PHYSICAL REVIEW B **80**, 220511(R) (2009)

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

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(Received 23 November 2009; published 30 December 2009)

Discontinuities in elastic constants are detected at the superconducting transition of layered organic conductors κ-(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 $A_{1g}+B_{1g}(d_{xy}+d_{z(x+y)})$ possibility is realized. Such clear symmetry-imposed signatures of mixed order parameters have not been observed in other superconducting compounds.

DOI: 10.1103/PhysRevB.80.220511 PACS number(s): 74.70.Kn, 74.25.Ld, 74.20.Rp

Unconventional, non-*s*-wave, superconductors in solids are ubiquitously associated with strong electronic correlations. This is the case in a wide variety of compounds that include heavy fermions, ruthenates, and cuprates. Although the symmetry of the order parameter is the most important information about a phase of matter, the exact symmetry of the unconventional superconducting order parameter is uncontroversial only in the cuprates. In addition to breaking $U(1)$ symmetry, superconducting phases in strongly correlated systems can also break crystal symmetry and that symmetry breaking is harder to detect.

Quasi-two-dimensional half-filled organic charge-transfer salts κ-(ET)$_2$X(ET=BEDT-TTF) (Ref. 1) play a special role in the above-mentioned class of superconductors. Indeed, they exhibit antiferromagnetism and Mott insulating behavior and they can be described in first approximation by the one-band Hubbard model, as the cuprates, albeit on a different lattice. In addition one can tune through the Mott transition with pressure. They are thus model systems to gain insight into strongly correlated superconductivity.

In this Rapid Communication, we establish the mixed character of the singlet order parameter in the orthorhombic compound κ-(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 $\vec{k}$-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[4–7] 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 the direction of both wave propagation and polarization. Attenuation experiments on UPt_3 (Refs. 11 and 12) and on Sr_2RuO_4 (Ref. 13) perfectly illustrate how the unconventional gap structure can be unraveled by this powerful 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 κ-(ET)$_2$Cu[N(CN)$_2$]Br compound,[14] but the interpretation of both velocity and attenuation results was complicated by a phase separation occurring even in highly ordered samples. Notwithstanding these difficulties, ultrasound *velocity* can be used to obtain insights into the nature of the superconducting (SC) state in layered organics. Lattice anomalies[15] and elastic constant changes[16,17] 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 κ-(ET)$_2$Cu(NCS)$_2$ and of orthorhombic κ-(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.[22–25]

We use an acoustic interferometer[14] where relative changes in frequency $\Delta f/f$ are transformed, after delay line correction, into velocity changes $\Delta V/V$ that allow us to extract the corresponding relative variations in the elastic constants C through $\Delta C/C=2\Delta V/V$. The κ-(ET)$_2$X crystals grow as platelets containing the highly conducting planes whose normal is oriented along $\vec{a}^*$ for monoclinic κ-(ET)$_2$Cu(NCS)$_2$ and along $\vec{b}$ for the orthorhombic κ-(ET)$_2$Cu[N(CN)$_2$]Br. Thus, ultrasonic plane waves can be propagated only along these normal directions by using shear and longitudinal polarized $LiNbO_3$ piezoelectric transducers (30 MHz fundamental frequency). Pure waves cannot be propagated along the $\vec{a}^*$ 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.[26] However, given the layered structure and the $\vec{a}$ axis orientation of about 110 instead of 90° from the plane, we neglect,

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	$C_{11}(a^*)$	$C_{22}(\vec{b})$
Transverse	$C_{55}(\vec{c})$	$C_{66}(\vec{a})$
Transverse	$C_{66}(\vec{b})$	$C_{44}(\vec{c})$

as a first approximation, the off-diagonal elements of the C_{ij} matrix that differentiate the monoclinic structure from the orthorhombic one. This simplifies the data treatment without affecting the conclusions. With this approximation the measured C_{ij}'s are given in Table I; since the bonding process of the transducer on organic crystals is not reversible, three different crystals of the same growth batch were used with appropriate transducer polarizations for each compound.

The κ-$(ET)_2Cu(NCS)_2$ 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. 1(a) the temperature dependence of the relative change of the ultrasonic frequency of the longitudinal mode below 20 K at 166 MHz. In zero magnetic field a negative discontinuity is obtained at T_c=9.5 K; the anomaly is completely quenched in a field of 12 T leaving only a monotonous decrease as the temperature increases. We notice the absence of magnetic

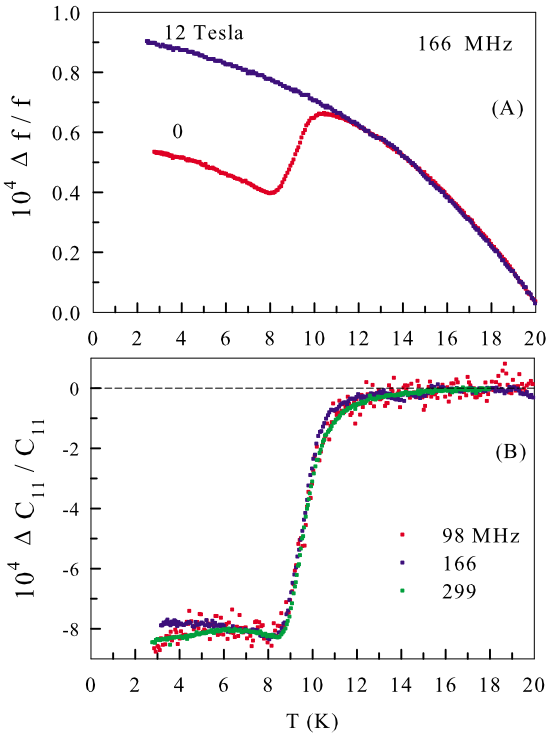

FIG. 1. (Color online) Longitudinal waves propagating along the $\vec{a}^*$ axis in κ-$(ET)_2Cu(NCS)_2$: (a) raw frequency data $\Delta f/f$ at 166 MHz for H=0 and 12 T; (b) $\Delta C_{11}/C_{11}$ at three frequencies.

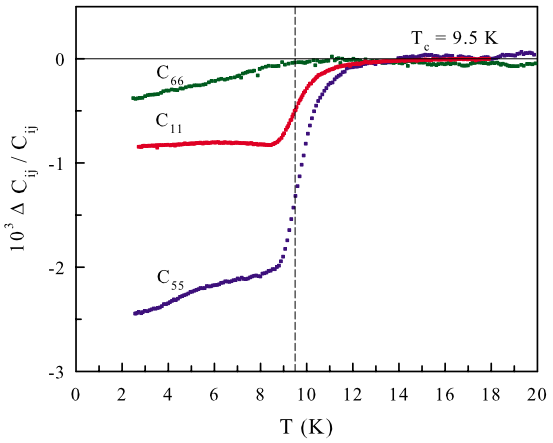

FIG. 2. (Color online) Temperature dependence of $\Delta C_{ij}/C_{ij}$ for the κ-$(ET)_2Cu(NCS)_2$ compound. The vertical dashed line indicates the SC critical temperature.

field effects above 12 K, an observation that excludes, contrary to the κ-$(ET)_2Cu[N(CN)_2]Br$ compound,[14] the presence of a coexisting phase in this temperature range. The difference between these two curves is directly proportional to a variation of the longitudinal velocity $\Delta V/V$ which yields the relative variation of the compressional constant C_{11} shown in Fig. 1(b) 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 quasitransverse 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 κ-$(ET)_2Cu[N(CN)_2]Br$, a higher magnetic field is needed to quench the SC state. We present in Fig. 3 the $\Delta C_{ij}/C_{ij}$ obtained by substracting the zero and 16 T velocity 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). This is because of phase separation.[14] 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 κ-$(ET)_2Cu(NCS)_2$ data (see Fig. 2) at T_c is remarkable: we still observe a negative discontinuity on $C_{22}(C_{11})$, a larger one on $C_{66}(C_{55})$ and only a change in 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. More-

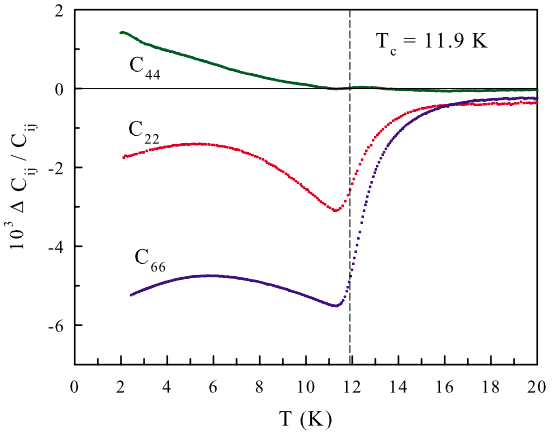

FIG. 3. (Color online) Temperature dependence of $\Delta C_{ij}/C_{ij}$ for the κ-$(ET)_2Cu[N(CN)_2]Br$ compound obtained with a 16 T magnetic field. The dashed line indicates the SC critical temperature.

over, 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,

$$F = a|\eta|^2 + g\epsilon_i|\eta|^2 + \frac{b}{2}|\eta|^4 + \sum_{i,j}\frac{1}{2}C_{ij}\epsilon_i\epsilon_j \qquad (1)$$

where η is the order parameter, b is a constant, ϵ_i 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 η shows that at the transition a negative discontinuity appears on the effective elastic constant $C'_{ii} = \partial^2 F/\partial\epsilon_i^2$. Such a linear coupling to $|\eta|^2$ is possible only if the strain ϵ_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 κ-$(ET)_2Cu(NCS)_2$, 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 II, ϵ_1 and ϵ_5 are invariant under the symmetry operations of the group, the corresponding elastic constants can couple linearly to $|\eta|^2$, leading to negative discontinuities. However, ϵ_6 is not invariant so there is no discontinuity at T_c. This explains the observations for κ-$(ET)_2Cu(NCS)_2$ and it does not impose any constraint on the symmetry of the order parameter.

TABLE II. Simplified character table, basis functions and transformation properties of the strains. The monoclinic C_{2h} group for κ-$(ET)_2Cu(NCS)_2$ has the character table of $C_2 \otimes i$, but inversion i always has character +1 for singlets so the above table for C_2 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. The **a** axis is tilted toward **c** (equivalently $x+y$) axis in the layers.

Irrep	E	$C_2^{\mathbf{b}}$	Basis functions	Strains
A_g	1	1	s, xy, $(x+y)z$	ϵ_1, ϵ_2, ϵ_3, ϵ_5
B_g	1	−1	x^2-y^2, $(x-y)z$	ϵ_4, ϵ_6

TABLE III. Simplified character table, basis functions and transformation properties of the strains for the orthorhombic $D_{2h} = D_2 \otimes i$ group appropriate for κ-$(ET)_2Cu[N(CN)_2]Br$. The **b** axis is perpendicular to the layers and the $x+y$ axis is along **a**.

Irrep	E	$C_2^{\mathbf{a}}$	$C_2^{\mathbf{b}}$	$C_2^{\mathbf{c}}$	Basis fcts	Strains
A_{1g}	1	1	1	1	s, xy	ϵ_1, ϵ_2, ϵ_3
B_{1g}	1	−1	−1	1	$(x+y)z$	ϵ_6
B_{2g}	1	−1	1	−1	x^2-y^2	ϵ_5
B_{3g}	1	1	−1	−1	$(x-y)z$	ϵ_4

In the orthorhombic κ-$(ET)_2Cu[N(CN)_2]Br$, because of the different conventions, the role of ϵ_5 in the monoclinic case is played by ϵ_6. The simplified character, Table III, for the D_{2h} group shows that the shear strain ϵ_6 is not invariant under the operations of the group.

Hence, the C_{66} negative discontinuity at T_c cannot be explained with simplest model Eq. (1). One must introduce an order parameter with two orthonormal basis functions with respective complex coefficients η_1 and η_2. Let us first neglect the strain terms and consider the most general free-energy functional that is invariant under point group and phase change operations,[29]

$$F_\eta = a_1|\eta_1|^2 + \frac{b_1}{2}|\eta_1|^4 + a_2|\eta_2|^2 + \frac{b_2}{2}|\eta_2|^4 + |\eta_1|^2|\eta_2|^2(\gamma + \delta\cos(2\Delta\theta)). \qquad (2)$$

In this expression, γ and δ are constants and $\Delta\theta$ is the phase difference between the two contributions to the order parameter. If δ is positive, this free energy will be minimized by $\Delta\theta = \pm\pi/2$, while if δ is negative $\Delta\theta = 0$ or π 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,

$$F_{\eta\epsilon} = g\epsilon_6|\eta_1||\eta_2|\cos(\Delta\theta) \qquad (3)$$

must be allowed by symmetry. Also, $\cos(\Delta\theta)$ should not vanish, thus removing the possibility of a time-reversal symmetry-breaking state. Since ϵ_6 transforms according to the B_{1g} representation, there are only two possibilities. Either one of the η is invariant (A_{1g}) and the other one transforms as B_{1g} or one of the contributions transforms like B_{2g} and the

other one such as 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 $F_{\eta\epsilon}$. Note that both of the above possibilities for η_1 and η_2 forbid a linear coupling to ϵ_4 since the latter transforms such as 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 axes, this forces us to choose an order parameter that has a mixed $A_{1g}+B_{1g}$ character, namely, $d_{xy}+d_{z(x+y)}$. 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 $d_{z(x+y)}$ contribution does not remove the nodes in the planes, but it clearly breaks mirror symmetry about the planes.

On general grounds, 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 Sr_2RuO_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}.[22] Although the present lattice is nearly triangular, the two contributions to the order parameter that we found do not coalesce into a single two-dimensional representation of the D_{6h} group.[30] 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 for all deviations of the monoclinic axis from 90°. Hence, we do not expect a large difference between the two T_c of the orthorhombic crystal. Our conclusions are unchanged even if there is an accidental degeneresence of the two T_c. Our experimental data in Fig. 3 show a rather broad transition with an extended region of SC fluctuations that is likely to mask a difference between two transitions.

The presence of a $d_{z(x+y)}$ contribution 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 two-dimensional purely electronic model.

In summary, symmetry and the observed discontinuities at T_c in the ultrasonic velocity data for two compounds of the layered κ-$(ET)_2X$ organic superconductors demonstrate that the order parameter must have at least two contributions in the orthorhombic compound κ-$(ET)_2Cu[N(CN)_2]Br$. Consistency with other experiments selects $A_{1g}+B_{1g}$ (equivalently $d_{xy}+d_{z(x+y)}$). The two contributions coalesce into a one-dimensional irreducible representation A_g in the monoclinic compound κ-$(ET)_2Cu(NCS)_2$. Nodes are not symmetry imposed but are symmetry allowed and are likely to occur in electronic pairing mechanisms. The $d_{z(x+y)}$ contribution of the order parameter suggests that further studies of interlayer coupling are called for.

The authors acknowledge stimulating discussions with Claude Bourbonnais, David Sénéchal, and Peter Hirschfeld, and they thank Mario Castonguay for technical support. This work was supported by grants from FQRNT and NSERC. A.-M.S.T. also acknowledges the support of the Tier I CRC program and of CIFAR.

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