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Symmetry-imposed signatures at the pseudogap crossover in κ-(BEDT-TTF)$_2X$ organic superconductors

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Very large softening anomalies are detected on particular shear elastic moduli at the pseudogap crossover line in the layered organic conductors κ-(ET)$_2X$, $X =$ Cu(SCN)$_2$ and Cu[N(CN)$_2$]Br. Symmetry properties at this crossover cannot be explained by a compressible Hubbard model with isotropic coupling to the lattice degrees of freedom. We observed that an anomaly is present or not on a shear modulus if, and only if, a corresponding anomaly appears at the superconducting transition. This observation suggests a symmetry driven correspondence between the superconducting phase and the pseudogap crossover in these layered organics. Since the mixed character $d_{xy} + d_{z(x+y)}$ was advanced for the superconducting phase, this suggests that a new theoretical approach to the pseudogap behavior is needed and reemphasizes the significance of the interlayer hopping which is implied in the $d_{z(x+y)}$ component.

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The Mott transition induced by electron-electron interactions is one of the key features observed in the phase diagram of the layered half-filled organic charge transfer salts κ-(ET)$_2X$ (ET = BEDT-TTF).[1] This first-order phase transition can be approached by varying pressure, temperature, or anionic substitution. The transition line ends at a second-order critical point (P_c, T_c), whose critical behavior has been extensively investigated.[2,3] Theoretically the physics of the Mott transition has been investigated successfully with the dynamical mean-field theory (DMFT).[4–6] The electronic degrees of freedom being the driving force of the transition, the critical end point has been associated with a diverging electronic response function χ_{el} (Refs. 7 and 8) in analogy with the liquid-gas transition.

The lattice degrees of freedom exhibit a strong coupling behavior in close proximity to the Mott transition as demonstrated by a discontinuous increase of the lattice spacing through the first-order metal-insulator transition line in the $(V_{1-x}\mathrm{Cr}_x)_2\mathrm{O}_3$ compounds.[9] For the κ-(ET)$_2X$ crystals, the frequency of some optical phonons has shown a nonmonotonic temperature dependence below 200 K (Ref. 10) that is theoretically related to the electronic spectral weight redistribution over the bandwidth.[11] Acoustic longitudinal phonons were also found to be strongly renormalized by the proximity of the Mott transition as revealed by a pronounced sound velocity anomaly[12,13] observed when crossing the so-called pseudogap line where the spin-lattice relaxation rate $1/T_1T$ reaches its maximum. A pressure-dependent study on the κ-(ET)$_2$Cu[N(CN)$_2$]Cl compound revealed a dramatic deepening of this velocity anomaly accounting for the expected diverging electronic compressibility near the critical endpoint.[14] In the framework of the DMFT, these effects were investigated within the compressible Hubbard model which retains both the electronic and lattice degrees of freedom[15] and the results compare favorably with those of the acoustic experiments on the longitudinal mode.

Joining the efforts to identify the superconducting pairing symmetry in these layered organic compounds, the sound velocity measurements were extended to transverse acoustic modes in the κ-(ET)$_2$Cu[N(CN)$_2$]Br compound.[16] However, a phase separation between metallic and magnetic insulating components over the same temperature range limited our ability to definitely address that question. This was later resolved by identical measurements performed on a compound located farther from the Mott transition line, κ-(ET)$_2$Cu(SCN)$_2$, allowing us to conclude on a clear symmetry-restricted mixed superconducting order parameter ($d_{xy} + d_{z(x+y)}$).[17] Suprisingly, the presence of a $d_{z(x+y)}$ contribution to the order parameter suggests that interlayer hopping is of fundamental relevance to the problem. Even though a symmetry breaking was indeed confirmed in the superconducting phase, a similar scenario at the pseudogap line was unlikely within the actual DMFT approach. We thus report here clear signatures of symmetry restrictions from a study of the giant ultrasonic velocity anomaly, appearing at the pseudogap line, for different polarizations of the acoustic waves. Though not directly linked to an order parameter, these intrinsic symmetry restrictions appear to be in clear correspondence with the ones observed in the superconducting phase. No theoretical model appears presently appropriate to explain these results.

In a pulse-echo experiment on the κ-(ET)$_2X$ crystals, ultrasonic waves can only propagate perpendicularly to the preferentially grown platelet plane which is the natural two-dimensional electron gas plane orientation. An acoustic interferometer is used to measure the variation of the sound velocity relative to a value at constant temperature $T_0 = 80$ K, $\Delta V/V = [V(T) - V(T_0)]/V(T_0)$, which can be related to the relative variation of the appropriate elastic modulus C_{ij} through the relation $\Delta C_{ij}/C_{ij} = 2\Delta V/V$. As explained in Ref. 17, the use of one longitudinal and two transverse waves allows access to three elastic moduli for each crystal: C_{22}, C_{66}, and C_{44} for orthorhombic κ-(ET)$_2$Cu[N(CN)$_2$]Br; and C_{11}, C_{55}, and C_{66} for monoclinic κ-(ET)$_2$Cu(SCN)$_2$, as indicated in Table I. This is, however, a simplification for the monoclinic structure since only quasilongitudinal and quasitransverse waves could be propagated along the a^* axis (the normal to the highly conducting planes). Since the bonding process of the piezoelectric transducer on organic crystals is not reversible,

TABLE I. Elastic constants C_{ij} with the appropriate polarization of the ultrasonic waves for two κ-(ET)$_2X$ compounds.

Waves	Cu(NCS)$_2$	Cu[N(CN)$_2$]Br
Longitudinal	C_{11} ($\vec{a}^*$)	C_{22} ($\vec{b}$)
Transverse	C_{55} ($\vec{c}$)	C_{66} ($\vec{a}$)
Transverse	C_{66} ($\vec{b}$)	C_{44} ($\vec{c}$)

three different crystals of the same growth batch were used with appropriate transducer polarizations for each compound. The $\Delta V/V$ data are not dependent on frequency over the range 100–300 MHz that is used here. We used the lowest frequency possible (105 MHz) to maximize the signal intensity that is experimentally limited by the quadratic frequency dependence of the attenuation.

We present in Fig. 1 the relative variation of the elastic moduli $\Delta C_{ij}/C_{ij}$ as a function of temperature below 80 K for the two κ-(ET)$_2X$ compounds. Two types of elastic anomaly are observed on these temperature dependencies for both compounds: a small anomaly ($\sim 10^{-3}$) at the superconducting temperature, $T_c = 9.5$ and 11.9 K, respectively, for $X =$ Cu(SCN)$_2$ and Cu[N(CN)$_2$]Br; and a giant softening anomaly ($\sim 10^{-2}$–10^{-1}) at the pseudogap line near 45 and 35–40 K, respectively. These two types of anomaly are consistent with the pressure-temperature phase diagram of which an example, mapped with the same ultrasound technique,[14] is given in Fig. 2 for the isostructural κ-(ET)$_2$Cu[N(CN)$_2$]Cl compound. In this diagram, we have indicated with dashed lines the position of the pseudogap anomaly at ambient pressure for the two compounds investigated here. Both types of elastic anomalies have always been observed with a high degree of reproducibility on crystals originating from different growth batches; the position of the pseudogap anomaly in temperature could vary by at most a few degrees from sample to sample due to the rapidly varying attenuation with crystal thickness. The anomalies in the superconducting phase were analyzed in Ref. 17 and we do not pursue their description here. However, these anomalies appear closely linked to the high temperature ones and they thus are part of the following discussion.

For the monoclinic compound κ-(ET)$_2$Cu(SCN)$_2$ in Fig. 1, the compression modulus C_{11} corresponds to quasilongitudinal waves propagating along the a^* axis: the softening anomaly around 45 K was previously reported[13] and analyzed as a function of hydrostatic pressure. It was shown that this anomaly is related to the pseudogap regime of the phase diagram. The anomaly shifts to higher temperatures, and its amplitude decreases with increasing pressure as the compound is more distant from the Mott critical point. The temperature behavior of the other two elastic moduli was never reported before and the features found are quite unexpected. If we understand the anomaly on C_{11} as a diverging compressibility due to a diverging electronic response χ_{el} in the compressible Hubbard model scheme,[15] no anomaly is to be expected on either shear elastic moduli. As seen in Fig. 1, there is no anomaly on C_{66} when there is definitively one on C_{55} with a much larger amplitude than on C_{11}. One can argue that the small change of slope around 45 K observed on C_{66} could be a signature of a remaining anomaly; for instance, this could be explained by mode mixing due to quasitransverse propagation in a monoclinic structure and/or to an error of the transducer's orientation relative to the in-plane crystal axes. We thus conclude that only the elastic shear

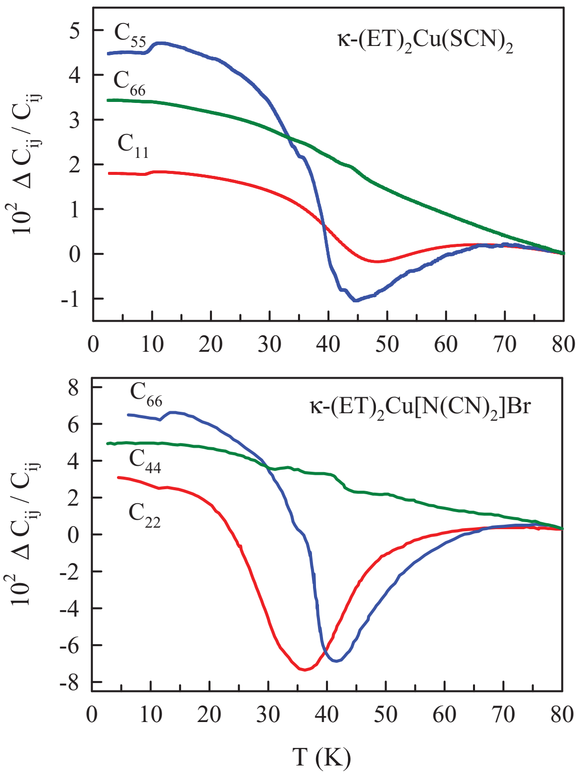

FIG. 1. (Color online) Temperature dependence of elastic moduli C_{ij} for two layered κ-(ET)$_2X$ organics.

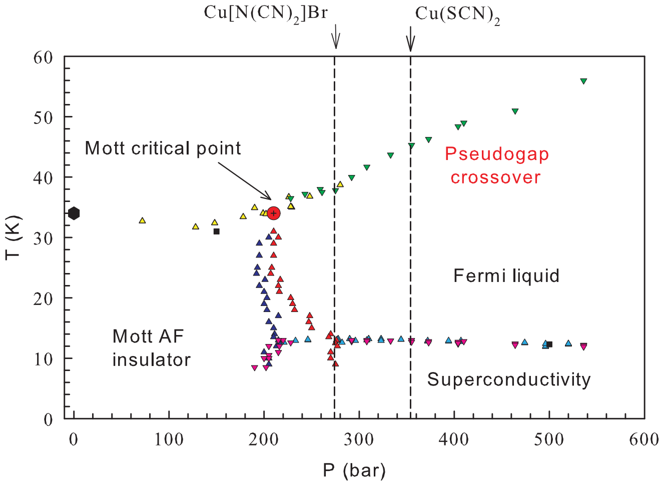

FIG. 2. (Color online) Temperature-pressure phase diagram of the layered κ-(ET)$_2$Cu[N(CN)$_2$]Cl organic compound taken from Ref. 14. The dashed lines indicate the position of the two compounds studied here, $X =$ Cu(SCN)$_2$ and Cu[N(CN)$_2$]Br, relative to the value of the pseudogap crossover temperature measured at ambient pressure.

modulus C_{55} shows a softening anomaly for the monoclinic compound.

Similar results are observed for the κ-(ET)$_2$Cu[N(CN)$_2$]Br crystal (Fig. 1). The amplitude of the softening anomalies is, however, much larger for this compound as it is located closer to the Mott critical point in the phase diagram, in agreement with the pressure study of the compressibility anomaly in the isostructural crystal κ-(ET)$_2$Cu[N(CN)$_2$]Cl (Ref. 14). The anomaly around 36 K on the compression modulus C_{22} was previously reported and analyzed as a function of hydrostatic pressure,[13] Again, the two shear moduli do not show the same temperature dependence: no anomaly is observed on C_{44} when a huge one is seen on C_{66} with a larger amplitude than on C_{22}. The C_{66} anomaly appears to be shifted to higher temperature compared to the C_{22} one; this shift, however, is most probably an experimental artifact related to the difficulty of tracking the wave velocity when the attenuation is very large (which is particularly the case for this transverse mode in the vicinity of the anomaly). The instabilities observed on C_{44} between 30 and 50 K are likely due to a small misalignment of the transducer's polarization relative to the crystal axes. As for the monoclinic compound, only one shear modulus C_{66} shows a pronounced softening anomaly. Finally, a small anomaly is observed around 35 K for both compounds on the shear moduli C_{55} ($X = \text{Cu(SCN)}_2$) and C_{66} ($X = \text{Cu[N(CN)}_2\text{]Br}$); as this anomaly is observed on the modulus which shows the largest elastic softening and attenuation for both compounds, its origin is believed to be extrinsic.

Hassan *et al.*[15] proposed that the longitudinal elastic softening anomaly likely originates from a linear coupling between the strain ϵ_i and an isotropic electronic response function χ_{el} which are both invariant under all the symmetry operations of the group to which they belong (monoclinic C_{2h} and orthorhombic D_{2h}). Our results show clearly that a response function that couples only to the compression strain ϵ_1 or ϵ_2 for the monoclinic or orthorhombic compound is not sufficient to explain the elastic anomaly on a shear moduli. It is known that these κ-(ET)$_2$ compounds have very similar anisotropic physical properties and, in particular, an identical Fermi surface. Then, it is not surprising to find that the same shear elastic moduli are affected the same way by the electronic degrees of freedom, anomaly on C_{55} (C_{66}) and nothing on C_{66} (C_{44}) for the monoclinic (orthorhombic) crystal structure.

An additional intriguing observation is the direct correspondence that can be established between elastic anomalies appearing in the superconducting phase[17] and the ones reported here in the pseudogap regime. The same selection rules related to symmetry arguments applied in both cases: the presence/absence of an anomaly occurs on the same elastic moduli with identical relative amplitude, suggesting common symmetry properties of the effective Hamiltonians leading to the superconducting phase and the pseudogap regime, respectively. For the superconducting phase it was suggested that the order parameter has a mixed character,[17] $A_{1g} + B_{1g}$ ($d_{xy} + d_{z(x+y)}$), implying that interlayer hopping is an important variable in these systems because of the presence of the $d_{z(x+y)}$ function. We foresee a similar underlying symmetry inside the pseudogap regime. Although experimental studies of the pseudogap symmetry in high T_c materials can be found in the literature (e.g., Ref. 18), a clear correspondence between superconductivity and pseudogap behavior in relation to the Mott transition appears to be a unique feature of these layered organic compounds.

For completeness, one should mention that the spin degrees of freedom may constitute an alternative to the transverse anomaly origin. The spin-lattice relaxation deduced in nuclear magnetic resonance experiments (NMR) on the κ-(ET)$_2X$ compounds is interpreted in terms of spin fluctuations whose energy scale coincides with a spin-gap opening and short spin-correlations.[19] Extensive NMR experiments demonstrate that the critical suppression of antiferromagnetic fluctuations is accompanied by the critical enhancement of the conductance.[20] the two criticalities showing the very same nonuniversal exponent. Our elastic data may highlight, in addition to the charge degrees of freedom, the high sensitivity of shear moduli to the spin degrees of freedom. Low-dimensional magnetic systems show wide softening anomalies when the elastic moduli are renormalized by magnetic fluctuations;[21,22] however, when considering a magnetoelastic coupling with a conventional magnetic order parameter, symmetry arguments limit the coupling to the longitudinal modes suggesting, as expected, that no conventional magnetic order appears to be involved in our case. Nonetheless, systems with complex magnetic exchanges generating magnetically driven nematic fluctuations can couple to shear modes and generate very wide anomalies without phase transition.[23] In the context of an exotic spin-fluctuation scenario, possibly related to the spin-frustration properties notorious in this family of organic compounds, the type of spin fluctuations that can couple with the appropriate strain field, as well as the correspondence with the superconducting phase, will have to be addressed theoretically.

The observation of very large softening anomalies on several elastic moduli could possibly signal the occurrence of a phase transition at the pseudogap line, but the absence of any clear signatures of such a transition on various physical properties investigated in these organic compounds disqualifies this assumption. The softening anomaly is rather directly linked to the Mott transition, since, as one changes pressure toward the Mott critical pressure, the pseudogap anomaly shifts toward the Mott critical temperature and its amplitude increases.[14] It has been shown experimentally that the critical behavior in these quasi-two-dimensional organics is not consistent with known universality classes obtained for a Mott transition in two dimensions.[24] The ultrasonic data presented here strongly suggest one take into account interplane correlations in both the superconducting phase and the pseudogap crossover region, confirming then the inadequacy of purely two-dimensional models to explain these experimental results.

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