Pressure-Induced Mott Transition in an Organic Superconductor with a Finite Doping Level

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Phys. Rev. Lett. **114**, 067002 — Published 9 February 2015

DOI: 10.1103/PhysRevLett.114.067002

Pressure-induced Mott transition in an organic superconductor at a finite doping level

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Abstract: We report the pressure study of a doped organic superconductor with Hall coefficient and conductivity measurements. We find that maximally enhanced superconductivity and a marginal-Fermi liquid appear around a certain pressure where mobile carriers increase critically, suggesting a possible quantum phase transition between strongly and weakly correlated regimes. This observation points to the presence of a criticality in Mottness for a doped Mott insulator with tunable correlation.

Main Text

The interaction strength and band filling are the parameters controlling electronic phases in strongly correlated electron systems, as depicted in Fig.1(a). For repulsively interacting electrons of the same number as the lattice sites (half-filled band), the on-site Coulomb repulsion U, when exceeding the kinetic energy characterized by the bandwidth W, prevents electrons from doubly-occupying a site, thus causing them to localize at each site. This interaction-induced insulator is called a Mott insulator. Decreasing U (or increasing W) by pressure along the blue line in Fig.1(a) causes the first-order Mott transition from the Mott insulator to a Fermi liquid or a superconductor at the Mott boundary $(U/W)_c$ [1], where a discontinuous increase in double occupancy occurs; roughly speaking, electrons are allowed to

doubly-occupy a site. If the band filling is varied from a half by removing electrons from the Mott insulator, the doped holes give rise to fascinating phenomena such as high-T_c superconductivity [2], non-Fermi liquid [3, 4], pseudogap [5], and self-organization of nanostructure [6-8]. However, questions remain regarding the case in which U/W is varied under doping because a doped conductor with tunable U/W across the critical value have not been available. The present study tackles this issue experimentally with an organic conductor, the highly compressible nature of which permits a wide range of variation in U/W.

The family of layered organic conductors, κ-$(ET)_2X$, with half-filled bands is well recognized as model systems for Mott physics under U/W control [9-12], where ET denotes bis(ethylenedithio)tetrathiafulvalene. Pressure experiments for these conductors have demonstrated a first-order phase transition from a Mott insulator to a Fermi liquid (FL) or a superconductor [13, 14] and have revealed its criticality [15]. The purple arrow in Fig.1(a) exemplifies a range of the pressure study for κ-$(ET)_2Cu_2(CN)_3$ (κ-$Cu_2(CN)_3$). While most κ-ET compounds have half-filled bands, the title compound κ-$(ET)_4Hg_{2.89}Br_8$ (κ-HgBr) with the nonstoichiometry in the Hg composition [16, 17] is an exceptional doped system and shows the non-monotonic pressure dependence of superconducting (SC) transition temperature T_c [18] and non-Fermi-liquid (NFL)-like resistivity [19] unlike the case of the half-filled κ-$(ET)_2X$. Assuming that the valences of Hg and Br ions are +2 and -1, respectively, the valence of an ET dimer is +1.11 due to the nonstoichiometry, while that in half-filled κ-$(ET)_2X$ is +1 where X is monovalent anion. Indeed, Raman spectroscopy has confirmed that the valence of the dimer deviates from unity [20]. According to the estimate of U/W based on the band-structure calculations, as described later in detail, κ-HgBr has a much larger value of U/W than those of half-filled Mott insulators such as κ-$Cu_2(CN)_3$ [21-23] and should be in a strongly correlated state, where electrons remain considerably prevented from the double occupancy while the 11%

hole doping makes the system metallic as located in Fig. 1(a) of the band filling-U/W phase diagram. Thus, the pressure study of κ-HgBr affords a chance to draw together two physics regimes under the variations of the correlation strength and band filling. With the aim of investigating how the doped system with strong correlation behaves as the prohibited double occupancy is allowed, we examine the nature of mobile carriers under pressure variation and characterize the normal-state transport properties and superconductivity in a pressure-temperature diagram.

To characterize the pressure dependence of the nature of mobile carriers in κ-HgBr, we measured the Hall coefficient with four probe technique as employed in ref. [24] The normal and SC states under pressure are characterized by contactless conductivity measurements, which utilize the technique of AC susceptibility measurements in the MHz frequency range. This method probes the resistivity in the normal state because the eddy current due to electromagnetic induction causes a diamagnetic response, which yields the characteristic length of flux penetration, namely the skin depth, δ (the so-called skin effect). Because δ depends on the resistivity, an analysis of the diamagnetic response enables us to evaluate the resistivity [25]. AC field was applied perpendicular to the conducting plane of the sample to probe the in-plane resistivity $\rho_{//}$. This method is superior to the conventional four-terminal method for the present study in that a single experimental run for an identical crystal yields information on both the normal-state transport and the SC diamagnetism probing the SC volume fraction. Details of experimental and analysis are described in supplemental material [26]. The single crystals of κ-HgBr used herein were grown by standard electrochemical methods.

The pressure dependence of the Hall coefficient R_H becomes more remarkable at lower temperatures (Fig. 1(b)). At 10 K, R_H steeply decreases for pressures up to 0.5 GPa and suddenly turns to leveling off. Note that the drastic change in R_H occurs in a metallic state,

which is reported to be stable [16, 18, 19]. Above 0.6 GPa, both magnitude and pressure dependences of R_H are similar to those of the half-filled metallic system κ-$(ET)_2Cu[N(CN)_2]Br$ [24], the R_H values of which well correspond to the cross-sectional area of Fermi surfaces as in other κ-ET compounds in a conventional metallic state [24, 32]. Therefore, κ-HgBr under pressures above 0.6 GPa is considered to be in a conventional metallic state with a large Fermi surface as in κ-$(ET)_2Cu[N(CN)_2]Br$. However, the enormously enhanced R_H values of κ-HgBr in the low-pressure range cannot be understood within the framework of the conventional metal in a weakly correlated regime because band filling is not likely to change under pressure as well as half-filled κ-ET compounds. Strong electronic correlation at ambient or low pressures is indicated by significantly enhanced electronic specific heat coefficient and nuclear magnetic resonance (NMR) relaxation rate [33, 34] and thus is likely responsible for the large R_H values in the low pressure. There are several ways to interpret the enhancement of R_H, as proposed theoretically in a strongly correlated regime [35-37]. A simple and widely argued scenario is that the prohibition of double occupancy decreases the density of mobile carriers. Simply assuming that only doped carriers are mobile, the mobile carrier density n equals to 0.11 per site, which corresponds to 5.0×10^{-2} cm^3/C in $1/ne$, where e is the elementary charge. The values of R_H below 0.4 GPa are of the order of this value. Another scenario is that anisotropic carrier conduction due to the enhanced spin fluctuations differentiates R_H from the value of the conventional metal as argued in the fluctuation-exchange theory [36] and t-t'-J model [37]. Considering that the spin fluctuations are enhanced due to the prohibition of double occupancy, both scenarios suggest that there occurs an anomaly in double occupancy around 0.5 GPa. The compressibility of $1/R_H$, which measures the density of mobile carriers, exhibits a sharp peak near 0.5 GPa, (see the inset of Fig. 1) [38]. Thus, 0.5 GPa is considered to be a critical pressure for the double occupancy, pointing to a sharp change from a strongly correlated state, in which

the double occupancy is strongly prohibited, to a FL (see also Fig.1(a)). In the heavy-fermion compound $YbRh_2Si_2$, where magnetic field is the tuning parameter of quantum criticality, R_H rapidly changes against field around the quantum critical point, and the slope of R_H against field increases sharply as temperature is lowered [39]. κ-HgBr shares the feature, as seen in the main panel of Fig.1 (b), indicating that the crossover from the strongly correlated state to FL state gets sharper at lower temperatures. However, the low-temperature sharpening of the crossover appears more moderate than in $YbRh_2Si_2$. This is possibly associated with the inhomogeneous nature of the strongly correlated state below 0.5 GPa and/or disorder, as discussed later.

SC diamagnetic responses are observed below the temperatures indicated by arrows in Fig. 2(a) and are imposed on eddy-current-induced diamagnetism in the normal state (discussed below). At ambient pressure and 0.2 GPa, the absolute value of χ_{rf}' extrapolated to 0 K did not reach the value of perfect diamagnetism, suggesting that both SC and non-SC regions coexist, where χ_{rf}' is the real part of the AC susceptibility. At 0.4 GPa and higher, however, the sample becomes fully superconducting. We confirmed the dome structure of T_c near 0.5 GPa (Fig. 2(b)). A SC transition was not observed above 1.7 GPa in the present study, which indicates that the SC transition observed above this pressure in the previous four-probe resistivity measurement [19] was not a bulk transition. Because the spatial inhomogeneity of SC at 0.2 GPa and lower is eliminated by the pressure, the emergence of inhomogeneity is likely inherent of the strongly correlated regime.

In the normal state, diamagnetic responses due to the skin effect were observed, and the in-plane resistivity $\rho_{//}$ was obtained from the analysis of AC susceptibility χ_{rf}'. Paramagnetic contribution, which is the order of 10^{-5} in κ-HgBr [33], is negligibly small in comparison to χ_{rf}', which is the order of 10^{-1} in the present measurements. As described in detail in supplementary information, the $\rho_{//}$ values are reliable when skin depth δ is shorter than sample size r. We

checked the reproducibility of their pressure and temperature dependence although absolute values $\rho_{//}$ are different from those measured for other samples by a factor of 3. Figure 3(a) shows $\rho_{//}$ for several pressures. At a low pressure of 0.3 GPa, $\rho_{//}$ exhibits a convex curve as a function of temperature, which characterizes the strongly correlated bad metal. At intermediate pressures, 0.6 GPa and 1.1 GPa, $\rho_{//}$ exhibits a linear temperature dependence down to T_c, clearly indicating the NFL (more specifically called marginal-Fermi liquid here) behavior that persists to T_c. At 1.4 GPa and higher, $\rho_{//}$ exhibits concave curves at low temperatures, where $\rho_{//}$ is well approximated by a form of $\rho_{//} = \rho_o + A T^2$. However, this behavior appears to cross over to a linear temperature dependence at higher temperatures (Fig. 3(b)). To further examine the FL and NFL regions in the pressure-temperature phase diagram, we performed an analysis to determine the "local" exponent, α, which is defined by $\alpha = d(\log(\rho_{//} - \rho_o))/d(\log(T))$, where ρ_o is the residual resistivity determined by fitting the form of $\rho_{//} - \rho_o \sim T^{\alpha}$ to the resistivity data below 15 K. The values of α are represented by a range of colors in the temperature-pressure plane in Fig. 4. The unexpected exponent of $\alpha < 1$ (corresponding to the concave curve) in the red-colored region well below 0.5 GPa likely reflects an inhomogeneous state leading to the imperfect SC discussed above. NMR line broadening observed below 40 K at ambient pressure is also an indication of inhomogeneity [33]. In the presence of strong electron correlation, doping is argued to cause spatially inhomogeneous phases because of their energetically competing electronic states [40-42], where disorder may work for the appearance of the inhomogeneity through spatially pinning and/or amplifying the inhomogeneity. The inhomogeneity in κ-HgBr may be a hallmark of a strongly correlated state. In between the red-colored region of the strongly correlated bad metal and the blue-colored FL region, a marginal-Fermi liquid region of $\alpha \sim 1$ appears and becomes confined between 0.5 GPa and 1.0 GPa at low temperatures. The linear-temperature dependence of resistivity is a hallmark of

marginal-Fermi liquid as observed in heavy electron systems, where the behavior appears around a quantum critical point separating the magnetically ordered phase and the heavy-electron state. Considering that the critical pressure of the double occupancy probed by the Hall coefficient falls in this range, the marginal-Fermi liquid behavior is most likely a manifestation of the critical fluctuations between the strongly correlated state and the FL.

Figure 4 indicates that as U/W decreases, the strongly correlated bad metal with inhomogeneous nature transforms into a FL through a marginal-Fermi liquid, the region of which becomes narrower in pressure at lower temperature to reside near the top of the SC dome. These features suggest that the crossover from the strongly correlated state to the FL may be sharpened into a quantum phase transition near the critical value, $(U/W)_c$. This is regarded as a generalization of Mott transition into a non-half-filled case in that the metal-to-metal transition (or sharp crossover) in the present doped case and the insulator-to metal transition in the non-doped case are both associated with a drastic change in Mottness, namely the degree of double occupancy.

We mention the possible effect of disorder or inhomogeneity. The narrowing of the marginal-Fermi liquid region toward low temperature in the present system is not so sharp as in $YbRh_2Si_2$ although sharper than in the ion pnictides, $BaFe_2(As_{1-x}P_x)_2$, supposedly quantum critical materials [43]. While disorder only causes to increase the residual resistivity in a Fermi liquid, it can be more significant in a critical region; that is, the non-negligible disorder indicated by the relatively large residual resistivity (~1 mΩcm) comparable to the Mott-Ioffe-Regel limit, most likely due to anion nonstoichiometry, may render the intrinsic phase transition less sharp [44]. Yet, the transition from the strongly correlated state with inhomogeneous nature may be unconventional. A quantum transition or a weak first-order transition as theoretically predicted in a clean limit [45] can become crossover-like in reality.

However, the anomalies around 0.5 GPa do not originate from disorder-induced phase transition, such as Anderson localization, which contradicts the maximum in the pressure dependence of T_c at 0.5 GPa and the finite carrier density below 0.5 GPa indicated by $1/R_H$, whose temperature dependence is shown in supplementary information, although there possibly exists an insulating phase in a hypothetical negative pressure range. Whether quantum phase transition exists in doped systems has been an intensively debated issue related to the high-T_c superconductivity [4, 46-52]. The present study shows that a quantum phase transition or a sharp crossover accompanies SC dome under variation of correlation strength.

The case for the critical value, $(U/W)_c$, in the present doped system should correspond to the Mott transition in the half-filled case. Thus, we compare $(U/W)_c$ of κ-HgBr with that of a half-filled system with a similar lattice geometry, κ-$Cu_2(CN)_3$, which exhibits a Mott transition at 0.15 GPa, to extend our discussion toward a comprehensive understanding of the band filling-U/W phase diagram (Fig.1(a)). The incommensurate structure of κ-HgBr makes the first-principle calculation difficult, so we employed the calculations based on extended Huckel and tight binding approximations. Although the absolute value of U/W depends on the methods of the calculations [21, 53], it is meaningful to compare the values calculated by the same method. At ambient pressure, the U/W values are 1.1 in κ-HgBr and 0.9 in κ-$Cu_2(CN)_3$, according to ref. [21]. Assuming that U/W decreases at a rate of approximately 4%/GPa for both compounds similarly to the case of κ-$(ET)_2Cu(NCS)_2$ [54], $(U/W)_c$ is estimated to be 1.07 for κ-HgBr and 0.88 for κ-$Cu_2(CN)_3$. Referring to these values, the doped and undoped compounds under pressure variation are located in the band filling-U/W phase diagram, as shown in Fig. 1(a). When moving from κ-$Cu_2(CN)_3$ to κ-HgBr in the diagram, the $(U/W)_c$ value is increased possibly due to doping. The mobile carriers generated by the doping enhance the screening effect and weakens the effective interaction, which explains the increase in $(U/W)_c$.

In conclusion, the pressure study of an organic superconductor with a band filling away from a half revealed that the top of the superconducting dome, the appearance of marginal-Fermi liquid behavior and a change in the electronic homogeneity all occur around a certain value of U/W where the density of mobile carriers shows a critical increase. In terms of the band filling-U/W phase diagram, the present observation adds information on the transition in U/W while at a finite doping level.

Acknowledgements We thank K. Murata for useful suggestions on high-pressure techniques. This work was supported in part by JSPS KAKENHI under Grant Nos. 20110002, 25220709, 24654101, and 11J09324 and the US National Science Foundation under Grant No. PHYS-1066293 and the hospitality of the Aspen Center for Physics.

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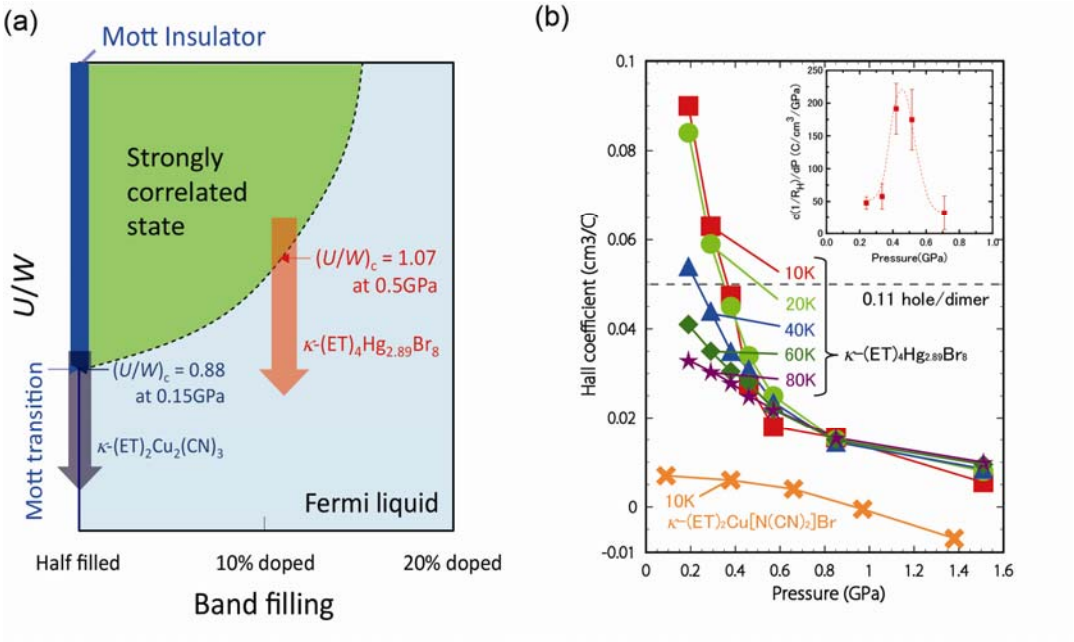

Figure 1 Generic U/W-carrier density phase diagram. (a) Schematic band filling-U/W phase diagram based on experimental results for κ-ET compounds. The double occupancy is considered to become allowed at the critical value in the doped organic conductor κ-$(ET)_4Hg_{2.89}Br_8$ under pressure as well as in the undoped systems. The critical value of U/W increases with doping. (b) Pressure dependence of R_H for κ-$(ET)_4Hg_{2.89}Br_8$ at several temperatures (the present study) and for the half-filled metallic system κ-$(ET)_2Cu[N(CN)_2]Br$ at 10K [24]. The inset shows pressure derivative of $1/R_H$ for κ-$(ET)_4Hg_{2.89}Br_8$ at 10K. The drastic pressure dependence suggests that 0.5 GPa is a critical pressure for electrons occupying a site.

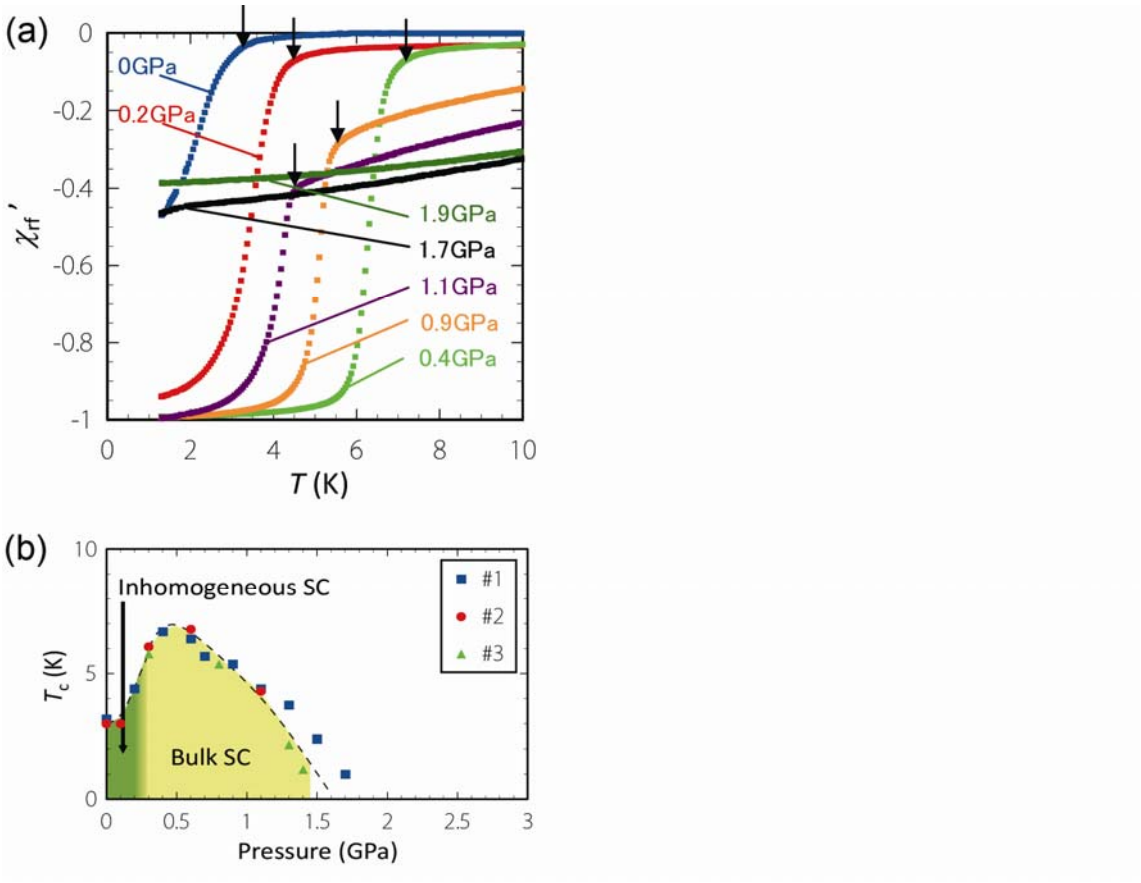

Figure 2 Superconducting transition probed by AC susceptibility and pressure dependence of the transition temperature. (a) χ_{rf}' of κ-$(ET)_4Hg_{2.89}Br_8$ under pressure. The arrows indicate SC transitions. The value of χ_{rf}' at pressures between 0.3 GPa and 1.3 GPa sharply saturates to the same value, which is interpreted as perfect diamagnetism. (b) Pressure dependence of T_c for the three samples investigated, #1, #2 and #3. The SC transitions occur in the pressure range of 0-1.5 GPa. At ambient pressure and 0.2 GPa, the SC diamagnetism is not perfect.

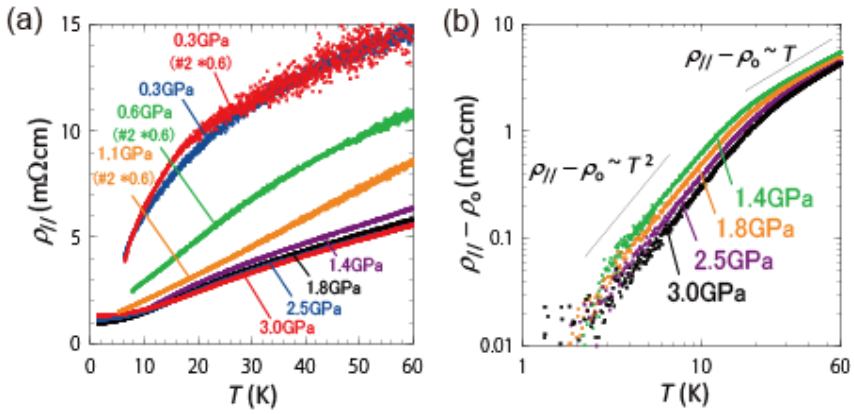

Figure 3 Temperature dependence of normal-state resistivity under pressures. (a) $\rho_{//}$ of κ-$(ET)_4Hg_{2.89}Br_8$ obtained from the analysis of χ_{rf}'. (b) Temperature dependence of $\rho_{//}-\rho_o$ in a pressure range of 1.4-3.0 GPa on a logarithmic scale.

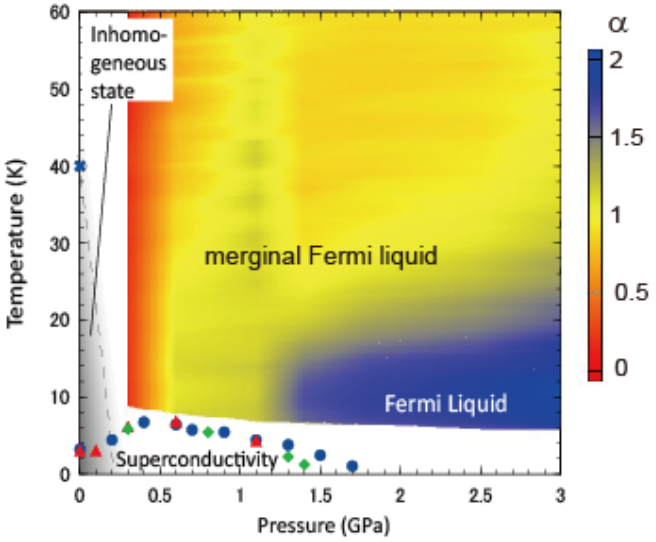

Figure 4 Pressure-temperature phase diagram for κ-$(ET)_4Hg_{2.89}Br_8$. At ambient pressure and 0.2 GPa, the SC is inhomogeneous. Likewise, the ^{13}C NMR line is broadened below 40 K at ambient pressure [27], indicating an inhomogeneous state. These signatures are reflected by the gray color. The dashed line serve as a guide to the eye. Contour plot of α in $\rho_{//}-\rho_o \sim T^{\alpha}$ are also shown. A blue-colored Fermi liquid region appears at low temperatures in a high-pressure range. A yellow-colored marginal-Fermi liquid region of $\alpha \sim 1$ becomes confined between 0.5 GPa and 1.0 GPa at low temperatures. At pressures below 0.3 GPa, the diamagnetic response due to the skin effect was too small to detect because the large value of $\rho_{//}$ increased the skin depth. Errors in the analysis preclude from obtaining the α value at low temperatures below 5K, but temperature dependence of $\rho_{//}-\rho_o$ suggests that FL behavior persists below 5K.