# Small-$q$ Phonon-Mediated Superconductivity in Organic $\kappa$-BEDT-TTF Compounds

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We propose a new picture for superconductivity in $\kappa$-(BEDT-TTF)$_2X$ salts arguing that *small*-**q** *electron-phonon* scattering dominates the pairing. We reproduce the distinct X-shaped $d$-wave gap reported recently by magneto-optic measurements and we argue that the *softness* of the momentum structure of the gap and the near degeneracy of $s$- and $d$-wave gap states may be at the origin of the experimental controversy about the gap symmetry. We show that a magnetic field applied parallel to the planes may induce extended gapless regions on the Fermi surface accounting for the experimental signatures of a Fulde-Ferrel-Larkin-Ovchinikov state and it may induce *gap symmetry transitions* as well.

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The fascinating physics of organic metals and superconductors (SC) continues to motivate intense investigations [1–3]. Particularly interesting are the quasi-two-dimensional organic SC based on the donor BEDT-TTF (bisethylenedithio-tetrathiafulvalene). The BEDT-TTF molecules are packed in various motifs (labeled by Greek letters) in layers which are separated by insulating ion planes. The $\kappa$ packed compounds exhibit numerous similarities with high-$T_c$ cuprates [1–4]. As verified by de Haas–van Alphen and Shubnikov–de Haas measurements [5,6] their carriers are usually quasidispersionless perpendicular to the planes exhibiting the behavior of almost perfectly two-dimensional metals. When associated to a monovalent ion $X$ (such as $I_3$ or $Cu(NCS)_2$ or $Cu[N(CN)_2]Br$ or $SF_5CH_2CF_2SO_3$, etc.) with stoichiometry $\kappa$-(BEDT-TTF)$_2X$ (usually abbreviated as $\kappa$-(ET)$_2X$) they show SC at temperatures that can exceed 10 K [1–3].

At least in $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br, $\kappa$-(ET)$_2$(SCN)$_2$, and $\kappa$-(ET)$_2$I$_3$, a number of measurements point clearly to the presence of gap nodes [7]. On the other hand, other experiments indicate instead a fully gapped superconducting state [8] and a striking experimental controversy persists [3]. In the most recent and accurate experiments on the best samples a surprising systematic trend emerges: Measurements involving a large in-plane field indicate a gap state with nodes probably $d$-wave [9], while in the absence of the field a nodeless $s$-wave state is reported [10]. There is no available theoretical understanding of such a systematic discrepancy.

Recently, a millimeter-wave magneto-optical technique (involving a large in-plane field) allowed measurement of the angular dependence of the gap in $\kappa$-(ET)$_2$Cu(NCS)$_2$ [11]. The SC gap exhibits a distinct X-shape pointing to an anisotropic $d$-wave structure with nodes along the **b** and **c** directions [11]. The reports of a $d$-wave gap motivated theoretical investigations of spin fluctuations (SF) mediated SC in $\kappa$-(ET)$_2X$ salts [12,13]. The potential relevance of SF has been justified by the proximity of antiferromagnetic (AFM) phases in the pressure-temperature phase diagram [14].

However, there is substantial experimental evidence suggesting that phonons are crucial for the pairing in $\kappa$-(ET)$_2X$ salts. *Isotope effect* measurements on $\kappa$-(ET)$_2$-Cu(SCN)$_2$ [15] report direct evidence for a phonon mechanism. Raman spectroscopy on $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br [16] also advocates a phonon mechanism. Inelastic neutron scattering studies report SC-induced frequency changes in the intermolecular phonon modes of $\kappa$-(ET)$_2$Cu(NCS)$_2$ [17] suggesting their involvement in the pairing. Moreover, the relevance of strong electron-phonon scattering is firmly established by the increase of the lattice conductivity (the phonon contribution to the thermal conductivity) at the SC transition [18]. Thermal expansivity measurements [19] confirm a strong electron-lattice coupling which may naturally dominate the pairing. All these experiments are in a puzzling apparent conflict with any measurement reporting a $d$-wave gap which is commonly attributed to a SF mechanism.

In the present Letter we introduce a new picture for SC in $\kappa$-(ET)$_2X$ salts. We show that *small*-**q** *phonon mediated* SC reproduces accurately the experimentally observed X-shaped *$d$-wave gap* in $\kappa$-(ET)$_2$Cu(NCS)$_2$ [11]. We emphasize the distinct qualitative behavior exhibited by our SC states which is related to the *softness* of the momentum structure of the gap and the possible near degeneracy of $s$- and $d$-wave gap symmetries which, we argue, is at the origin of the experimental controversies in $\kappa$-(ET)$_2X$'s. We report for the first time $s$-$d$ gap symmetry transitions induced by an in-plane magnetic field. The high field gap states are systematically $d$-wave as in the experiments. At sufficiently high fields, our $d$-wave states exhibit surprisingly extended gapless regions around the nodes which may be responsible for recent experimental signatures of inhomogeneous SC near the in-plane critical field.

The $\kappa$-packing motif is illustrated in Fig. 1a where each stick corresponds to a BEDT-TTF molecule. There are two different types of pairs of closely packed BEDT-TTF molecules called *dimers* and a unit cell is constituted by two dimers, one of each type. Because the intradimer hoping is more than twice the interdimer one and the

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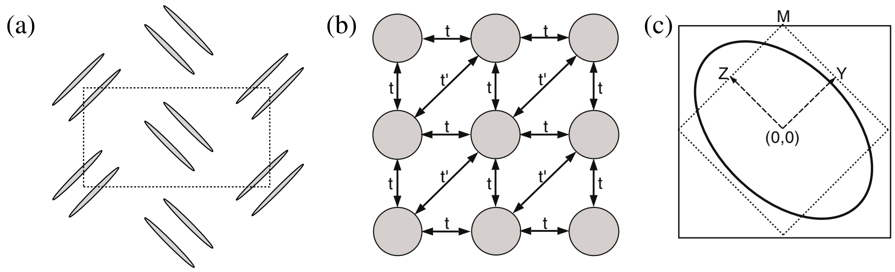


FIG. 1. (a) The $\kappa$ packing motif. Each stick corresponds to a BEDT-TTF molecule. (b) The effective frustrated lattice scheme in the dimer model approximation. (c) The FS (thick line) of the dimer model in the extended BZ scheme. The original BZ is shown with dotted lines. In the real system, there is a small gap opening at the intersection of the dimer model FS with the original BZ leading to a holelike FS sheet around the $Z$ point and a quasi-1D sheet along the $z$ axis.

splitting between the bonding and antibonding orbitals is about twice the intradimer hoping, only the antibonding orbitals contribute to the Fermi surface. This allows us to consider a dimer as the effective basic structural unit making the so-called *dimer model approximation* [20,21] which leads to an effective frustrated lattice model illustrated in Fig. 1b and to an extended Brillouin zone (BZ) scheme (see Fig. 1c). Shubnikov–de Haas measurements [20] confirmed the relevance of the dimer approach in $\kappa$-$(ET)_2X$ salts which corresponds to an electronic dispersion of the form

$$\xi_{\mathbf{K}} = 2t(\cos K_y + \cos K_z) + 2t' \cos(K_y + K_z), \quad (1)$$

where $t'/t \approx 0.8$ and $K_y, K_z$ refer to the new coordinates in the extended dimer model BZ which are *rotated* by $\pi/4$ compared to those of the original BZ (see Fig. 1c).

A system in which Coulomb correlations are screened to be short range (Hubbard type) may generically show electron-phonon scattering *dominated by forward processes* [22,23]. In that case the effective pairing potential takes the following form in momentum space [23]: $V(\mathbf{k},\mathbf{k}') = -\frac{V}{\mathbf{q_c}^2+(\mathbf{k}-\mathbf{k}')^2} + \mu^*(\mathbf{k}-\mathbf{k}')$. The pairing kernel is characterized by a smooth momentum cutoff $\mathbf{q_c}$ which selects the small wave vectors in the attractive phonon part while at larger wave vectors the repulsive Coulomb pseudopotential $\mu^*(\mathbf{k}-\mathbf{k}')$ may prevail. This type of potential has been considered for high-$T_c$ cuprates [23–27] and heavy fermion systems [28]. Screening by *short range* Hubbard-like Coulomb terms is necessary for obtaining such an effective small-$q$ phonon pairing [22,23] and thus we may naturally observe it in systems in which the insulating phases show *AFM correlations* as in $\kappa$-$(ET)_2X$ salts.

Self-consistent solutions of the BCS gap equation with the small-**q** pairing kernel and the electronic dispersion of the dimer model are obtained using a fast Fourier transform technique. The extended BZ (Fig. 1c) has been discretized with a $256 \times 256$ momentum grid. Our $d$-wave solutions (see Fig. 2a) have an X-shape remarkably similar to the experimental one [11]. The angular position of the nodes and maxima in the calculated and measured order parameters are in full agreement (experimental notations refer to the rotated coordinates of the original BZ) corroborating both the relevance of the experimental technique employed in Ref. [11] and that of our picture in $\kappa$-$(ET)_2X$'s. Our $d$-wave solutions are in competition with anisotropic $s$-wave solutions such as the one shown in Fig. 2b. With a local Coulomb pseudopotential $\mu^*/V \approx 0.1$, for $q_c < \pi/4.5$ the $d$-wave solution prevails while for $q_c > \pi/4.5$ the gap is anisotropic $s$ wave.

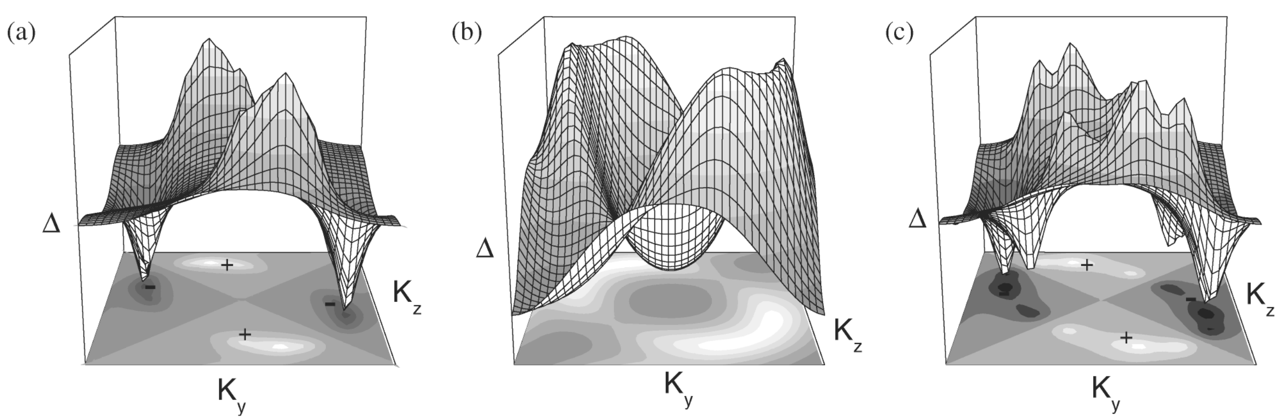


FIG. 2. Self-consistent gap solutions with small-$q$ pairing over the extended BZ of the dimer model: (a) typical $d$-wave solution, (b) competing anisotropic $s$-wave solution, and (c) $d$-wave solution obtained when $t'/t = 1$.

Engineering a physical situation in which $t'/t \approx 1$, possibly by applying uniaxial pressure, may be useful for distinguishing which one of the small-$\mathbf{q}$ or the SF pairing pictures is relevant. In our scheme the $t'/t = 1$ system is still a SC showing a multipeak structure in the momentum structure of the gap which could perhaps be observable in an experiment such as in Ref. [11]. We show in Fig. 2c a typical $d$-wave SC gap solution obtained with our kernel and $t'/t = 1$. Moreover, enhancing $t'/t$ within our scheme gives an advantage to $d$-wave solutions in their close competition with anisotropic $s$ wave. In a spin fluctuations mechanism instead, when $t'/t = 1$ *there are no SC correlations* for $U/t < 16$ [12] while for $U/t \gg 1$ the problem is mapped to a Heisenberg model on a regular triangular lattice which is a well-studied frustrated system [30].

When small-$\mathbf{q}$ processes dominate the pairing, we have the situation of *Momentum Decoupling* (MD) in SC, meaning a tendency for decorrelation of the SC behavior in the various regions of the FS [23,24] resulting from the reduction of the mixing scattering between FS regions. This *loss of rigidity* of the momentum structure of the gap leads to a distinct SC behavior exhibiting density of states (DOS) driven anisotropies and a gradual *marginalization* of the SC gap symmetry for the condensation free energy [23,29]. The position of the gap maxima at the intersection of the dimer FS with the original BZ in Fig. 2a, the anisotropic character of the $s$-wave solution in Fig. 2b, and the multipeak structures in Fig. 2c reflect corresponding anisotropies of the DOS. In fact, the gap equation could be viewed schematically as a convolution product of the pairing kernel with a functional having the shape of the DOS. By reducing $q_c$, the shape of the kernel approaches gradually that of a Dirac $\delta$-function and the resulting gap takes the shape of the DOS since $\delta$ is the identity element of the convolution product. Doping induced variations of the effective Coulomb pseudopotential and other details in the pairing kernel [23,29] or variations in the concentration of impurities or disorder [25] have been shown to induce transitions between anisotropic $s$- and $d$-wave SC. The conflicting reports about the presence of nodes in $\kappa$-$(\mathrm{ET})_2X$ SC are probably signatures of the *momentum softness* of the SC gap and/or of the resulting marginality of the gap symmetry. In the case of SF pairing the gap structure is instead *rigid* and all experiments should report a $d$-wave gap.

Our picture for the origin of the experimental conflicts about the gap symmetry in $\kappa$-$(\mathrm{ET})_2X$ is strongly supported by our study of the influence of an in-plane magnetic field. Our SC states exhibit a distinct qualitative behavior which is in remarkable qualitative agreement with the experimental one. In the presence of a Zeeman field $H_Z$ we solve the BCS gap equation

$$\Delta_{\mathbf{k}} = \sum_{\mathbf{k}'} \frac{V_{\mathbf{k},\mathbf{k}'}}{4\sqrt{\xi_{\mathbf{k}'}^2 + \Delta_{\mathbf{k}'}^2}} \left[ \tanh\frac{\sqrt{\xi_{\mathbf{k}'}^2 + \Delta_{\mathbf{k}'}^2} + \mu_B H_Z}{2T} + \tanh\frac{\sqrt{\xi_{\mathbf{k}'}^2 + \Delta_{\mathbf{k}'}^2} - \mu_B H_Z}{2T} \right]. \tag{2}$$

This equation accounts for the Pauli effects on SC and is particularly relevant when the field is applied *parallel to the conducting planes* in which case orbital effects are negligible. We illustrate the effect of the field using a simplified two-dimensional square lattice model with nearest neighbors hopping $\xi_{\mathbf{k}} = t(\cos k_x a + \cos k_y a)$.

We show in Fig. 3 the evolution of the $d$-wave gap with the applied field along the first quarter of the FS [connecting the $(\pi, 0)$ and $(0, \pi)$ points]. For fields larger than about $H_c/3$, the shape near the nodes is modified significantly. Approaching $H_c$ ($H_Z > 0.8Hc$) we observe surprisingly *extended effectively gapless regions around the nodes* whose extension grows with the applied field. The unusual extension of the gapless regions is a direct consequence of the *softness* of the gap shape in the MD regime. Because in this regime the mixing scattering between different FS regions is weak, SC can survive in the proximity of such extended gapless regions. This behavior may have significant experimental consequences. For example, the $T$ exponent of the penetration depth at low $T$ depends on the gap shape near the node. Moreover, the coexistence of similarly extended gapless and SC regions on the FS is the essential characteristic of the Fulde-Ferrel-Larkin-Ovchinikov state [31] and recent experiments claim the observation of signatures of such a state in $\kappa$-$(\mathrm{ET})_2\mathrm{Cu(NCS)}_2$ [32]. An inhomogeneous SC state like the one shown in Fig. 3 near $H_c$ may naturally be at the origin of the observations in Ref. [32].

Moreover, we obtain for the first time gap symmetry transitions induced by the magnetic field. We show in the inset of Fig. 3 the evolution of the condensation free energy as a function of the field in two characteristic cases of $\mu^*/V$ when $q_c = \pi/6$. Enhancing the field we may obtain at low-$T$ transitions from $s$-wave to $d$-wave ($\mu^*/V = 0.053$) or even *reentrant* transitions from $d$-wave to $s$-wave and then back to $d$-wave SC ($\mu^*/V = 0.057$) at high fields. Systematically, the high field state is *$d$-wave* providing a plausible explanation to the discrepancy between the recent reports of $d$-wave SC from experiments like NMR involving large *in plane* fields [9] and the recent reports of $s$-wave SC from specific heat measurements in the absence of a field [10]. The $d$-wave SC state dominates at high fields because it can coexist with extended gapless areas on the FS as shown in Fig. 3. Our $s$-wave state instead cannot coexist with field-induced gapless areas and disappears abruptly at the $s$-wave critical field.

In conclusion, we have shown that phonon mediated pairing dominated by forward processes reproduces accurately the recently reported X-shaped $d$-wave gap in $\kappa$-$(\mathrm{ET})_2X$ salts. We argue that the experimental conflicts about the gap symmetry in these salts are signatures of the

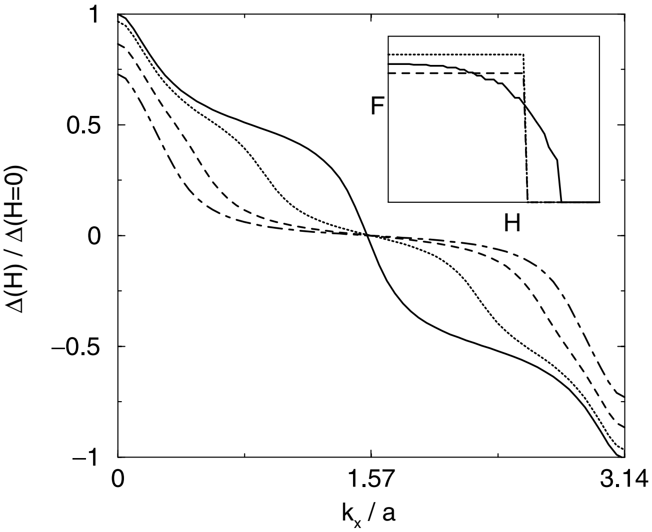


FIG. 3. Typical evolution of the $d$-wave gap in the small-$q$ pairing scheme ($q_c \approx \pi/10$) over the first quadrant of the BZ of a nearest-neighbor hoping square lattice model with $H_Z = 0$ (full line), $H_Z = 0.75H_c$ (dotted line), $H_Z = 0.9H_c$ (dashed line), and $H_Z = 0.975H_c$ (dotted-dashed line). In the inset is shown the evolution of the absolute condensation free-energy $F$ as a function of the field $H$ applied parallel to the planes (both in arbitrary units) for the $d$-wave (full line) and the $s$-wave states with $\mu^*/V = 0.53$ (dotted line) and $\mu^*/V = 0.57$ (dashed line) when $q_c = \pi/6$ (the $d$-wave state is insensitive to a local $\mu^*$).

*softness* of the momentum shape of the gap and the plausible near degeneracy of $s$- and $d$-wave SC gap states in our picture. We show that a magnetic field applied parallel to the planes may induce gap symmetry transitions, the high-field gap states being systematically of $d$-wave type as in the experiments. Near the critical fields, our $d$-wave states exhibit a coexistence of comparably extended gapless and SC regions accounting for recent experimental indications of a FFLO state in $\kappa$-(ET)$_2X$ salts.

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