High-resolution photoemission and x-ray absorption study of quasi-one-dimensional DCNQI-Cu salt

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We have made a high-resolution photoemission (PES) and x-ray absorption (XAS) study of quasi-one-dimensional partially deuterated (DMe-DCNQI)2Cu. The PES spectra in the metallic phase exhibit a power-law dependence on the electron binding energy \( \omega \) on a high energy scale (\( -0.3 \text{ eV} > |\omega| > -0.05 \text{ eV} \)) or at high temperatures (\( T > 300 \text{ K} \)) while a weak but finite intensity is found at the Fermi level at low temperatures, indicating a weak 3D character. From the N 1s and Cu 2p XAS spectra, we clearly observe the mixed valence state of Cu and the strong anisotropy of the electronic structure although 3D character is also found.

1. INTRODUCTION

Organic quasi-1D DCNQI-Cu salts have attracted great interest due to their unusual physical properties in these several years [1-4]. These salts have substantial 3D character due to the presence of Cu 3d orbitals bridging the 1D p-x chains of DCNQI molecules [5-7]. (MeBr-DCNQI)2Cu, (MeCl-DCNQI)2Cu, some deuterated (DMe-DCNQI-d7)2Cu, etc., undergo a MI transition as a function of temperature [2,8-10] accompanied by a three-fold periodical lattice distortion along the chain. The lattice distortion is associated with ordering of Cu+ and Cu2+ with ratio Cu+:Cu2+ = 2:1 [3,4,11]. An important point is that the DCNQI-Cu salts are not simple 1D conductors.

On the other hand, theoretical and experimental studies of quasi-one-dimensional interacting electron systems have made much progress in recent years. If there is finite interaction between electrons, the Fermi-liquid state of a 1D metal becomes unstable and the system becomes a Tomonaga-Luttinger liquid (TLL) [12]. The single-particle spectral function of the TLL has a power-law dependence on the electron energy measured from the Fermi level \( E_F \), \( \rho(\omega) \propto |\omega|^{\theta} \), where \( \theta \) determines the power-law exponents of the asymptotic behavior in the spin- and charge-correlation functions [13]. Photoemission spectroscopy (PES) is a suitable tool to test the TLL behavior since it probes the single-particle spectral function. Indeed, PES spectra near \( E_F \) were reported for several quasi-1D compounds [14-18] and their intensity is suppressed near \( E_F \), suggesting that a TLL may be realized in these systems.

In this paper, we report on a high-resolution PES [19] and x-ray absorption (XAS) study of a deuterated (DMe-DCNQI-d7)2Cu, which undergoes a sharp metal-insulator (MI) transition at \( T_c \sim 80 \text{ K} \) [9]. Our interest is whether high-resolution PES spectra near \( E_F \) of the DCNQI-Cu salt behave as a TLL like the spectra of other quasi-1D conductors or not and whether we observe the anisotropy of the unoccupied electronic states by linearly polarized XAS spectra or not.

2. EXPERIMENTAL

Single crystals of (DMe-DCNQI-d7)2Cu were prepared by the diffusion method [20]. PES measurements were performed using a spectrometer equipped with a He discharge lamp (\( h\nu = 21.2 \text{ eV} \)). XAS measurements were made at the soft x-ray undulator beam line BL-2 having a 10-m grazing incidence monochromator at Photon Factory, National Laboratory for High Energy Physics. In order to obtain clean surfaces, the samples were fractured in situ at each measuring temperature. All the PES spectra reported here were recorded within \(-1 \text{ hour} \) after cleaving. The XAS spectra did not
change within several hours after cleaving. The energy resolution was ~40 meV for PES, ~0.1 eV for N 1s XAS and ~0.5 eV for Cu 2p XAS.

3. RESULT AND DISCUSSION

3.1 PES spectra

Temperature dependence was observed near \( E_F \) as shown in Fig. 1. The spectrum at 55 K is suppressed near \( E_F \) compared to those taken in the metallic phase, clearly indicating the opening of a gap of at least ~0.1 eV in the insulating phase.

Recently a band-structure calculation has been made for (DMe-DCNQI)\(_2\)Cu using the local density approximation (LDA) by Miyazaki et al. [7]. We have simulated the PES spectra using the appropriately broadened density of states as shown in Fig. 2. While the LDA calculation relatively well reproduces the spectrum from ~0.5 eV to ~1.8 eV, the emission intensity is strongly suppressed compared to the LDA calculation within ~0.3 eV of \( E_F \), where the conduction band derived from the \( p\pi \) orbitals of the DCNQI molecules is mixed with the Cu 3d orbitals.

The single-particle spectral function of a TLL near \( E_F \) is described by a power-law of the electron binding energy at zero temperature. Therefore we have fitted using the least-squares method the spectra near \( E_F \) in the metallic phase (within ~0.3 eV of \( E_F \)) to a model function

\[
\varrho(\omega) = A|\omega|^\theta, \tag{1}
\]

where \( -\omega \) is the electron binding energy measured from \( E_F \) and \( A \) is a constant. [\( \varrho(\omega) = 0 \) for \( \omega > 0 \) for PES spectra.] On the other hand, the anisotropy of the electrical conductivity in the DCNQI-Cu salts is only about 10:1 [5], and a 3D Fermi surface has been observed by de Haas-van Alphen measurements [6] as predicted by the band-structure calculations [4,6,7]. In order to take into account the Fermi-liquid aspects of the conduction electrons, we have also fitted the spectra to a model function similar to Eq.(1) but with a Fermi edge at \( \omega = 0 \),

\[
\varrho(\omega) = \max(B|\omega|^\theta, C), \tag{2}
\]

where \( B \) and \( C \) are positive constants. Appropriate

![Fig. 1](image1.png)

**Fig. 1** Valence band PES spectra of (DMe-DCNQI-d\(_2\))\(_2\)Cu.

![Fig. 2](image2.png)

**Fig. 2** Comparison of the PES spectrum (dots) with the band-structure calculation by Miyazaki et al. [7] (solid line).

instrumental and thermal (FWHM ~3.8 \( k_B T \)) broadening have also been included in the analysis. Equation (1) reproduces the experimental spectra reasonably well. However, the measured spectra, particularly that taken at \( T = 190 \) K show excess intensities at \( E_F \); Equation (2) yields a slightly but distinctly better fit than Eq.(1). Thus the spectra in the metallic phase are consistent with the 3D character of the conduction electrons as suggested by the de Haas-van Alphen and transport results. Detailed line-shape analysis of the spectra using Eq.(1) and Eq.(2) is reported in [19].

The exponent \( \theta \) is estimated to be ~0.9 at 295 K
and -1.1 at 190 K. These values are much larger than the upper limit for the single-band Hubbard model θ=1/8 [22] whereas θ can be arbitrarily large when the electron-electron interaction is long-ranged [23]. Therefore, we conclude that electron-electron interaction between the conduction electrons in (DMe-DCNQI)₂Cu is long-ranged. Here it should be noted that the TLL scaling in a 1D metal is guaranteed only below a characteristic electron-electron interaction energy [24]. In the case of long-range Coulomb interaction, the average electron-electron interaction energy is given by $e^2/εr_s^2/2$-0.3 eV, where ε is the optical dielectric constant and $r_s$ ~7Å is the average electron-electron distance. This explains why the TLL scaling is valid up to 10K as large as ~0.3 eV in the photoemission spectra. The estimated θ at 190 K is larger than that at 295 K. For the SU(N) model (N=2 corresponds to the single-band model with spin 1/2), the exponents of the spin and charge correlation function increase with decreasing θ [25]. Therefore we may consider that the correlations at lower temperatures become rather long-ranged than those at higher temperatures.

3.2 XAS spectra

Figure 3 shows linearly polarized N 1s XAS spectra of (DMe-DCNQI-d₇)₂Cu in the metallic phase. Sharp peaks at 399 eV and 401 eV, and broad structures at 404 eV, 408 eV and 414 eV are observed in both spectra. Appropriately broadened density of states derived from the LDA calculation [7,26] is also shown in Fig. 3. The calculated density of states is in good agreement with the E//c spectrum although the simulated PES spectrum does not reproduce the experimental PES spectra near $E_F$ as described above. The reason is unclear at present. The peak at 399 eV is greatly reduced in the E⊥c spectrum compared with that in the E//c spectrum. It is known that the conduction band is mainly derived from the 1D pₓ band dispersing along the c-axis. Therefore this observation is a reflection of the strong anisotropy of the conduction band in the DCNQI-Cu salt. However, the 399 eV peak does not completely vanish in the E⊥c spectrum. Contrary to the peak at 399 eV, the peak at 401 eV shows no anisotropy. This peak corresponds to the second lowest unoccupied band. Thus we consider that this band is quite isotropic and is three-dimensional.

Fig. 3 Linearly polarized N 1s XAS spectra (solid line and dots) compared with the band-structure calculation by Miyazaki [26] (dashed line).

Fig. 4 Linearly polarized Cu 2p₃/₂ XAS spectra of (DMe-DCNQI-d₇)₂Cu.

Linearly polarized Cu 2p₃/₂ XAS spectra in the metallic phase are shown in Fig. 4. In these spectra, peaks are observed at 931 eV and 935 eV. The peak at 931 eV is clearly different between the spectrum for $φ$=0° (E//c) and that for $φ$=60° although the peak at 935 eV has little anisotropy. Therefore we consider that the peak at 935 eV and that at 931 eV correspond to absorption at the Cu⁺ sites and that at the Cu²⁺ sites, respectively. These spectra directly show the evidence for the mixed valence state of the Cu.

It is thought that holes on the Cu²⁺ site occupy the Cu 3dₓᵧ orbital and that the other Cu 3d orbitals have negligibly small number of holes [6,27]. If
this is the case, the peak originated from the Cu$^{2+}$ in the $\phi=0^\circ$ spectrum should be very weak because of the selection rule. However, the $\phi=0^\circ$ spectrum has fairly large intensity at the Cu$^{2+}$ peak position (at 931 eV), which probably originates from the $d_{yz}$ and $d_{zx}$. Nevertheless, the Cu$^{2+}$ peak in the $\phi=60^\circ$ spectrum is stronger than in the $\phi=0^\circ$ spectrum. From these results, we conclude that the Cu 3$d$ holes mainly exist in the $d_{xy}$ orbital but that the number of holes in the other 3$d$ orbitals is not negligible.

4. CONCLUSION

In conclusion, the PES spectra of (DMe-DCNQI-$d_{7}$)$_2$Cu obey a TLL scaling on a high energy scale while the intensity at the Fermi level is finite characteristic of a 3D Fermi liquid. This signifies that a crossover occurs from 1D to 3D with decreasing temperature and energy scale. The results also imply how a quasi-1D metal approaches a 3D metal as the mass anisotropy decreases. The large exponent $\theta$ means that electron-electron interaction is long-ranged. As for the unoccupied band structure, we clearly observed a strong anisotropy in the XAS spectra. This is derived from the 1D character of the conduction band. However, we also observed 3D character from the spectra. The Cu $2p$ XAS spectra indicate that the holes of Cu 3$d$ are mainly originated from 3$d_{xy}$ orbital.

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