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 FS accounting for the experimental signatures of a Fulde-Ferrel-Larkin-Ovchinnikov (FFLO) 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 [4]. As verified by de Haas-van Alphen and Shubnikov-de Haas measurements [4] their carriers are usually quasi-dispersionless perpendicular to the planes exhibiting the behavior of almost perfectly two-dimensional metals. When associated to a monovalent ion X (like $I_3$ or $Cu(NCS)_2$ or $Cu[N(CN)_2]Br$ or $SF_6CH_2CF_2SO_3$ etc.) with stoichiometry $\kappa-(BEDT-TTF)_2X$ (usually abbreviated as $\kappa-(ET)_2X$) they show SC at temperatures that can exceed 10K [4]. At least in $\kappa-(ET)_2Cu[N(CN)_2]Br$, $\kappa-(ET)_2(SCN)_2$ and $\kappa-(ET)_2I_3$, specific heat, NMR relaxation, thermal conductivity and some penetration depth measurements point clearly to the presence of gap-nodes [4]. On the other hand, other similar experiments indicate instead a fully gapped superconducting state [4] and a striking experimental controversy persists [4].

Recently, a millimeter-wave magneto-optical technique allowed to measure the angular dependence of the gap in $\kappa-(ET)_2Cu(NCS)_2$ [4]. The SC gap exhibits a distinct X-shape pointing to an anisotropic d-wave structure with nodes along the b and c directions [4]. The reports of a d-wave gap motivated theoretical investigations of spin fluctuations (SF) mediated SC in $\kappa-(ET)_2X$ salts [4]. The potential relevance of SF has been justified by the proximity of antiferromagnetic (AFM) phases in the pressure-temperature phase diagram [4].

However, there is substantial experimental evidence suggesting that phonons are crucial for the pairing in $\kappa-(ET)_2X$ salts. Isotope effect measurements on $\kappa-(ET)_2Cu(SCN)_2$ [4] report direct evidence for a phonon mechanism. Raman spectroscopy on $\kappa-(ET)_2Cu[N(CN)_2]Br$ [4] also advocate a phonon mechanism. Inelastic neutron scattering studies report SC-induced frequency changes in the intermolecular phonon modes of $\kappa-(ET)_2Cu(NCS)_2$ [4] 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 [4]. Thermal expansivity measurements [4] confirm a strong electron-lattice coupling which may naturally dominate the pairing.

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 $\kappa-(ET)_2Cu(NCS)_2$. 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 near degeneracy of s- and d-wave gap symmetries which may be at the origin of the experimental controversies in $\kappa-(ET)_2X$'s. We study the effect of an in-plane magnetic field on our SC state which is shown to account for recent experimental signatures of inhomogeneous SC near the in-plane critical field and may plausibly induce s-d gap symmetry transitions.

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 splitting between the bonding and antibonding orbitals is about twice the intradimer hoping, only the antibonding orbitals contribute to the Fermi surface. This allows to consider a dimer as the effective basic structural unit making the so called dimer model approximation [4][5] 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 [4] confirmed the relevance of the dimer approach.
in $\kappa - (ET)_{2}X$ salts which corresponds to an electronic dispersion of the form

$$\xi_{\mathbf{K}} = 2t'(\cos K_y + \cos K_z) + 2t' \cos(K_y + K_z)$$  \hspace{1cm} (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 \cite{2,21}. In that case the effective pairing potential takes the following form in momentum space \cite{21}: 

$$V(\mathbf{k}, \mathbf{k}') = -\frac{V}{q_{c} \pi} \cdot \frac{1}{(\mathbf{k} - \mathbf{k}')^2} + \mu^*(\mathbf{k} - \mathbf{k}')$$

The pairing kernel is characterized by a smooth momentum cut-off $q_c$ which selects the small wavevectors in the attractive phonon part while at larger wavevectors the repulsive Coulomb pseudopotential $\mu^*(\mathbf{k} - \mathbf{k}')$ may prevail. This type of potential has been considered for high-$T_c$ cuprates \cite{21,27} and heavy fermion systems \cite{21}. Screening by short range Hubbard-like Coulomb terms is necessary for obtaining such an effective small-$q$ phonon pairing \cite{21} and thus we may naturally observe it in systems in which the insulating phases show AFM correlations as in $\kappa - (ET)_{2}X$ 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 momentum grid. Our dimer model are obtained using a fast Fourier transform method. The extended BZ (Fig. 1c) has been discretized with a 256 momentum grid. Our dimer model is characterized by a smooth momentum cut-off $q_c$. Screening by short range Hubbard-like Coulomb terms is necessary for obtaining such an effective small-$q$ phonon pairing \cite{21} and thus we may naturally observe it in systems in which the insulating phases show AFM correlations as in $\kappa - (ET)_{2}X$ salts.

When small-$q$ 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 \cite{21,22}. This loss of rigidity of the momentum structure of the gap leads to a distinct SC behavior exhibiting density of states driven anisotropies and a gradual marginalization of the SC gap symmetry for the condensation free energy \cite{21,22}. 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 multipole structures in Fig. 2c reflect corresponding anisotropies of the density of states. Doping induced variations of the effective Coulomb pseudopotential and other details in the pairing kernel \cite{21,27} or variations in the concentration of impurities or disorder \cite{23} have been shown to induce transitions between anisotropic s and d-wave SC. The conflicting reports about the presence of nodes in $\kappa - (ET)_{2}X$ SC are probably singularities 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.

We show below that in the MD regime an in-plane magnetic field involved for example in NMR experiments may also influence significantly the momentum shape of the gap and possibly induce gap symmetry transitions as well. In the presence of a Zeeman field $H_Z$ we solve the BCS gap equation

$$\Delta_{\mathbf{k}} = \sum_{\mathbf{k}'} \frac{V_{\mathbf{k},\mathbf{k}'}'}{\sqrt{\xi_{\mathbf{k}'} + \Delta_{\mathbf{k}'}}} \left( \tanh \frac{\sqrt{\xi_{\mathbf{k}'} + \Delta_{\mathbf{k}'}} + H_Z}{2T} + \tanh \frac{\sqrt{\xi_{\mathbf{k}'} + \Delta_{\mathbf{k}'}} - H_Z}{2T} \right)$$  \hspace{1cm} (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 $H_c$ ($H_Z > 0.8H_c$) we observe extended effectively gapless regions around the nodes whose extension grows with the applied field. 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 extended gapless regions with
SC regions on the FS is the essential characteristic of the Fulde-Ferrell-Larkin-Ovchinikov state [29] and recent experiments claim the observation of signatures of this state in $\kappa - (ET)_2Cu(NCS)_2$ [30]. An inhomogeneous SC state like the one shown in Fig. 3 near $H_c$ may possibly be at the origin of the observations in Ref. [31]. Furthermore, we may obtain 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 $q_\perp = \pi/6$. 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 ($\mu^*/V = 0.057$). A detailed study of the field effects will be reported elsewhere, it is however plausible that such field-induced s-d transitions may be responsible for the quasi-systematic reports of d-wave SC from experiments like NMR involving large in plane fields while specific heat measurements in the absence of a field usually report a nodeless state.

In conclusion, we have shown that phonon mediated pairing dominated by forward processes reproduces accurately the angular dependence of the gap in $\kappa - (ET)_2X$ salts reported recently. We argue that the experimental conflicts about the gap symmetry may be simple consequences of the softness of the momentum shape of the gap and the possible near degeneracy of s- and d-wave SC in our picture. We show that magnetic fields applied parallel to the planes may induce extended gapless regions accounting for recent indications of a FFLO state and may plausibly induce gap symmetry transitions as well.

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[1] T. Ishiguro, K. Yamaji and G. Saito, Organic Superconductors, Springer, Berlin-Heidelberg (1998).
[2] M. Lang, Supercond. Rev. 2, 1 (1996).
[3] For related short reviews see e.g. the articles by J.F. Annett, p. 1, M. Dressel p. 89, J. Wosnitza p. 98 and E. Balthes et al. p. 108 in Anomalous Complex Superconductors, Ed. P.B. Littlewood and G. Varelogiannis, Physica C (Elsevier), Vol. 317 - 318, (1999).
[4] R.H. McKenzie, Science 275, 820 (1997).
[5] J. Wosnitza, Fermi surface of low-dimensional organic metals and superconductors, Springer, Berlin (1996).
[6] J. Singleton, Rep. Prog. Phys. 63, 1111 (2000).
[7] K. Kanoda et al., Phys. Rev. Lett. 65, 1271 (1990); L.P. Le et al., ibid 68, 1923 (1992); H. Mayaffre et al., ibid 75, 4122 (1995); S.M. de Soto et al. Phys. Rev. B 52, 10364 (1995); K. Kanoda et al., ibid 54, 76 (1996); M. Pinterič et al., Phys. Rev. B 61, 7033 (2000).
[8] D.R. Harshman et al., Phys. Rev. Lett. 64, 1293 (1990); O. Klein et al., ibid 66, 655 (1991); M. Lang et al., ibid 69, 1443 (1992); T. Takahashi et al., Physica C 235-240, 2461 (1994); H. Elsinger et al., Phys. Rev. Lett. 84, 6098 (2000).
[9] J.M. Schrama et al., Phys. Rev. Lett. 83, 3041 (1999). There is some controversy about this technique: Hilt et al., Phys. Rev. Lett. 86 3451 (2001); T. Shibauchi et al., ibid 3452 (2001); J.M. Schrama et al., ibid 3453 (2001).
[10] H. Kondo and T. Moriya, J. Phys. Soc. Jpn. 67, 3695 (1998).
[11] H. Kino and H. Kontani, J. Phys. Soc. Jpn. 67 3691 (1998); J. Schmalian, Phys. Rev. Lett. 81, 4232 (1998); M. Vojta and E. Dagotto, Phys. Rev. B 59, 713 (1999).
[12] S. Lefebvre et al., Phys. Rev. Lett. 85, 5420 (2000).
[13] A.M. Kini et al., Physica C 264, 81 (1996); Synth. Met. 85, 1617 (1997).
[14] D. Pedron et al., Physica C 276, 1 (1997).
[15] L. Pintschovius et al., Europhys. Lett. 37, 627 (1997).
[16] S. Bélin, K. Behnia and A. Deluzet, Phys. Rev. Lett. 81, 4728 (1998).
[17] J. Müller et al., Phys. Rev. B 61, 11739 (2000).
[18] J. Caulfield et al., J. Phys.: Cond. Mat. 6, 2911 (1994).
[19] H. Kino and H. Fukuyama, J. Phys. Soc. Jpn. 64, 2726 (1995); ibid 65, 2159 (1996).
[20] K.J. von Szczepanski and K.W. Becker, Z. Phys. B 89, 327 (1992); M.L. Kulic and R. Zeyher, Phys. Rev. B 49, 4395 (1994); M. Grilli and C. Castellani, ibid 50, 16880 (1994).
[21] G. Varelogiannis, Phys. Rev. B 57, 13743 (1998).
[22] G. Varelogiannis et al., Phys. Rev. B 54, R6877 (1996); G. Varelogiannis, Phys. Rev. B 57, R732 (1998); A. Perali and G. Varelogiannis, Phys. Rev. B 61, 3672 (2000).
[23] A.A. Abrikosov, Phys. Rev. B 53, R8910 (1996).
[24] A.J. Leggett, Phys. Rev. Lett. 83, 392 (1999).
[25] M. Weger and M. Peter, Physica C 317 - 318, 252 (1999).
[26] D.F. Agterberg, V. Barzykin and L.P. Gorkov, Phys. Rev. B 60, 14868 (1999).
[27] G. Varelogiannis, Sol. St. Commun. 107, 427 (1998).
[28] P.W. Anderson, Mater. Res. Bull. 8, 153 (1973).
[29] P. Fulde and R.A. Ferrel, Phys. Rev. 135, A550 (1964); A.I. Larkin and Yu.N. Ovchinikov, Sov. Phys. JETP 20, 762 (1965).
[30] J. Singleton et al., J. Phys.: Condens. Matter 12, L641 (2000).
FIG. 1. a) The κ 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 hole-like FS sheet around the Z point and a quasi-1D sheet along the z-axis.

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 \( t'/t = 1 \).

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 NN 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 \( \mu^* \)).
