Collapse of the charge order in $(DI\text{-}DCNQI)_2Ag$ by dimensional crossover

T. Itou,[1,2,*] K. Kanoda,[1,2] K. Hiraki,[3] T. Takahashi,[3] K. Murata,[4] and T. Matsumoto[5]
[1]*Department of Applied Physics, University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan*
[2]*CREST, Japan Science and Technology Agency (JST), Saitama 332-0012, Japan*
[3]*Department of Physics, Gakushuin University, Toshima-ku, Tokyo 171-8588, Japan*
[4]*Graduate School of Science, Osaka City University, Sumiyoshi-ku, Osaka 558-8585, Japan*
[5]*National Institute for Materials Science, Tsukuba, Ibaraki, 305-0047, Japan*
(Received 5 July 2005; published 22 September 2005)

The nature of the electron liquid phase in a quasi-one-dimensional charge-ordering system composed of uniform chains is investigated by means of comparison between the parallel and perpendicular resistivity under pressures. At lower pressures, the liquid phase is the one-dimensional liquid where electrons are confined in the conducting chains. At higher pressures where the charge-ordering transition vanishes, however, it acquires the three-dimensional Fermi-liquid nature at low temperatures away from the one-dimensional liquid. This result shows that the collapse of the charge order is due to the "dimensional crossover."

DOI: 10.1103/PhysRevB.72.113109 PACS number(s): 71.30.+h, 71.20.Rv

Quasi-one-dimensional electronic systems with quarter-filled bands often exhibit charge ordering, where electrons are localized on alternate sites in a chain, due to the electron correlation. In particular, the charge ordering in the TMTTF (tetramethyltetrathiafulvalene) salts has been intensively studied.[1–17] They have, however, inherent lattice-dimerization and interchain anisotropy, which complicate the situation. The former causes a two-body electron-electron (*e-e*) umklapp scattering in addition to a four-body *e-e* umklapp scattering[18] and thus the insulating phases have not only the charge-ordering nature but also the Mott-insulating nature. The latter causes the intricate hierarchy structure in the dimensionality; in the low- and high-energy scale the systems are regarded as three-dimensional (3D) and 1D ones, respectively, while in the intermediate-energy scale they can be regarded as 2D systems.

$(DI\text{-}DCNQI)_2Ag$ under the present investigation has a tetragonal interchain arrangement without the intrachain dimerization and thus is regarded as the prototype of quasi-one-dimensional systems.[19] The space group of the crystal structure is $I4_1/a$.[20,21] In the crystal, the planer DI-DCNQI molecules stack along the *c* axis, forming one-dimensional conducting columns. Since the monovalent Ag^+ ion coordinated between the DCNQI columns forms the closed shell, the DI-DCNQI molecule has a half of conduction electron on average. Although this system has an ideal quasi-one-dimensional quarter-filled DCNQI-LUMO (lowest unoccupied molecular orbital) band, the resistivity shows insulating behavior below room temperature.[21] This is revealed to come from the charge order (or its fluctuations) by nuclear magnetic resonance (NMR) (Ref. 22) and x-ray diffraction (XRD) (Ref. 23) experiments, which indicate charge disproportionation on alternate molecules in a column below $\sim$210 K. This is representative of the charge ordering in the weakly coupled chains with quarter-filled bands.

Our previous study showed that the charge order in $(DI\text{-}DCNQI)_2Ag$ is collapsed by pressure and established its pressure-temperature phase diagram.[24] As the mechanism of the pressure-induced charge-ordering collapse, two scenarios are conceivable. One is the "dimensional crossover," namely, the confinement-deconfinement crossover, which has often been discussed in TMTTF/TMTSF salts.[11–17] Under low pressures, the electrons are confined in the conducting chains and behave as the one-dimensional liquid. The commensurate quarter-filling of the one-dimensional band gives rise to the singular enhancement of four-body *e-e* umklapp scattering, which causes a charge gap accompanied by $4k_F$-charge-ordering fluctuations, if the electron correlation exceeds a certain value. The fluctuations grow to a long-range ordering at lower temperatures by three dimensionality. If pressure makes the bare interchain transfer integral larger than the intrachain charge gap, the system comes to acquire the three-dimensional Fermi-liquid nature at low temperatures, where the umklapp scattering is depressed by warping of the Fermi surfaces and consequently the charge-ordered state is suppressed. In this case, the charge-ordering collapse by pressure accompanies the deconfinement, or the lifting of the one-particle dimensionality. The other scenario is a picture of three-dimensional melting. The three-dimensional Fermi liquid needs stronger electron correlation to give way to the charge-ordered state than the one-dimensional liquid, because the singularity of the umklapp scattering is suppressed. According to the first-principles band-structure calculation,[25] however, the bandwidth of DI-DCNQI compounds is narrow compared with TMTTF/TMTSF salts, and is likely compared to the intersite Coulomb interaction. This feature could make the charge ordering feasible even if $(DI\text{-}DCNQI)_2Ag$ has one-particle three dimensionality. In this scenario, the collapse of the charge order by pressure is attributed to the increase of the bandwidth.

The purpose of the present work is to clarify which mechanism is the case, by measuring resistivity parallel and perpendicular to the conducting *c* axis (hereafter denoted by $\rho_\parallel$ and $\rho_\perp$, respectively).

High-quality single crystals whose forms are rectangular parallelepipeds with clean planes and edges are required particularly for measuring $\rho_\perp$. After several trials, we succeeded in growing single crystals with a typical size of $0.03\times0.03\times3$ mm. The magnetic impurity, which gave the Curie component in the susceptibility, was less than 0.1% in molecular concentration. Pressure was applied with the dual-

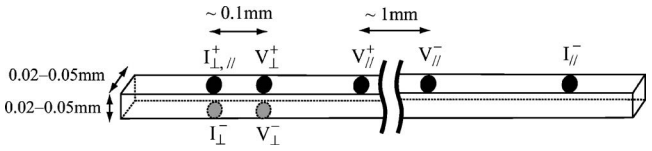

FIG. 1. Geometry of the four-terminal configuration of the electrodes.

structured cell made of BeCu and NiCrAl. Pressure medium used is the Daphne 7373 oil. As it is solidified around 19 kbar at room temperature, we heated the pressure cell up to about 50 °C by a ribbon heater wound around the cell to keep the applied pressure hydrostatic, when pressurizing the samples beyond 18 kbar. We measured $\rho_{\parallel}$ and $\rho_{\perp}$ down to 1.6 K under pressures up to 23 kbar in the four probe arrangement. Figure 1 shows the four-terminal configuration of the electrodes for measuring $\rho_{\parallel}$ and $\rho_{\perp}$ simultaneously for one crystal. The terminals were connected with 15-μm-ϕ gold wires, using the conductive carbon paste. The measurements were performed under different levels of injected currents and the data in the ohmic region were taken as the intrinsic data free from the Joule heating. When electric current is applied along the c axis, current density is expected to be almost uniform over the cross section of the sample because of the sample shape of a fine needle. Thus, the absolute value of $\rho_{\parallel}$ calculated from the measured resistance and the geometrical sizes is meaningful within the ambiguity of a factor of two or less in the estimation of the sample cross-sectional area. On the other hand, when $\rho_{\perp}$ is measured in the configuration of Fig. 1, the current density is not uniform, which does not allow one to estimate the absolute value of $\rho_{\perp}$. Thus, we show only normalized values, $\rho_{\perp}(P,T)/\rho_{\perp}(1\ \text{bar}, 300\ \text{K})$, in this report.

Figure 2 shows the temperature dependence of $\rho_{\parallel}$ and normalized $\rho_{\perp}$ at several pressures below 17.8 kbar. Under pressures below 15.1 kbar, $\rho_{\perp}$ shows nonmetallic behavior in the whole temperature range although $\rho_{\parallel}$ behaves metallically at high temperatures. According to the conventional Fermi-liquid theory, $\rho_{\parallel}$ and $\rho_{\perp}$ should have much the same temperature dependence due to an almost identical scattering rate even if the system has an anisotropic band structure with a large $\rho_{\parallel}/\rho_{\perp}$ value. This situation is realized in $(DI\text{-}DCNQI)_2Cu$ salts,[26] where a three-dimensional π-d networked Fermi liquid is likely realized. The contrasting behavior in the present system means that the Fermi-liquid picture breaks down, or that the one-dimensional liquid with the electrons confined in the chains is realized.

The one-dimensional liquid with a commensurate quarter-filled band often becomes insulating at low temperatures due to the singular four-body e-e umklapp scattering, where the charge fluctuations develop. In such a case, the long-range ordering of the charge fluctuations should occur due to the three dimensionality at a much lower temperature than the insulating crossover temperature. This scenario explains why there exists a wide fluctuation region of the charge order in $(DI\text{-}DCNQI)_2Ag$ as was revealed in the previous paper.[24]

By the way, the confinement of electrons is generally achieved only in higher energy region than the interchain transfer energy. According to the first-principles band-

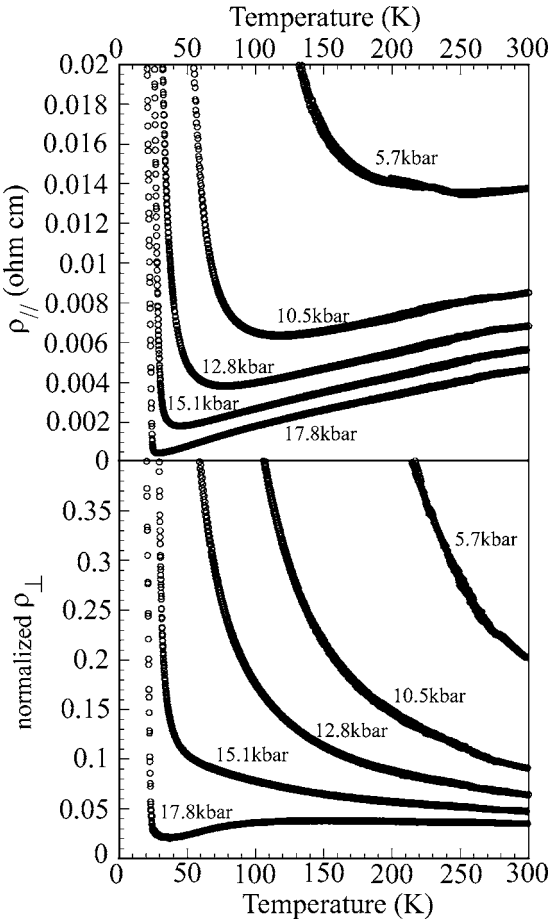

FIG. 2. Temperature dependence of $\rho_{\parallel}$ (upper) and normalized $\rho_{\perp}$ defined by $\rho_{\perp}(P,T)/\rho_{\perp}(1\ \text{bar}, 300\ \text{K})$ (lower) at several pressures below 18 kbar.

structure calculations,[25] however, the bare transfer energy of $(DI\text{-}DCNQI)_2Ag$, $t_{\perp}$, at ambient pressure is 0.03 eV, which is larger than the thermal energy below room temperature. In the context of the confinement, our result implies that the effective interchain transfer integral $t_{\perp}^{\text{eff}}$ is diminished by electron correlation, as was also discussed in the TMTTF/TMTSF salts.[11–17]

The data of $\rho_{\perp}$ under higher pressures are shown in Fig. 3. In contrast to the behavior below 15.1 kbar, the metallic temperature dependence appears in $\rho_{\perp}$ under 17.8 kbar and higher pressures. At 17.8 kbar, the temperature dependence of $\rho_{\perp}$ is nonmetallic around room temperature, while it crosses over into the metallic behavior around 100 K. This reflects that the system begins to acquire the Fermi-liquid nature at low temperatures away from the one-dimensional liquid. At about 40 K, the system becomes insulating in both directions. Under further higher pressures, the nonmetallic behavior of $\rho_{\perp}$ at high temperatures is gradually changed to the metallic one, which shows that the system gets closer to the Fermi-liquid state. Particularly at low temperatures, the system is considered to be in the Fermi-liquid state. Note that, it is in this pressure region that the metal-insulator transition observed in $\rho_{\parallel}$ changes from the second order into the first order and at last vanishes.[24] Above 19.3 kbar, unfortunately we could not measure reliable $\rho_{\perp}$ behavior at low

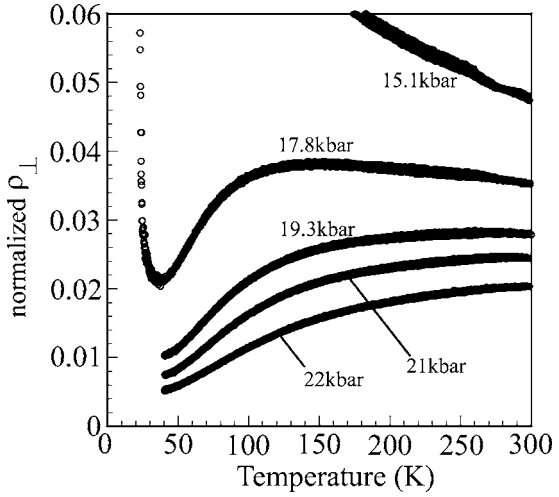

FIG. 3. Temperature dependence of normalized $\rho_\perp(\rho_\perp(P,T)/\rho_\perp(1\ \mathrm{bar},300\ \mathrm{K}))$ at several pressures above 15 kbar.

temperatures because the observed resistance becomes quite low while contact resistance increases much more by an unknown reason. Thus, above 19.3 kbar, we only show the reliable data above 40 K.

Figure 4 shows the pressure-temperature phase diagram of this system. As discussed in our previous paper,[24] closed circles indicate the second-order transition temperatures defined by that giving the peak in $d \ln \rho_\parallel / d(1/T)$, open squares indicate the temperature of minimum in $\rho_\parallel$ as a measure of the fluctuation onset, and closed squares show the first-order transition. The characteristic temperatures probed by the present transverse-transport measurements are indicated by open and closed triangles. Open triangles, which are defined by the $\rho_\perp$ peak, indicate the onset temperatures of the crossover from the one-dimensional liquid to the Fermi liquid. Closed triangles, where $\rho_\perp$ shows inflection against temperature (i.e., $d^2\rho_\perp/dT^2=0$), mean the offset of the crossover.

The phase diagram indicates that the liquid phase at low pressures is the confined one-dimensional liquid, but comes to acquire the Fermi-liquid nature at higher pressures where the charge order vanishes. The collapse of charge order is, therefore, attributed to the "dimensional crossover" due to an increase of $t_\perp^{\mathrm{eff}}$. Under lower pressures, the electrons are confined in the DCNQI chains, where the singular four-body *e-e* umklapp scattering leads to the $4k_\mathrm{F}$ charge order. The electrons are deconfined under higher pressures, where depression of the umklapp scattering leads to the vanishing of $4k_\mathrm{F}$ charge order. In this context, there is a possibility that the first-order insulating transition appearing at high pressures is not the charge-order one driven by the four-body *e-e* umklapp scattering but a density-wave transition driven by the nesting of Fermi surfaces, because it appears in the pressure region where the Fermi-liquid feature is enhanced.

Lastly, we mention the temperature dependence of $\rho_\parallel$ at low temperatures in the high-pressure region above 20 kbar. In this region, electrons are deconfined and thus the Fermi-liquid state is considered to be realized; in other words, the quasiparticles introduced by Landau are well-defined. Nevertheless, a curious temperature dependence, $\Delta\rho_\parallel \propto T^3$, was observed below 30 K, as reported in our previous paper.[24]

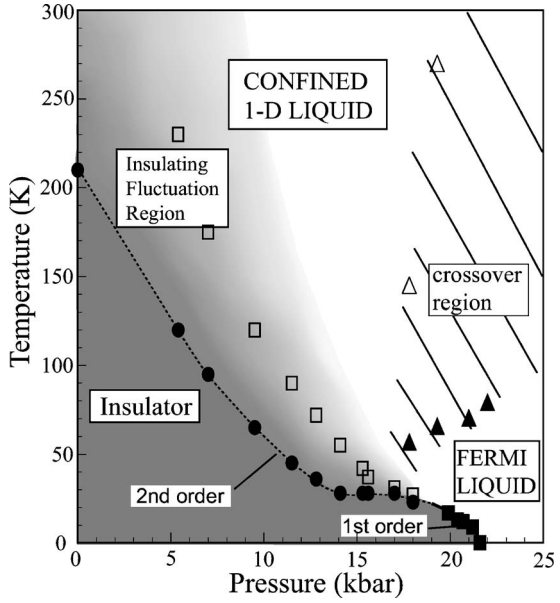

FIG. 4. Summarized *P-T* phase diagram of $(\mathrm{DI\text{-}DCNQI})_2\mathrm{Ag}$. Closed circles indicate the second-order insulating transition and open squares indicate the fluctuation onset, while closed squares shows the first-order transition. (See Ref. 24.) Open triangles show onset temperatures of the crossover from the one-dimensional liquid to the Fermi liquid, which is defined by the peak of $\rho_\perp$. Closed triangles mean the offset of the crossover defined by a inflection point of $\rho_\perp$.

We consider that it is due to the absence of the two-body umklapp scattering of the quasiparticles which causes the normal T^2 dependence.

In conclusion, we measured the parallel and perpendicular resistivity $\rho_\parallel$ and $\rho_\perp$ of $(\mathrm{DI\text{-}DCNQI})_2\mathrm{Ag}$ under pressures to clarify why the charge order is collapsed by pressure. Under lower pressures, $\rho_\parallel$ and $\rho_\perp$ show contrasting behavior, which means that electrons are confined in the one-dimensional chains. Under higher pressures, however, electrons become deconfined and at the same time the charge order vanishes. The charge order is, therefore, caused by an enhanced *e-e* umklapp scattering which is present only in the one-dimensional liquid. Pressurizing causes the "dimensional crossover" which makes the charge order unstable. Different from TMTTF/TMTSF salts, the insulating phase of $(\mathrm{DI\text{-}DCNQI})_2\mathrm{Ag}$ is the pure charge-ordered state without Mott-insulator nature and its phase diagram has no intermediate 2D-conductor region. The revealed phase diagram epitomizes the "dimensional crossover" physics in the quasi-one-dimensional charge-ordered system with a quarter-filled band.

The authors thank K. Miyagawa, H. Taniguchi, and K. Yokogawa for experimental support and H. Fukuyama, N. Nagaosa, M. Imada, Y. Nogami, J. Kishine, M. Tsuchiizu, H. Seo, A. Furusaki, and H. Yoshioka for valuable discussions. This work was partially supported by MEXT Grant-in-Aid for Scientific Research on Priority Area of Molecular Conductors (No. 15073204) and by JSPS Grant-in-Aid for Scientific Research (No. 15104006).

*Present address: Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-8501, Japan.

[1] H. Seo and H. Fukuyama, J. Phys. Soc. Jpn. **66**, 1249 (1997).
[2] S. Mazumdar, S. Ramasesha, R. T. Clay, and D. K. Campbell, Phys. Rev. Lett. **82**, 1522 (1999).
[3] R. T. Clay, S. Mazumdar, and D. K. Campbell, Phys. Rev. B **67**, 115121 (2003).
[4] F. Nad, P. Monceau, and J. M. Fabre, Eur. Phys. J. B **3**, 301 (1998).
[5] F. Nad, P. Monceau, C. Carcel, and J. M. Fabre, Phys. Rev. B **62**, 1753 (2000).
[6] D. S. Chow, F. Zamborszky, B. Alavi, D. J. Tantillo, A. Baur, C. A. Merlic, and S. E. Brown, Phys. Rev. Lett. **85**, 1698 (2000).
[7] F. Zamborszky, W. Yu, W. Raas, S. E. Brown, B. Alavi, C. A. Merlic, and A. Baur, Phys. Rev. B **66**, 081103(R) (2002).
[8] T. Nakamura, T. Nobutoki, Y. Kobayashi, T. Takahashi, and G. Saito, Synth. Met. **70**, 1293 (1995).
[9] T. Nakamura, R. Kinami, T. Takahashi, and G. Saito, Synth. Met. **86**, 2053 (1997).
[10] S. Fujiyama and T. Nakamura, Phys. Rev. B **70**, 045102 (2004).
[11] C. Bourbonnais and D. Jérome, Science **281**, 1155 (1998).
[12] V. Vescoli, L. Degiorgi, W. Henderson, G. Gruner, K. P. Starkey, and L. K. Montgomery, Science **281**, 1181 (1998).
[13] J. Kishine and K. Yonemitsu, Int. J. Mod. Phys. B **16**, 711 (2002).
[14] M. Tsuchiizu and Y. Suzumura, Phys. Rev. B **59**, 12326 (1999).
[15] Y. Suzumura and M. Tsuchiizu, J. Phys. Chem. Solids **62**, 93 (2001).
[16] S. Biermann, A. Georges, T. Giamarchi, and A. Lichtenstein, cond-mat/0201542 (unpublished).
[17] J. Moser, M. Gabay, P. Auban-Senzier, D. Jérome, and J. M. Fabre, Eur. Phys. J. B **1**, 39 (1998).
[18] See, for example, H. Yoshioka, M. Tsuchiizu, and Y. Suzumura, J. Phys. Soc. Jpn. **69**, 1594 (2000), and references therein.
[19] DI-DCNQI stands for an organic molecule, 2,5-diiodo-*N*, *N*′-dicyanoquinonediimine.
[20] R. Kato, H. Kobayashi, and A. Kobayashi, J. Am. Chem. Soc. **111**, 5224 (1989).
[21] K. I. Hiraki and K. Kanoda, Phys. Rev. B **54**, R17276 (1996).
[22] K. Hiraki and K. Kanoda, Phys. Rev. Lett. **80**, 4737 (1998).
[23] Y. Nogami, K. Oshima, K. Hiraki, and K. Kanoda, J. Phys. IV **9**, 357 (1999).
[24] T. Itou, K. Kanoda, K. Murata, T. Matsumoto, K. Hiraki, and T. Takahashi, Phys. Rev. Lett. **93**, 216408 (2004).
[25] T. Miyazaki and K. Terakura, Phys. Rev. B **54**, 10452 (1996).
[26] Y. Kashimura, H. Sawa, S. Aonuma, R. Kato, H. Takahashi, and N. Mori, Solid State Commun. **93**, 675 (1995).