

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

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The phase diagram of the organic superconductor κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl has been investigated by ultrasonic velocity measurements under helium gas pressure. Different phase transitions were identified through 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 anomaly of the sound 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 the understanding of 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: V₂O₃ [1], Ni(S, Se)₂ [2], and the family of organic conductors κ -(BEDT-TTF)₂X [3].

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) [4].

One of the recent predictions of DMFT is that the compressibility of electronic degrees of freedom κ_e diverges at the critical point that terminates the first-order Mott transition line [5,6]. Such a divergence of κ_e can be observed experimentally by measuring the sound velocity which is proportional to the square root of the compression modulus $C_{22} \sim \kappa_e^{-1} + \kappa_l^{-1} + \kappa_{el}^{-1}$ where κ_l is the lattice compressibility and κ_{el} is a term depending on the strength of the electron-lattice interaction. A divergence of κ_e should thus show up as a dip in the velocity. In this Letter, we present the first ultrasonic study of κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl (denoted as κ -Cl), using

a hydrostatic helium gas pressure cell. The study, summarized in the phase diagram shown in Fig. 1, shows (a) A very large anomaly in the sound velocity at the critical point associated with the predicted huge dip in the compression modulus C_{22} . (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 pseudo-gap features identified in the magnetic [7], transport [8,9], and elastic [9] properties of the other compounds of the family corresponding to higher chemical pressure, $X = \text{Cu}(\text{NCS})_2$ and $\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$. This suggests a common origin to the phenomena. (c) In addition, we show

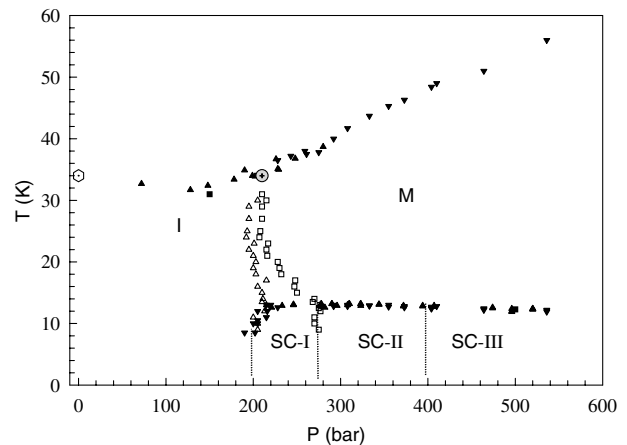


FIG. 1. Temperature vs pressure phase diagram of κ -Cl. Different symbols are associated with different anomalies gathered on three different crystals (crystal I, \blacktriangle , \triangle , and \square ; crystal II, \blacktriangledown ; crystal III, \blacksquare) from temperature sweeps (full symbols) 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).

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 [10]. 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 [9]. Considering the geometry of single crystals synthesized by the standard electrocrystallization technique [11], only longitudinal waves propagating along a direction perpendicular to the layers could be generated; for the orthorhombic structure, the velocity of these waves, V , is related to the C_{22} compression modulus and density ρ via the relation $V = \sqrt{C_{22}/\rho}$. Because of multiple bonds and an intrinsically large attenuation at low temperatures, the measurements could be done only at the fundamental frequency of the piezoelectric 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 $1.0 \times 1.0 \times 0.4 \text{ mm}^3$. The points on the phase diagram of Fig. 1 come from these three crystals, so their dispersion represents our accuracy. Cooling was slow ($\sim 0.6 \text{ K/min}$) to avoid any residual disorder of ethylene end groups. We tested, simultaneously, the quality of our $\kappa\text{-Cl}$ crystals at ambient pressure by measuring the microwave resistivity at low temperatures [12].

Several elastic anomalies are identified on the relative variation of the longitudinal ultrasonic velocity ($\Delta V/V$) from isothermal sweeps. As shown typically in Fig. 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.

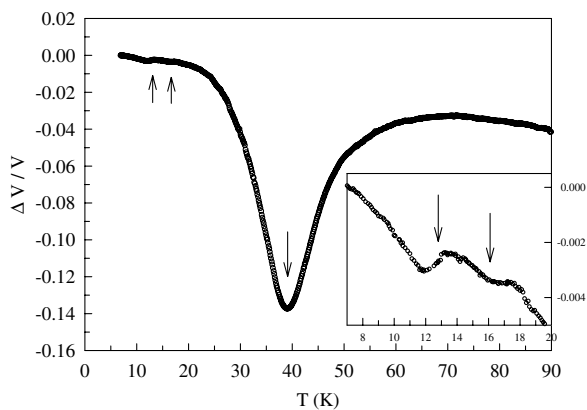


FIG. 2. Temperature dependence of $\Delta V/V$ at 270 bars. The velocity variation is relative to the value at 7 K. Inset: low temperature portion. (Arrows indicate the anomalies).

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 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 Fig. 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 temperature 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 [10,13].

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 Fig. 4 for various pressures. The amplitude of the dip increases

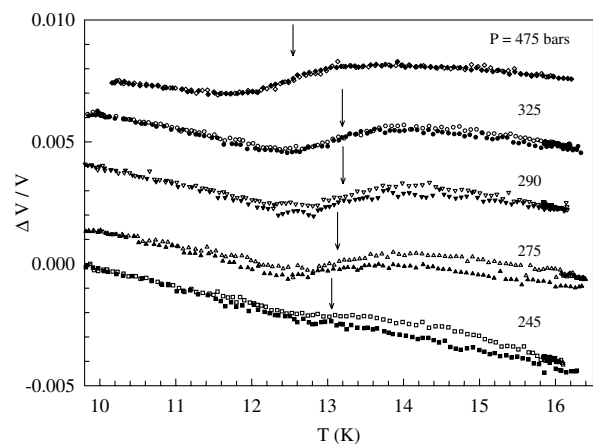


FIG. 3. $\Delta V/V$ around 13 K for various pressures (solid symbols: increasing temperature sweeps; open symbols: decreasing temperature sweeps). The velocity variation is relative to the value at 9.8 K. The curves have been shifted vertically for a better view. The arrows indicate the transition temperature.

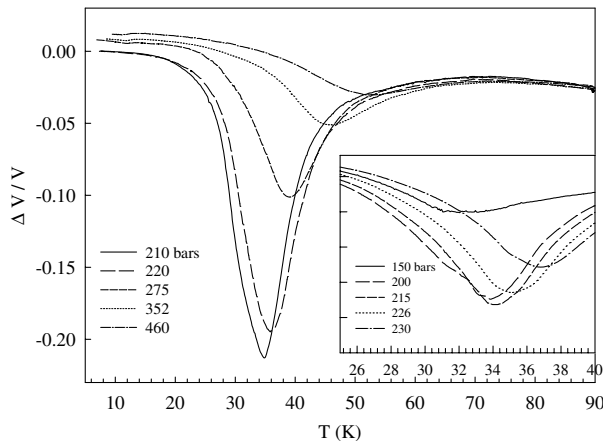


FIG. 4. Temperature dependence of $\Delta V/V$ at various pressures. The velocity variation is relative to the value at 90 K. Inset: position and amplitude of the anomaly below 230 bars.

tremendously and shifts to lower temperatures as the pressure is decreased from 460 bars. It reaches its maximum amplitude ($> 20\%$) near 34 K and $P \approx 210$ 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. Such a huge dip on the ultrasonic velocity is likely related to the contribution of the electronic degrees of freedom to the compression modulus. Using DMFT, Merino and McKenzie [14] have shown that, when the electron-electron interactions are sufficiently large, phonon frequencies (consequently elastic moduli) can have a nonmonotonic temperature dependence similar to the one observed here. Moreover, a near 40% decrease of the compression modulus at the critical point may correspond to a compressibility divergence of the electronic degrees of freedom, which has been described recently as a generic feature of the finite-temperature critical point of the Mott transition [5,6]. We have reported, in Fig. 1, the temperature of the minimum of $\Delta V/V$ as a function of pressure (full squares). These points correspond, at high pressure ($P > 210$ bars), to the crossover line (defined by the peak in $d\rho/dT$ [8]) between incoherent and coherent metallic phases, not only in the κ -Cl compound but also in the $X = \text{Cu}(\text{NCS})_2$ and $\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$ ones where a similar important ultrasonic anomaly is observed [9]. 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) [12]. These results therefore allow a better understanding of the transport properties of these compounds: 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 [13]. In the region above the two crossover lines in Fig. 1, 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 quasivertical transition line in the P - T phase diagram of Fig. 1. Since vertical lines are better identified from pressure sweeps, we present, in Fig. 5, two series of increasing pressure sweeps for different temperatures. 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 dip-type 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 dashed arrow at 200 bars indicates a change in slope coincident with the point where a magnetic field study has signaled the onset of a metastable SC phase

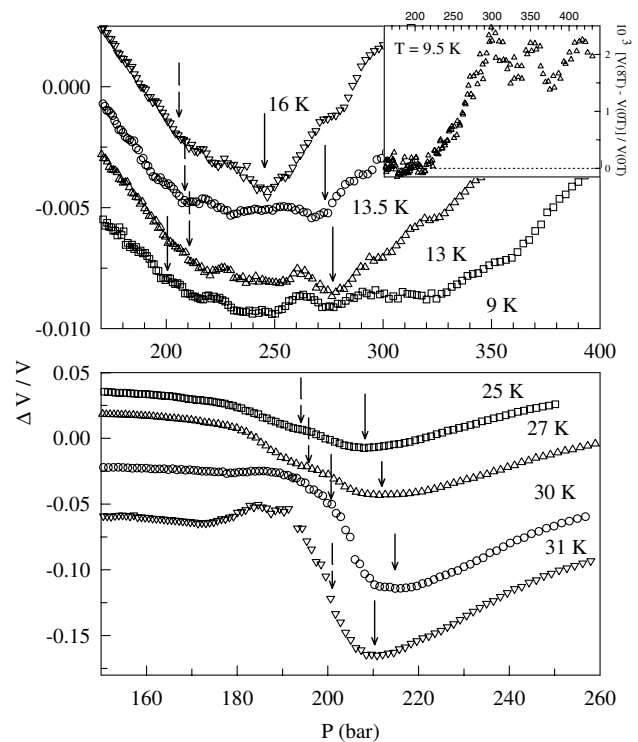


FIG. 5. $\Delta V/V$ as a function of increasing pressure at fixed temperatures. The velocity variation is relative to the value at 150 bars. Curves have been shifted vertically for a better view. Solid arrows signal the maximum softening and dashed ones indicate the 200 bar feature. Inset: effect of a 8 T magnetic field on the velocity at 9.5 K, $[V(8T) - V(0T)]/V(0T)$, signaling the onset of the metastable SC phase around 200 bars and SC transition at 275 bars.

(inset of Fig. 5). 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 dip 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 dip has maximum amplitude ($\sim 20\%$) 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), the pressure sweeps of the crossover line yield a dip anomaly that corresponds with the anomaly observed in the temperature sweeps (Fig. 4).

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 [10] and following the same trajectory in the P - T diagram, 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 depth of the velocity dip increases dramatically to reach near 20% at the critical point, before it joins with the crossover lines. 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 [10,13].

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 [15], 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 κ -Cl organic conductor allowed the first detailed study of the critical point region and they are consistent with the predictions of the DMFT. The very large dip in the velocity at the critical point corresponds to the predicted compressibility divergence of the electronic degrees of freedom [5,6] that joins continuously with two crossover lines. This is consistent with phonon anomalies due to strong electronic correlations [14]. We note the similarity with the two crossover lines identified in the Ni(S, Se)₂

compounds [2]. Most importantly, our data reveal that the high pressure crossover line coincides with the pseudogap features previously observed in magnetic [7], transport [8,9], and elastic [9] 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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