, 936, 951, and 956 eV in all the spectra. The former two peaks are Cu $2p_{3/2}$ peaks and the latter are Cu $2p_{1/2}$ peaks. We attribute the peak at 931 eV to absorption at the Cu $2p_{1/2}$ site because an oxidized Cu plate shows a peak at 931 eV due to absorption at Cu $2p_{1/2}$ site as shown in Fig. 7. On the other hand, the peak at 936 eV corresponds to absorption at the Cu $2p_{3/2}$ site and therefore we consider that these spectra reflect the mixed valence state of the Cu in the DCNQI-Cu salt. The Cu $2p_{3/2}$ site signal at 936 eV is largely due to the absorption into the $4s$ conduction band, and therefore should not show appreciable polarization dependence. Therefore we have normalized the spectra to the intensity of the 936-eV peak. The 931-eV peak is then clearly more intense in the $E\parallel c$ spectra than in the $E\perp c$ spectra as shown in Fig. 7(a). Because the $2p\rightarrow 3d_{xy}$ absorption is allowed only in the $E\parallel c$ spectra, the enhancement of the peak in the $E\parallel c$ spectra indicates that the Cu 3$d$ holes mainly occupy the $d_{xy}$ orbital. This is consistent with the band-structure calculations. On the other hand, the 931-eV peak in the $E\parallel c$ spectra is appreciable. If the holes occupy only the Cu 3$d_{xy}$ orbital and that the other Cu 3$d$ orbitals have negligibly small numbers of holes, the 931-eV peaks in the $E\parallel c$ spectra should not be observed because of selection rules. From these results, we conclude that the holes in the DCNQI-Cu salt are predominantly $d_{xy}$-like but that the number of holes in the $d_{xz}$ and $d_{yz}$ orbitals is not negligible.

As for the changes in the Cu $2p$ spectra between the metallic and insulating phases, they are small but distinctly larger than the changes in the N $1s$ spectra. The intensity of the 931-eV peak in the insulating phase is high compared with that in the metallic phase. The same phenomenon is seen for both the $E\parallel c$ and $E\perp c$ spectra. The results indicate that the number of Cu$^{2+}$ sites in the insulating phase is slightly larger than that in the metallic phase and that the mean valence of Cu is slightly larger in the insulating phase. In the insulating phase, Cu$^{+}$ and Cu$^{2+}$ sites are ordered to form the threefold periodic lattice and the mean valence of Cu is thought to be $+4/3$. Therefore, we can conclude that the mean valence of Cu in the metallic phase is slightly less than $+4/3$. A recent theoretical study has suggested that the mean valence of Cu increases at the transition from the metal to the insulator, consistent with our result. For a simple Peierls transition to occur within the 1D $p\pi$ band, the ordering of Cu with different valences does not need to be commensurate with the lattice periodicity. The change of the mean Cu valence at the MIT indicates that there is a driving force to make the Cu charge ordering commensurate with the CDW periodicity. This means the MIT is not a simple Peierls transition but a Peierls transition coupled with the Cu 3$d$ electrons, as has been pointed out by previous experimental and theoretical studies.

IV. CONCLUSION

We have studied the unoccupied electronic states of the DCNQI-Cu salt, which undergoes a MIT as a function of temperature, by linearly polarized XAS. We have clearly observed the anisotropy of the electronic structure in the N $1s$ and Cu $2p$ XAS spectra. The N $1s$ spectra indicate that the LUMO orbitals of the DCNQI molecule strongly overlap...
along the c axis to form the 1D conduction band. The spectra also indicate that the LDA band-structure calculation well reproduces the N 1s E∥c spectra. In the Cu 2p spectra, we have observed the mixed valence state of Cu and analyzed the character of the Cu 3d holes. The Cu 2p spectra show that the holes of Cu 3d mainly originate from the 3d_xy orbital but that the number of holes in the other 3d orbitals is not negligible. As for the changes in the spectra between the metallic and insulating phases, the N 1s spectra show little change while the change of the Cu 2p spectra is substantial. Namely, the XAS peak due to Cu 2+ in the insulating phase is enhanced compared to that in the metallic phase. This suggests that the number of Cu 2+ sites increases, that is, the valence of Cu increases when the DCNQI-Cu salt undergoes the transition from the metallic phase to the insulating phase.

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23. We assume that the 2p→3d↑,↓ absorption is negligible because these levels are lower than other 3d orbitals and thought to be fully occupied.