Superconductivity Mediated by Charge Fluctuations in Layered Molecular Crystals

Jaime Merino* and Ross H. McKenzie

Department of Physics, University of Queensland, Brisbane 4072, Australia
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We consider the competition between superconducting, charge ordered, and metallic phases in layered molecular crystals with the θ and β'' structures. Applying slave-boson theory to the relevant extended Hubbard model, we show that the superconductivity is mediated by charge fluctuations and the Cooper pairs have d_{xy} symmetry. This is in contrast to the κ-(BEDT-TTF)$_2$X family, for which theoretical calculations give superconductivity mediated by spin fluctuations and with $d_{x^2-y^2}$ symmetry. We predict several materials that should become superconducting under pressure.

The issue of the interplay of superconductivity, magnetism, and charge ordering is relevant to a wide range of strongly correlated electron materials. Examples include the copper-oxide (high-temperature) superconductors [1], colossal magnetoresistance materials [2], heavy fermion compounds [3], vanadium oxides [4], and organic molecular crystals [5–7]. In particular, for the cuprate superconductors there is controversy about the relative importance of charge fluctuations (associated with dynamical "stripes") and antiferromagnetic spin fluctuations (associated with the Mott insulator which occurs when there is an average of one electron or hole for every lattice site). For some heavy fermion compounds recent experiments support the idea that the superconductivity is mediated by spin fluctuations [3].

The family κ-(BEDT-TTF)$_2$X [8] of molecular crystals has similarities to the cuprates [6] including the proximity of superconductivity to a Mott insulator in the phase diagram. Although there is an average of half a hole per molecule the necessary condition of one hole per lattice site is met because the molecules are paired up (dimerized) within the κ-type crystal structure. Theoretical calculations [9] suggest that the superconductivity has $d_{x^2-y^2}$ symmetry (as in the cuprates) and is mediated by antiferromagnetic spin fluctuations. However, there is controversy about whether experiments support this [10]. In this Letter, we show theoretically that the organic superconductors listed in Table I are quite different from the κ-type materials and the superconductivity is mediated by charge fluctuations and has d_{xy} symmetry. Our results may also be relevant to the recent discovery that the quasi-one-dimensional vanadium bronzes β-Na$_{0.33}$V$_2$O$_5$ (which is a charge ordered insulator) and β-Cu$_{0.65}$V$_2$O$_5$ become superconducting under pressure [4]. Previously, it was suggested by Scalapino, Loh, and Hirsch [11] that spin fluctuations could mediate $d_{x^2-y^2}$ pairing and charge fluctuations could mediate d_{xy} pairing.

The materials considered here consist of layers of donor molecules [e.g., BEDT-TTF = bis-(ethylenedithiatetrathiafulvalene)] alternating with insulating layers of anions [e.g., X = SF$_5$CH$_2$CF$_2$SO$_3$]. For the θ and β'' crystal structures the donor molecules are not dimerized

and so noninteracting electron models (band structure calculations) predict a metallic state due to a band which is one-quarter filled with holes. However, some of these materials are insulators at low temperatures. Mott insulators (resulting from the Coulomb repulsion between electrons on a single site) occur only for a half-filled band. However, the localization of charge (and associated insulating behavior) could result from charge ordering due to the Coulomb repulsion between electrons on neighboring sites. Indeed, such charge ordering is observed in some of these materials and is reflected in a disproportion of charge between neighboring donor molecules (see Ref. [7] for a brief review of how this is determined experimentally). Depending on the anion, temperature, and pressure, the materials can be either a charge-ordered insulator, a metal, or a superconductor. (A schematic phase diagram of the θ materials is shown in Fig. 1 of Ref. [7].) The common feature of the superconductors listed in Table I is that in the phase diagram the superconductivity occurs in close proximity to the insulating and/or charge-ordered phase. Five of the superconductors have the very unusual property that as the temperature decreases the resistivity is increasing before entering the superconducting phase.

The simplest possible strongly correlated electron model which can describe the competition among the above phases is an extended Hubbard model at quarter filling on a square lattice [7]. The Hamiltonian is

$$H = t \sum_{\langle ij \rangle, \sigma} (c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma}) + U \sum_i n_{i\uparrow} n_{i\downarrow}$$
$$+ V \sum_{\langle ij \rangle} n_i n_j - \mu \sum_{i\sigma} n_{i\sigma}, \tag{1}$$

where the operator $c_{i\sigma}^\dagger$ creates an electron in site i with spin σ. t is the amplitude for electrons to go from one site to a nearest-neighbor one, V is a nearest-neighbor Coulomb interaction, and U is the electron-electron interaction at a given site. μ is the chemical potential. A further simplification on model (1) can be made considering the fact that $U \gg V, t$, so we can fix $U = \infty$. We have previously studied charge ordering within this model [7] and here we briefly summarize the main results. For $V \gg t$, the model has an insulating phase with checkerboard

TABLE I. Organic superconductors described by our theory. All materials (except the last one) have an average of half a hole per donor molecule. This corresponds to a quarter-filled band. T_c is the superconducting transition temperature at the given pressure. Five of the materials have the unusual property that the resistivity, ρ, decreases with increasing temperature above T_c suggesting a direct transition from an insulating phase into a superconducting phase ($d\rho/dT < 0$). There is evidence of charge ordering (CO) and/or an insulating phase (with a metal-insulator transition temperature T_{MI}) in close proximity to the superconducting phase. θ-(BEDT-TTF)$_2$I$_3$ is close to a charge-ordered insulator as when the anion, I$_3$, is replaced with RbZn(SCN)$_4$, CsZn(SCN)$_4$, CsZn(SCN)$_4$, or CsCo(SCN)$_4$, the material becomes a charge-ordered insulator [25]. [$Y = (C_2O_4)_3 \cdot$ PhCN].

Material	Pressure	T_c (K)	Ref.	$\frac{d\rho}{dT} < 0$	Pressure	CO	T_{MI} (K)	Ref.
θ-(BEDT-TTF)$_2$I$_3$	1 bar	3.6	[26]	No				
β''-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$	1 bar	5.2	[27]	No	1 bar	Yes		[28]
(BEDT-TTF)$_2$ReO$_4$	4 kbar	2	[29]	No	1 bar	Yes	77	[30]
β''-(BEDT-TTF)$_4$Pd(CN)$_4$H$_2$O	7.0 kbar	1.2	[31]	Yes	1 bar		70	[31]
β''-(BEDT-TTF)$_4$Pt(CN)$_4$H$_2$O	6.5 kbar	2.0	[25]	Yes	1 bar		120	[25]
β''-(BEDT-TTF)$_4$H$_3$OFeY	1 bar	8.5	[32]	No	1 bar	Yes		[33]
β''-(BEDT-TTF)$_4$H$_3$OCrY	1 bar	5.5	[32]	No	1 bar	Yes		[33]
θ-(BETS)$_2$(Cl$_2$TCNQ)	3.5 kbar	1.3	[34]	Yes	8.5 kbar		22	[34]
β''-(BEDO-TTF)$_2$ReO$_4 \cdot$ H$_2$O	1 bar	2–3	[35]	Yes				
θ-(DIETS)$_2$Au(CN)$_4$	10 kbar uniaxial	8	[36]	No	1 bar		220	[37]
β''-(BEDT-TTF)$_3$Cl$_2 \cdot$ 2H$_2$O	16 kbar	2–3	[38]	Yes	1 bar	Yes	150	[39]

charge ordering (i.e., the wave vector associated with charge modulation is (π, π); see Fig. 3 in Ref. [7]). The spins in the charge-ordered state are antiferromagnetically coupled due to a fourth order ring-exchange process. For $V/t < (V/t)_c \approx 0.69$ we find a metallic phase with homogeneous charge density while for $V/t > (V/t)_c$ the system becomes charge ordered. Hence, we find a quantum phase transition from a metallic phase to a charge-ordered phase with a quantum critical point at $(V/t)_c$. It should be stressed that this charge-ordering instability is not associated with nesting of the Fermi surface since at quarter filling the Fermi surface diameter is much smaller than the length of the (π, π) wave vector [12]. We now give a brief outline of our new theoretical calculations which show how charge fluctuations near this quantum critical point produce superconductivity. Our main results are summarized in Fig. 1.

First, we extend the SU(2) spin symmetry of (1) to SU(N) by allowing the index σ to run from 1 to N. We have used slave-boson theory [13] combined with a $1/N$ expansion [14], where N is considered to be large. This type of approach has previously been applied to a wide range of strongly correlated electron systems including the Kondo model [13–15], heavy fermions [16], the Hubbard model [17], and models for the cuprate superconductors [18,19]. It has been successful in describing the physics of the Kondo effect [15] and, for the Hubbard model, it can describe the Mott-Hubbard metal-insulator transition [17]. The mean-field theory in the slave bosons corresponds to the Gutzwiller approximation [17], and so the $1/N$ expansion provides a systematic method to calculate corrections to this approximation. We briefly outline the main steps of the approach; details can be found elsewhere [7,14,18]. The condition $U \rightarrow \infty$ precludes doubly occupied sites and so it is convenient to introduce the following representation [13] for the electron operators: $c_{i\sigma}^{\dagger} = f_{i\sigma}^{\dagger}b_i$, where $f_{i\sigma}^{\dagger}$ represents a fermion at site i which carries spin σ, and

b_i is a boson associated with the electron charge located at site i. We impose the constraint that either a fermion or a boson can be at each lattice site, $f_{i\sigma}^{\dagger}f_{i\sigma} + b_i^{+}b_i = N/2$, by introducing a Lagrange multiplier λ_i at each lattice site. We expand to the next-to-leading order corrections in $1/N$, arriving at a Hamiltonian which describes an
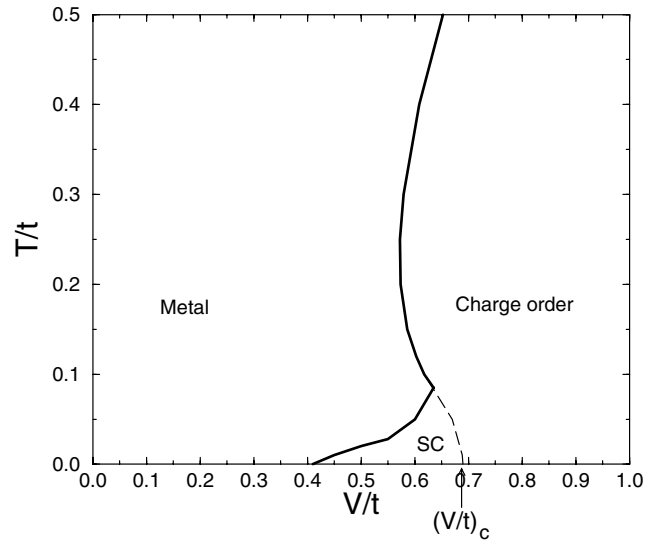

FIG. 1. Phase diagram showing competition between metallic, superconducting (SC), and charge-ordered phases. The symmetry of the Cooper pairs in the superconducting phase is d_{xy}. The phase diagram is for the extended Hubbard model [defined by the Hamiltonian (1)] with an average of one hole per two molecules (a quarter-filled band) in the limit of infinite Coulomb repulsion energy U for two holes on the same molecule. This is the simplest model Hamiltonian which can describe the organic superconductors listed in Table I. The vertical axis is the ratio of the temperature T to the intermolecular hopping integral t. The horizontal axis is the ratio of the nearest-neighbor Coulomb repulsion energy V between electrons on neighboring molecules to t. Note that the unconventional superconductivity is found near the quantum critical point [at $(V/t)_c$] separating the metallic and charge-ordered phases.

effective coupled fermion-boson problem: $H = H^f + H^b + H^{f-b}$. H^f is the result of taking the average of the boson fields, $b = \langle b_i \rangle$ and $\lambda = \langle \lambda_i \rangle$, and describes fermions moving in a renormalized band with energy dispersion given by $\epsilon_{\mathbf{k}} = \frac{-tb^2}{N} T_{\mathbf{k}} + \lambda - \mu + 4V \frac{\langle n \rangle}{N}$, with $T_{\mathbf{k}} = 2[\cos(k_x) + \cos(k_y)]$, being the Fourier transform of the hopping operator in units of the nearest-neighbor hopping t. $\langle n \rangle$ is the average occupation number of the electrons at each lattice site. The effect of Coulomb interactions is then twofold: (i) renormalization of the free electron energies by a factor $b^2 = N/2 - \langle n \rangle$ and (ii) upward shift in the position of the band which is given by $\lambda = \sum_{\mathbf{k}} f(\epsilon_{\mathbf{k}})(tT_{\mathbf{k}} + 4V)$. For $N = 2$ and a quarter-filled band, $\langle n \rangle = \frac{1}{2}$, and so the effective mass of the quasiparticles is enhanced by a factor of $m^*/m = 1/b^2 = 2$.

The bosonic part of the Hamiltonian, H^b, describes the dynamical and spatial fluctuations about the mean-field solution. The field λ_i describes fluctuations in the no-double occupancy constraint at each lattice site. The real charge fluctuations are described by b_i. These boson fields propagate according to $\hat{D}^0(\mathbf{q}, i\nu_n)$, where $\mathbf{q}$ is the momentum of the boson and $\nu_n = 2\pi n T$ is a Matsubara frequency with T being the temperature and n an integer number. Finally, H^{f-b} couples the fermions and the bosons so that they propagate according to $\hat{D}(\mathbf{q}, \nu_n) = \frac{1}{N}[\hat{D}^0(\mathbf{q}, \nu_n)^{-1} - \hat{\pi}(\mathbf{q}, \nu_n)]^{-1}$, where $\hat{\pi}(\mathbf{q}, \nu_n)$ is the self-energy of the bosons. These bosons originate from the electron-electron repulsion and produce interaction between the quasiparticles. In particular, they can induce Cooper pairing of quasiparticles. This is in analogy to the pairing of electrons due to phonons in elemental metals. However, the mechanism of the pairing in the present case is the charge fluctuations. The scattering amplitude in the particle-particle channel between a quasiparticle with momentum $\mathbf{k}$ and another with momentum $-\mathbf{k}$ which scatter to $\mathbf{k}'$ and $-\mathbf{k}'$ is denoted $\Gamma(\mathbf{q} = \mathbf{k} - \mathbf{k}')$. It can also be understood as the effective potential between the quasiparticles forming the Cooper pairs. A divergence in the effective interaction occurs at the charge-ordering instability [7,19]. We find that as the ratio V/t is increased, the potential varies its shape, developing singularities at $(\pm\pi, \pm\pi)$ when $V/t \to (V/t)_c \approx 0.69$, at zero temperature. This signals the onset of checkerboard charge ordering.

In order to look for superconducting instabilities near the charge-ordering instability we compute Fermi surface averages [11,18] of the effective potential, $\Gamma(\mathbf{q})$, weighted with the different cubic harmonics, into which the effective potential can be decomposed. These have different symmetries and they read

$$g_{s^*}(\mathbf{k}) = \cos(k_x) + \cos(k_y),$$
$$g_{d_{x^2-y^2}}(\mathbf{k}) = \cos(k_x) - \cos(k_y),$$
$$g_{d_{xy}}(\mathbf{k}) = \sin(k_x)\sin(k_y),$$
$$g_{p_x}(\mathbf{k}) = \sin(k_x).$$

(2)

From these Fermi surface averages, we find that there is attraction between the quasiparticles forming Cooper pairs with d_{xy} symmetry at $V/t \gtrsim 0.4$ and zero temperature. Cooper pairing with other symmetries is found to be repulsive for all values of V/t. This is in contrast to the $d_{x^2-y^2}$ symmetry found for κ-(BEDT-TTF)$_2$X within renormalized spin-fluctuation calculations [9].

The finite-temperature phase diagram obtained is shown in Fig. 1. The line separating the metal from the charge-ordered phase is defined from the divergence at $\mathbf{q} = (\pi, \pi)$ of the quasiparticle scattering amplitude, $\Gamma(\mathbf{q})$. The dashed line in Fig. 1 is the extension of this line, but we do not compute the transition from the charge-ordered phase to the superconducting phase. As the temperature is lowered it is possible to go from the charge-ordered state directly into the superconducting phase. This reentrant behavior [20] might explain the most unusual property ($d\rho/dT < 0$) of five of the materials listed in Table I.

The qualitative features of the phase diagram, including the d_{xy} pairing symmetry, turn out to be *insensitive to the details of the band structure and the type of charge ordering.* First, we have changed the shape of the Fermi surface by introducing a next-nearest neighbor hopping along one of the diagonals of the square lattice, t' [21]. We find that varying the ratio, t'/t, in the range $0 \leq t'/t \leq 1$ changes the shape of the Fermi surface significantly (see Fig. 5 in Ref. [7]) but does not destroy the d_{xy} pairing instability. Second, introducing a next-nearest neighbor repulsion, V', changes the momentum dependence of the scattering amplitude. Furthermore, for sufficiently large values of the ratio V'/V the singularities in $\Gamma(\mathbf{q})$ shift from (π, π) to $(0, \pm\pi)$ and $(\pm\pi, 0)$. This is because for $V'/V > 1$, it is energetically more favorable to produce charge ordering either along the x or y direction, rather than along both of them. We find that there is still a quantum critical point, and superconducting pairing with d_{xy} symmetry persists, although the strength of the effective interaction within the Cooper pairs decreases somewhat as compared to the square lattice case. The robustness of the d_{xy} superconducting instability can be understood from the fact that the charge-ordering instability is *not* associated with Fermi surface nesting. Furthermore, it means our results should also be applicable to the β'' materials for which the Fermi surface is more complicated than for the θ materials.

Proposed experimental tests.—(i) We identify several materials that might become superconducting under pressure. Pressure in the θ materials decreases the hopping parameter t, driving the materials into the insulating phase [22]. Therefore, θ materials such as θ-(BETS)$_2$Ag(CN)$_2$, θ-(BETS)$_4$Cu$_2$(Cl)$_6$, and θ-(BO)$_2$Cl(H$_2$O)$_3$, which are all metallic at ambient pressure, should become superconducting under pressure. These materials would then be located in the metallic side of our phase diagram (see Fig. 1), and pressure would increase V/t driving them into a superconducting state with d_{xy} symmetry before becoming insulating. (ii) Polarization-dependent Raman scattering should be done in the superconducting state because it can

distinguish d_{xy} and $d_{x^2-y^2}$ states [23]. (iii) Measurements of the nuclear magnetic resonance relaxation rate and Knight shift should be done in the metallic phase for the superconductors in Table I. There should be no enhancement of the Korringa ratio. This is in contrast to the large enhancements seen in κ-(BEDT-TTF)$_2$X superconductors which are close to the Mott insulator [24].

In conclusion, we have identified 11 molecular superconductors which we predict to have pairing of d_{xy} symmetry due to charge fluctuations. This is based on a systematic many-body calculation using slave-boson theory for an extended Hubbard model. Materials with the θ and β'' crystal structures are at quarter filling and are described by quite different physics from β, κ, and λ structures which are essentially at half filling.

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*Present address: Max Planck Institut für Festkörperforschung, D-70506 Stüttgart, Germany.
Email address: J.Merino@fkf.mpg.de

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