Transport criticality of the first-order Mott transition in a quasi-two-dimensional organic conductor, $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl

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An organic Mott insulator, $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl, was investigated by resistance measurements under continuously controllable He gas pressure. The first-order Mott transition was demonstrated by observation of clear jump in the resistance variation against pressure. Its critical endpoint at 38 K is featured by vanishing of the resistive jump and critical divergence in pressure derivative of resistance, $\left| \frac{\partial R}{\partial T} \right|$, which are consistent with the prediction of the dynamical mean field theory and have phenomenological correspondence with the liquid-gas transition. The present results provide the experimental basis for physics of the Mott transition criticality.

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, $\kappa$-(BEDT-TTF)$_2$X, 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. In the conducting layer, the BEDT-TTF dimers form anisotropic triangular lattice, and the dimer band is half-filled [1]. The salt of X = Cu[N(CN)$_2$]Cl (denoted as $\kappa$-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 $\kappa$-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. The pressure is quite effective to drive the Mott transition in organics, which are highly compressible. 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 [4] and theoretically [5, 6, 7].

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 [8, 9, 10], the critical nature of Mott transition has remained to be seen. Recently, ac susceptibility and NMR studies for $\kappa$-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 endpoint, and given the pressure-temperature ($P$-$T$) phase diagram [11]. Moreover, the ultrasonic study by Fournier et al. has shown an anomaly related to (iii) the divergence of charge compressibility at the possible endpoint [12]. These three characters seem to support the criticality predicted by the dynamical mean field theory (DMFT) [11, 12, 13]. 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 $\kappa$-Cl under He gas pressure in Ref.14, where the hysteretic resistive anomaly associated with the Mott transition was observed and the possible endpoint was also supported. However, the resistive transition was smooth and the criticality on the endpoint was not clear, leading to the conclusion that the Mott transition in $\kappa$-Cl include a complex physics and can’t be described simply by the DMFT [11], 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 $\kappa$-Cl crystals with high quality under the He gas pressure. In contrast with the previous report [14], we observed the first-order Mott transition with huge discontinuous resistance jump and sharp criticality of the endpoint. 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.

The size of the $\kappa$-Cl crystal used here is $1.8 \times 1.4 \times 1.2$ 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 $\pm 50$ 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 ($P$) - temperature ($T$) - resistance ($R$) 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 non-metallic 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 to 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, $|\frac{\partial R}{\partial P}|$, 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 $|\frac{\partial R}{\partial P}|$ is divergent around the critical point of $(P_C, T_C) = (23.2 \text{ MPa}, 38.1 \text{ K})$ roughly as $\sim (T - T_C)^{-(0.9 \pm 0.1)}$ against temperature along the crossover line. This transport criticality observed here should be related to divergence in the charge compressibility suggested experimentally [10] and predicted theoretically [12, 13]. As for the
FIG. 3: The pressure derivative of resistance, $|\frac{1}{R} \frac{∂R}{∂P}|$, against pressure at several temperatures. The value of $|\frac{1}{R} \frac{∂R}{∂P}|_{\text{max}}$ is plotted against temperature in the inset. The arrow indicates the critical temperature, 38.1 K, determined by 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.

liquid-gas transition, the compressibility, $|\frac{1}{V} \frac{∂V}{∂P}|$, is divergent at the critical point. The phenomenological correspondence implies the possibility that the Mott transition belongs to the same universality class with the liquid-gas transition, namely the Ising universality class. The exponent which we extracted above corresponds to so-called '$\gamma$' in the scaling law. Although the use of $|\frac{1}{R} \frac{∂R}{∂P}|$ in order to extract '$\gamma$' in the Mott transition leaves room to be considered, the tentative value of $0.9 \pm 0.1$ is close to $\gamma \sim 1$ in the mean field theory and $\gamma \sim 1.25$ in the 3D 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. 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 endpoint 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) [15], where the first-order MIT changes to the crossover. We suppose that the absence of the resistance jump and sharp criticality in the previous report [14] is ascribable to the effect of disorder, which can make the simple nature inherent in the Mott transition sophisticated.

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 SC-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 SC domains are induced progressively in the insulating host phase by pressure at a zero field but are destroyed at 11 T [16]. At 10.1 K (Fig. 2 (e)), the resistance under a zero field decreases continuously and falls below the noise level around $\sim 27$ 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. 4(c). This is consistent with the previous work by NMR [9], which shows coexistence of AFI and SC phases at a certain pressure (broken lines shown in Fig. 4).

Figure 4 shows the $P$-$T$ phase diagram of $\kappa$-Cl, where the closed and open red circles represent points giving the resistance jumps (first-order transition) and maximum $\partial R/\partial P$ (crossover point), respectively, and the superconducting transition defined by the resistance vanishing is marked by closed blue triangles. Figure 4 is consistent with the Lefebvre’s diagram [11], after which the broken line is drawn as a bulk SIT line.

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, $\Delta$, 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 of $\Delta(P) \sim (P_C - P)^{0.4 \pm 0.1}$ 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 predicted that the density of states at the Fermi energy, $\rho(0)$, shows continuous change against temperature and the change is sharpened at the endpoint [11]. 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.

To conclude, the Mott transition in the quasi-two-dimensional organic system, $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl, is accompanied by the gigantic resistive jump and the first-order transition line has an endpoint at $(P_C, T_C) = (23.2$ MPa, 38.1 K), where the transition is changed to the crossover. The endpoint has the following critical behaviors: (i) the pressure derivative of resistance, $\frac{1}{\Omega} \frac{\partial R}{\partial P}$, 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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