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Electronic states in the valence-fluctuating organic conductors $(DCNQI)_2Cu$ (DCNQI=N,N'-dicyanoquinonediimine) studied by ultraviolet photoemission spectroscopy

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Ultraviolet photoemission spectra near the Fermi level of quasi-one-dimensional organic conductors, $(DME\text{-}DCNQI)_2Cu$ and $(Me,Br\text{-}DCNQI)_2Cu$, where DMe is dimethyl, have been studied using undulator radiation. We have found no evidence for sharp Fermi edges in both salts, as was observed in other one-dimensional conductors; the existence of Cu $3d$ character was found near the Fermi level in $(DME\text{-}DCNQI)_2Cu$. This indicates that, in the metallic DCNQI-Cu systems, $3d$ electrons are hybridized with the p_π conduction band at the Fermi level, which is consistent with the valence-fluctuation picture of Cu. We have also observed the gap opening in $(Me,Br\text{-}DCNQI)_2Cu$, where Me is methyl, below the critical temperature of the metal-insulator transition.

In recent years, $(2,5\text{-}R_1,R_2\text{-}DCNQI)_2Cu$, where DCNQI is N, N'-dicyanoquinonediimine and $R_1,R_2 = CH_3$, CH_3O, Cl, Br, I, etc., has provoked a great deal of interest for its intriguing electric, magnetic, and structural properties.[1,2] DCNQI's are π-acceptor molecules which are stacked along a certain axis forming the one-dimensional $p\pi$-conduction band. Cu salts show metal-to-insular (MI) transitions accompanied by a three-fold periodical lattice distortion through the formation of a charge-density wave along the stacking axis.[3] Therefore, the mean valence of the Cu ion has been considered to be $\frac{4}{3}$ for the degenerate $p\pi$ conduction band of DCNQI which is $\frac{1}{3}$ filled. Some of the DCNQI-Cu salts, e.g., $(DME\text{-}DCNQI)_2Cu$, where DMe is dimethyl, do not show a MI transition down to the lowest temperature studied,[4] but under pressure, they show a reentrant-type MI transition.[5–7]

In a previous paper, we have reported an x-ray photoemission spectroscopy (XPS) study of $(DME\text{-}DCNQI)_2Cu$ and concluded that the $[Cu^+]:[Cu^{2+}]$ ratio is nearly 2:1.[8] This result has been confirmed by a subsequent infrared absorption study of $(Me,Br\text{-}DCNQI)_2Cu$.[9] Based on the analysis of the XPS spectra, we have suggested that the Cu $3d$ electrons are basically localized and the system can be viewed as a valence-fluctuating material.[8] The question that we must address now is the nature of the electronic states near the Fermi level of these Cu salts. In this paper, we report on the results of an ultraviolet photoemission spectroscopy (UPS) study of $(DME\text{-}DCNQI)_2Cu$ and $(MeBr\text{-}DCNQI)_2Cu$ to provide new information on the electronic states of these organic systems.

The UPS measurements were performed at beam line BL-19A of Photon Factory (PF), National Laboratory for High Energy Physics (KEK), using undulator radiation from a 2.5-GeV positron storage ring.[10,11] The maximum

photon flux at the focal point amounts to $\sim 7\times 10^{13}$ photons/(sec/mm^2) at the photon energy of 90 eV and the ring current of 300 mA. In this experiment, the resolution was 220 meV for the pass energy of an electron-energy analyzer (a PHI-15-235G double-stage cylindrical mirror analyzer) of 20 eV. All the UPS spectra reported here were normalized to the incident photon flux. The undulator radiation never hangs out of a very thin, needlelike sample prepared by the diffusion method [reaction with CuI in acetonitrile (CH_3CN)] whose width was ~ 0.4 mm for (DMe-DCNQI)$_2$Cu and ~ 0.1 mm for (MeBr-DCNQI)$_2$Cu. This was made possible because the undulator radiation was so collimated that the front-end slit of the beam line could be narrowed without significant loss of intensity to such an extent that the beam was found to be an almost rectangular spot of ~ 50 μm$\times\sim 2$ mm at the sample position. The samples were introduced to the spectrometer via an airlock and were mounted on a liquid-nitrogen cryostat. As in the XPS measurements,[8] we could obtain fresh, clean surfaces by gently scraping the samples with a diamond file in an ultrahigh vacuum chamber (with a base pressure of $<8\times 10^{-11}$ Torr) to remove the surface layers.

The valence-band UPS spectra obtained in this way (Fig. 1) show almost the same profiles as the recent UPS spectra measured on *in situ* prepared thin films by Schmeisser *et al.*[12] In both spectra, roughly six structures are identified. We could see two additional structures in the higher binding-energy region ~ 15–25 eV.[10] Furthermore, as reported,[12] the resonance effects at the Cu $3p$ threshold were not pronounced also in our measurements. In this paper, we concentrate on the photon energy and temperature dependence of the UPS spectra near the Fermi level.

The UPS spectra near the Fermi level of (DMe-DCNQI)$_2$Cu taken for several photon energies at liquid-nitrogen temperature are shown in Fig. 2. Since (DMe-DCNQI)$_2$Cu is metallic down to low temperatures, one would expect that the valence band extends to the Fermi level and a Fermi edge will be observed. However, the center of each emission edge, i.e., the midpoint of the steeply rising slope, is shifted to higher binding energy from the Fermi level determined by subsequent UPS measurement on a gold film evaporated on the sample, and is considerably broadened. These shifts were $\sim 400\pm 20$ meV for all the photon energies studied, and the widths of the emission edges were about 1.5–3.0 times larger than the instrumental resolution (220 meV). Therefore, we believe that these broad emission edges are not originated from an experimental artifact such as charging, but from an intrinsic property of the disappearance of the Fermi edges in quasi-one-dimensional systems. On this subject, Dardel *et al.*[13] have recently carried out high-resolution photoemission experiments on typical quasi-one-dimensional metallic compounds, and have shown that Fermi edges are not observed even above the Peierls transition temperatures. In addition to the previous explanations such as large Peierls fluctuation effects[14] and the excitations of high-energy phonons in the photoemission process due to strong electron-phonon coupling,[15] they proposed another possibility to account for this unusual property from the viewpoint of a Tomonaga-Luttinger liquid.[16] Since the conduction electrons of the DCNQI salts actually exhibit a sign of electron correlation, i.e., $4k_F$ lattice instability in addition to the $2k_F$ one in the salts of monovalent cations,[17] we have also to keep that proposal in mind when we discuss the UPS spectra around the Fermi level of the DCNQI salts.

Figure 3 shows the UPS spectra near the Fermi level of (MeBr-DCNQI)$_2$Cu, which shows a MI transition at $T_{MI}=160$ K, at room temperature and liquid-nitrogen temperature. The center of the emission edge is seen to

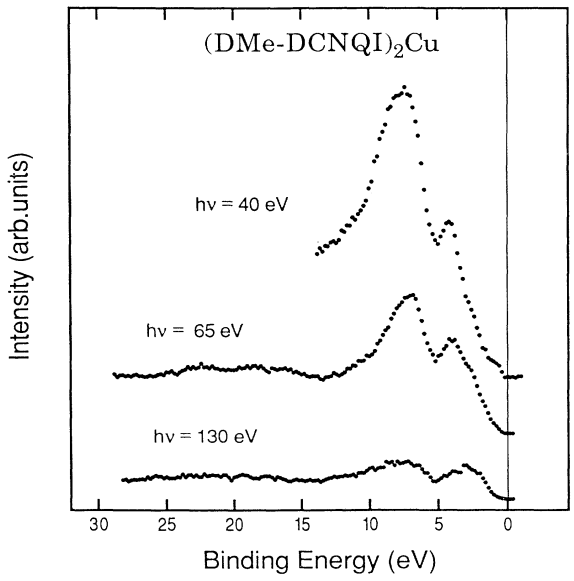

FIG. 1. Valence-band UPS spectra of (DMe-DCNQI)$_2$Cu measured at liquid-nitrogen temperature.

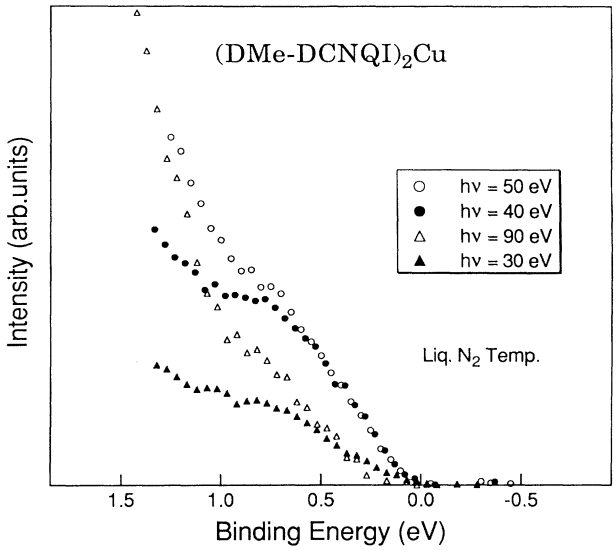

FIG. 2. UPS spectra of (DMe-DCNQI)$_2$Cu near the Fermi level measured at liquid-nitrogen temperature. The centers of the emission edges are located ~ 400 meV below the Fermi level. For details, see text.

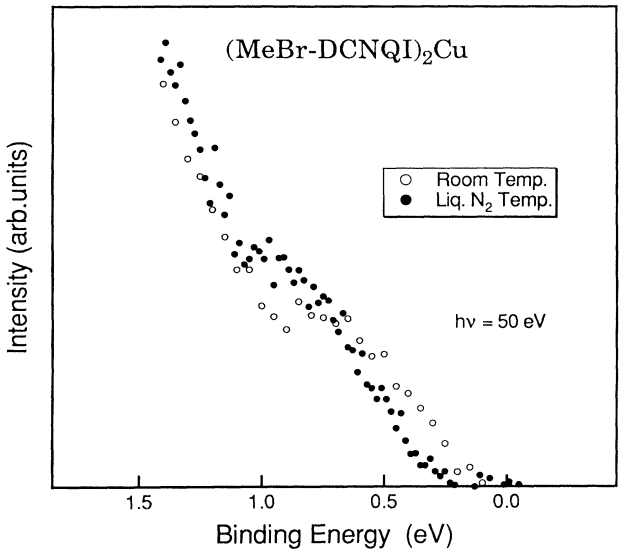

FIG. 3. UPS spectra of (Me,Br-DCNQI)$_2$Cu ($T_{MI}=160$ K) near the Fermi level at room temperature and at liquid-nitrogen temperature (~ 80 K). Below T_{MI}, the photoemission intensity at the emission edge is decreased and that around 0.8 eV is enhanced.

be shifted and broadened also in this salt. As the temperature is lowered from room temperature to liquid-nitrogen temperature (~ 80 K), the photoemission intensity at the emission edge is decreased. This phenomenon would be related to the creation of a Peierls gap at the Fermi level which leads to the MI transition. In addition, we observe that the density of states disappearing from the emission edge is piled up around 0.8 eV associated with the formation of the Peierls gap. It is interesting to note that the spectral change occurs down to ~ 0.8 eV below E_F, which is one to two orders of magnitude larger than T_{MI} or the activation energy in the insulating state.[18]

Since the photon-energy dependence of the photoionization cross section for copper $3d$ electrons is very different from that for nitrogen and carbon $2p$ electrons,[19] to investigate the photon energy dependence of the photoemission intensity at the emission edge clarifies the character of the conduction electrons at the Fermi level. As shown in Fig. 2, the photoemission intensity at the emission edge in (DMe-DCNQI)$_2$Cu increases as the photon energy decreases from 90 to 50 eV; this tendency is common to both the $3d$ electrons and the $2p$ electrons. However, for further decrease of the photon energy, the intensity reaches a maximum at 40–50 eV and then drops toward ~ 30 eV. This type of behavior is what is expected for the photoionization cross section of the $3d$ electrons but not for the $2p$ electrons. Therefore, it seems reasonable to suppose that the "nearly localized" Cu $3d$ electrons are hybridized into the $p\pi$ electrons around the Fermi level and are involved in the formation of the Fermi surfaces; in this case, the Fermi surfaces are considered to be no longer those of typical quasi-one-dimensional metals due to the hybridization between the $p\pi$ electrons of different DCNQI columns mediated by the intervening Cu $3d$ electrons. This $3d$-$p\pi$ hybridization in the metallic phase is consistent with the result of an optical conductivity study, which shows finite optical conductivity perpendicular to the c axis only in the metallic state.[20] It should be noted that in the UPS spectra shown in Fig. 2, the Cu $3d$ character is apparently enhanced due to the large $\sigma(3d)/\sigma(2p)$ relative cross sections (~ 10). The spectral weight of Cu $3d$ character at the Fermi level is actually small and the Fermi surfaces are considered to be still dominated by the one-dimensional $p\pi$ character.

Therefore, we may consider that electrons near the Fermi level are influenced by two different characters: one is the electron correlation within the one-dimensional $p\pi$ conduction electrons, which causes the emission edges to be shifted away from the Fermi level and become broader, and the other is that due to hybridization between the itinerant $p\pi$ conduction electrons and the nearly localized $3d$ electrons. Through these correlation effects, a narrow quasiparticle band may be formed at the Fermi level, leading to the observed enhancement of the electronic specific coefficient,[21] namely, to the high quasiparticle density of states at the Fermi level $N(E_F)$. However, the photoemission intensity near the Fermi level generally remains unenhanced[22] since the photoemission spectral function $\rho(E_F)$ is given by

$$\rho(E_F)=Z\times N(E_F)\ ,$$

where $Z(<1)$ is the bandwidth renormalization factor.

As we have discussed previously,[8] the hybridization $V_{pd\pi}$ between the localized Cu $3d$ electron and the $p\pi$ conduction electron is weak in comparison with the energy difference between the two relevant $3d$ configurations ($3d^9$ and $3d^{10}$ on a Cu ion). On the other hand, we have also discussed that in the DCNQI-Cu systems, there exists a strong p_σ-d hybridization ($d^9\pi$-$d^{10}\underline{L}_\sigma\pi$, where π denotes an electron at the Fermi level of the $p\pi$ conduction band, and $\underline{L}\sigma$ denotes a ligand hole on $p\sigma$ orbitals) in the Cu-N_4 local complex, which lowers the energy of the Cu^{2+} ground state $\Psi_g(Cu^{2+})=\cos\theta|3d^9\pi\rangle -\sin\theta|3d^{10}\underline{L}_\sigma\pi\rangle$, relative to that of the Cu^+ ground state $\Psi_g(Cu^+)=|3d^{10}\rangle$, and leads to the near degeneracy of $\Psi_g(Cu^{2+})$ and $\Psi_g(Cu^+)$.[8] When the energy difference between these two states δ is of order $V_{pd\pi}$, valence fluctuation between them will take place, and a "singlet" ground state, which is stabilized by the energy of $\sim k_B T_K$, is realized. T_K is a Kondo temperature given by

$$T_K\sim\exp\left[-\frac{\delta}{N_0(E_F)|V_{pd\pi}|^2}\right]\ ,$$

where $N_0(E_F)$ is the bare p_π-electron density of state at the Fermi level. If the ground state is such a singlet, we can understand the Pauli paramagnetic behavior of this salt even in the presence of Cu^{2+} states as well as the mass enhancement of the conduction electrons. Therefore, when the temperature is low enough compared with T_K, the ground state is a nonmagnetic mixed-valence state between Cu^+ and Cu^{2+}; and above T_K, the Curie-Weiss magnetic susceptibility is recovered. In this pic-

ture, $(DMe\text{-}DCNQI)_2Cu$ would be characterized by a large T_K, which is at least larger than room temperature, and the salt is in the so-called mixed-valence regime of valence fluctuation. The resistivity of $(DMe\text{-}DCNQI)_2Cu$ and $(DMeO\text{-}DCNQI)_2Cu$ at low temperatures under pressure has previously been attributed to a dense Kondo effect with smaller T_K (~ 100 K), but recently it has alternatively been explained as a result of competition between the Peierls instability in the Luttinger liquid and the three dimensionality due to the coupling between the DCNQI chains.[23] Actually, that the mass of the conduction electrons is not so extremely enhanced [$\gamma = 45$ mJ/(mol/K^2) (Ref. 21)] is consistent with the relatively large T_K. In a recent theoretical study[23] starting from the band picture of the d electrons, it has been shown that the $[Cu^+]$:$[Cu^{2+}]$ ratio is forced to be 2:1 in the metallic state as a natural consequence of strong correlation among the Cu $3d$ electrons.

In conclusion, the strong and collimated undulator radiation has made it possible to perform the UPS measurements on such thin, needlelike samples of $(DMe\text{-}DCNQI)_2Cu$ and $(Me,Br\text{-}DCNQI)_2Cu$ with *in situ* surface cleaning. The UPS spectra of these salts did not show such sharp emission edges at the Fermi level as those of ordinary three-dimensional metals; this phenomenon is considered as due to the intrinsic properties of quasi-one-dimensional conductors. The Cu $3d$ character near the Fermi level was observed in $(DMe\text{-}DCNQI)_2Cu$; this result leads us to consider that the DCNQI-Cu salts are valence-fluctuating materials with large T_K. We also observed the gap opening in $(Me,Br\text{-}DCNQI)_2Cu$ below the critical temperature T_{MI}.

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