In an ultrasonic experiment, we have investigated the temperature profile of the velocity of longitudinal elastic waves propagating along a direction perpendicular to the layers in the organic superconductors \( \kappa-(\text{BEDT-TTF})_2\text{X} \), \( \text{X} = \text{Cu(SCN)}_2 \) and \( \text{Cu}[\text{N(CN)}_2]\text{Br} \). Although a small decrease of the velocity is observed at the superconducting transition, the most anomalous behavior is obtained in the normal metallic state where an important softening is identified around 40-50 K. In order to characterize the origin of this anomaly, we have studied its behavior under the application of hydrostatic pressure. The observed behavior is found to mimic those of the transport and magnetic properties of these materials which have been attributed to the magnetic fluctuations. Following the example of one-dimensional insulating systems where coupling between longitudinal acoustic waves and magnetic fluctuations is known to occur, our results suggest that the pseudo-gap regime of these two-dimensional organic superconductors is dominated by a similar mechanism.

Organic compounds of the \( \kappa-(\text{BEDT-TTF})_2\text{X} \) family are highly anisotropic, layered, extreme type II superconductors which show the highest superconducting transition temperatures known to date. They are continuing to attract considerable attention because of their similarity to the high \( T_c \) cuprates and the possibility that they also have a non-conventional pairing state. In these materials the superconducting phase is in close proximity to an antiferromagnetic (AF) phase. Indeed, at ambient pressure, the compounds with \( \text{X} = \text{Cu}[\text{N(CN)}_2]\text{Br} \) and \( \text{Cu(SCN)}_2 \) are showing superconducting ground states around 10 K, while an insulating one with antiferromagnetic ordering is obtained below 25 K for \( \text{X} = \text{Cu}[\text{N(CN)}_2]\text{Cl} \). However, the latter compound shows also a superconducting ground state around 12 K under a small hydrostatic pressure of 300 bar. In view of the strong dimerization of the BEDT-TTF molecules, this pressure induced metal-insulator transition results from the competition between the repulsive Coulomb energy (U) and the bandwidth (W) in the effectively half-filled electronic band structure (Mott transition). In the \( \text{Cu}[\text{N(CN)}_2]\text{Br} \) and \( \text{Cu(SCN)}_2 \) salts, the proximity of the AF magnetic phase can be inferred from the transport and magnetic properties of the normal state. In NMR experiments the maximum of \((\text{T}_1/\text{T})^{-1}\) around 50 K and the rapid decrease of the Knight shift below 50 K were attributed to both AF magnetic fluctuations and to a pseudo-gap. At the same temperature, the intra- and inter-layer resistivity data suggest a change of regime (peak in \( \text{dR/dT} \)) around the same temperature. All these features observed on the magnetic and transport properties are highly sensitive to pressure and they completely disappear above 2 kbar.

Ultrasonic techniques can be used to study quasiparticle and magnetic excitations effects on the elastic properties of superconductors and attenuation measurements are probably the key experiments that are still to be performed on organic and high \( T_c \) superconductors to assess the nature of the superconducting state. Indeed, the smallness of the crystals prohibits the application of standard ultrasonic methods to these materials. Nevertheless few measurements of the ultrasonic velocity \( V \) in the superconducting state have been performed on organic materials. In this paper a modified ultrasonic technique is used to investigate the elastic velocity in organic superconductors \( \kappa-(\text{BEDT-TTF})_2\text{X} \), \( \text{X} = \text{Cu(SCN)}_2 \) and \( \text{Cu}[\text{N(CN)}_2]\text{Br} \) in their normal state. In addition to a small velocity anomaly found at the superconducting transition temperature, we observe, for both compounds, a very large softening in the normal state. This peak is likely the result of a coupling between magnetic fluctuations and acoustic phonons. An investigation of these anomalies under hydrostatic pressure allows to obtain a phase diagram which establishes a clear connection between the temperatures of the superconducting transition and the pseudo-gap.

Single crystals of the organic superconductors \( \kappa-(\text{BEDT-TTF})_2\text{Cu}[\text{N(CN)}_2]\text{Br} \) and \( \kappa-(\text{BEDT-TTF})_2\text{Cu(SCN)}_2 \) were synthesized by the electrocrystallization technique described elsewhere. Because of their quasi-two-dimensional structure, the crystals have generally the shape of small shiny platelets or cubes. In our ultrasonic technique, the parallel faces identifying the highly conducting planes are the only faces that can be used properly to generate and detect acoustic waves propagating along a direction perpendicular to the layers. The crystals with typical surface area of 1 mm\(^2\) (layer plane) and thickness of 0.3 mm (transverse direction) were used in a pulse transmission experiment. The usual pulse echo method cannot, however, be utilized directly since the propagation length (~ 0.3 mm) does not allow time separation of transmitted and reflected echoes. We have thus used a modified set-up for the measurement. One parallel face of the crystal is first...
glued on the surface of a CaF$_2$ delay line (buffer length $\sim$ 7 mm). Then, a LiNbO$_3$ piezoelectric transducer bonded on the other parallel face generates longitudinal waves, at 30 MHz and odd overtones, that will propagate through the crystal-delay line ensemble and will be detected by a second piezoelectric transducer at the other end of the buffer. The ultrasonic velocity is measured with a pulsed acoustic interferometer and GE silicon sealant was used for all the bonds. The ultrasonic experiment can also be performed in a pressure cell using a liquid (maximum value 8 kbar). The temperature is monitored with a Si diode sensor and stabilized with a LakeShore controller. Magnetic field measurements up to 9 Tesla can also be done with this set-up.

The velocity of longitudinal waves propagating along a direction perpendicular to the layers has a rather low value around 2000 m/sec, in agreement with the 2D character of the structure. In this work we are interested in the temperature profile of the velocity only. This is obtained by monitoring the phase ($\phi$) of the transmitted signal as a function of the temperature. However, since two terms, $\phi = k_1 t_1 + k_2 t_2$ where $k_1$, $k_2$, $t_1$ and $t_2$ are respectively the ultrasonic wave vectors and the lengths of the crystal (1) and the delay line (2), contribute to the total phase of the transmitted signal, it is necessary to subtract the delay line contribution ($k_2 t_2$) to isolate the crystal one ($k_1 t_1$). The latter is measured in a pulsed reflection experiment in the delay line only at the same frequency and for identical experimental conditions. The crystal velocity data have not been corrected to take into account thermal expansion effects since these are orders of magnitude too small. No frequency effects could be detected on the ultrasonic velocity data. All the data presented in this paper have been obtained at 100 MHz.

We present in figure 1 the relative change of the velocity, $\Delta V/V = (V - V_0)/V_0$ where $V_0$ is the velocity at 200 K, as a function of temperature in the range 2-150 K for the $\kappa$-BEDT-TTF)$_2$Cu[N(CN)$_2$]Br and $\kappa$-(BEDT-TTF)$_2$Cu(SCN)$_2$ organic superconductors obtained at a pressure of a few mbar of helium gas. For both compounds, a weak softening of the velocity ($10^{-3}$) is observed at the superconducting transition temperature $T_c = 11.3$ and 9.2 K respectively for the Cu[N(CN)$_2$]Br and Cu(SCN)$_2$ crystals. A similar type of anomaly in the superconducting state has previously been reported in both compounds. As the temperature is increased above $T_c$, both velocity profiles reveal a very large dip centered at 38 and 50 K respectively for the Cu[N(CN)$_2$]Br and Cu(SCN)$_2$ compounds. The relative velocity softening is much larger for the Cu[N(CN)$_2$]Br crystal ($\sim$ 6%) than for the Cu(SCN)$_2$ one ($\sim$ 2%). No additional anomalous behavior is observed up to room temperature where the profile is dominated by the usual anharmonic contribution. As observed in transport experiments, rapid cooling of the crystals below 90 K decreases slightly the superconducting character and shifts a little the dip to higher temperatures. Although the application of a magnetic field perpendicularly to the layers decreases $T_c$ and eventually suppresses completely the superconducting state, no effects could be detected on the softening anomaly up to 9 Tesla . It is worth mentioning that recent measurements of thermal expansion have also revealed an anomalous behavior of that quantity along the direction perpendicular to the layers in the Cu[N(CN)$_2$]Br crystal: a peaked anomaly centered around 40 K was observed in agreement with our results.

A few scenarios can be suggested to explain the anomalous elastic behavior of these superconductors in the normal state. First, this could be the result of a structural phase transition. However, no such transition has ever been reported in either of these compounds, although indications of a second-order transition around 80 K have been obtained in several experiments. In relation to the onset of conformational order among the terminal ethylene groups of the donor molecules. The appearance of a structurally disordered state below 80 K can be induced easily by a rapid cooling process. This has been also verified on our ultrasonic velocity data as mentioned previously. The data presented here were obtained with the slowest possible cooling in order to avoid disorder. Although structural order clearly affects the low temperature properties, they cannot be responsible for the observed elastic feature around 40-50 K.

In a metal, the ultrasonic wave can also interact with the conduction electrons: the softening or hardening of an elastic constant (and the velocity) is then related to the augmentation or reduction in the quasiparticle screening of ion potential. In order to appreciate possible quasiparticle screening in our crystals, we present in figure 2 the microwave transverse resistivity of both compounds as a function of temperature. Even if the absolute values are 2 to 3 orders of magnitude higher, the temperature profile shown here is identical to the in-plane resis-
FIG. 2. Microwave transverse resistivity (17 GHz) as a function of temperature: $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br (full line) and $\kappa$-(BEDT-TTF)$_2$Cu(SCN)$_2$ (dotted line).

This gives an indication that the transverse transport is diffusive in these highly anisotropic conductors. As the temperature is decreased below the resistivity maximum around 80-90 K, a metallic regime first sets in and the resistivity decreases with a rate $d\rho/dT$ which is the largest at respectively 38 and 50 K for the Cu[N(CN)$_2$]Br and Cu(SCN)$_2$ crystals. Then, the expected decrease of the resistivity is observed when entering in the superconducting state at $T_c$. Since the softening elastic dip and the resistivity decrease in the normal state occur exactly at the same temperature values in both compounds, this is suggestive of a common mechanism. However no direct correlation can be established between these two features. Indeed, quasiparticle screening cannot explain an elastic softening which shows the temperature profile of a dip and, moreover, it should yield a larger acoustic anomaly when the compounds enter in the superconducting state, an observation which is not supported by the data presented in Fig.1.

In transport measurements, it has been suggested that the rapid decrease of the resistivity around 40-50 K is related to the presence of both a pseudo-gap regime and AF magnetic fluctuations in the normal state. These fluctuations have been clearly identified in NMR experiments in one-dimensional (1D) insulating systems. It is known that AF magnetic fluctuations can couple to longitudinal acoustic phonons and yield a softening of the ultrasonic longitudinal velocity along the 1D direction. The magneto-elastic coupling is then the result of the modulation of the spin exchange constant $J$ by the acoustic phonons. In such a 1D model, the softening occurs within a rather wide temperature domain with a maximum at $T \sim J$. Now one can ask the following question: is it possible to support a similar explanation in a 2D conducting system in which AF magnetic fluctuations are present? We will try to answer this question by investigating further the softening observed on the ultrasonic velocity by applying hydrostatic pressure. From NMR experiments (nuclear relaxation and Knight shift), the magnetic fluctuations and the pseudo-gap in these organic superconductors are indeed suppressed by a pressure of a few kbar. We present in figure 3 the temperature profile of the ultrasonic velocity at different pressures in the range 0.4-2.5 kbar. The observed trend with pressure is identical for both compounds: in addition to the decrease of the superconducting transition temperature $T_c$ with increasing pressure, there is a depression and a shift of the dip to higher temperatures in the normal state. No anomaly can be detected above 2.5 kbar, although the superconducting transition is still observed. These data confirm that the elastic anomaly shows temperature and pressure dependences which are similar to the ones observed on the transport and magnetic properties. We thus believe that it can be the result of a coupling between acoustic phonons and magnetic fluctuations. The absence of magnetic field effects (up to 9 Tesla) on the anomaly is not necessarily in contradiction with the magneto-elastic coupling picture. Indeed, field effects would be expected to be observed only if the Zeeman field energy is approaching $J_{\perp}$, namely the interlayer exchange constant which is not known for the moment.

In figure 4 we show the phase diagram which is obtained for the two organic conductors when the superconducting temperature $T_c$ (lower panel) and the temperature of the dip $T_M$ (upper panel) are plotted as a function of pressure. The variation of $T_c$ with pressure is
in full agreement with already published data. The variation of +25 K/kbar for $T_M$ with pressure is similar for the two materials. Although there is a 12 K separation between the $T_M$’s at zero pressure, this difference tends to be reduced as pressure is increased; a similar trend is observed for the $T_c$’s. This diagram is coherent with the fact that, in these materials, the superconducting phase is in close proximity to an antiferromagnetic phase. Moreover, magnetic fluctuations appear to be an important ingredient to obtain a superconducting state at high temperatures. Indeed, the Cu[N(CN)]$_2$Br crystal presents a higher $T_c$ than the Cu(SCN)$_2$ one at zero pressure, while the magnetic fluctuation effects manifest themselves at a lower temperature $T_M$. Finally, it is worth mentioning a special feature observed for the Cu[N(CN)]$_2$Br crystal. In figure 3, we notice that the anomaly obtained at 0.44 kbar has a larger amplitude and a smaller $T_M$ than the 0.36 kbar one. For the moment we cannot decide if this effect is real or not because we do not have enough precision on the pressure; one will need a gas pressure cell instead of a liquid to overcome this difficulty.

In summary, we have identified an important softening on the temperature profile of longitudinal ultrasonic waves propagating along a direction perpendicular to the conducting layers in 2D organic superconductors. Its pressure dependence suggests that this anomaly is related to the presence of magnetic fluctuations in this temperature range, as it was previously observed on the magnetic properties. The anomaly could then result from a coupling between acoustic phonons and AF magnetic fluctuations. Although similar anomalies have been observed in 1D insulating magnetic systems, our data give the first observation of such a phenomenon in an organic conductor having a 2D character. Considering the large amplitude of the anomaly, this signifies an important coupling between the lattice and the spin degrees of freedom.

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1. J. M. Williams et al., in Organic Superconductivity, edited by V. Kresin and W.A. Little (Plenum Press, New York, 1990).
2. R.H. McKenzie, Science 278, 820 (1997).
3. H. Urayama et al., Chem. Lett. 1988, 5; A.M. Kini et al., Inorg. Chem. 29, 2555 (1990).
4. U. Welp et al., Phys. Rev. Lett. 69, 840 (1992); K. Miyagawa et al., Phys. Rev. Lett. 75, 1174 (1995).
5. S. Lefebvre et al., unpublished.
6. J.M. Williams et al., Inorg. Chem. 29, 3274 (1990).
7. K. Kanoda, Physica C 282-287, 299 (1997).
8. A. Kawamoto et al., Phys. Rev. Lett. 74, 3455 (1995).
9. H. Mayaffre et al., Europhys. Lett. 28, 205 (1994).
10. Y.V. Shushko et al., J. Phys. I, 1, 1375 (1991).
11. M. Yoshizawa et al., Sol. State Comm. 89, 701 (1994).
12. K. Frikach et al., Synthetic Metals 103, 2081 (1999).
13. A.M. Kini et al., Inorg. Chem. 29, 2555 (1990).
14. M. Poirier et al., Phys. Rev. B 41, 4869 (1990).
15. M. Kund et al., Physica B 203, 129 (1994).
16. M. Lang et al., unpublished data.
17. X. Su et al., Phys. Rev. B57, R14056 (1998).
18. Y. Trudeau et al, Phys. Rev. B46, 169 (1992).
19. B. Dumoulin et al., Synth. Metals 86, 2243 (1997).
20. J.E. Schriber et al., Physica C152, 157 (1988).
21. Y. V. Sushko et al., J. Phys. France 1, 1375 (1991).