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Fermi-liquid versus Luttinger-liquid behavior and metal-insulator transition in *N*,*N*′-dicyanoquinonediimine-Cu salt studied by photoemission

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We have made a high-resolution photoemission study of quasi-one-dimensional partially deuterated $(\text{DMe-DCNQI})_2\text{Cu}$, where DMe-DCNQI denotes dimethyl *N*,*N*′-dicyanoquinonediimine. The spectra in the metallic phase exhibit a power-law dependence on the electron binding energy $|\omega|$ on a high-energy scale ($0.3 \gtrsim |\omega| \gtrsim 0.05$ eV) or at high temperatures ($T \gtrsim 300$ K) while a weak but finite intensity is found at the Fermi level at low temperatures, consistent with the existence of a Fermi edge. These results imply how a crossover occurs from a one-dimensional Luttinger liquid to a three-dimensional Fermi liquid as a function of excitation energy, temperature, and mass anisotropy.

In recent years, theoretical and experimental studies on quasi-one-dimensional interacting electron systems have made much progress. If there is finite interaction between electrons, the Fermi-liquid state of a one-dimensional (1D) metal becomes unstable and the system becomes a Luttinger liquid.[1] The momentum distribution function of a Luttinger liquid shows a power-law singularity at the Fermi momentum, which in turn determines the power-law exponents of the asymptotic behavior in the spin- and charge-correlation functions.[2] The single-particle spectral function also has a power-law dependence on the electron energy near the Fermi level (E_F), $\rho(\omega) \propto |\omega|^\theta$, the exponent θ being identical to that of the momentum distribution function.[3] Photoemission spectroscopy is a suitable tool to test the Luttinger-liquid behavior because it probes the single-particle spectral function. Indeed, photoemission spectra near E_F were reported for several quasi-1D compounds[4–8] and their intensity is suppressed near E_F, suggesting that a Luttinger liquid may be realized in these systems. However, the exponents observed by photoemission are generally large, $\theta \gtrsim 1$, much larger than that predicted for the Hubbard model ($\theta \leqslant 1/8$),[5,8] indicating that a more realistic microscopic model is required to describe the real quasi-1D systems. Furthermore, it is not known how the interchain interaction in the real systems influence the 1D character.

In this paper, we have made a high-resolution photoemission spectroscopy study of an organic quasi-1D conductor $(\text{DCNQI})_2\text{Cu}$ salt,[9–12] which has substantial 3D character due to the presence of Cu $3d$ orbitals bridging the 1D $p\pi$ chains of DCNQI (*N*,*N*′-dicyanoquinonediimine) molecules.[13–15] The sample we have studied is a deuterated $(\text{DMe-DCNQI-}d_7)_2\text{Cu}$ (where DMe denotes dimethyl), which undergoes a sharp metal-insulator (MI) transition at $T_t \sim 80$ K.[16] The spectral intensity is strongly suppressed near E_F even in the metallic phase, suggesting Luttinger-liquid behavior. Nevertheless, the intensity at E_F appears to remain finite, reminiscent of a Fermi edge in 3D metals. In the insulating phase, the band edge does not show the $|\omega|^{-1/2}$ divergence expected for a 1D insulator,[17] possibly reflecting the three-dimensionality of the $(\text{DCNQI})_2\text{Cu}$ compounds.

The $(\text{DCNQI})_2\text{Cu}$ salts have recently attracted great interest due to their unusual physical properties. $(\text{MeBr-DCNQI})_2\text{Cu}$, $(\text{MeCl-DCNQI})_2\text{Cu}$, some deuterated $(\text{DMe-DCNQI-}d_x)_2\text{Cu}$, etc., undergo a MI transition as a function of temperature[10,16,18,19] accompanied by a threefold periodical lattice distortion along the chain. The lattice distortion is associated with ordering of Cu^+ and Cu^{2+} states with the ratio $\text{Cu}^+:\text{Cu}^{2+} = 2:1$.[11,12,20]

Single crystals of $(\text{DMe-DCNQI-}d_7)_2\text{Cu}$ were prepared by the diffusion method.[20] Photoemission measurements were performed using a spectrometer equipped with a He discharge lamp ($h\nu = 21.2$ eV). The base pressure of the analyzer chamber was $\sim 2 \times 10^{-10}$ Torr. In order to obtain clean surfaces, the samples were fractured *in situ* at measuring temperatures. All the spectra reported here were recorded within ~ 1 h after cleaving. Because the fractured surfaces were irregular and the spectra did not show appreciable angular dependence, we believe that our spectra are angle-integrated ones and hence represent the k-integrated single-particle spectral function of $(\text{DMe-DCNQI-}d_7)_2\text{Cu}$. The Fermi level was determined by evaporating Au on the samples. The energy resolution was ~ 40 meV.

Figure 1 shows the valence-band spectrum of $(\text{DMe-DCNQI-}d_7)_2\text{Cu}$. The spectrum is close to those of undeuterated compounds reported previously.[7,21,22] The predominant peak at 8 eV originates from the C, N $2p\sigma$ orbitals of the DCNQI molecule, and the peak at 4 eV originates from the Cu $3d$ orbitals. Temperature dependence was observed near E_F, as shown in Fig. 2. 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 $(\text{DMe-DCNQI})_2\text{Cu}$ using the local density approximation (LDA) by Miyazaki *et al.*[15] We have simulated the photo-

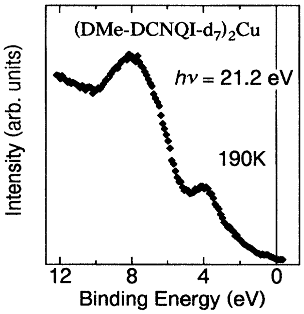

FIG. 1. Valence-band spectrum of (DMe-DCNQI-d_7)$_2$Cu.

emission spectra using the appropriately broadened density of states as shown in Fig. 3. Here, the different cross sections for the C, N $2sp$ and Cu $3d$ atomic orbitals have been taken into account. While the LDA calculation has relatively well reproduced the spectrum from $\sim$0.5 eV to $\sim$1.8 eV, the spectrum is strongly suppressed compared to the LDA calculation within $\sim$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. In the following analysis, we do not differentiate between the $p\pi$ and Cu $3d$ orbitals because the electron-electron interaction strength is nearly the same for the $p\pi$ and Cu $3d$ electrons, as indicated by a recent Auger-electron spectroscopic study.[23]

The single-particle spectral function of a Luttinger liquid 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 $\sim$ 0.3 eV of E_F) to a model function

$$\rho(\omega)=A|\omega|^{\theta}, \tag{1}$$

where $-\omega$ is the electron binding energy measured from E_F and A is a constant. [$\rho(\omega)\equiv 0$ for $\omega>0$ for photoemission spectra.] On the other hand, the anisotropy of the electrical conductivity in the DCNQI-Cu salts is only about 10:1,[13] and a three-dimensional Fermi surface has been observed by de Haas–van Alphen measurements[14] as predicted by the band-structure calculations.[12,14,15] The electrical resistivity of undeuterated (DMe-DCNQI)$_2$Cu shows a T^2 dependence above $T\sim$ 30 K (Ref. 11) characteristic of a 3D Fermi liquid. 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 $\omega=0$,

$$\rho(\omega)=\max(B|\omega|^{\theta},C), \tag{2}$$

where B and C are positive constants. Appropriate instrumental and thermal [full width at half maximum (FWHM) $\sim 3.8k_BT$] broadening have also been included. Figure 4(a) shows that Eq. (1) reproduces the experimental spectra reasonably well. However, the measured spectra, particularly that taken at $T=190$ K, show excess intensities at E_F; Eq. (2) yields a slightly but distinctly better fit than Eq. (1), as shown in Fig. 4(b). The ratio C/B converged to similar values for the spectra taken at various temperatures, indicating that the least-squares fitting is reliable. 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.

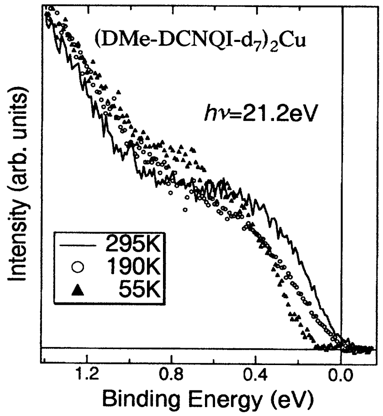

FIG. 2. Valence-band spectra near E_F of (DMe-DCNQI-d_7)$_2$Cu.

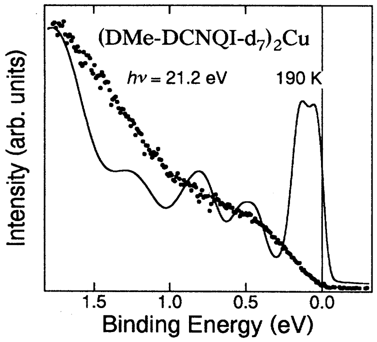

FIG. 3. Comparison of the spectrum near E_F (dots) with the band calculation by Miyazaki *et al.* (Ref. 15) (solid line).

Figure 4 shows, however, that in the spectrum taken at 295 K, there is little difference between the best fit result of Eq. (1) and that of Eq. (2). This is due to the strong thermal broadening at $\sim$ 300 K, indicating that a clear distinction between pure 1D and weak 3D is lost and therefore that a 1D description may recover at higher temperature. Polarized re-

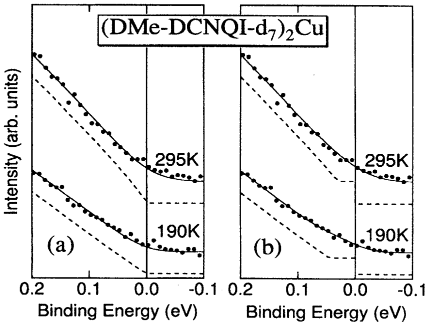

FIG. 4. Spectra near E_F fitted to Eq. (1) (a) and Eq. (2) (b) with the instrumental and thermal broadening taken into account. Curves without broadening are also shown by dashed curves.

flectance spectra of the DCNQI-Cu salts by Yakushi *et al.* have indicated a decrease and/or a broadening of the Drude weight perpendicular to the chain direction with increasing temperature, also suggesting a 1D-3D crossover.[24] Dimensionality crossover as a function of temperature has previously been suggested in an optical study of (tetramethyltetraselenafulvalene)$_2$PF$_6$.[25]

The crossover between 1D and 3D with varying temperature can be naturally understood as follows: The conduction bands of (DCNQI)$_2$Cu have weak dispersions perpendicular to the chain due to the transfer integral $t_\perp^*$ between the chains (renormalized from the bare $t_\perp$ by electron correlation), which is much smaller than the transfer integral $t_\parallel^*$ parallel to the chain. At lower temperatures, $k_BT \ll t_\perp^*$, the 3D character becomes evident and the Fermi edge is observable in the photoemission spectra. At higher temperatures, $k_BT \gg t_\perp^*$, the perpendicular dispersion is obscured because of thermal disturbance. Indeed, the photoemission intensity at E_F of NbTe$_4$, TaTe$_4$, and (NbSe$_4$)$_3$I seems to be a little increased at low temperatures compared to that at room temperature.[6] Contrary to this, in BaVS$_3$ the photoemission intensity near E_F is suppressed compared to the power-law dependence with decreasing temperature,[8] possibly due to a larger mass anisotropy in BaVS$_3$. The present spectra also show a crossover from 3D to 1D with increasing electron binding energy: The spectra at $|\omega| \gg t_\perp^*$ are not influenced by the weak 3D character and appear to obey the Luttinger-liquid scaling. A recent theoretical study has shown that in a quasi-1D electron system with interchain interaction, electrons with energy above a characteristic value behave as 1D conduction electrons although electrons in the vicinity of E_F behave as a Fermi liquid,[26] consistent with our observation.

We may interpret the spectra in the metallic phase in terms of Fermi-liquid theory as follows. The photoemission intensity at E_F is much reduced compared to the intensity predicted by the band-structure calculation, the reduction factor being ~ 0.03 at 190 K. Using the electron self-energy $\Sigma(k,\omega)$, this factor is given by $m_k/m_b \equiv [1+(m_b/k)\partial \mathrm{Re}\Sigma(k,\omega)/\partial k]^{-1}$,[27,28] where m_k is the k mass and m_b is the unrenormalized band mass. $m_k/m_b < 1$ means the nonlocality of $\Sigma(k,\omega)$ due to the nonlocal nature of the electron-electron interaction and the long-range spatial correlation between electrons. The mass enhancement factor $m^*/m_b \equiv (m_k/m_b)(m_\omega/m_b)$ deduced from the electronic specific heat coefficient $\gamma \sim 22$ mJ/K^2 mol (Ref. 29) and the LDA band-structure calculation is ~ 1.7, which yields the ω mass ratio $m_\omega/m_b \sim 70$. This large m_ω/m_b is consistent with the tiny coherent spectral weight around E_F compared to the large incoherent spectral weight at $|\omega| \gg 0.3$ eV (centered at $|\omega| \sim 1$ eV) since the coherent-to-incoherent spectral weight ratio is given by $\sim m_b/m_\omega : (1-m_b/m_\omega)$. Considering the relatively weak mass enhancement ($m^*/m_b \sim 1.7$) and the extremely strong deviation of the spectra ($m_k/m_b \ll 1$ and $m_\omega/m_b \gg 1$) from the LDA band calculation, we speculate that with decreasing one-dimensional mass anisotropy, m_k/m_b and m_ω/m_b increases and decreases, respectively, approaching a 3D correlated metal.[28]

The exponent θ 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, $\theta = 1/8$,[30] whereas θ can be arbitrarily large when the electron-electron interaction is long-ranged (e.g., in the $1/r^2$ model).[31] Therefore, we conclude that electron-electron interaction between the conduction electrons in (DMe-DCNQI)$_2$Cu is long-ranged. This is in accordance with the small value of m_k/m_b as discussed above. Here it should be noted that the Luttinger-liquid scaling in a 1D metal is guaranteed only below a characteristic electron-electron interaction energy. In the case of long-range Coulomb interaction, the average electron-electron interaction energy is given by $e^2/\varepsilon r_s \sim 0.3$ eV, where $\varepsilon \sim 5$ is the optical dielectric constant and $r_s \sim 7$ Å is the average electron-electron distance. This explains why the Luttinger-liquid scaling is valid up to $|\omega|$ as large as ~ 0.3 eV in the photoemission spectra.

Finally, in the insulating phase, the density of states of a 1D insulator should show a $\sim |\omega|^{-1/2}$ divergence at the band edge irrespective of the interaction form and strength.[17,32] However, Fig. 2 shows that such a divergence is not observed in the spectrum taken at 55 K. The expected divergence may appear on a smaller energy scale than our instrumental resolution or the interchain interaction may have obscured the $\sim |\omega|^{-1/2}$ divergence. The band edge is located ~ 0.1 eV below E_F so that the gap $2\Delta \gtrsim 0.1$ eV. Therefore, $2\Delta/k_BT_t \gtrsim 12$, which is much larger than the mean-field value ~ 3.5, indicating that fluctuation effect or electron correlation effect is strong in this system.

In conclusion, the photoemission spectra of (DMe-DCNQI-d_7)$_2$Cu obey a Luttinger-liquid scaling on a high-energy scale (0.3 eV$\gtrsim |\omega| \gtrsim$0.05 eV) while the intensity at the Fermi level is a 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 θ means that the electron-electron interaction is long-ranged. The insulating gap does not show a $\sim |\omega|^{-1/2}$ divergence, which is expected for a 1D insulator. In order to test the Luttinger-liquid versus Fermi-liquid behavior, systematic studies of various quasi-1D conductors of different mass anisotropies would be required. Angle-resolved photoemission will yield more detailed information about the coherent quasiparticle excitations near E_F and incoherent excitations at higher energies.[26] Detailed studies of quasi-1D insulators would also give useful insight into the 1D versus 3D behavior in strongly correlated systems.

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