Mixed pairing symmetry in $\kappa$-(BEDT-TTF)$_2$X organic superconductors from ultrasonic velocity measurements

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Discontinuities in elastic constants are detected at the superconducting transition of layered organics $\kappa$-(BEDT-TTF)$_2$X by longitudinal and transverse ultrasonic velocity measurements. Symmetry arguments show that discontinuities in shear elastic constants can be explained in the orthorhombic compound only if the superconducting order parameter has a mixed character that can be of two types, either $A_{1g} + B_{1g}$ or $B_{2g} + B_{3g}$ in the classification of irreducible representations of the orthorhombic point group $D_{2h}$. Consistency with other measurements suggests that the $A_{1g} + B_{1g}$ ($d_{xy} + d_{x^2-y^2}$) possibility is realized. Such clear symmetry-imposed signatures of mixed order parameters have not been observed in other superconducting compounds.

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Unconventional, non s-wave, superconductors in solids seem ubiquitously associated with strong electronic correlations. This is the case in a wide variety of compounds that include heavy fermions, ruthenates, cuprates as well as quasi-two-dimensional half-filled organic charge transfer salts $\kappa$-(ET)$_2$X (ET = BEDT-TTF) [1]. In most cases gaps with nodes are observed, but the exact symmetry of the unconventional superconducting order parameter is controversial only in the cuprates.

In this letter, we focus on the layered organics that exhibit antiferromagnetism and Mott insulating behavior, as the cuprates, and establish the two-component nature of the singlet order parameter in the orthorhombic compound only if the superconducting order parameter has a mixed character $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br. Previous studies suggest $d$-wave pairing with nodes, although $s$-wave symmetry is sometimes seen. Measurements sensitive to the $\tilde{k}$-space dispersion, such as scanning tunneling spectroscopy [2] and thermal conductivity [3], favor $d_{xy}$ symmetry, namely nodes along the nearest neighbor bonds (or equivalently, between the orthorhombic axes). Moreover, theoretical calculations based either on spin-fluctuation mediated superconductivity [4, 5, 6, 7] or on quantum cluster methods [8, 9] and variational approaches [10] for the Hubbard model, support the anisotropic $d$-wave picture with a prevailing $d_{x^2-y^2}$ symmetry. Nevertheless, none of these calculations has considered interlayer hopping, which, as we will show, is necessary to explain the experimental data that we present.

The ultrasonic probe is extremely sensitive to gap anisotropies as the attenuation and velocity depend on both the direction of wave propagation and the direction of polarization. Attenuation experiments on UPT$_3$ [11, 12] and of Sr$_2$RuO$_4$ [13] perfectly illustrate how the unconventional gap structure can be unraveled by such a versatile technique. In organic charge transfer salts however, attenuation experiments are hampered by the small size and the shape of single crystals. Nevertheless, one experiment was successful for the $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br compound [14], but the interpretation of the results was complicated by a phase separation occurring even in highly ordered samples. Notwithstanding these difficulties, ultrasound velocity can also be used to obtain insights into the nature of the superconducting (SC) state in layered organics. Lattice anomalies [15] and elastic constant changes have been identified, but no consistent effort has been yet dedicated to identify the SC order symmetry.

We report anomalies observed at the SC transition temperature $T_c$ on three elastic constants of monoclinic $\kappa$-(ET)$_2$Cu(NCS)$_2$ and of orthorhombic $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br. Even though these compounds belong to different point groups, we expect similarities in the SC order parameters because of their nearly identical electronic properties. To understand discontinuities in elastic constants one can invoke Landau-Ginzburg arguments [18, 19] or perform detailed BSC type calculations [20, 21]. Since we focus on symmetry properties, a Ginzburg-Landau (GL) approach will suffice [22, 23, 24, 25].

We use an acoustic interferometer [14] to measure relative changes in velocity $\Delta V/V$ that allow us to extract the corresponding relative variations in the elastic constants $C$ through $\Delta C/C = 2\Delta V/V$. The $\kappa$-(ET)$_2$X crystals grow as platelets containing the highly conducting planes whose normal is oriented along $\tilde{a}^*$ for monoclinic $\kappa$-(ET)$_2$Cu(NCS)$_2$ and along $\tilde{b}$ for the orthorhombic $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br. Thus, ultrasonic plane waves can be propagated only along these normal directions. Pure longitudinal and transverse waves cannot be propagated along the $\tilde{a}^*$ axis of the monoclinic structure so, strictly speaking, it is not possible to measure the $C_{ij}$'s individually as it is the case for the orthorhombic material [20]. However, given the layered structure and the $\tilde{a}$ axis orientation of about $110^\circ$ instead of $90^\circ$ from the plane, we neglect, as a first approximation, the off-diagonal ele-

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The $\kappa$-(ET)$_2$Cu(NCS)$_2$ crystal will be considered as our reference compound since it is located far enough from the Mott transition line on the high pressure side of the P-T diagram with no indication of a phase separation. To extract the elastic change caused by the onset of superconductivity, we applied a magnetic field perpendicular to the highly conducting plane to quench the SC state. We show in Fig. 1A the temperature dependence of the relative change of the longitudinal velocity below 20 K at 166 MHz. In zero magnetic field a negative discontinuity of the velocity is obtained at $T_c = 9.5$ K; the anomaly is completely quenched in a field of 12 Tesla leaving only a monotonous decrease of the velocity as the temperature increases. We notice the absence of magnetic field effects above 12 K, an observation that excludes, contrary to the $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br compound [14], the presence of a coexisting phase in this temperature range. The difference between these two curves yields the relative variation of the compressional constant $C_{11}$ shown in Fig. 1B at different frequencies. As expected, no frequency dependence is observed: the onset of the SC phase yields a negative discontinuity at $T_c$ that extends over a few degrees due to important SC fluctuations above and below the superconducting temperature defined as the maximum slope. At lower temperatures $\Delta C_{11}/C_{11}$ is practically constant. A similar procedure was used for the two transverse acoustic modes yielding, over the same temperature range, $\Delta C_{55}/C_{55}$ and $\Delta C_{66}/C_{66}$. The three relative elastic constant variations are compared in Fig. 2. While a negative discontinuity is expected on $C_{11}$ [18], the appearance of a discontinuity on the shear constant $C_{55}$ is unusual. The amplitude of the discontinuity is larger than that of $C_{11}$ by approximately a factor two, excluding the simple explanation of mode mixing for a quasi-transverse wave. These discontinuities are larger than in other non conventional superconductors [27, 28] by two to three orders of magnitude. No discontinuity is observed for $\Delta C_{66}/C_{66}$; only a small change of slope is obtained at $T_c$.

In the highly ordered $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br compound, the coexistence of antiferromagnetic (AF) and SC phases complicates the analysis of the SC state [14]. Moreover, a higher magnetic field is needed to quench the SC state. We present in Fig. 2 the $\Delta C_{ij}/C_{ij}$ obtained by substracting the zero and 16 Tesla curves. We notice that magnetic field effects are observed in the normal state up to 20 K on $C_{22}$ and $C_{66}$ ($\Delta C_{ij}/C_{ij}$ is not zero). The temperature dependence below $T_c = 11.9$ K is also not monotonous and the SC fluctuations appear on a wider temperature range above $T_c$. Notwithstanding these differences, the comparison with the $\kappa$-(ET)$_2$Cu(NCS)$_2$ data (see Fig. 2) at $T_c$ is remarkable: we still observe a negative discontinuity on $C_{22}$ ($C_{11}$), a

| Waves          | $\text{Cu(NCS)}_2$ | $\text{Cu[N(CN)}_2\text{]Br}$ |
|----------------|--------------------|-------------------------------|
| Longitudinal   | $C_{11}$ ($a^2$)   | $C_{22}$ ($b$)                |
| Transverse     | $C_{55}$ ($c^2$)   | $C_{66}$ ($a$)                |
| Transverse     | $C_{66}$ ($b$)     | $C_{44}$ ($c$)                |

TABLE I: Elastic constants $C_{ij}$ with the appropriate polarisation of the ultrasonic waves for two $\kappa$-(ET)$_2$X compounds.
larger one on $C_{66}$ ($C_{55}$) and only a change of slope on $C_{44}$ ($C_{66}$). These observations clearly establish the similarity of the couplings between the SC order parameter and the elastic strains, although the crystal symmetry groups differ because of the tilting of the axis normal to the planes. Moreover, they confirm that the negative discontinuity on $\Delta C_{55}/C_{55}$ for the monoclinic compound is intrinsic and that it cannot be attributed to mode mixing.

Experiment has established that the layered organics are singlet superconductors [1]. In the simplest GL model then, discontinuities in elastic constants at the superconducting transition are easily explained through the free energy functional

$$F = a|\eta|^2 + g\varepsilon_1|\eta|^2 + \frac{b}{2}|\eta|^4 + \sum_{i,j} \frac{1}{2} C_{ij}\varepsilon_i\varepsilon_j$$

where $\eta$ is the order parameter, $b$ is a constant, $\varepsilon_1$ is the strain, $C_{ij}$ the matrix of elastic constants, while $a$ is proportional to $(T - T_c)$. If one of the strains is coupled linearly through the constant $g$ to the order parameter, the minimization with respect to $\eta$ shows that at the transition a negative discontinuity appears on the effective elastic constant $C_{ii}^{\eta} = \partial^2 F/\partial \varepsilon_i^2$. Such a linear coupling to $|\eta|^2$ is possible only if the strain $\varepsilon_i$ is invariant under all the operations of the point group because $|\eta|^2$ is. Higher order coupling terms in the free energy would only lead to the change of slope or curvature observed below $T_c$ for all $C_{ii}$, and these are not considered here.

Table II shows a simplified character table for the irreducible representations of the monoclinic $C_{2h}$ group of $\kappa$-(ET)$_2$Cu(NCS)$_2$, along with the transformation properties of the strains and examples of basis functions for the order parameter. Note that the $x$ and $y$ axes are not perpendicular. They lie along the atomic bonds, which are along the diagonal formed by the $b$ and $c$ axes. Since, according to Table III, $\varepsilon_1$ and $\varepsilon_5$ are invariant under

| irrep | $E$ | $C_{2h}^b$ | Basis functions | Strains |
|-------|-----|-----------|-----------------|--------|
| $A_g$ | 1   | 1         | $s, x, y, (x+y)z$ | $\varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_5$ |
| $B_g$ | 1   | -1        | $x^2 - y^2, (x-y)z$ | $\varepsilon_4, \varepsilon_6$ |

TABLE II: Simplified character table, basis functions and transformation properties of the strains. The monoclinic $C_{2h}$ group for $\kappa$-(ET)$_2$Cu(NCS)$_2$ has the character table of $C_2 \otimes i$, but inversion $i$ always has character $+1$ for singlets so the table of $C_2$ shown above suffices. The names of the irreducible representations are those of $C_{2h}$. The last column shows the transformation properties of the strains and the next to last column examples of basis functions for the order parameter. The $a$ axis is tilted towards $c$ (equivalently $x+y$) axis in the layers.

The symmetry operations of the group, the corresponding elastic constants can couple linearly to $|\eta|^2$, leading to negative discontinuities. However, $\varepsilon_5$ is not invariant so there is no discontinuity at $T_c$. This explains the observations for $\kappa$-(ET)$_2$Cu(NCS)$_2$ and does not impose any constraint on the symmetry of the order parameter.

In the orthorhombic $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br, because of the different conventions, the role of $\varepsilon_5$ in the monoclinic case is played by $\varepsilon_6$. The simplified character table for the $D_{2h}$ group shows that the shear strain $\varepsilon_6$ is not invariant under the operations of the group. Hence, the $C_{66}$ negative discontinuity at $T_c$ cannot be explained with the simplest model Eq. (1). One must introduce an order parameter with two orthonormal basis functions with respective complex coefficients $\eta_1$ and $\eta_2$. Let us first neglect the strain terms and consider the most general free energy functional that is invariant under the point group and phase changes of the order parameter

$$F_\eta = a_1|\eta_1|^2 + b_1\frac{1}{2}|\eta_1|^4 + a_2|\eta_2|^2 + b_2\frac{1}{2}|\eta_2|^4$$

$$+|\eta_1|^2|\eta_2|^2(\gamma + \delta \cos(2\Delta \theta)).$$

In this expression, $\gamma$ and $\delta$ are constants and $\Delta \theta$ is the phase difference between the two components of the order parameter. If $\delta$ is positive, this free energy will be minimized by $\Delta \theta = \pm \pi/2$, while if $\delta$ is negative $\Delta \theta = 0$ or $\pi$ will be the minimum. The case $\Delta \theta = \pm \pi/2$ corresponds to a complex order parameter, hence it breaks time reversal symmetry.
To explain the discontinuity in the transverse elastic constant, the coupling free energy
\[ F_{\text{ge}} = g \epsilon_6 |\eta_1| |\eta_2| \cos(\Delta \theta) \]
must be allowed by symmetry. Also, \( \cos(\Delta \theta) \) should not vanish, thus removing the possibility of a time-reversal symmetry-breaking state. Since \( \epsilon_6 \) transforms according to the \( B_{1g} \) representation, there are only two possibilities. Either one of the \( \eta \) is invariant (\( A_{1g} \)) and the other one transforms as \( B_{1g} \) or one of the components transforms like \( B_{2g} \) and the other one like \( B_{3g} \). This can be checked by showing that the product of the characters in Table III is unity for all group operations applied to \( F_{\text{ge}} \). Note that both of the above possibilities for \( \eta_1 \) and \( \eta_2 \) forbid a linear coupling to \( \epsilon_4 \) since the latter transforms like \( B_{3g} \). This explains the absence of a discontinuity in the corresponding elastic constant.

Since both scanning tunneling spectroscopy [2] and thermal conductivity [3] suggest nodes along the \( x \) and \( y \) axis, this forces us to choose an order parameter that has a mixed \( A_{1g} + B_{1g} \) character, namely \( d_{xy} + g_{(x+y)} \). The nodeless \( s \) case has the same symmetry as \( d_{xy} \) so more generally it should be included but it suffices that its amplitude be smaller than that of \( d_{xy} \) for the nodes of \( s + d_{xy} \) to survive. They are just shifted from their position in the \( d_{xy} \) case. The \( d_{z(x+y)} \) component does not remove the nodes in the plane, but it clearly breaks mirror symmetry about the planes.

On general grounds, the free energy Eq. (2) predicts two different \( T_c \)’s since there is no a priori reason why \( a_1 \) and \( a_2 \) should vanish at the same \( T \). That is different from the case of \( \text{Sr}_2\text{RuO}_4 \) where the two components of the order parameter necessary to explain the data belong to a single two-dimensional representation \( E_{2u} \) of the point group \( D_{4h} \). Although the present lattice is nearly triangular, the two components of the order parameter that we found do not coalesce into a single two-dimensional representation of the \( D_{4h} \) group [22]. Nevertheless, the mixed \( A_{1g} + B_{1g} \) representation for the orthorhombic crystal does coalesce into the one-dimensional \( A_g \) representation of its monoclinic cousin, leading to a single \( T_c \) in that case. Hence, we do not expect a large difference between the two transition temperatures of the orthorhombic crystal. Our experimental data in Fig. 3 show a rather broad transition with an extended region of SC fluctuations that could mask this difference between the two transitions.

The presence of a \( d_{z(x+y)} \) component to the order parameter suggests that interlayer hopping is an important variable in the problem. The value of this parameter has been estimated from angle-dependent magnetoresistance oscillations [31]. Thermal expansion data [32] also disclose a striking anisotropy and dependence of \( T_c \) on interlayer effects [33] that are unlikely to be captured by a 2D purely electronic model.

In summary, symmetry and the observed discontinuities at \( T_c \) in the ultrasonic velocity data for two compounds of the layered \( \kappa-(\text{ET})_2\text{X} \) organic superconductors demonstrate that the order parameter must have at least two components in the orthorhombic compound \( \kappa-(\text{ET})_2\text{Cu[N(CN)]}_2\text{Br} \). Consistency with other experiments selects \( A_{1g} + B_{1g} \) (equivalently \( d_{xy} + d_{z(x+y)} \)). The two components coalesce into a one-dimensional irreducible representation \( A_g \) in the monoclinic compound \( \kappa-(\text{ET})_2\text{Cu(NCS)}_2 \). Nodes are not symmetry imposed but are symmetry allowed and are likely to occur in electronic pairing mechanisms. The \( d_{z(x+y)} \) component of the order parameter suggests that further studies of interlayer coupling are called for.

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