Mott Transition, Antiferromagnetism, and *d*-Wave Superconductivity in Two-Dimensional Organic Conductors

B. Kyung and A.-M. S. Tremblay

*Département de Physique and Regroupement Québécois sur les Matériaux de Pointe, Université de Sherbrooke,
Sherbrooke, Québec, J1K 2R1, Canada*

We study the Mott transition, antiferromagnetism, and superconductivity in layered organic conductors using the cellular dynamical mean-field theory for the frustrated Hubbard model. A *d*-wave superconducting phase appears between an antiferromagnetic insulator and a metal for $t'/t = 0.3$–0.7 or between a nonmagnetic Mott insulator (spin liquid) and a metal for $t'/t \gtrsim 0.8$, in agreement with experiments on layered organic conductors including κ-(ET)$_2$Cu$_2$(CN)$_3$. These phases are separated by a strong first-order transition. The phase diagram gives much insight into the mechanism for *d*-wave superconductivity. Two predictions are made.

Strong electronic correlations lead to fascinating phenomena such as high-temperature superconductivity and metal-insulator (Mott) transitions. In that context, layered organic conductors κ-(BEDT-TTF)$_2$X (X denotes an anion) play a special role. They share many features with high-temperature superconductors (HTSC) [1,2], such as the existence of *d*-wave superconductivity and antiferromagnetism. But they have an even richer phase diagram since they also display a Mott transition and possibly a $T = 0$ spin liquid phase. Microscopically, they are described by the two-dimensional one-band Hubbard model, just as HTSC, albeit on an anisotropic triangular lattice instead of a square lattice. The various phases of HTSC are explored essentially by changing doping. The phases of organic conductors, on the other hand, are controlled by pressure and by frustration, two variables over which one has very little control in the HTSC. In this Letter, we will see that we can capitalize on recent theoretical progress on the theory of HTSC to understand organic conductors. In return, the agreement that we find between theory and experiment for these compounds leads to much insight into the origin of *d*-wave superconductivity in the one-band Hubbard model in general.

Experimentally, metallic (*M*), paramagnetic insulating [spin liquid (SL)], antiferromagnetic (AF), and unconventional superconducting (SC) phases are all found, for example, in the pressure vs temperature phase diagram of $X = $ Cu[N(CN)$_2$]Cl [3]. The broken-symmetry states overlap through a first-order boundary that merges with the first-order line of the Mott metal-insulator transition in the normal state. Various experiments suggest that the superconductivity has line nodes [4] that are strongly suggestive of *d*-wave character. Changing the anion modifies the frustration in the lattice. The anion [$X = $ Cu$_2$(CN)$_3$] [5], which corresponds to large frustration, has attracted considerable attention because of the transition from *d*-wave SC to a possible SL state where no magnetic long-range order was found down to a very low temperature (23 mK), in contrast to other layered organic materials.

The intriguing behaviors observed in layered organic conductors have prompted theoretical studies using various analytical and numerical methods. These include a path-integral renormalization group study of the frustrated Hubbard model by Morita *et al.* [6], cellular dynamical mean-field theory (CDMFT) [7] by Parcollet *et al.* [8], a variational Monte Carlo (VMC) study by Liu *et al.* [9] and Watanabe *et al.* [10], a U(1) gauge theory by Lee *et al.* [11], and a Gutzwiller projection method for the Hubbard-Heisenberg model by Powell *et al.* [12] and Gan *et al.* [13].

The layered organic conductors are described by the frustrated two-dimensional Hubbard model [14]

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

where $c_{i\sigma}^{\dagger}$ ($c_{i\sigma}$) are creation (annihilation) operators for electrons of spin σ, and $n_{i\sigma} = c_{i\sigma}^{\dagger} c_{i\sigma}$ is the density of σ spin electrons. The hopping amplitude t_{ij} determines the anisotropic bare dispersion $\varepsilon_{\vec{k}} = -2t(\cos k_x + \cos k_y) - 2t' \cos(k_x + k_y)$. [The HTSC have an additional $2t' \cos(k_x - k_y)$ in their dispersion.] U is the on-site repulsive interaction, and μ is the chemical potential controlling the electron density. Physically relevant parameters for layered organic conductors are $U/t = 5$–10 at half-filling ($n = 1$) and $t'/t = 0.5$–1.1.

Our results are summarized by the U/t vs t'/t phase diagram in Fig. 1. A *d*-wave SC phase appears in a relatively narrow region between metallic (*M*) and AF phases or between metallic (*M*) and SL phases. The phase transition lines are all first-order, except for the SC-metal transition that is also first-order but eventually turns second-order (dashed line) for sufficiently large t'/t. Three phases *M*-AF-SC meet at the triple point near $t'/t = 0.25$ and $U/t = 2.75$, satisfying the Gibbs phase rule. There is a jump for all order parameters so that this point does not exhibit SO(5) symmetry [15]. The SL phase (paramagnetic Mott insulator) appears only for large t'/t (large frustration) and large U/t (strong correlations). If we
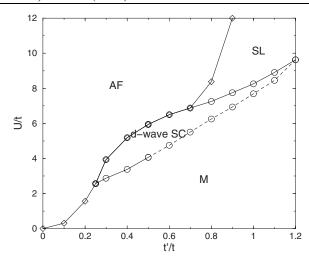
FIG. 1. Phase diagram of the frustrated two-dimensional Hubbard model at zero temperature in the U/t vs t'/t plane. AF, SL, SC, and M denote antiferromagnetic, spin liquid (nonmagnetic insulator), d-wave superconducting, and metallic phases, respectively.

do not allow for broken symmetry, we obtain a normal state that has a first-order Mott metal-insulator transition that coincides with the first-order line that separates SC from either AF or SL. That first-order line, however, ends at a critical point for t'/t close to 0.5.

Predictions.—Based on the calculated phase diagram, we predict a class of new materials (with $t'/t \sim 0.8$–0.9) which would undergo a series of phase transitions from an AF insulator to a paramagnetic Mott insulator (SL) to a d-wave superconductor to a metal with increasing pressure. Also, we predict that if AF and SC are destroyed with an external symmetry-restoring perturbation (magnetic field), the first-order transition that separates them should remain as a first-order Mott metal-insulator transition. In the following, we describe the method and results that lead to the above phase diagram. We then discuss the remarkable agreement with existing experiments.

Method.—We use CDMFT [7], a cluster approach that allows one to extend dynamical mean-field theory to include momentum dependence of the self-energy. CDMFT has been benchmarked and is accurate even in one dimension [16,17]. The infinite lattice is tiled with identical clusters of size N_c, and the degrees of freedom in the cluster are treated exactly while the remaining ones are replaced by a bath of noninteracting electrons that is determined self-consistently. To solve the quantum cluster embedded in an effective SC medium, we consider a cluster-bath Hamiltonian of the form [18,19]

$$H = \sum_{\langle \mu\nu\rangle,\sigma} t_{\mu\nu} c^\dagger_{\mu\sigma} c_{\nu\sigma} + U\sum_\mu n_{\mu\uparrow} n_{\mu\downarrow} + \sum_{m,\sigma,\alpha} \varepsilon^\alpha_{m\sigma} a^{\dagger\alpha}_{m\sigma} a^\alpha_{m\sigma}$$
$$+ \sum_{m,\mu,\sigma,\alpha} V^\alpha_{m\mu\sigma}(a^{\dagger\alpha}_{m\sigma} c_{\mu\sigma} + \text{H.c.})$$
$$+ \sum_{m,n,\alpha} \Delta_{mn}(a^\alpha_{m\uparrow} a^\alpha_{n\downarrow} + \text{H.c.}). \quad (2)$$

Here the indices μ, $\nu = 1, \cdots, N_c$ label sites within the cluster, and $c_{\mu\sigma}$ and $a^\alpha_{m\sigma}$ annihilate electrons on the cluster and the bath, respectively. $t_{\mu\nu}$ is the hopping matrix within the cluster, $\varepsilon^\alpha_{m\sigma}$ are the bath energies, and $V^\alpha_{m\mu\sigma}$ are the bath-cluster hybridization matrices. Δ_{mn} represents the amplitude of SC correlations on the bath with a given gap symmetry. Because superconductivity and antiferromagnetism are allowed to compete on equal footing, $\varepsilon^\alpha_{m\sigma}$ and $V^\alpha_{m\mu\sigma}$ carry a spin variable σ explicitly. In the present study, we used $N_c = 4$ sites for the cluster and $N_b = 8$ sites for the bath with $m = 1, \ldots, 4$, $\alpha = 1, 2$. To deal with superconductivity, the Nambu spinor representation is used for the cluster operators so that the Weiss field, the cluster Green's function, and the self-energy constructed from these operators are 8×8 matrices. The exact diagonalization method [20] is used to solve the cluster-bath Hamiltonian equation (2) at zero temperature, which has the advantage of computing dynamical quantities directly in real frequency and of treating the large U regime without difficulty. Although the present study focuses on a 2×2 cluster with additional 8 bath sites, we expect our results to be robust with respect to an increase in the cluster size. This was verified by our recent low (but finite) temperature CDMFT + QMC (quantum Monte Carlo) calculations [21], where, at intermediate to strong coupling, a 2×2 cluster accounts for more than 95% of the correlation effect of the infinite size cluster in the single-particle spectrum. Recent variational cluster perturbation theory calculations [22] for the same Hamiltonian also confirmed that results on a 2×2 cluster are quantitatively similar to those on larger clusters.

Normal state Mott transition.—We first present the evidence of a first-order line of metal-to-insulator transition in the normal state. That line also turns out to coincide with the phase boundary between AF and SC phases for $t'/t > 0.5$. The present results obtained in the normal state at $T = 0$ would be relevant when the temperature is slightly higher than T_c and T_N or in regions where broken symmetries are destroyed at zero temperature by an external symmetry-restoring perturbation. The first plot in Fig. 2(a) shows the double occupancy $\langle n_\uparrow n_\downarrow \rangle$ (circles) for two different t'/t. For $t'/t = 0.7$ it jumps discontinuously to a lower value near $U/t = 7.0$, while for $t'/t = 1.0$ the first-order transition occurs near $U/t = 8.5$, which is comparable to the value obtained by Parcollet *et al.* [8] in CDMFT + QMC calculations and Watanabe *et al.* [10] in VMC calculations. To show hysteresis associated with a first-order transition, we also calculated the double occupancy [diamonds in Fig. 2(a)] with the insulating solution as an initial guess. In this case, the first-order transition occurs for a value of U that is typically smaller by 0.5–0.75t. A very similar hysteresis is found for all the first-order transitions shown in this Letter, but for the rest of the Letter we show results obtained only with the metallic solution as an initial guess. The critical U_c shown in Fig. 2(b) decreases monotonically with decreasing t'/t
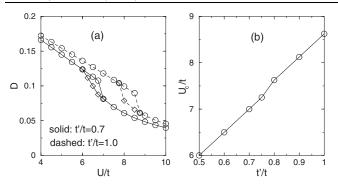
FIG. 2. (a) Double occupancy $D = \langle n_\uparrow n_\downarrow \rangle$ as a function of U/t for $t'/t = 0.7$ (solid curve) and $t'/t = 1.0$ (dashed curve); (b) critical U_c/t as a function of t'/t in the normal state. The diamond symbols in (a) are obtained with the insulating solution as an initial guess.

until the first-order transition disappears near $t'/t = 0.5$, close to $t'/t \leq 0.4$ found by Watanabe *et al.* [10].

While various studies [6,8,10–13] suggested the existence of a first-order transition for the frustrated Hubbard model in static quantities, here we present the strongest evidence of a first-order transition from a metal to an insulator by presenting dynamical quantities $A(\vec{k}, \omega)$. For $U/t = 6.9$ slightly smaller than critical U_c/t for $t'/t = 0.7$, the spectral function has a sharp quasiparticle peak near the Fermi wave vectors [Fig. 3(a)] consistent with a Fermi liquid picture. It is more evident from the fact that $A(\vec{k}, \omega)$ becomes sharper as $\vec{k}$ approaches the Fermi surface. When U/t is increased only by a tiny fraction (less than 1%), the first-order metal-to-insulator transition manifests itself as the massive reshuffling of the spectral weight. An insulating gap is present in the whole Brillouin zone, reminiscent of the spectral function in the two-dimensional Hubbard model at half-filling [18], where the low energy bands inside the Hubbard bands are caused by short-range spin correlations.

Broken-symmetry states.—Next we study the existence of broken-symmetry states in the frustrated model and the role of the first-order transition in those states. Because of
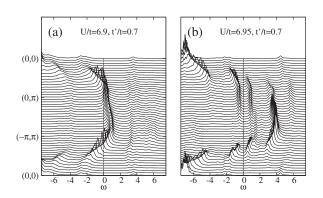
the possible coexistence of AF and SC phases, the two order parameters are treated on equal footing. For a SC phase, two symmetries are considered $d_{x^2-y^2}$ and d_{xy}. For all the parameters studied, $d_{x^2-y^2}$ symmetry always dominates over d_{xy} (see caveat [23]). For $t'/t = 0.7$ [Fig. 4(a)], AF and SC phases abruptly terminate near $U/t = 7$, the same U_c as in the normal state where a metal-to-insulator transition occurs. We have not found evidence of homogeneous states with nonzero AF and SC order parameters simultaneously, in contrast to the case of the square lattice t-t'-U model for HTSC at finite doping, where AF can have some itinerant character [24,25]. With enough frustration, $t'/t = 1.0$ [Fig. 4(b)], a direct first-order transition from a paramagnetic Mott insulator to a superconductor occurs near $U/t = 8.25$, in agreement with other recent theoretical works [10–12]. This result is also in agreement with the study [26] of the J-J' Heisenberg model in which the Néel order persists up to $J'/J = 0.6$–0.7 ($t'/t = 0.77$–0.84). Nevertheless, we have to leave open the possibility that magnetically ordered phases different from AF are more stable than the SL.

Contact with experiment.—In the first approximation, the effect of pressure is to decrease the ratio U/t, [1] even though t'/t should also change slightly [27]. We now demonstrate that our phase diagram (Fig. 1) accounts for a surprisingly large number of experimental results if we assume that pressure only decreases the U/t ratio at fixed t'/t, the various compounds being associated to a given t'/t. For $t'/t = 0.7$ [Fig. 4(a)] which is relevant to κ-(ET)$_2$Cu[N(CN)$_2$]Cl, Fig. 1 shows that, as observed experimentally [3]: (a) as pressure increases (U/t decreases), one crosses a first-order transition between AF and SC phases; (b) the maximum SC order parameter occurs at the phase boundary; and (c) in the normal state there is a first-order Mott-insulator transition, at essentially the same t/U ratio. The d-wave SC in our phase diagram, however, exists in a relatively small region of t/U in Fig. 4. In the experimental phase diagram [3], the SC region

FIG. 3. Spectral function $A(\vec{k}, \omega)$ along some symmetry directions for (a) $U/t = 6.9$ and (b) $U/t = 6.95$ for $t'/t = 0.7$ in the normal state.
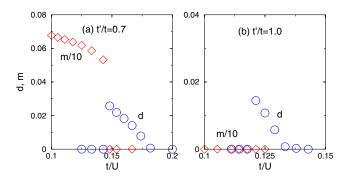

FIG. 4 (color online). Order parameters of the frustrated two-dimensional Hubbard model as a function of pressure (modeled as t/U) at zero temperature for (a) $t'/t = 0.7$ and (b) $t'/t = 1.0$. d (circles) and m (diamonds) denote the d-wave SC and AF order parameters, respectively. m is multiplied by 0.1 to fit in the plots.

extends far beyond the AF + SC phase boundary in the pressure vs temperature plane, but, in the absence of a precise scale connecting pressure and t/U, this cannot be taken as a real disagreement. For $t'/t = 1.0$, close to the value for κ-(ET)$_2$Cu$_2$(CN)$_3$, the AF phase is not stabilized even for large U/t due to too strong frustration and the transition is between a SL and SC [Fig. 4(b)], consistent with recent experiments by Shimizu *et al.* [5].

Another clear overall trend in our results is that the maximum value of the SC order parameter decreases monotonically with t'/t (0.0276, 0.0258, 0.0228, 0.0186, 0.0145 for $t'/t = 0.6, 0.7, 0.8, 0.9, 1.0$, respectively). This trend is remarkably consistent with experiments where compounds with weaker frustration (smaller t'/t) have higher T_c, for instance [1,10], $T_c = 11.6, 10.4$, and 3.9 K for $X = $ Cu[N(CN)$_2$]Br$(t'/t = 0.68)$, $X = $ Cu(NCS)$_2$($t'/t = $ 0.84), and $X = $ Cu$_2$(CN)$_3$($t'/t = 1.06$), respectively.

Mechanism for d-wave superconductivity.—Along the AF-SC and SL-SC phase transition lines, the maximum value of the SC order parameter increases with U until $U \sim$ 6t and then it starts to decrease, as does the value of $J = 4t^2/U$. In previous studies of HTSC [19,28], the maximum value of the doping dependent SC order parameter was found to scale similarly with interaction strength. In the organics, at fixed t'/t the SC order parameter always increases with increasing U until it drops to zero at the phase boundary. The SC region is broadest near $t'/t = 0.5$ and becomes narrower for both smaller and larger t'/t, vanishing near $t'/t = 0.25$ and $t'/t = 1.2$, respectively. If there is not enough frustration in the system, as in the case of near perfect nesting at small t'/t, AF long-range order is stabilized, suppressing the SC phase. Increasing frustration then helps d-wave SC, as suggested for the cuprates [29]. However, too strong frustration at large t'/t suppresses even short-range singlet correlations on which pairing correlations may build up so that SC disappears again for $t'/t \gtrsim 1.2$. Note that the ratio of interaction strength U to hopping integral t is of the same order in the organics and in HTSC but that the energy scale set by the hopping integrals is an order of magnitude smaller in these compounds than in the HTSC.

In conclusion, we obtained the phase diagram for layered organic conductors using CDMFT. The calculated sequence of phases and the nature of the transitions between them are consistent with observations in that class of compounds. In addition, the observed maximum value of T_c near the Mott transition is consistent with the calculated maximum SC order parameter. This allows us to predict a new class of materials. In conjunction with results for HTSC [19,28], the present results also allow us to understand more deeply the role of exchange interactions and of frustration for d-wave superconductivity.

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