Mott transition, antiferromagnetism, and unconventional superconductivity in layered organic superconductors

S. Lefebvre$^{1,2}$, P. Wzietek$^3$, S. Brown$^3$, C. Bourbonnais$^2$, D. Jérome$^1$, C. Mézière$^4$, M. Fourmigué$^4$ and P. Batail$^4$

$^1$Laboratoire de Physique des Solides (CNRS, U.R.A.2), Bâtiment 510 Université de Paris-sud, 91405 Orsay, France

$^2$CERPEMA, Département de Physique, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1

$^3$Department of Physics and Astronomy, University of California at Los Angeles

Los Angeles, CA 0025, USA

$^4$Institut des Matériaux de Nantes, 44072 Nantes, France

The phase diagram of the layered organic superconductor $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Cl has been accurately measured from a combination of $^1$H NMR and AC susceptibility techniques under helium gas pressure. The domains of stability of antiferromagnetic and superconducting long-range 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 is found to merge with another first order line related to the metal-insulator transition in the paramagnetic region. This transition is found to evolve into a crossover regime above a critical point at higher temperature. The whole phase diagram features a point-like region where metallic, insulating, antiferromagnetic and non s-wave superconducting phases all meet.

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 [4]. A pressure-driven metal-insulator transition can be thus 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 $\kappa$-(BEDT-TTF)$_2$X 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 [33], whereas AF order is shown to become in turn stable on the deuterated X= d$^a$-Cu[N(CN)$_2$]Br compound [33].

Among all members of the series $\kappa$--(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl, denoted as $\kappa$-- Cl [33], 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 few hundred bars [33]. 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 AF critical point is missing so far [33]. 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 [33].

The experiments that are presented in this work were undertaken in order to yield an accurate phase diagram of $\kappa$-- Cl, which is shown in Figure 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 AF or SC state is stable have been unraveled. Both phases meet at $(P^*, T^*) \approx (282$ 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 [1]. Temperature and pressure sweeps were sufficiently slow to show no dependance on the sweeping rate ($\sim 0.07$ K/min, $\sim 1$ bar/min). In order to ensure hydrostatic pressure conditions, our measurements are restricted to the region above the Helium solidification
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 $T_M(P)$ (MI: open circles) lines were obtained from the AC susceptibility. The AF-SC boundary (double dashed line) is determined from the inflexion point of $\chi'(P)$ and, for 8.5 K, from sublattice magnetization. This boundary line separates two regions of inhomogeneous phase coexistence (shaded area).

Different field and 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 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 Figure 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; 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 to determine the fraction of the sample that becomes either AF or SC. From Figure 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 Figure 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 Figure 4 where the AF order parameter at \( T = 8.5 \text{ K} \) shows a slow decrease under pressure followed by an abrupt drop at \( P_1 = 290 \text{ bar} \).

At this point, a few remarks are in order. Although our results do show evidence of coexisting phases, they do not allow to determine if a macroscopic or mesoscopic (e.g., stripes) 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. The nature of the point \((P^*, T^*)\) in the phase diagram is also of interest. Since it exhibits hysteresis (Figs. 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 have used the NMR spectra 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. By looking at the modification of internal field distribution in NMR line shape as function of the static field orientation at \( P \approx 300 \text{ bar} \) and down to 3K, however, we failed to detect any decrease of the AF part of the spectra when the static field is oriented along the so-called ‘lock-in’ direction. This orientation corresponds to the situation of intrinsic pinning of vortices between the conducting planes and where vortex cores should sustain a sizeable reduction of their magnetic component. Our results then indicate that the vortex cores are non-magnetic, 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 (Figure 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. When the temperature is increased, the jump in the diamagnetic susceptibility evolves towards a smooth concave profile above some point \((P_0, T_0) \approx (220 \text{ bar}, 32.5 \text{ K})\). 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 Figure 4).
Within experimental accuracy, the MI line also starts from \((P_0, T_0)\) where all other phases meet [5]. The end point \((P_0, T_0)\) can then be conjectured to be a critical point.

Refering to Figure 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 (Figure 2) and would quench a sizeable part of the spin 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.

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 [6]. 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 a complete AF phases. This confirms previous inferences made about the absence of itinerant antiferromagnetism in \(\kappa-(BEDT-TTF)_2X\) [3] and the relevance of a description of magnetic ordering in terms of interacting spins localized on dimers [2,4]. 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 function of pressure.

The existence of the point-like 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 [1].

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[9] One should note that the determination of \(T_N(P)\) from the position of the peak of nuclear relaxation rate may introduce some uncertainty so we cannot discard the possibility that the MI and AF lines actually merge slightly above \(T^*\).
[10] We are assuming a larger density for the metallic state.
[11] There is no contradiction here with the Gibbs phase rule because at least one line (SC) is found to be critical at this point.
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