Transport criticality of the first-order Mott transition in the quasi-two-dimensional organic conductor κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Cl$

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The Mott transition in a quasi-two-dimensional organic conductor, κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Cl$ was investigated by resistance measurements under continuously controllable He gas pressure. We constructed the resistance diagram as functions of temperature and pressure, which has unveiled the phase diagram and the critical characteristics of the Mott transition. The observation of the huge resistance jump by nearly two orders of magnitude provides an unambiguous evidence for the first-order nature of the Mott transition. At elevated temperatures, the jump is diminished gradually and vanishes at a critical end point 38 K, above which the resistance variation against pressure is continuous. It is also found that the end point is featured by critical divergence in pressure derivative of resistance, $|(1/R)\partial R/\partial P|$, which was consistent with the prediction of the dynamical mean-field theory and has phenomenological correspondence with the liquid-gas transition. The present results provide the experimental basis for physics of the Mott transition criticality.

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The Mott transition is one of the metal-insulator transitions (MIT) which are representative phenomena in highly correlated electrons. The family of quasi-two-dimensional layered organic conductors κ-$(BEDT\text{-}TTF)_2X$ are model systems for the study of the Mott transition in two dimensions, where BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene and X stands for various kinds of anions. They have layered structures composed of the conducting BEDT-TTF layers and the insulating X layers. In the conducting layer, the BEDT-TTF dimers form anisotropic triangular lattice. In a dimer, two degenerate highest occupied molecular orbitals (HOMO) belonging to the neighboring BEDT-TTF's are split into bonding and antibonding HOMO's, which form respective bands due to the interdimer transfer integrals. According to the band-structure calculations, the two bands are separated in energy. Since one hole is introduced to one dimer by the anion X, the upper band, which is the antibonding HOMO band, is half filled.[1]

The salt of $X=Cu[N(CN)_2]Cl$ (denoted as κ-Cl hereafter) is an antiferromagnetic insulator (AFI) with a commensurate order at ambient pressure and thus is understood as a Mott insulator driven by the strong electron correlation.[2] When κ-Cl is pressurized, it becomes metallic and undergoes a superconducting transition at $T_{SC}\sim 13$ K under a pressure of 30 MPa.[3] It is considered that the pressure induces the Mott transition. On the other hand, the salts of $X=Cu[N(CN)_2]Br$ and $X=Cu(NCS)_2$ behave like the pressurized κ-Cl with superconducting ground states.[4] The metallic states are found to have strong electron correlation by the ^{13}C-NMR study.[5] Thus, the pressure and the replacement of anion X, which is equivalent to discrete pressure control,[1] are quite effective to drive the Mott transition in the organics. Moreover, since they have no orbital degree of freedom, they give a prototype of the Mott transition. These aspects make organics suitable for pursuing the fundamentals of the Mott transition both experimentally[1] and theoretically.[6–8]

The behavior near the MIT is a key to comprehension of the Mott transition. However, since most of the previous experiments have been performed under the chemical or discrete pressure control,[3,5,9] the critical nature of Mott transition has remained to be seen. Recently, ac susceptibility and NMR studies for κ-Cl under continuously controllable He gas pressure by Lefebvre *et al.* have revealed (i) the first-order nature of the Mott transition, suggested (ii) the existence of the critical end point, and given the pressure-temperature (P-T) phase diagram.[10] Moreover, the ultrasonic study by Fournier *et al.* has shown an anomaly related to (iii) the divergence of charge compressibility at the possible end point.[11] These three characters seem to support the criticality predicted by the dynamical mean-field theory (DMFT).[12–14] In order to confirm these qualitative features and go further to a substantial stage in the study of the Mott transition criticality, the electron-transport measurements, which can detect the MIT directly, are highly desired.

Quite recently, Limelette *et al.* have reported transport measurements of κ-Cl under He gas pressure in Ref. 15, where the hysteretic resistive anomaly associated with the Mott transition was observed and the possible end point was also supported. However, the resistive transition was *smooth* and the criticality on the end point was not clear, leading to the conclusion that the Mott transition in κ-Cl includes a complex physics and can not be described simply by the DMFT,[12] which predicts that the Mott transition is in the same regime of the liquid-gas transition. Thus, the criticality of the Mott transition is controversial. In the present work, we have performed resistance measurements for κ-Cl crystals with high quality under the He gas pressure. In contrast with the previous report,[15] we observed the first-order Mott transition with huge *discontinuous resistance jump* and *sharp criticality* of the end point. These behaviors, which are consistent with those of the liquid-gas transition in the Ising universality class as is suggested by the DMFT, give the experimental basis for the criticality of the Mott transition.

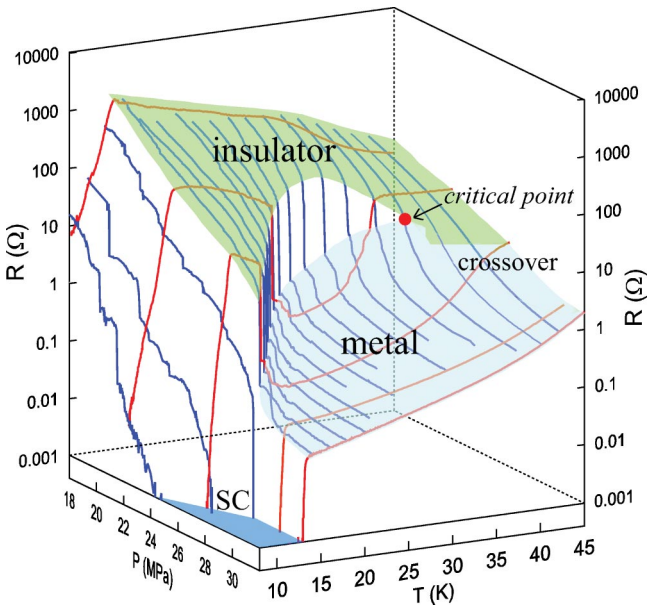

FIG. 1. (Color online) Overview of the resistance behavior around the Mott transition against pressure and temperature. The resistance (vertical axis) is in a logarithmic scale. The resistance curves are taken under isobaric temperature sweep and isothermal pressure sweep, respectively.

Single crystals were grown by electrochemical oxidation of BEDT-TTF in the mixture of 1.1.2-trichloroethane and 10% ethanol in the presence of CuCl, tetraphenylphosphonium-$[N(CN)_2]$. In one or two months, single crystals were obtained. The size of the κ-Cl crystal used here is $1.8\times1.4\times1.2$ mm^3. The sample was mounted in the Be-Cu cell and pressurized by compressing the He gas. The in-plane resistance was measured with the standard dc four-probe method under both isothermal pressure sweep and isobaric temperature sweep. In the isothermal process, the pressure sweep was made so slowly that the temperature deviation was within ± 50 mK. During the isobaric temperature sweep, which requires more care because the temperature sweep inevitably causes pressure change, the He gas inflow (outflow) to (from) the cell was finely controlled so that the pressure deviation was maintained within ± 0.05 MPa. To ensure the hydrostatic nature of pressure, the present experiments were performed except the P-T region of the He solidification. Below T_{SC}, the measurements were also made under a field of 11 T normal to the conducting layer, which is much higher than the upper critical field H_{C2} in the temperature range studied here.

The overall feature of the present results around the Mott transition is visualized in a pressure-temperature-resistance (P-T-R) diagram shown in Fig. 1, where blue and red curves are data taken under the isothermal pressure sweep and the isobaric temperature sweep, respectively. At low pressures, the system is highly resistive with nonmetallic temperature dependence ($\partial R/\partial T<0$), while at high pressures it is conductive with metallic temperature dependence ($\partial R/\partial T>0$). The transition between the two regimes occurs with a huge discontinuous resistance jump on a well-defined line in the P-T plane. It is also seen that the resistive jump becomes diminished at elevated temperatures and eventually vanishes at a certain critical point, above which the resistance variation is continuous. Replacing the label of z axis, R (Ω), in Fig. 1 by volume V of the classical liquid-gas system, one can see intuitively that the present P-T-R diagram of the Mott transition has correspondence with the textbook P-T-V diagram of the liquid-gas transition. At low temperatures below 13 K, superconductivity appears at a high-pressure region and even in the low-pressure side resistance decrease with temperature is observed. The data of the pressure dependence are classified into three temperature regions of $T>38$ K, 38 K$>T>$13 K ($\sim T_{SC}$), and $T<13$ K, which are discussed in detail below.

As an example of the behaviors at higher temperatures above 38 K, the data at 40.1 K are shown in Fig. 2(a), where neither anomaly nor hysteresis is observed. Since the temperature derivative of resistance, $\partial R/\partial T$, is changed from negative to positive by pressure (see Fig. 1), the resistance variation against pressure is regarded as crossover from insulator to metal. As seen in Fig. 2(b), the variation gets steeper with temperature decreased. One can define a crossover pressure at which the pressure derivative of resistance, $|(1/R)\partial R/\partial P|$, shows a peak as shown in Fig. 3. The peak grows as temperature approaches 38.1 K, where it is divergent (see the inset of Fig. 3), namely, the $|(1/R)\partial R/\partial P|$ is divergent around the critical point of $(P_C,T_C)=(23.2\ \text{MPa},38.1\ \text{K})$ roughly as $\sim(T-T_C)^{-(0.9\pm0.1)}$ against temperature along the crossover line. This transport criticality observed here should be related to divergence in the charge compressibility suggested experimentally[11] and predicted theoretically.[13,14] As for the liquid-gas transition, the compressibility $|(1/V)\partial V/\partial P|$ is divergent at the critical point. The exponent which we extracted above corresponds to the so-called "γ" in the scaling law. Although the use of $|(1/R)\partial R/\partial P|$ in order to extract γ in the Mott transition leaves room to be considered, the tentative value of 0.9 ± 0.1 is close to $\gamma\sim1$ in the mean-field theory and $\gamma\sim1.25$ in the three-dimensional Ising model.

Below 38 K, the resistive crossover is changed into the resistive transition of the first-order, which is evidenced by hysteresis and the resistance jump ΔR. The observation of the clear resistance jump means not only the first-order nature but also the consistency with the DMFT, which predicts the criticality relevant to the vanishing of discontinuous nature around the end point like the discontinuity of the volume, ΔV, at the liquid-gas transition. Shown in Fig. 2(c) are the data at 14.1 K, where the magnitude of the jump at 28.1 MPa amounts to nearly two orders of magnitude and a small hysteresis of ~0.3 MPa larger than the experimental error of ~0.1 MPa is appreciable. The huge resistive jump indicates a bulky transition. Additional small jumps and slightly irreversible resistance traces extended around the bulk transition are likely to come from inhomogeneous internal pressure in the sample, although the possibility of intrinsic phase separation with only tiny fraction of the secondary phase is not ruled out. As temperature is increased, the magnitude of the resistive jump decreases with the hysteresis diminished and eventually vanishes at the critical point (23.2 MPa, 38.1 K),[16] where the first-order MIT changes to the crossover. We

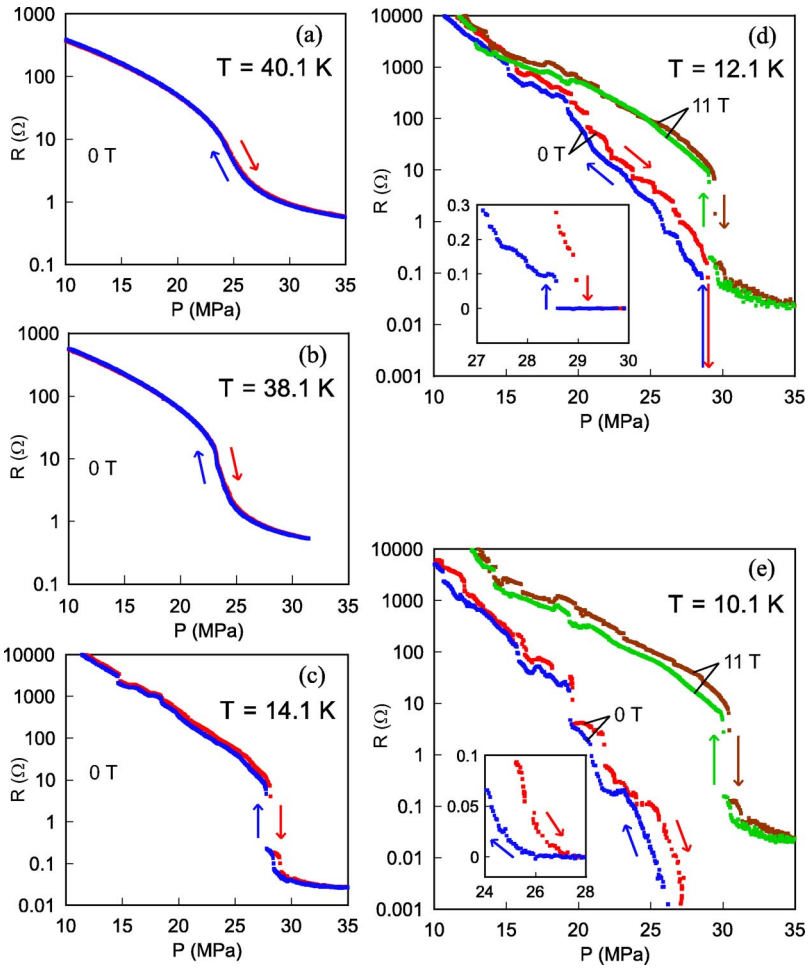

FIG. 2. (Color online) Isothermal pressure dependence of resistance under ascending and descending pressures at a zero field [(a)–(e)] and a field of 11 T [(d) and (e)]. Insets of (d) and (e) are enlarged views of each main panel in linear scales around the pressure where the resistance vanishes under a zero field.

suppose that the absence of the resistance jump and sharp criticality in the previous report[15] is ascribable to the effect of disorder, which can make the simple nature inherent in the Mott transition sophisticated.

As is seen above, the analogy between the system volume in the liquid-gas transition and the resistance in the Mott transition goes well. The resistance is not a thermodynamic quantity but a transport coefficient determined by the numbers of the electron double occupancies, holes, scattering rate, and so on. However a basis for the intuitive analogy is given by a theoretical treatment,[17] which points out that the resistivity shows a singular behavior at the critical point and discontinuity at the first-order phase boundary, playing the role of the order parameter of Mott transition in the vicinity of the critical point. Understanding of the criticality in the microscopic level is a future issue.

At lower temperatures below 13 K, superconductivity, which is a specific phase to the electronic systems, appears under pressure. The data at 12.1 K under a zero field and 11 T are shown in Fig. 2(d). At a zero field, the resistance suddenly vanishes around 28.5–29.0 MPa with large hysteresis against pressure, indicating the bulky superconductor-insulator transition (SIT) of the first order. By application of 11 T, the SIT was converted into MIT with the transition pressure nearly unchanged. It is seen that the field dependence of resistance is large even in the low-pressure region below 28.5 MPa. It is considered that tiny superconductor (SC) domains are induced progressively in the insulating host phase by pressure at a zero field but are destroyed at 11 T.[18] At 10.1 K [Fig. 2(e)], the resistance under a zero field decreases continuously and falls below the noise level around ~27 MPa, where the growing SC fraction is considered to be percolated before occurrence of the bulky SIT at a higher pressure. Actually a bulky MIT under 11 T was at a higher pressure, 30.4 MPa, as seen in Fig. 2(e). This is consistent with the previous work by NMR,[10], which shows coexistence of AFI and SC in a wide pressure range and drastic exchange of the volume fractions of AFI and SC phases at a certain pressure (broken lines shown in Fig. 4).

Figure 4 shows the P-T phase diagram of κ-Cl, where the closed and open circles represent points giving the resistance jumps (first-order transition) and maximum $|(1/R)\partial R/\partial P|$ (crossover point), respectively, and the superconducting transition defined by the resistance vanishing is marked by closed triangles. Figure 4 is consistent with the Lefebvre's diagram,[10] after which the broken line is drawn as a bulk SIT line. In the insulating region, AF phase appears at low temperatures,[2,10] although the phase boundary is not drawn here. The competition between the neighboring AF insulating and SC phases as in the κ-(BEDT-TTF)$_2X$ family[19] has often been discussed in terms of SO(5) theory,[20,21] which treats the AF and SC orders in a unified way of the five-dimensional superspin. The SO(5) theory tells that the phase

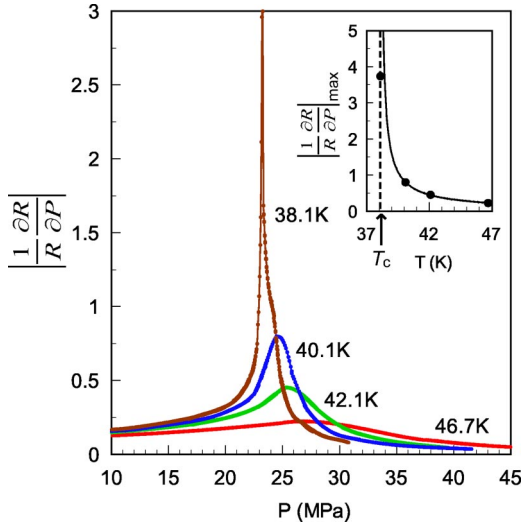

FIG. 3. (Color online) The pressure derivative of resistance, $|(1/R)\partial R/\partial P|$, against pressure at several temperatures. The value of $|(1/R)\partial R/\partial P|_{max}$ is plotted against temperature in the inset. The arrow indicates the critical temperature 38.1 K determined by the disappearance of the resistance jump. The divergence is described by the solid curve of $\sim(T-T_C)^{-0.9}$ with T_C of 38.1 K.

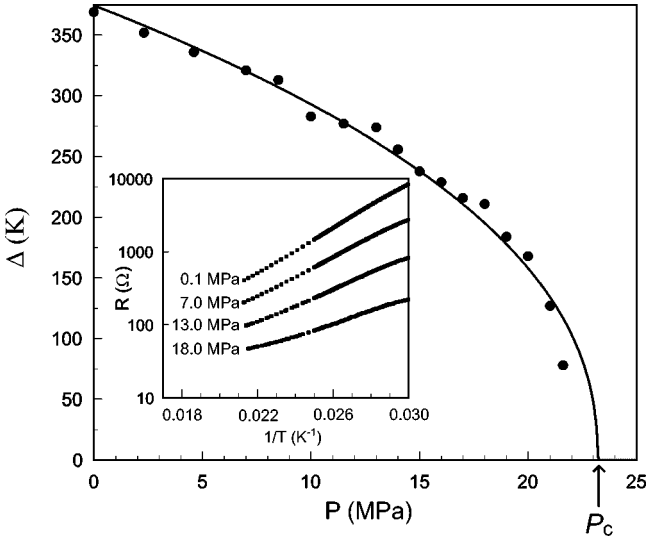

FIG. 5. Pressure-dependence of the effective charge gap. The gap Δ defined by $R\sim\exp(\Delta/T)$ is estimated from the Arrhenius plot of resistance as shown in the inset. The arrow indicates the critical pressure 23.2 MPa determined by the disappearance of the resistance jump. The pressure dependence of the gap is described by the solid curve of $\sim(P_C-P)^{0.4}$ with P_C of 23.2 MPa.

diagram has a bicritical point at the end of a first-order transition line separating the AF and SC phases in the phase diagram. The present results show that the first-order line is extended to the high-temperature nonordered region. This is beyond the scope of the SO(5) theory, which needs to be extended so as to incorporate the Mott transition.[17]

We now examine the charge gap profile on the insulating side near the critical point. The inset of Fig. 5 shows the Arrhenius plot of the resistance. In a restricted temperature range from 50 K to 33 K, the data are nearly on straight lines, the slope of which gives the activation energy. The effective charge gap Δ defined by $R\sim\exp(\Delta/T)$ is shown against pressure in the main panel of Fig. 5. It is seen that the gap reasonably closes around the critical point. The overall profile of the gap closing seems to be described by a form $\Delta(P)\sim(P_C-P)^{0.4\pm0.1}$ with $P_C=23.2$ MPa. This is an additional criticality of the Mott transition and unique to the electronic systems. In the context of the DMFT, Kotliar *et al.* predicted that the density of states at the Fermi energy, $\rho(0)$, shows continuous change against temperature and the change is sharpened at the end point.[12] The similar behavior is also expected against pressure. The criticality of the charge gap can be related to the growth of $\rho(0)$ and its neighboring profile.

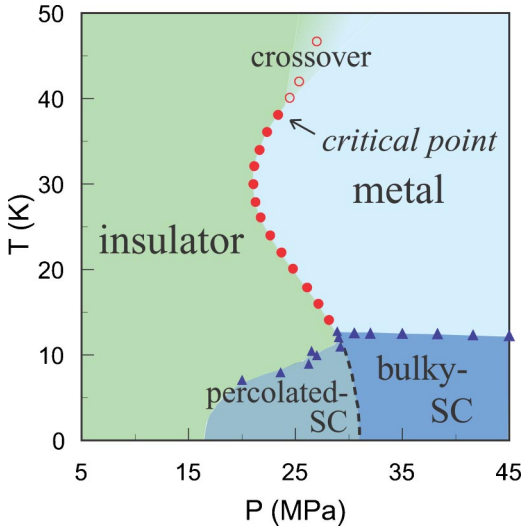

FIG. 4. (Color online) Pressure-temperature phase diagram of κ-Cl. Closed circles and open circles represent points at which resistance shows jump (first-order transition) and $|(1/R)\partial R/\partial P|$ is maximum (crossover point), respectively. The superconducting transition defined by the resistance vanishing is marked by closed triangles. The broken line is taken after Lefebvre *et al.* (Ref. 10) as the bulky SIT boundary.

To conclude, the Mott transition in the quasi-two-dimensional organic system κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Cl$ is accompanied by the gigantic resistive jump and the first-order transition line has an end point at $(P_C,T_C)=(23.2\text{ MPa},38.1\text{ K})$, where the transition is changed to the crossover. The end point has the following critical behaviors; (i) the pressure derivative of resistance, $|(1/R)\partial R/\partial P|$, is divergent, reflecting the divergence in the charge compressibility, (ii) the resistance jump vanishes, and (iii) the effective charge gap closes. The criticalities (i) and (ii) establish the phenomenological correspondence between the Mott transition of correlated electrons and the liquid-gas transition of molecules or atoms as predicted by the dynamical mean-field theory. The present results provide the experimental basis for physics of the Mott transition criticality.

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