Mott Transition, Antiferromagnetism, and Unconventional Superconductivity in Layered Organic Superconductors

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The phase diagram of the organic superconductor κ-$(ET)_2Cu[N(CN)_2]Cl$ has been accurately measured from ^{1}H NMR and ac susceptibility techniques under helium gas pressure. The domains of stability of antiferromagnetic and superconducting orders in the pressure vs temperature plane have been determined. Both phases overlap through a first-order boundary that separates two regions of inhomogeneous phase coexistence. The boundary curve merges with the first-order line of the metal-insulator transition which ends with a critical point at higher temperature. The whole phase diagram features a pointlike region where metallic, insulating, antiferromagnetic, and non-s-wave superconducting phases all meet.

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The determination of the conditions giving rise to superconductivity (SC) in layered organic conductors constitute one of the chief objectives in understanding the physics of these strongly correlated electronic materials [1]. Closely bound to the now classical issue of proximity of antiferromagnetism (AF) in the emergence of superconductivity stands the problem of the "normal" phase which, depending on pressure conditions in these systems, is either a Mott insulator (MI) or an unconventional metal [2]. A pressure-driven metal-insulator transition can thus be revealing of the strong coupling conditions for electrons that are responsible for broken symmetry states [3].

In this matter, the phase diagram of the series of layered organic superconductors κ-(BEDT-TTF)$_2X$ as a function of both hydrostatic and chemical (or anion X substitution) pressures is set to stand out of the debate. By chemical means, the study of anion substituted compounds has allowed few discrete shifts of the pressure scale. Thus for $X = Cu[N(CN)_2]Br$ and $X = Cu(NCS)_2$, experiments adduce growing evidence for an unconventional metal and a non-s-wave SC state [3,4], whereas AF order is shown to become in turn stable on the deuterated $X = d^n$-$Cu[N(CN)_2]Br$ compound [5].

Among all members of the series κ-(BEDT-TTF)$_2Cu[N(CN)_2]Cl$, denoted as κ-Cl [6], is the prototype compound of the series showing the complete sequence of states, namely, the Mott-insulating, antiferromagnetic, metallic, and superconducting states, within a pressure interval of a few hundred bars [2,5]. Despite the numerous experimental efforts recently expended on the properties of this salt, the information collected from experiments done under pressure remained until now scattered and limited by the selectivity of the experimental probe used. Regions of stability of the metallic and superconducting phases have been investigated, whereas the information about the pressure profile of the AF critical point is missing so far [2,3,5]. Our knowledge on the multicritical structure of opposing phases and the nature of the MI transition under pressure is also partial so that a major part of the phase diagram remained until now grounded on a conjectural rather than an empirical basis [1,3].

The experiments that are presented in this Letter were undertaken in order to yield an accurate phase diagram of κ-Cl, which is shown in Fig. 1. An hydrostatic helium gas pressure technique has been used in order to cover the P-T phase diagram from both isothermal and isobar sweeps. ^{1}H NMR and ac susceptibility techniques were simultaneously employed, and separated sectors of the phase diagram where either the AF or the SC state is stable have been unraveled. Both phases meet at $(P^*, T^*) \simeq$ (282 bar, 13.1 K), a point that ends a first-order AF-SC boundary, which in turn separates two regions of inhomogeneous coexistence of AF and SC phases. As pressure is swept in the high-temperature paramagnetic domain, one crosses a first-order line associated with the Mott transition and which evolves towards a crossover above a critical point where the MI transition line ends.

All measurements under pressure were performed on single crystals of approximately $0.85 \times 0.75 \times 0.075$ mm^3, synthesized and grown by standard electrochemical methods [6]. In order to ensure hydrostatic pressure conditions, our measurements are restricted to the region above the helium solidification line. Results presented here were obtained on slowly cooled samples (0.35 K/min through 80 K) [7].

^{1}H NMR measurements were done in a low static field of 0.5 T oriented perpendicular to the conducting layers, which essentially allows one to obtain a zero field phase diagram. For ac susceptibility, we used a null-phase feedback loop to track the rf resonance frequency of the NMR circuit with a sensitivity of a few ppm. No static field was applied and the ac magnetic field was approximately 0.05 Oe in a direction parallel to the layers—in order to also statisfy NMR requirements. Different field and

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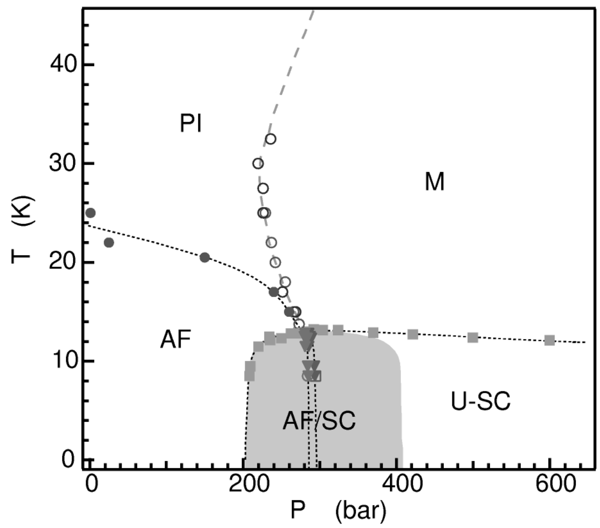

FIG. 1. Temperature vs pressure phase diagram of κ-Cl. The antiferromagnetic (AF) critical line $T_N(P)$ (dark circles) was determined from NMR relaxation rate while $T_c(P)$ for unconventional superconductivity (U-SC: squares) and the metal-insulator $T_{\mathrm{MI}}(P)$ (MI: open circles) lines were obtained from the ac susceptibility. The AF-SC boundary (double-dashed line) is determined from the inflection point of χ'(P) and, for 8.5 K, from sublattice magnetization. This boundary line separates two regions of inhomogeneous phase coexistence (shaded area).

temperature conditions, namely, 1 T and 3 K in the vortex—lock-in—orientation, have been applied at about 300 bar in a clamp pressure cell in an attempt to detect the presence of AF vortex cores and to establish the stability of the coexistence region down to 3 K.

The results for the temperature dependence of the nuclear relaxation rate T_1^{-1} are shown in Fig. 2 for various pressures. The singular peak of T_1^{-1}, which marks the onset of critical AF ordering at the Néel temperature T_N is gradually suppressed under pressure with the value $dT_N/dP \simeq -0.025$ K/bar for the pressure coefficient. Above 275 bar, there is no peak indicating the absence of a magnetic transition. A plateau of T_1^{-1}, however, persists up to 40 K or so, which marks a sizable enhancement due to short-range AF correlations.

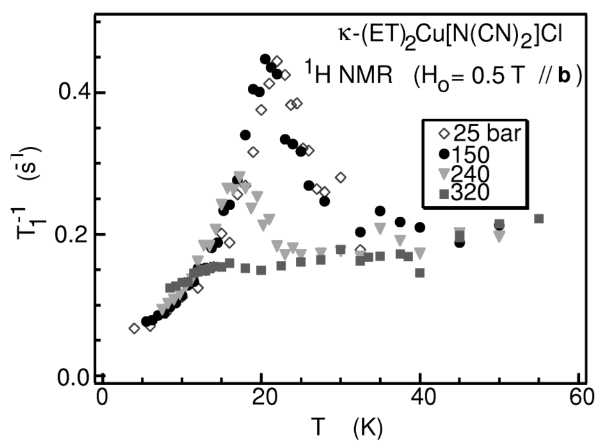

FIG. 2. Temperature dependence of ^{1}H NMR relaxation rate for κ-$(ET)_2Cu[N(CN)_2]Cl$ at various pressures. The static magnetic field (0.5 T) was applied perpendicular to the layers.

An accurate determination of superconducting order in the phase diagram can be obtained from the ac susceptibility measurements as shown in Fig. 3 for selected temperature and pressure sweeps, respectively. In the high pressure domain above 400 bar, the $T_c(P)$ line below which there is a finite density of superconducting condensate slowly decreases in agreement with previous results ($dT_c/dP \simeq -3.8$ K/kbar, squares in Fig. 1) [2]. As pressure is reduced below 400 bar, lower saturation levels are recorded indicating a gradual suppression of the superconducting order down to 200 bar where it vanishes; $T_c(P)$ thus crosses $T_N(P)$ and the regions of stability for SC and AF overlap.

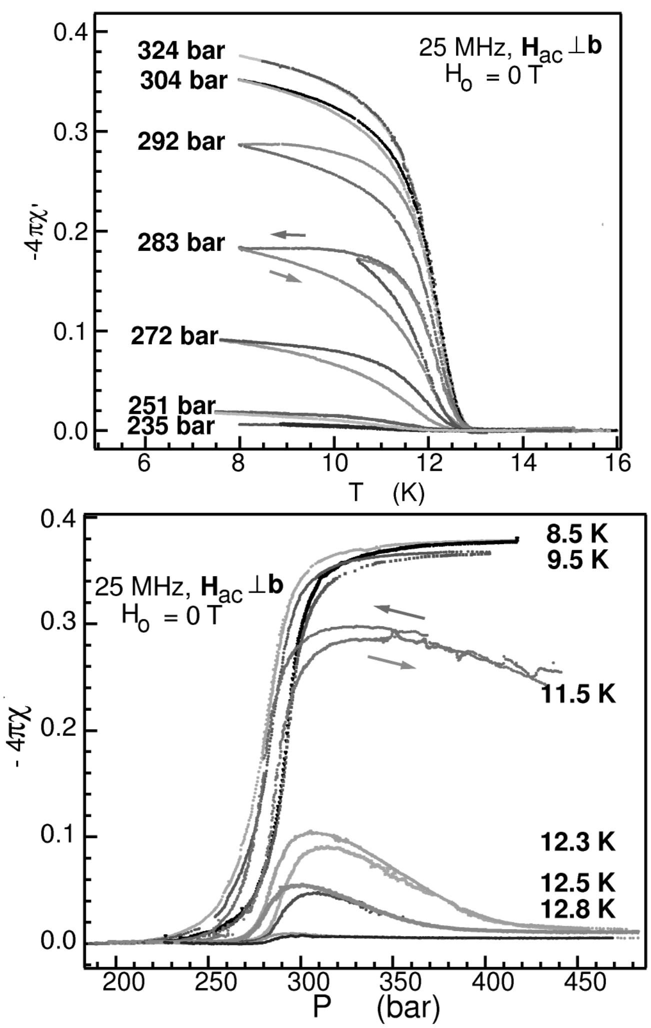

FIG. 3. Real part of ac susceptibility of κ-Cl for (top) temperature sweeps at selected pressures and (bottom) for pressure sweeps at selected temperatures.

When the variation of the superconducting condensate is analyzed under pressure between 8.5 and 12.8 K (Fig. 3, bottom), there is a rapid change of the diamagnetic signal centered around a transition pressure denoted P_1—defined at the inflection point. At 8.5 K, $P_1 \simeq 290$ bar, and P_1 slightly moves downward as temperature is raised to finally reach P^* at T^* (double dashed line in Fig. 1). According to Fig. 3, an hysteresis can be found in a given interval of pressure and temperature. This region of coexistence which conveys some metastability of the transition is delimited by the shaded area in Fig. 1.

The nature of this region of the phase diagram can be further sharpened by first looking at the pressure dependence of the ^{1}H NMR line shape as shown in Fig. 4 for 8.5 K. In the AF phase at $P = 15$ bar, the signal is split into a number of discrete peaks, a characteristic of commensurate AF order [5]; this structure persists up to 200 bar, above which a narrow peak close to the origin grows in importance concomitant with a reduction of the AF line shape structures. At high pressure, where the system is completely in the SC state, this peak dominates the spectrum. A simulation of the line shape then allows one to determine the fraction of the sample that becomes either AF or SC. From Fig. 4 (right inset), there is a gradual suppression of AF order which becomes steepest at $P_1 \simeq 290$ bar and is tied to a concomitant increase of the SC order. The 10 bar hysteresis at P_1 is in accordance with the ac susceptibility measurements of Fig. 3.

A further, more direct, confirmation of the first-order character of the AF-SC transition line is provided by the pressure variation of the AF order parameter as obtained from the NMR spectral line shape. This is exhibited in the left inset of Fig. 4 where the AF order parameter at

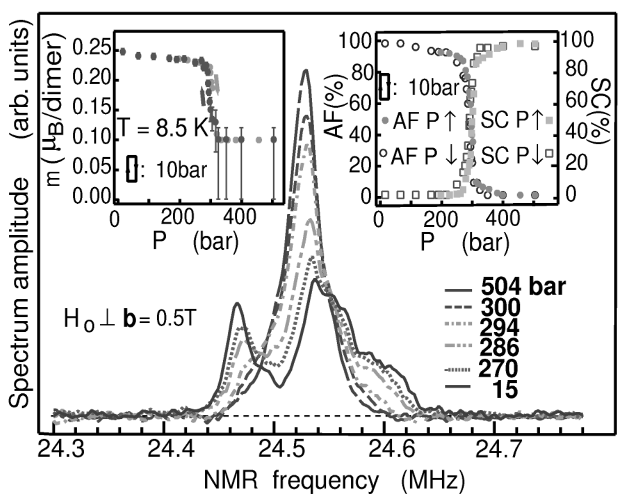

FIG. 4. ^{1}H NMR spectra of κ-Cl for different pressures at 8.5 K. Insets: Pressure dependence of AF magnetization (left) and proportion of nuclear spins in the AF and SC states (right) as extracted from the spectrum. (Note that the determination of the AF magnetization becomes uncertain above 350 bar because the AF component merges with the tails of the SC spectrum.)

$T = 8.5$ K shows a slow decrease under pressure followed by an abrupt drop at $P_1 = 290$ bar.

At this point, a few remarks are in order. Although our results do show evidence of coexisting phases, they do not allow one to determine if a macroscopic or mesoscopic (e.g., stripes [8]) type of coexistence is taking place. Given here the constant band filling (half-filling) under pressure, the stripe formation, if it exists, would be of different nature than for high-T_c materials [8]. The nature of the point (P^*, T^*) in the phase diagram is also of interest. Since it exhibits hysteresis (Fig. 3), it can hardly be classified as a bicritical point, which is second order in character. As we will see shortly, however, the point (P^*, T^*) also belongs to another transition line associated with the MI transition between two unbroken symmetry states, that is, the Mott insulating and the metallic states.

We used the NMR spectrum with the static field oriented along the lock-in direction to check if superconducting vortices with AF cores may be part of the SC-rich sector—AF vortices are predicted in the SO(5) scenario for unification of magnetism and superconductivity [9]. This orientation corresponds to the situation of intrinsic pinning of vortices between the conducting planes leading to the disappearance of vortex cores. We failed to detect any reduction of the AF component of the spectra at $P \simeq 300$ bar and down to 3 K, for this field orientation. Our results then indicate that the vortex cores are nonmagnetic, at the very least in this region of the phase diagram.

When ac susceptibility measurements are performed under pressure in the paramagnetic temperature domain, a jump in the diamagnetic signal, albeit small in amplitude, is clearly found (Fig. 5). It reveals an increase of diamagnetism when the system enters in the metallic phase—through skin depth effect. These observations corroborate previous electrical transport measurements by Ito *et al.,* who located the MI transition in the same pressure and temperature domain [2].

When the temperature is increased, the jump in the diamagnetic susceptibility evolves towards a smooth concave profile above some point $(P_0, T_0) \simeq (220 \text{ bar}, 32.5 \text{ K})$. Well below this point, the diamagnetic susceptibility shows a small but detectable hysteresis that decreases in amplitude as the temperature is raised from (P^*, T^*), indicating that the MI transition is first order in character (inset of Fig. 5). Within experimental accuracy, the MI line also starts from (P^*, T^*) where all other phases meet [10]. The end point (P_0, T_0) can then be conjectured to be a critical point.

Referring to Fig. 1, over most part of the MI-metal equilibrium curve dP/dT is negative. According to the Clausius-Clapeyron relation a negative dP/dT would indicate a reduction of the spin entropy on the insulator side below the metallic level. A reasonable explanation for this could come from low dimensional short-range AF correlations, which extend relatively deep in the paramagnetic domain (Fig. 2) and would quench a sizable part of the spin

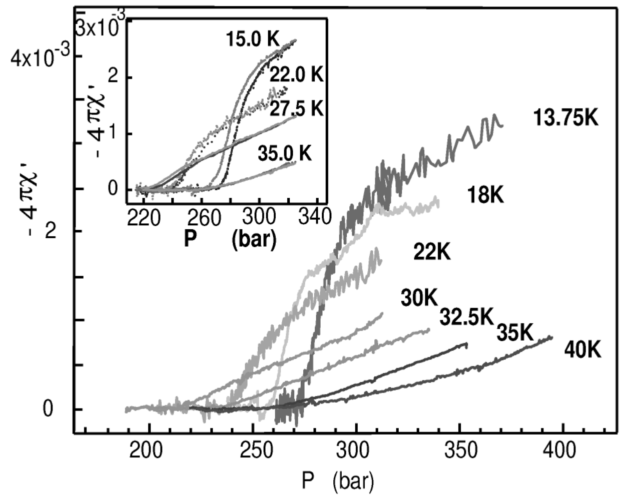

FIG. 5. The MI transition seen by the pressure dependence of ac susceptibility in the paramagnetic phase. The inset shows the variation of hysteresis effects at different temperatures.

entropy in the vicinity of $T_N(P)$. Sufficiently far from the AF transition, however, entropies nearly balance so that dP/dT is close to zero around 30 K or so [11].

As for global phase diagram, important conclusions may be drawn about the description of this series of layered organic superconductors. It is noticeable in the first place that the MI transition is discontinuous and clearly evolves toward a mere crossover above a critical point (P_0, T_0). To our knowledge, it seems to be the first time that a genuine electronic transition that combines all these characteristics is discovered in a quasi-two-dimensional system at half-filling [12]. In the second place, the joining of the MI line with $T_N(P)$ at (P^*, T^*) is of great interest since it shows within experimental accuracy the absence of boundary between the metallic and complete AF phases. This confirms previous inferences made about the absence of itinerant antiferromagnetism in κ-(BEDT-TTF)$_2X$ [3] and the relevance of a description of magnetic ordering in terms of interacting spins localized on dimers [1,13]. The fact that SC and AF phases overlap below P^* indicates that superconductivity can be directly stabilized from the insulating phase. An inescapable outcome of this result is the obvious exclusion of a weak coupling scenario for the emergence of unconventional pairing in layered organic superconductors as a function of pressure.

The existence of the pointlike region at (P^*, T^*) where metal, Mott insulator, antiferromagnet, and non-*s*-wave superconductor all meet demonstrates that strong electron correlations and broken symmetry variables are equally important for a unified theory of antiferromagnetism and non-*s*-wave superconductivity in these compounds [14].

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