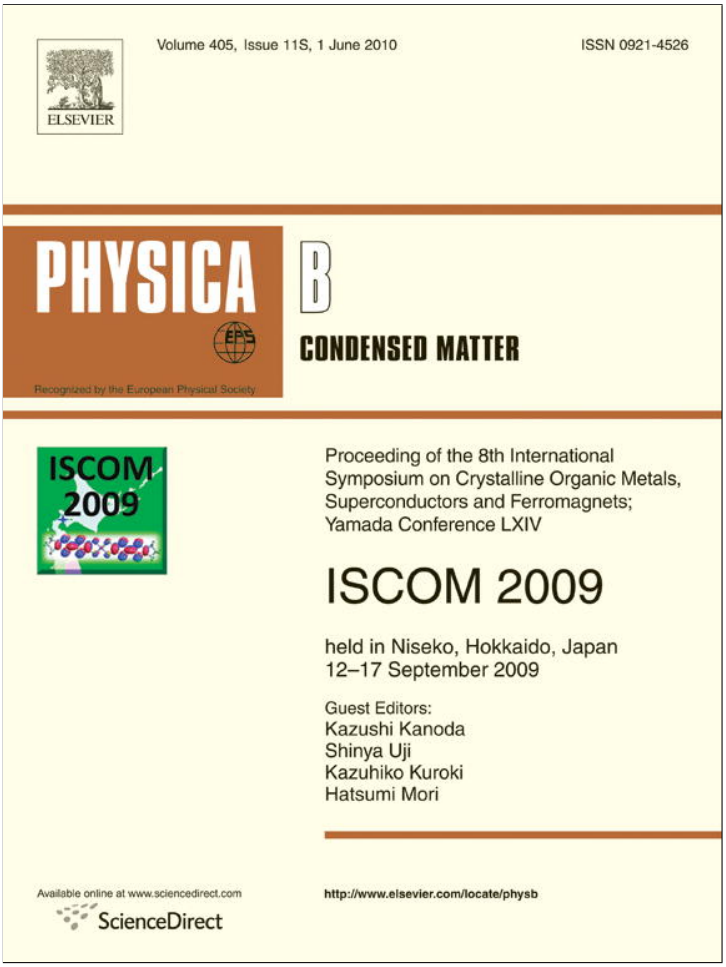

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Bipolaron density-wave driven by antiferromagnetic correlations and frustration in organic superconductors ☆

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ABSTRACT

We describe the paired electron crystal (PEC) which occurs in the interacting frustrated two-dimensional $\frac{1}{4}$- filled band. The PEC is a charge-ordered state with nearest-neighbor spin singlets separated by pairs of vacant sites, and can be thought of as a bipolaron density wave. The PEC has been experimentally observed in the insulating state proximate to superconductivity in the organic charge-transfer solids. Increased frustration drives a PEC-to-superconductor transition in these systems.

Cuprate high T_c and organic charge transfer solid (CTS) superconductors share quasi-two-dimensionality (quasi-2D), strong electron–electron (e–e) interactions and unconventional superconductivity (SC). Consequently, ideas first applied to the cuprates, such as spin fluctuation-mediated SC, have also been applied to the CTS [1]. In the present work we report exact numerical calculations that cast severe doubt on this mechanism.

While antiferromagnetism (AFM) is adjacent to SC in some CTS, most notably the κ-$(ET)_2X$, there are exceptions. In other CTS the insulating phase adjacent to SC is charge ordered (CO) or has a spin gap (SG), or both. In analogy to the spin fluctuation mechanism, mean-field theories of charge fluctuation-mediated SC have been proposed. Separate mechanisms for different classes of CTS superconductors seem unlikely, given the similarities in crystal structure and molecular makeup between CTS. In the second part of this work we propose a single mechanism that can explain the exotic insulating states and unconventional SC in the CTS.

SC in exotic superconductors often occurs at specific electron concentrations, a feature that is beyond the scope of the BCS theory. CTS superconductors have a carrier concentration ρ of one hole or electron per two molecules (i.e., $\rho = 0.5$). We present here a mechanism for frustration-driven transition from AFM to the PEC in the $\rho = 0.5$ 2D CTS. Further increase in frustration drives a PEC-to-superconductor transition that we believe gives the proper mechanism of SC in the CTS. We believe that our mechanism of SC applies to other exotic superconductors that share carrier density of 0.5, strong e–e and electron–phonon (e–p) interactions, and lattice frustration with the CTS.

Mean-field calculations find a region of SC in the $\frac{1}{2}$- filled ($\rho = 1$) anisotropic triangular lattice Hubbard model. We report exact calculations that find no indication of SC. We consider a periodic 2D 4×4 lattice with nearest-neighbor (n.n.) hopping t and frustrating hopping t'. In Fig. 1 we plot the $d_{x^2-y^2}$ pair-correlation function $P(r)$ as a function of U for several different distances r measured in units of the lattice constant. $P(r)$ decreases monotonically with increasing U. A weak increase in onsite and n.n. $P(r)$ (not shown) simply reflects the increase in strength of n.n. AFM correlations with U. Other numerical approaches have reached the same conclusion [3,4]. Claims of SC within the model appear to be artifacts of the mean field approximation. We believe that mechanisms of "charge-fluctuation mediated SC" based on mean-field approximations also suffer from similar problems.

We now discuss $\rho = 0.5$, which we believe is more appropriate to the CTS. For not too strong n.n. Coulomb interaction V, the ground state in 1D in the presence of e–e *and* e–p interactions is CO with charge pattern $\cdots 1100 \cdots$, where 1 (0) indicates charge $0.5+\delta$ ($0.5-\delta$). Sites labeled "1" are coupled by a singlet bond in the spin-gapped spin-Peierls (SP) state [6]. This 1D bond-charge density wave is the simplest example of the PEC. Another PEC is found in the zigzag ladder (see Fig. 2(a)). CO is again the $\cdots 1100 \cdots$ pattern now along the zigzag direction, and interchain spin singlets give a SG ground state [5].

The PEC structure in the $\rho = 0.5$ zigzag ladder gives a hint as to what to expect in the 2D triangular lattice. For $\rho = 1$, rectangular ladders possess rung-based spin singlets. When multiple ladders are coupled, however, the 2D lattice is AFM rather than SG because each site now has four *singly occupied* n.n. sites [7]. Very different scenarios emerge when $\rho = 0.5$ zigzag ladders are similarly coupled, as is shown in Figs. 2(b) and (c). Each "occupied" site continues to have only two "occupied" neighbors,

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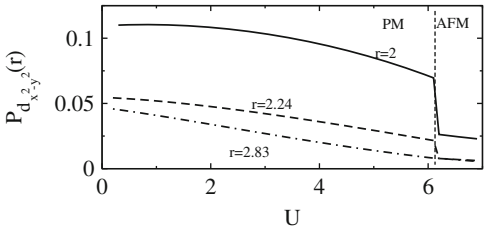

Fig. 1. Exact d-wave SC pair correlation functions versus distance r, for the $\frac{1}{2}$ filled 4×4 periodic anisotropic triangular lattice for $t'/t=0.5$. SC correlations similarly decrease monotonically with increasing U for all t'/t [2].

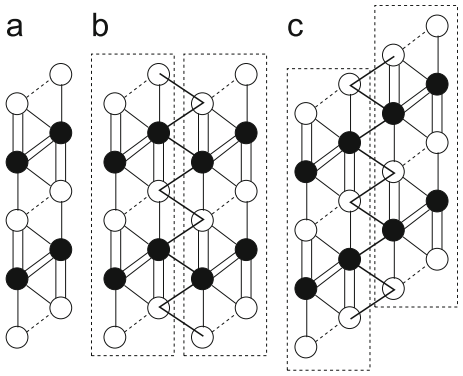

Fig. 2. (a) The $\rho=0.5$ zigzag ladder [5]. Ladders combine to form a 2D lattice in two ways, forming either horizontal stripe (b) or diagonal stripe (c) CO patterns. Black and white circles denote charge-rich and charge-poor sites. Double bonds between the charge-rich sites indicate spin singlets.

as in 1D. Thus stripe formation ("horizontal" or "diagonal"), along with n.n. spin singlets are to be *expected* in the 2D $\rho=0.5$ triangular lattice. In terms of the n.n. V interaction both CO patterns have the same static energy [8,9]. The strong tendency to spin-singlet formation is a characteristic of the particular electron density as well as of frustrated systems. Coupled rectangular ladders, for example, have site populations of 0.5 each.

Based on the above, it is natural to speculate that the PEC persists in the $\rho=0.5$ triangular lattice. We have recently confirmed this within the 2D extended Hubbard Hamiltonian with n.n. e–e repulsion and inter- and intrasite e–p couplings [10]. We started with the same periodic 4×4 lattice as above, and performed self-consistent calculations. For diagonal hopping t' less than a critical t'_c, the square lattice is dimerized along one direction, with in-phase dimerization on all chains, and AFM spin–spin couplings between the dimer unit cells. This explains the AFM in the bulk of the κ-$(ET)_2X$. For $t'>t'_c$ we find a clear frustration-driven transition from the AFM to the PEC of Fig. 2(b). We refer to the original work for details [10].

The PEC has been found in a number of 2D CTS with different crystal structure, α, β′, θ and also κ [10]. The CO pattern is $\cdots1100\cdots$ along two crystal directions and $\cdots1010\cdots$ along the third [10]. In the following we discuss the most notable cases.

The PEC shown in Fig. 2(b) is found in the θ-$(ET)_2MM'(SCN)_4$, where a SG occurs at T_{SG} [12]. The high T_{SG} (~60 K) precludes a simple 1D SP transition, which occurs at 10–20 K in the CTS. With decreasing temperature the lattice parameter along the weakest hopping direction decreases sharply, leading to increased frustration giving the transition to the PEC [10].

The PEC pattern in Fig. 3(a) is seen in some β′-$X[Pd(dmit)_2]_2$ [13]. Weakly frustrated systems are AFM, but SGs occur in systems closer to being isotropic triangular ($X=Et_2Me_2Sb$ and $X=EtMe_3P$) [13]. For $X=EtMe_3P$, the charge densities and intermolecular distances are exactly as in Fig. 3(a) [13,10].

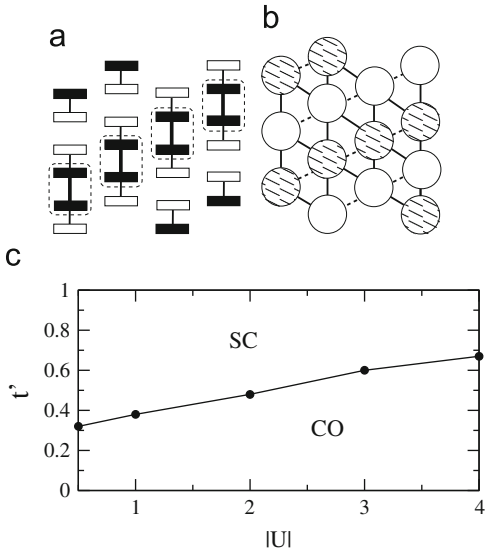

Fig. 3. (a) PEC in the β′ CTS. Singlets indicated by heavy line and dashed boxes. (b) Effective $-|U|$, $+V$, t', t model. Pairs of singlet-bonded sites (vacancies) are mapped to a single doubly occupied (vacant) site in the effective model. (c) Phase diagram of the effective model for $V=1$ [11].

Another CTS with a similar structure, β-(*meso*-$DMET)_2PF_6$, has the same CO/bond arrangement [14]. Pressure-induced transition to SC occurs in both systems.

Among the κ-$(ET)_2X$ CTS, $X=Cu_2(CN)_3$ has a nearly isotropic triangular lattice and does not display AFM order [15]. Although specific heat data appear to show no gap [16] thermal conductivity shows a small SG [17]. We propose that the ground state of this CTS is a PEC, driven by frustration larger than that in the other κ- salts. Because of near perpendicular orientations of neighboring dimers, multiple ways of forming singlet-bonds between charge-rich sites are possible, making any SG very small [10]. Experimental evidences that support our proposal of CO here include, (i) NMR line broadening at low temperature, [18], (ii) strong role of the lattice near the 6 K transition as seen in thermal expansion measurements [19], and (iii) frequency-dependent dielectric constant measurements that indicate unequal charges within the ET dimers [20]. Note in particular that site charge occupancies $1=0\ldots0=1$ along the "stacks" provides a simple explanation of the antiferroelectricity observed by these authors.

We have proposed that the $\rho=0.5$ PEC can be mapped to an effective $\rho=1$ CO in which the singlet-bonded sites are replaced with an effective doubly occupied single site (Figs. 3(a) and (b)) [11]. The effective $\rho=1$ system is described by a negative (attractive) U and repulsive V. To understand pressure-effects we refer to ab initio calculations for κ-$(ET)_2X$ [21]. We assume similar charge-distribution in κ as in Fig. 3(a). Then the strong intradimer t_1 bond is 1–0, which is unchanged by pressure [21]. Careful comparison of Fig. 1(c) in Ref. [21] and Fig. 3(a) shows that the 1–1 and 0–0 bonds correspond to the t_3 bonds in κ−ET. These increase with pressure [21], but are irrelevant within the effective model of Fig. 3(b) where the 1–1 and 0–0 sites are replaced by effective double occupancies and vacancies. The bonds *between* the effective double occupancies are derived from t_2 and t_4, which increase with pressure [21]. The 2–2 and 0–0 bonds of Fig. 3(b) thus become stronger, even as the 2–0 bonds remain relatively unchanged, *thus increasing the frustration within the effective model.* We have shown that a CO-to-SC transition, driven by the frustration t'/t occurs within this effective model (see Fig. 3(c)) [11].

Other exotic $\rho=0.5$ superconductors, with proximate exotic insulating states, include spinels $LiTi_2O_4$ [22], and $CuRh_2X_4$

($X = S, Se$) [23]. There are 0.5 d-electrons per atom after Jahn-Teller distortion breaks the t_{2g} orbital symmetry. There is evidence for PEC formation in $CuIr_2S_4$, isostructural and isoelectronic with $CuRh_2S_4$; CO $\cdots 1100 \cdots$ and n.n. singlets are both found [24]. $Na_{0.5}CoO_2$ is another example with both CO and AFM phases at $\rho = 0.5$ [25]. Several common features, viz., $\rho = 0.5$, strong e–e interactions, lattice effects showing electron–phonon (e–p) interactions, and geometrically frustrated lattices, link these seemingly unrelated materials. Our proposed theory unveils the relationship between them.

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