Cooperative effects of electron correlation and charge ordering on the metal-insulator transition in quasi-one-dimensional deuterated (DMe-DCNQI)$_2$Cu

T. Takahashi, T. Yokoya, A. Chainani, H. Kumigashira, and O. Akaki

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

R. Kato

Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan

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We study the changes in the electronic structure of a quasi-one-dimensional organic conductor, deuterated (DMe-DCNQI)$_2$Cu, across the CDW/M-I (charge-density-wave/metal-insulator) transition at $T_c = 60$ K, using temperature-dependent (30–300 K) high-resolution photoemission spectroscopy. Above the mean-field (MF) transition temperature ($T_{MF} \sim 4T_c$), the system shows typical metallic behavior with small but finite density of states at E_F. The spectral weight in the vicinity of E_F decreases systematically upon decreasing temperature below T_{MF} even in the metallic phase, resulting in a pseudogap formation above T_c. This behavior continues across T_c and causes the M-I transition. The spectral weight is transferred to energies much larger than the gap, indicating a cooperative effect of strong electron correlation and structural changes which imply decreases in interchain coupling across the M-I transition.

I. INTRODUCTION

Recently, much theoretical and experimental work has been carried out on quasi-one-dimensional (1D) metals with particular emphasis on effects of strong electron-electron correlations in the framework of the Luttinger liquid.[1] One of the peculiar results of studies on a variety of quasi-1D systems using high-resolution photoemission spectroscopy is the absence of a typical Fermi edge in the metallic phase,[2–6] though transport measurements imply a finite density of states (DOS) at the Fermi level (E_F). The single-particular spectral function is expected to show a power-law dependence on energy close to E_F, $\rho(w) \sim w^\theta$, with the exponent θ being the same as for the momentum distribution function.[7] Theoretical predictions based on the 1D Hubbard model with $U = \infty$ or large but finite U show that $\theta = -\frac{3}{8}$ or $\theta \lesssim \frac{1}{8}$, respectively,[8,9] though the experimentally observed θ is generally large with $\theta \gtrsim 1$ (Refs. 3 and 6). These observations indicate the presence of additional effects in real 1D systems. In particular, since 1D metals are inherently unstable with respect to the Peierls-Fröhlich instability causing a lattice distortion that leads to charge-density-wave (CDW) formation and a possibly accompanying metal-insulator (M-I) transition, important changes are expected in the DOS across the transition. In fact, earlier studies on the 1D metals have been carried out on the high-temperature phase of the CDW systems, but there is no clear evidence for changes that can be directly attributed to the theoretically expected changes in the DOS across the Peierls transition.[10]

In this work, we study the CDW transition in a quasi-1D deuterated (DMe-DCNQI-α,α'-d_2)$_2$Cu, where DCNQI = dimethyl-dicyanoquinonediimine [Fig. 1(a)] using high-resolution temperature dependent photoemission spectroscopy. Nondeuterated (DMe-DCNQI)$_2$Cu consists of planar DCNQI molecules stacked along the tetragonal c-axis, producing a quasi-1D $p\pi$ conduction path.[11,12] The copper atoms are tetrahedrally coordinated by N-cyano groups of DCNQI molecules, forming "bridges" between one-dimensional DCNQI columns [Fig. 1(b)]. Thus the interplay between the one-dimensional $p\pi$ electrons and the three-dimensional network via Cu 3d electrons is expected to directly influence the electronic structure in DCNQI-Cu compounds. The nondeuterated (DMe-DCNQI)$_2$Cu remains metallic down to very low temperature at ambient pressure,[11] it being free from the Peierls/CDW transition usually observed in low-dimensional materials. However, it undergoes a M-I transition in a function of temperature under the application of pressure,[13] or on replacing a methyl group by a halogen atom such as bromine [(MeBr-DCNQI)$_2$Cu] (Ref. 14) as well as on deuteration of hydrogen atoms.[15] The M-I transition is accompanied by a tripling of the unit cell along the c-axis establishing a CDW transition. The replacement of the methyl group within a halogen atom as well as deuteration is regarded as a "chemical pressure" effect. The M-I transition is of first order and the magnetic susceptibility in the insulating phase obeys the Curie-Weiss law with the
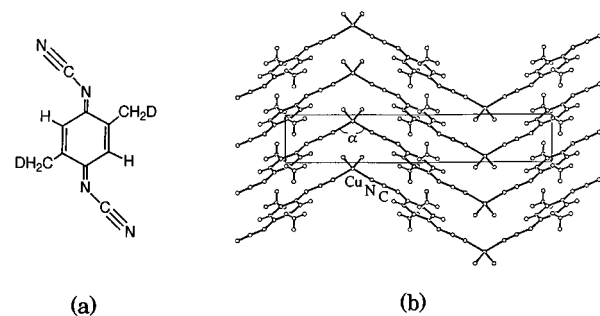

FIG. 1. (a) Molecular structure of DMe-DCNQI-α,α'-d_2 and (b) crystal structure of (DMe-DCNQI-α,α'-d_2)$_2$Cu. For clarity, two of the four DCNQI molecules that coordinate to a Cu atom are omitted.

Curie constant corresponding to $\frac{1}{3}$ mol of Cu^{2+} (Ref. 16), suggesting that a threefold charge ordering along the c axis ($-Cu^{1+}-Cu^{1+}-Cu^{2+}-Cu^{1+}-$) drives the M-I transition. A recent study[17] using x-ray core-level photoemission spectroscopy on *in situ* synthesized compounds has shown that the average valence of Cu atoms is close to 1.33 only for the compound exhibiting a M-I transition, but deviates substantially from this value for the metallic $(DMe-DCNQI)_2Cu$. Deuterated $(DMe-DCNQI-\alpha,\alpha'-d_2)_2Cu$ (hereafter called d_2-DCNQI-Cu) exhibits a CDW/M-I transition at $T_c=60$ K with the properties described above.[18] It is followed by a reentrant metallic phase at 20 K, but unfortunately, due to experimental limitations we could only probe the changes in the DOS down to 30 K. Since it is well known[10] that a decreasing interchain coupling in the Peierls system in the presence of fluctuations leads to a pseudogap formation above T_c and below T_{MF} (mean-field transition temperature, $\sim 4T_c$), we could nonetheless systematically study the changes in the DOS from above T_{MF} to below T_c. Our results show that above T_{MF}, a small but finite DOS is observed at E_F like a typical metal; it decreases systematically in the metallic phase as a function of temperature with a concomitant pseudogap formation above T_c. This spectral change continues across T_c, being responsible for the M-I transition, but the transfer of spectral weight is over a much larger energy range compared to the gap. We attribute this behavior to a cooperative effect of electron-electron correlations and structural change implying decrease in the interchain coupling leading to the CDW formation.

II. EXPERIMENT

Polycrystalline d_2-DCNQI-Cu was synthesized *in situ* in a vacuum chamber directly connected to the photoemission spectrometer as follows: (1) In the synthesis chamber, acetonitrile (CH_3CN) solution containing neutral (DMe-DCNQI-α, α'-d_2) molecules was frozen using liquid nitrogen and the chamber was evacuated to 10^{-7} Torr. (2) After closing the gate value to the pump, the frozen solution was gradually warmed to a liquid at room temperature. The chamber was pumped again after refreezing the solution. The above procedure was repeated several times to purify the solution as well as to obtain a clean ambient. (3) Then a clean copper block was dipped in the solution at room temperature. In the solution, fine black fiberlike crystals of the DCNQI-Cu salt grew on the surface of the copper block. After several hours, the block was totally covered with a thin layer of fiberlike DCNQI-Cu crystals. The block was taken out from the solution and dried under vacuum of 10^{-7} Torr. (4) Without breaking the vacuum, the sample copper block was transferred to the photoemission chamber and mounted on a holder connected to the cold head of a closed-cycle cryostat. The whole process of synthesis was thus carried out under ultrahigh vacuum, with negligible surface contamination due to oxidation. The powder x-ray diffraction pattern of thus prepared sample was compared with that of a single crystal grown by the conventional diffusion method. The patters were identical except for the peak width of the present sample being slightly broader, which is indicative of smaller crystal domain size, and such a comparison has been reported earlier for $(DMe-DCNQI)_2Cu$ (Ref. 19).

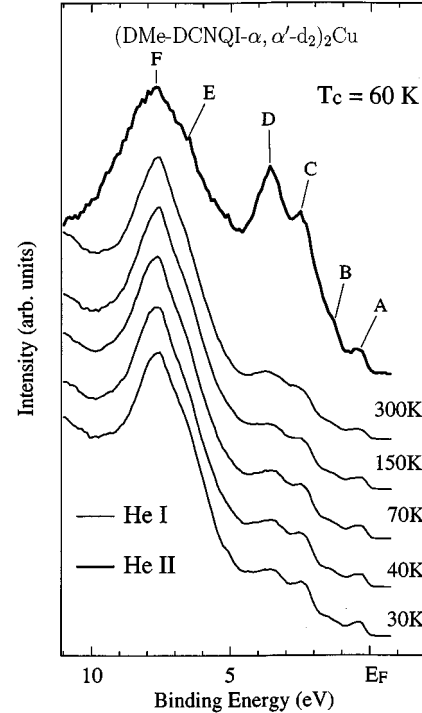FIG. 2. Valence-band photoemission spectra of $(DMe-DCNQI-\alpha,\alpha'-d_2)_2Cu$ across the CDW/M-I transition temperature at $T_c=60$ K measured using He I radiation (21.2 eV). The He II (40.8 eV) spectrum at 300 K is also shown to identify the primarily Cu 3d-derived states.

Photoemission measurements were carried out in a home-built high-resolution photoemission spectrometer that has a VSW 300-mm-diameter hemispherical electron energy analyzer and a high brightness discharge lamp. The instrumental energy resolution was about 45 meV at $T=30$ K as estimated using the Fermi-edge cutoff of gold. The base pressure of the spectrometer was 3×10^{-11} Torr. Photoelectrons were excited using the He I (21.2 eV) and He II (40.8 eV) resonance lines. Prolonged exposure to ultraviolet light resulted in changes in the recorded spectrum as is also known from earlier work on quasi-one-dimensional compounds.[20] So utmost care was taken to obtain reproducible spectra at every temperature from several spots of the sample surface within 10 min of exposure to ultraviolet radiation. Also, the measurements were carried out while cooling and heating by cycling across the transition temperature and the spectral changes were reproducible, indicating that the changes are intrinsic and not due to surface contamination or degradation. The Fermi level of the sample was referred to that of a gold film deposited on the sample at each temperature and its position was accurate to better than 2 meV. The sample temperature was monitored by a Pt resistor embedded in the sample holder to an accuracy of ± 2 K.

III. RESULTS AND DISCUSSION

Figure 2 shows photoemission spectra in the valence-band region of d_2-DCNQI-Cu measured at several temperatures from 30 to 300 K using He I radiation. Also shown is the He II spectrum at 300 K (uppermost spectrum in Fig. 2), from which we identify the primarily Cu 3d-derived contri-

bution to the DOS as its relative photoionization cross section is strongly enhanced compared to the C and N $2p$ states.[21] The spectra show six features marked $A-F$ and it is to be noted that the spectral profile of d_2-DCNQI-Cu closely resembles that of the nondeuterated (DMe-DCNQI)$_2$Cu (Refs. 19 and 22), suggesting that the deuteration does not remarkably modify the gross electronic structure over this wide energy scale. Comparing with earlier photon-energy-dependent photoemission studies[19,22] as well as Hückel molecular orbital calculations,[23] the following assignment is in order. The prominent features E and F at 6–8-eV binding energy are due to the C and N $2p\sigma$ states of the quinone ring. Features C and D at 2–4-eV binding energy are dominated by the Cu $3d$ states, with shoulder B due to the C and N $2p$ states of the cyano group. Note that features C and D have an energy separation of about 1 eV corresponding to the crystal-field splitting expected of Cu in a tetrahedral geometry.[24] The energy position of the Cu $3d$-derived states (2–4 eV) is in contrast to a recent first-principles band-structure calculation in which the Cu $3d$ states are found to occur between 0.5 and 2.0 eV.[25] Feature A is due to the C and N $2p\pi$ states of the cyano group and correspond to the lowest unoccupied molecular orbital band, which is partially occupied and responsible for the changes in the properties as a function of temperature. In order to see the changes in detail, we measure photoemission spectra near E_F with high resolution as a function of temperature.

Figure 3 shows photoemission spectra in the vicinity of E_F measured at five different temperatures from 30 K (below the M-I transition temperature $T_c = 60$ K) to 300 K (above the mean-field transition temperature $T_{MF} \sim 240$ K). At 300 K, the photoemission band corresponding to feature A in Fig. 2 is broad and shows a small but finite intensity at E_F like that of a typical metal. With decreasing temperature, the feature gradually becomes narrower and the intensity of E_F decreases systematically even in the metallic phase. The decrease in the photoemission intensity at E_F continues across T_c. To see these changes clearly, we have superimposed the 70-K spectrum on the 150- and 40-K spectra in Fig. 3. In going from 150 to 70 K and further to 40 K, the spectral weight at and within ~ 300 meV of E_F decreases and is simultaneously transferred to energies up to more than 600 meV. This indicates that we have a pseudogap forming even before the M-I transition at 60 K, which continues further on decreasing temperature. Such a transfer of spectral weight and a pseudogap formation are expected to occur due to change of the interchain coupling in the presence of fluctuations,[10] but in the calculated case, the changes in the DOS are expected to occur only within 2Δ from E_F, where Δ is the gap value. The estimated gap from resistivity measurements is about 100 meV,[15] and is much larger than T_c or T_{MF}. While photoemission spectra at 40 and 30 K have negligible intensity at E_F consistent with the semiconducting character below 60 K, a clear energy gap at E_F is not observed. But as shown in the inset to Fig. 3, a shift of about 100 meV in the leading edge is observed in going from 300 to 30 K. It is to be remarked that the signature of fluctuation effects, namely, diffuse scattering in the XRD, which should be observed above T_c along with the pseudogap formation, is not seen for the deuterated compounds.[15,18] On the other hand, it is known that the local arrangement around the cop-
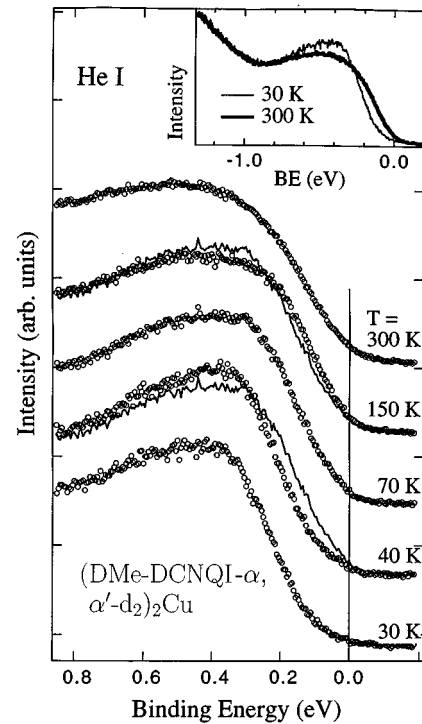

FIG. 3. Photoemission spectra in the vicinity of the Fermi level of (DMe-DCNQI-α,α'-d_2)$_2$Cu at temperatures from below the CDW transition temperature $T_c = 60$ K to above the mean-field transition temperature $T_{MF} \sim 240$ K. The photoemission intensity is normalized to the area under the curve until 0.8-eV binding energy. The 70-K spectrum is superimposed on the 150- and 40-K spectra with solid lines to see the temperature-induced change. The inset shows a comparison of the 30- and 300-K spectra near E_F, indicating a shift of about 100 meV in the leading edge and a simultaneous transfer of spectral weight extending to more than 600 meV.

per ion, in particular the bond angle of N-Cu-N (α) [see Fig. 1(b)] plays a key role for the occurrence of the phase transition in DCNQI-Cu compounds.[15,18] This is because for a copper ion in a tetrahedral geometry with T_d symmetry ($\alpha = 109.5°$), the crystal-field splitting results in triply degenerate t_{2g} (d_{xy}, d_{yz}, d_{zx}) and doubly degenerate e_g (d_{z^2}, $d_{x^2-y^2}$) orbitals. In the crystal, the copper ion is in the distorted tetrahedral D_{2d} crystal field with a larger α value (124.8° at room temperature), resulting in further splitting of the t_{2g} orbital with the b_{2g} (d_{xy}) pushed above the e_g (d_{xz} and d_{yz}) orbitals. The energy separation between the b_{2g} and e_g orbitals increases with increasing α value, which increases gradually in the metallic phase on decreasing temperature, but changes sharply across the CDW transition to 128.5° (Refs. 14 and 15). The strong p-d mixing[17,25,26] then guarantees that states at E_F responsible for the transition are directly affected as a consequence of the change in α. Note that we too observe a bigger change across 70–40 K compared to 150–70 K, being consistent with the changes in α as a function of temperature. Also note that the change in α may be viewed as a decrease in interchain coupling, which causes the transfer of spectral weight as discussed earlier. Furthermore, it would also cause a redistribution of charge between the copper ions and the DCNQI stacks, facilitating the threefold charge-ordered Peierls state.

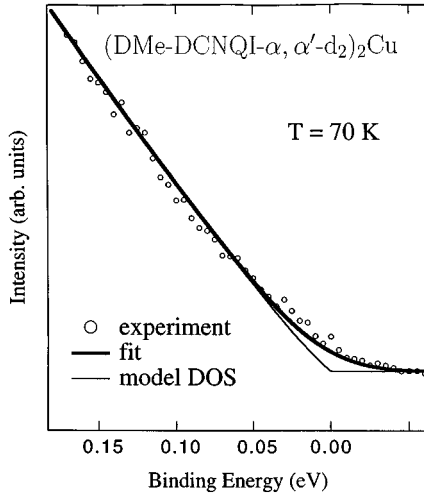Having established the role of structural changes to the

FIG. 4. The photoemission spectrum at 70 K, just above $T_c=60$ K, showing the absence of a Fermi edge. A least-squares fit (thick line) using a model DOS $\rho(w)=Aw^{\theta}$ (thin line) gives an exponent $\theta=1.1$.

M-I transition we next point out the role of electron-electron correlations in d_2-DCNQI-Cu. An important indicator of correlation effects comes from Fig. 4 where we plot the 70-K spectrum near E_F compared with a least-squares fit to the data using a power-law model DOS. A power-law model DOS was used because it is the asymptotic energy dependence of the spectral function calculated for a Luttinger liquid at zero temperature,[7] and the spectral function for the real case including temperature is not yet known. The model DOS was appropriately broadened by the instrumental and thermal ($\sim 3.8 k_B T$) broadening at 70 K. As is seen in Fig. 4, a good fit was obtained using the model DOS $\rho(w)=Aw^{\beta}$, giving $\theta=1.1$. This procedure has been used to show that the spectral weight near E_F is suppressed compared to the case of a typical Fermi liquid[3,6] and is believed to be representative of Luttinger liquid behavior. Also, the photoemission intensity at E_F seems strongly suppressed compared to the calculated density of states obtained from band-structure calculations.[25] While the calculated electronic specific-heat coefficient γ is 12.8 mJ/mol/K^2 (Ref. 25) the experimental value is about 20 mJ/mol/K^2 (Ref. 27), and the discrepancy may be due to correlation effects. Though there are no Hall effect measurements reported to date, the high electrical conductivity and Pauli susceptibility in the metallic phase [the experimental χ of $\sim 0.5 \times 10^{-3}$ emu/mol (Ref. 28) is also larger than the calculated χ of $\sim 0.18 \times 10^{-3}$ emu/mol (Ref. 25] are again indicative of a large density of states at E_F. Thus the negligible intensity at E_F in the 70-K photoemission spectrum seems to be in contrast to the calculated DOS

as well as the thermodynamic measurements. This observation is, however, consistent with similar recent photoemission studies on other quasi-one-dimensional metals,[2-6] suggesting that the quasi-one-dimensionality results in modifying the photoemission spectral function. It is to be pointed out that very recent theoretical work[8] for the 1D Hubbard model shows that the DOS at E_F can be finite for the $U=\infty$ case with a dependence on energy near E_F with $\theta=-\frac{3}{8}$. The important observation we would like to point out is that while the spectral weight is suppressed near E_F, it gets transferred to higher energies over an energy range much larger than the gap. A similar observation in the high-temperature metallic phase has been reported for the CDW transition in $K_{0.3}MoO_3$ (Ref. 2). Qualitatively speaking, this is consistent with the fact that since correlation effects suppress spectral weight near E_F, the transfer of weight takes place to energies only beyond this suppression, in contrast to the theoretical expectation for the uncorrelated Peierls transition.[9] A recent theoretical work has shown that the M-I transition in the DCNQI-Cu salts can be considered as a cooperative CDW transition in the quasi-1D DCNQI stacks and a Mott transition in the Cu $3d$-derived states.[29] Our results also indicate that combined effects of electron-electron correlations and structural changes are responsible for the changes in the DOS as a function of temperature.

IV. CONCLUSION

We studied the changes of the electronic structure of quasi-1D deuterated d_2-DCNQI-Cu across the CDW transition, from above the mean-field transition temperature T_{MF} (~ 240 K) to below the M-I transition temperature T_c (60 K). A small finite DOS at E_F above T_{MF} indicates typical metallic behavior, which decreases systematically with a transfer of spectral weight over an energy range much larger than the gap and causes the M-I transition at T_c. The spectral changes are attributed to cooperative effects of electron-electron correlations, which suppress the spectral weight near E_F in the metallic phase above T_c, and structural changes which imply decrease in the interchain coupling across the CDW transition.

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