Mott Transition, Compressibility Divergence and P-T Phase Diagram of Layered Organic Superconductors: An Ultrasonic Investigation.

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The phase diagram of the organic superconductor $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl has been investigated by ultrasonic velocity measurements under helium gas pressure. Different phase transitions were identified trough several elastic anomalies characterized from isobaric and isothermal sweeps. Our data reveal two crossover lines that end on the critical point terminating the first-order Mott transition line. When the critical point is approached along these lines, we observe a dramatic softening of the velocity which is consistent with a diverging compressibility of the electronic degrees of freedom.

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Electronic properties of metals or semiconductors at energies of the order of room temperature or less can usually be understood by simple models that take into account a few electronic bands near the Fermi level. In the absence of broken symmetries, it suffices to take into account the effects on the bands of small residual electron-electron and electron-phonon interactions to explain the observed electronic properties. In the last decade, a flurry of activity has centered on materials that cannot be understood using the above textbook procedure. In these materials, only one or a few bands should be relevant to understand electronic properties but the residual interactions are so strong that electronic eigenstates can become localized, leading to a complete breakdown of the band picture. A few compounds have become prototype materials for the study of these so-called strong correlation effects: $V_2O_3$, Ni(S,Se)$_2$ and the family of organic conductors $\kappa$-(BEDT-TTF)$_2$X.

In these compounds, one observes a pressure-induced finite-temperature first-order phase transition (MI) between an insulating (I) and a metallic (M) phase. Pressure (hydrostatic or chemical) increases the bandwidth, reducing the effects of residual interactions. This first-order phase transition seems to correspond to the so-called Mott transition, as it has become understood in the last few years through dynamical mean-field theory (DMFT).

One of the recent predictions of DMFT, is that the compressibility of electronic degrees of freedom diverges at the critical point that terminates the first-order Mott transition line. Observation of this phenomenon would help confirm the picture of the Mott transition proposed by DMFT. In this letter, we present the first ultrasonic study of $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl (denoted as $\kappa$-Cl), using an hydrostatic helium gas pressure cell. The study, summarized in the phase diagram shown in figure 1, shows (a) A very large softening of the sound velocity at the critical point, corresponding to the predicted divergence of the compressibility of the electronic degrees of freedom. (b) Two crossover lines - joining at the critical point - where a similar although smaller compressibility anomaly is observed. Most remarkably, while the compressibility anomalies decrease in size as one moves away from the critical point, the crossover line at high pressure coincides with the well-known pseudogap features identified in the magnetic, transport and elastic properties of the other compounds of the family corresponding to higher chemical pressure, X = Cu(NCS)$_2$ and Cu[N(CN)$_2$]Br. This suggests a common origin to the phenomena. (c) In addition, we show that much smaller signatures in our ultrasonic velocity measurements confirm the superconducting (SC) phase boundaries previously identified mostly on the metallic side of the Mott transition. Curiously, our measurements are not sensitive to the antiferromagnetic phase boundary on the insulating side of the Mott transition, although one of the crossover lines is not far from that phase boundary.

The difficulty to carry out ultrasonic experiments in organic conductors is primarily due to their very small dimensions. An additional difficulty in the $\kappa$-Cl compound comes from small desirable pressure effects (a crystal embedded in vacuum grease experiences a pressure of a few hundreds bars) that can be induced when the piezoelectric transducers are glued to the crystal faces. Considering the geometry of single crystals synthesized by the standard electrocrystallization technique, only longitudinal waves propagating along a direction perpendicular to the layers (compression mode) could be generated. Because of multiple bonds and an intrinsically large attenuation at low temperatures, the measurements could only be done at the fundamental frequency of the transducer, namely 32 MHz. To ensure hydrostatic pressure conditions, we restricted the temperature range to the region above the helium solidification line. Results presented here were repeated on three crystals having approximate dimensions 1.0 x 1.0 x 0.4 mm$^3$. The points on the phase diagram of Fig.1 come from these three crystals, so their dispersion represents our accuracy. Cooling was slow ($\sim$ 0.6 K/min) to avoid any residual disorder of ethylene end groups. We tested, simultaneously, the quality of our $\kappa$-Cl crystals at am-
FIG. 1: Temperature vs pressure phase diagram of κ-Cl. Different symbols are associated to different anomalies gathered on three different crystals from temperature sweeps (full symbols) and pressure sweeps (open symbols). The zero pressure point (dotted hexagon) was obtained from a microwave resistivity measurement. The gray circle indicates the critical point \( (P_0, T_0) \).

ambient pressure by measuring the microwave resistivity at low temperatures \([13]\).

Several elastic anomalies are identified on the relative variation of the longitudinal ultrasonic velocity \( (\Delta V/V) \) from isothermal sweeps. As shown typically in figure 2, three anomalies can be easily identified at \( P = 270 \) bars, two small ones at 13 and 16 K and a huge dip centered at 38 K.

The small anomaly at 13 K characterizes the superconducting order; this has been confirmed by analyzing the magnetic field dependence of the anomaly. As previously shown in other compounds of the family \([9]\), a small softening anomaly appears in \( \Delta V/V \) below the superconducting critical temperature \( T_c \). The latter is determined by the maximum rate of softening on decreasing temperature sweeps. We present, in figure 3, low temperature sweeps of \( \Delta V/V \) at selected pressures in the range 200-500 bars. The pressure range can be divided in three regions I (200-275 bars), II (275-400 bars) and III (over 400 bars). In region I \( (P = 245 \) and 275 bars), the anomaly shows a significant hysteresis over a wide temperature range above \( T_c \); for increasing temperature sweeps, the anomaly’s amplitude is much smaller than for decreasing sweeps. Moreover, both the amplitude and \( T_c \) increase with pressure. In region II \( (P = 290 \) and 325 bars), the hysteresis is much smaller and it merely represents a tiny shift of \( T_c \) between increasing and decreasing temperature sweeps. In region III \( (P = 475 \) bars), no hysteresis is observed. We have reported in Fig.1 the \( T_c(P) \) deduced from the temperature sweeps (full triangles). This \( T_c(P) \) line is fully consistent with the results of Lefebvre et al. \([10]\). Our ultrasound data confirm the metastability of the SC phase in pressure regions I and II. Although we cannot specify the nature of the other phase coexisting with the SC one, NMR and AC susceptibility data have indicated an inhomogeneous antiferromagnetic phase \([10]\). Above 400 bars, the finite density condensate SC-III is characterized by a slowly decreasing \( T_c \) with pressure in agreement with previous results \([10, 12]\).

We now examine the anomaly in \( \Delta V/V \) giving rise to the huge dip observed at 38 K for \( P = 270 \) bars (Fig.2). Its temperature profile is shown in figure 4 for various pressures. The amplitude of the dip increases tremendously and shifts to lower temperatures as the pressure is decreased from 460 bars. It reaches its maximum am-

FIG. 2: Temperature dependence of \( \Delta V/V \) at 270 bars. The velocity variation is relative to the value at 7 K. Inset: low temperature portion. (Arrows indicate the anomalies).

FIG. 3: \( \Delta V/V \) around 13 K for various pressures (Full symbols: increasing temperature sweeps; open symbols: decreasing temperature sweeps). The velocity variation is relative to the value at 9.8 K. The curves have been shifted vertically for a better view. The arrows indicate the transition temperature.
plitude (> 20%) near 34 K and $P \simeq 210$ bars, these values of temperature and pressure defining the critical point ($P_0$, $T_0$). Below 210 bars, the anomaly is still observable but its amplitude decreases progressively as the pressure is lowered to 150 bars, where its position is stabilized around 32 K. This huge velocity anomaly, which implies a decrease of the perpendicular compression elastic constant of almost 40% at the critical point, is likely due to a strong coupling between longitudinal acoustic phonons and electronic degrees of freedom. This points to a compressibility divergence, which has been described recently as a generic feature of the finite temperature critical point of the Mott transition [5, 6]. A similar velocity anomaly has also been observed in compounds $X = \text{Cu(NCS)}_2$ and $\text{Cu[N(CN)}_2\text{]Br}$ having a higher chemical pressure [9]. We have reported, in Fig.1, the temperature of the softening dip as a function of pressure (full squares). These points correspond, at high pressure ($P > P_0$), to the crossover line between incoherent and coherent metallic phases in $\kappa$-Cl and $X = \text{Cu(NCS)}_2$ and $\text{Cu[N(CN)}_2\text{]Br}$ compounds (line defined by the peak in $d\rho/dT$ [8]). Surprisingly, this line does not terminate at the critical point ($P_0$, $T_0$), but continues in the low pressure range reaching a plateau near 32 K at the lowest pressure attained in our experiment (75 bars). This line connects smoothly with the microwave resistivity point at $P = 1$ bar (dotted hexagon) [3]. These results therefore allow a better understanding of the transport properties within the PI phase: at high pressures ($P > P_0$) along the crossover line, $d\rho/dT$ is positive and it shows a peak which moves to higher temperature with increasing pressure whereas, along the low pressure portion of the line ($P < P_0$), $d\rho/dT$ is rather negative and shows a dip [12]. Above the critical point, one can then pass continuously from an incoherent metal to an insulator.

The small anomaly in $\Delta V/V$ observed around 16 K for a pressure of 270 bars (Fig.2) is due to the crossing of a quasi vertical transition line in the $P - T$ phase diagram of Fig.1. Since vertical lines are better identified from pressure sweeps, we present, in figure 5, two series of increasing pressure sweeps for different temperature ranges. In the top panel, we examine the crossing of the superconducting phase boundary near 13 K. As the pressure is increased above 170 bars all the $\Delta V/V$ curves show a softening anomaly: at 9 K, the minimum of the anomaly extends from 200 to 350 bars, while, at 13 K, the pressure range is shortened to 200-275 bars, a trend which is still more pronounced at 13.5 K. This clearly indicates that, at 13.5 K, we have crossed the superconducting phase boundary. We defined the small minimum around 275 bars (indicated by a solid arrow) as a clear transition, while the 200 bars feature, corresponding to a slope variation (dashed arrow), signals the onset of the metastable SC phase. Above 13.5 K, the minimum progressively deepens and moves to lower pressure (16 K curve in Fig.5). This trend is more clearly observed at higher temperatures (lower panel of Fig.5): the amplitude of the softening anomaly increases and its position (solid arrows) shifts with temperature; there is also a clear change of slope (200 bars feature indicated by dashed arrows) on the low pressure side. The anomaly
has maximum amplitude (∼20%) in the vicinity of the critical point \((P_0, T_0)\). The 30 and 31 K curves of Fig. 5 show a small stiffening of the velocity around 190 bars, when the horizontal crossover line, previously identified in the temperature sweeps, is approached. Finally, for \(T > 34\) K (not shown), a softening anomaly without the 200 bars feature is still obtained: its amplitude decreases and it moves rapidly to high pressure along the crossover line.

The two features indicated by arrows in the pressure sweeps have been reported in the phase diagram of Fig. 1. The right vertical line (open squares) presents two parts. From 9 to 13.2 K, a transition line centered at 275 bars separates two regions where a metastable superconducting state is found. Then, this line, starting from the same point (275 bars, 13.2 K), denoted \((P^*, T^*)\) in Lefebvre et al. paper [11], has a negative slope at low temperatures before going vertical as it approaches the critical point \((P_0, T_0)\) indicated by a gray circle. Along this line, the softening of the velocity increases dramatically to reach near 20% at the critical point, before it joins with the crossover line. The left vertical line (open triangles) defines, with the right one, a region where strong hysteresis is found in the temperature sweeps (hysteresis is also observed in pressure sweeps although it cannot be quantified). This region begins at the SC-I boundary and, then, shrinks to zero at the critical point where both lines merge and join with the crossover lines. This hysteretic region coincides with the previously observed first-order Mott transition [10][12].

We mention, finally, that, in the low pressure range, we could not identify any clear anomaly related to a AF ordering transition. This is highly surprising and unexpected since ultrasonic waves couple generally quite easily with spin degrees of freedom [14], although the absence of anomaly could signify a very small coupling for this particular acoustic mode (longitudinal polarized perpendicularly to the planes).

Beyond the confirmation of the \(P - T\) diagram of a typical Mott MI material, our ultrasonic data on the \(\kappa\)-Cl organic conductor allowed the first detailed study of the critical point region. The very large softening of the velocity at the critical point corresponds to the predicted compressibility divergence of the electronic degrees of freedom and validates then, the DMFT picture of the Mott transition [3][8]. Two crossover lines joining at the critical point were also obtained from a similar, although smaller, compressibility anomaly. We note the similarity with the two crossover lines identified in the \(\text{Ni}(\text{S,Se})_2\) compounds [9]. Most importantly, our data reveal that the high pressure crossover line coincides with the pseudogap features previously observed in magnetic [1], transport [3][10] and elastic [11] properties of organic compounds of the same family having a higher chemical pressure. Since a Mott insulating phase is present in underdoped high-\(T_c\) compounds, this suggests that the Mott critical point could play an important part in the origin of the pseudogap in these materials. It should then be interesting to investigate the pseudogap feature with an ultrasonic measurement in high-\(T_c\) compounds.

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[13] We have measured the parallel and perpendicular microwave resistivities at ambient pressure as a function of temperature with a contactless microwave cavity perturbation technique at 17 GHz. Below 50 K, the Mott-insulating state is signaled by a rapid increase of the resistivity; we observed, however, a change in the rate of increase (dip in \(d\rho/dT\)) around 34 ± 2 K just above the AF transition [10], which is signaled at 27 K on the resistivity by a strictly linear temperature dependence. This dip in \(d\rho/dT\) in the insulating phase has its counterpart in the metallic phase where a peak in \(d\rho/dT\), associated to the crossover line, is rather observed. This dip in \(d\rho/dT\) at \(T = 34\) K and \(P = 1\) bar is indicated as a dotted hexagon on the phase diagram of Fig. 1.
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