Charge ordering and antiferromagnetic exchange in layered molecular crystals of the θ type

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We consider the electronic properties of layered molecular crystals of the type θ-D_2A where A is an anion and D is a donor molecule such as bis-(ethylenedithia-tetrathiafulvalene) (BEDT-TTF), which is arranged in the θ-type pattern within the layers. We argue that the simplest strongly correlated electron model that can describe the rich phase diagram of these materials is the extended Hubbard model on the square lattice at one-quarter filling. In the limit where the Coulomb repulsion on a single site is large, the nearest-neighbor Coulomb repulsion V plays a crucial role. When V is much larger than the intermolecular hopping integral t the ground state is an insulator with charge ordering. In this phase antiferromagnetism arises due to a novel fourth-order superexchange process around a plaquette on the square lattice. We argue that the charge ordered phase is destroyed below a critical nonzero value V, of the order of t. Slave-boson theory is used to explicitly demonstrate this for the SU(N) generalization of the model, in the large-N limit. We also discuss the relevance of the model to the all-organic family β''-(BEDT-TTF)$_2$SF$_5Y$SO$_3$ where $Y=$CH$_2$CF$_2$, CH$_2$, CHF.

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I. INTRODUCTION

Layered organic molecular crystals based on the bis-(ethylenedithia-tetrathiafulvalene) (BEDT-TTF) molecule[1–3] are rich examples of strongly correlated electron systems in low dimensions. The κ-(BEDT-TTF)$_2X$ family has many similarities to the cuprate superconductors, such as the proximity of superconductivity to an antiferromagnetic Mott-Hubbard insulating phase.[4–6] It has recently been argued that the simplest strongly correlated electron model that can describe this family is a Hubbard model on an anisotropic triangular lattice at one-half filling.[6] This model should also describe the β-(BEDT-TTF)$_2X$ family.[7,8] As the anion X or pressure is varied the θ-(BEDT-TTF)$_2X$ family exhibits metallic, superconducting, insulating, antiferromagnetic, charge-ordered, and spin-gapped phases.[9,10] The family[11] θ-(BETS)$_2X$ [where BETS is bis-(ethylenedithio-tetraselenafulvalene)] is also found to exhibit a metal-insulator transition with a transition temperature that varies with the anion.[12] The recently synthesized family β''-(BEDT-TTF)$_2$SF$_5Y$SO$_3$ where $Y=$CH$_2$CF$_2$, CH$_2$, CHF has attracted considerable interest from chemists because the anion is purely organic and $Y=$CH$_2$CF$_2$ is the first purely organic superconductor.[13] Insulating, charge-ordered, and spin-gapped phases are observed for different anions.[14]

Given the complexity of the details of the chemistry, crystal structure, and band structures of these materials it is important to define the simplest possible many-body Hamiltonian that can capture the essential physics. This is similar in spirit to the way one studies the Hubbard and t-J models on a square lattice in order to understand the cuprate superconductors.[15] Several previous studies[16,12] of the metal-insulator transition and the magnetic properties of the insulating phase[17] of the θ family have been interpreted in terms of the Hubbard model. However, this is inadequate because, at one-quarter filling, the Hubbard model is expected to be metallic. Following Seo,[18] we argue that the nearest-neighbor Coulomb repulsion V plays a crucial role in these materials. This has been emphasized before for other organic compounds.[10,19–21]

Specifically, the simplest possible strongly correlated electron model that can describe the competition between all of the above phases is the extended Hubbard model (or a t-V model with no double occupancy) at one-quarter filling on a square lattice. We show that in the charge-ordered insulating phase antiferromagnetic interactions arise due to a novel fourth-order superexchange around a plaquette on the square lattice. We then consider the SU(N) generalization of the t-V model and perform a slave boson study that becomes exact in the limit of large N. We find there is a critical value of the ratio V/t, above which the metallic Fermi-liquid phase undergoes an instability to a charge-ordered state.

II. REVIEW OF EXPERIMENTAL PROPERTIES OF θ-(BEDT-TTF)$_2X$

Properties of the θ-(BEDT-TTF)$_2X$ family have recently been reviewed by Mori *et al.*[16,22] and Seo.[18] The arrangement of the BEDT-TTF or BETS molecules within a layer of the θ structure is shown in Fig. 1. For most anions, X, the materials undergo a metal-insulator transition at a temperature that decreases with increasing bandwidth; the latter is directly correlated with the angle between the molecules within the layers[16] (see Fig. 2). The temperature at which the metal-insulator transition occurs generally increases with increasing pressure.[12,23]

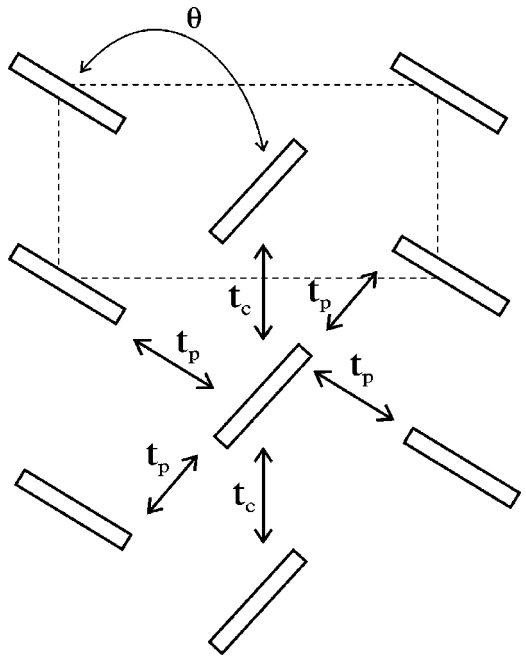

FIG. 1. Arrangement of the donor molecules D (for example BEDT-TTF) within a layer for the θ-D_2X molecular crystals. The dashed rectangle denotes the unit cell. Typical values of the hopping integrals t_p and t_c are given in Table I. Note that this geometry defines a tight binding model on an anisotropic triangular lattice which also can be viewed as a square lattice with hopping along one of the diagonals. The angle θ, and consequently the value of t_p, varies with pressure or change in anion X.

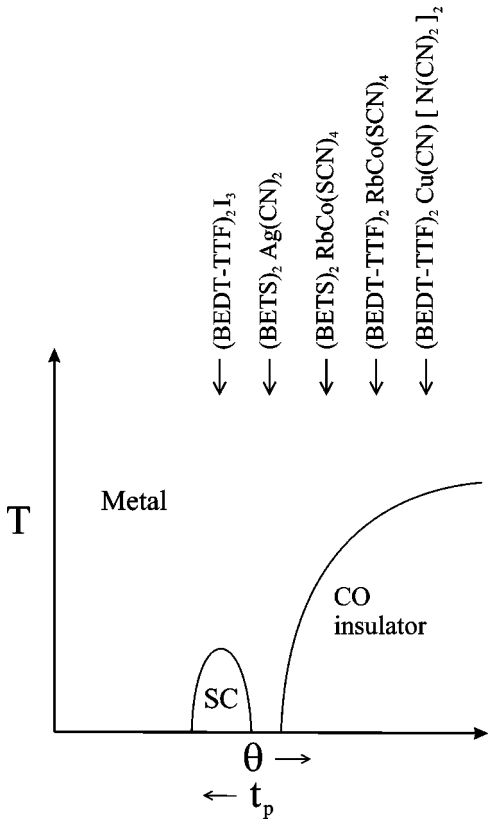

FIG. 2. Schematic phase diagram of the θ-$(\mathrm{BEDT\text{-}TTF})_2X$ and θ-$(\mathrm{BETS})_2X$ families (Refs. 9 and 12) showing competition between metallic, superconducting (SC), and charged ordered (CO) insulating phases. The horizontal axis is proportional to the angle θ (see Fig. 1) which is related to the hopping integral t_p. Generally, increasing θ decreases the bandwidth and so increases the importance of the electronic correlations. The vertical arrows denote the location of various materials at ambient pressure. The effect of pressure is to drive each material towards the right (Refs. 12 and 23).

Evidence for short-range charge ordering along the c-axis direction (the vertical direction in Fig. 1) was found in the insulating phase of $X=\mathrm{CsCo(SCN)_4}$ by x-ray scattering.[24] For $X=\mathrm{CsZn(SCN)_4}$, the principal axes of the g tensor associated with electron spin resonance undergo a rotation at 20 K; this has been interpreted as a change in the electronic state.[25] For $X=\mathrm{RbZn(SCN)_4}$ there is a metal-insulator transition at 190 K; there is then a dimerization in the c direction.[16] The magnetic susceptibility shows no features at this transition and between 50 and 190 K has been fitted to that for a two-dimensional antiferromagnetic Heisenberg model with exchange $J=100$ K. Below 50 K the susceptibility is consistent with a spin gap of about 45 K. There is evidence from nuclear magnetic resonance for charge ordering below 190 K and of a spin gap below 10 K.[26] For $X=\mathrm{Cu_2(CN)[N(CN)_2]_2}$ there is a metal-insulator transition at 220 K; the charge gap at low temperatures is about 200 meV.[27] The magnetic susceptibility shows no features at this transition and between 33 and 220 K has been fitted to that for a two-dimensional antiferromagnetic Heisenberg model with $J=48$ K. There is no sign of Néel order but below 30 K the susceptibility decreases rapidly, suggesting formation of a spin gap.

The only member of the θ-$(\mathrm{BEDT\text{-}TTF})_2X$ family that is superconducting is $X=\mathrm{I_3}$, which has a transition temperature of 3.6 K. The Fermi surface of the metallic phase has been mapped out using angular-dependent magnetoresistance and magnetic oscillations.[28] Several of the θ-$(\mathrm{BETS})_2X$ family undergo a metal-insulator transition and several are metallic down to 4 K (see Table I).

θ-$(\mathrm{BDT\text{-}TTP})_2\mathrm{Cu(NCS)_2}$ [where BDT-TTP is 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathia-pentalene] undergoes a metal-insulator transition at 250 K.[29] At low temperatures the charge gap deduced from the activation energy of the conductivity is about 100 meV. Raman-active vibrational modes (associated with the stretching of carbon-carbon double bonds) of the BPT-TTP molecules are sensitive to the charge on the molecule. In the insulating phase these modes split, consistent with charge ordering.[29]

θ-$(\mathrm{C_1TET\text{-}TTF})_2\mathrm{Br}$ [where $\mathrm{C_1}$TET-TTF is bis(methylthio)ethylenedithio-tetrathiofulvalene] is an insulator with a charge gap of 600 meV.[17] The magnetic susceptibility between 8 and 290 K has been fit to that for a two-dimensional antiferromagnetic Heisenberg model with $J=6$ K. Below 3 K the susceptibility depends on the field direction, suggesting the formation of Néel order. As emphasized by Mori *et al.*,[30] and illustrated schematically in Fig. 2, Table I shows the general trend that as the bandwidth (which is roughly proportional to t_p) increases the transition temperature of the metal-insulator transition decreases.

TABLE I. Hopping integrals for various θ-type crystals calculated by the Hückel method. Two values are given for the case where the unit cell is larger. The temperature of the metal-insulator transition, T_{MI}, is also given. Note the general trend, observed by Mori (Ref. 30), that as t_p increases T_{MI} decreases (Ref. 73).

Material	t_p (meV)	t_c (meV)	Reference	T_{MI} (K)
$(BEDT\text{-}TTF)_2I_3$	42	64	31	–
$(BEDO\text{-}TTF)_2H_5O_2Cl_2$	140	100	74	<0.03
$(BETS)_2Ag(CN)_2$	392,398	$-1,38$	12	<4
$(BETS)_4Cu_2Cl_6$	380–467	-12 to $+56$	75	<4
$(BETS)_2CsCo(SCN)_4$	366	-2	12	10?
$(BETS)_2CsZn(SCN)_4$	372	-10	12	10?
$(BETS)_2RbCo(SCN)_4$	382	-72	12	20
$(BETS)_2RbZn(SCN)_4$	347	-46	12	?
$(BEDT\text{-}TTF)_2CsCo(SCN)_4$	106	-5	30	20
$(BEDT\text{-}TTF)_2CsZn(SCN)_4$	108	-10	30	20
$(BETS)_4TaF_6$	-30	110	76	70
$(BEDT\text{-}TTF)_2RbCo(SCN)_4$	99	-33	30	190
$(BEDT\text{-}TTF)_2RbZn(SCN)_4$	94	-24	30	190
$(BEDT\text{-}TTF)_2Cu_2(CN)[N(CN)_2]_2$	79	-30	27	220
$(BEDT\text{-}TTF)_2TlCo(SCN)_4$	100	-48	30	250
$(BDT\text{-}TTP)_2Cu(NCS)_2$	$-86,-91$	-41	17	250
$(C_1TET\text{-}TTF)_2Br$	$-54,-43$	-58	17	>300

III. THE EXTENDED HUBBARD MODEL

The arrangement of the BEDT-TTF molecules within a layer of θ-$(BEDT\text{-}TTF)_2X$ is shown schematically in Fig. 1. Values of the intermolecular hopping integrals, calculated using the Hückel approximation are given in Table I. If there is complete charge transfer of one electron onto each anion X, there is an average of half a hole per molecule and so the electronic bands will be one-quarter filled with holes.

Band structure calculations[14,17,27,30,31] predict that all these materials are metallic. Hence, the different phases must be due to electronic interactions. The Hubbard interaction U describing the Coulomb repulsion between two electrons on the same BEDT-TTF molecule has been estimated from quantum chemistry calculations to be about 4 eV.[32,33] Thus U is much larger than the bandwidth associated with the hopping integrals given in Table I, confirming that these are strongly correlated materials. The Hubbard model on the square lattice at one-quarter filling is expected to be metallic and so one must consider longer-range Coulomb interactions to explain the existence of insulating, charge-ordered, and antiferromagnetic phases. The nearest-neighbor Coulomb repulsion between various arrangements of pairs of BEDT-TTF molecules has also been estimated from quantum chemistry calculations[33,32,34] and is generally found to have a value of about 2–3 eV. It is approximately given by Coulomb's law $V \simeq 14$ eV/R, where R is in Å. Mori calculated V as a function of the angle θ; variations of about 10% occur in the range of angles (98°–130°) relevant to the θ-type materials. These calculations involve isolated pairs of molecules and so one expects that the values of U and V in a molecular crystal to be less than the values given above due to screening. Hubbard has discussed this for the case of TTF-TCNQ [tetrathiafulvalene-tetracyanoquinodimethane], arguing that screening decreases both U and V by a factor of about 2.[35] Actually in Sec. IV, from experimentally determined charge gaps, we estimate values of V of the order of a few hundred meV. In materials consisting of dimers of BEDT-TTF molecules the difference U-V can be estimated from the charge transfer excitation seen in optical absorption measurements. For $(BEDT\text{-}TTF)HgBr_3$ it is estimated to be 0.7 eV.[36] Thus we are led to the extended Hubbard model on the anisotropic triangular lattice at one-quarter filling.

Table I shows that for many of the θ materials, $t_c \ll t_p$ and so, as a first approximation, we neglect the diagonal hopping t_c. This means we are left with a square lattice model. In Sec. V we will show that this diagonal term has only a small effect on the metal-insulator transition. The Hamiltonian is

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

where U is the Coulomb repulsion between two electrons on the same site, V is the nearest-neighbor Coulomb repulsion, $\langle ij \rangle$ denotes nearest neighbors, and μ is the chemical potential.

If we consider the large U limit, and so preclude doubly occupied sites, the Hamiltonian then reduces to

$$H = t \sum_{\langle ij \rangle, \sigma} P(c^\dagger_{i\sigma} c_{j\sigma} + c^\dagger_{j\sigma} c_{i\sigma}) P + V \sum_{\langle ij \rangle} n_i n_j - \mu \sum_{i\sigma} n_{i\sigma}, \tag{2}$$

where P projects out the doubly occupied states. We refer to this as the t-V model. For large V/t the ground state is an

insulator with charge ordering (Sec. IV). We expect that for small V/t a metallic phase exists because the quarter-filled Fermi surface is poorly nested. Hence, as V/t decreases the charge ordering should be destroyed at a nonzero value of V/t. We are not aware of any previous study of this model on the square lattice. Mazumdar, Clay, and Campbell[21] have studied coupled chains of the extended Hubbard model at one-quarter filling. Most of their numerical results are for $U=6t_{\|}$ and $V_{\|}=t_{\|}$ (where the $\|$ refers to the chain direction) so that $V_{\|}$ is smaller than the critical value necessary to form the charge ordered state considered here. They find that when interactions with phonons are included there is a tendency to formation of a bond-order wave. Henley and Zhang recently considered a similar model involving spinless fermions on the square lattice.[37] Mila considered the extended Hubbard model on the square lattice at a one-quarter filling with finite U and infinite V.[38] In Sec. V we consider the SU(N) generalization of the t-V model and show that in the large-N limit, slave boson theory implies that there is a critical value of V/t above which the metallic phase becomes unstable to formation of charge ordering.

We now briefly review previous work on the extended Hubbard model (in the large-U limit) at one-quarter filling on different lattices. Numerical calculations show that a single chain undergoes a transition from a Luttinger liquid to a charge-density wave insulator at $V=2t$.[39] The one-dimensional t-V model can be solved exactly via the Bethe ansatz.[40] It is equivalent to two decoupled XXZ spin chains and so will undergo a metal-insulator transition at $V=2t$. We note that the ring exchange process responsible for antiferromagnetic interactions discussed above will be absent in a single chain. Vojta, Hübsch, and Noack[41] recently studied the model (1) on a ladder using the density matrix renormalization group (DMRG). They find that the charge ordered phase is destroyed for $V<2.5t$ but claim that there will be a charge gap for all V/t. The model in infinite dimensions was studied by Pietig, Bulla, and Blawid using dynamical mean-field theory.[42] At low temperatures they found that for $U=2t$, charge ordering occurred for $V>0.5t$.

IV. ANTIFERROMAGNETIC EXCHANGE IN THE CHARGE-ORDERED PHASE

For large V/t there will be charge ordering and the ground state will be an insulator with a charge gap of magnitude $3V$. There will be two possible ground states with the checkerboard covering of the lattice (Fig. 3). This defines a new square lattice rotated by 45° with respect to the original square lattice. It should be stressed that these ground states are distinct from the commensurate charge density waves, associated with a lattice distortion, and seen in some organic compounds. To zeroth order in t/V all possible spin states will be degenerate. We consider a single plaquette (Fig. 3) containing two spins. To second order in t/V both the singlet and triplet states have their energy lowered by $-4t^2/3V$. The degeneracy of the singlet and triplet states is only broken to fourth order in t/V. We show below that this results in an effective antiferromagnetic exchange interaction

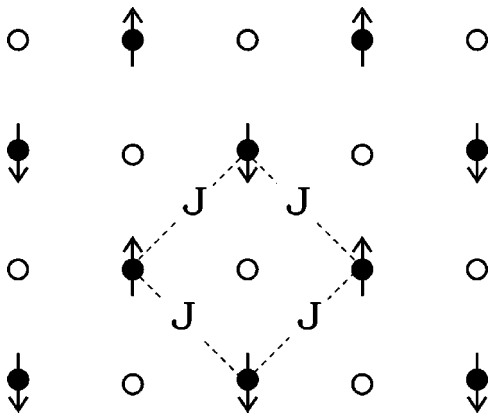

FIG. 3. Charge-ordered insulating ground state of the extended Hubbard model at one-quarter filling in the limit $t \ll V \ll U$. An antiferromagnetic interaction J occurs between spins along the diagonals. The spin degrees of freedom are described by the antiferromagnetic Heisenberg model on the square lattice.

$$J=\frac{4t^4}{9V^3} \tag{3}$$

that acts along the diagonals of the original square lattice. Thus the spin degrees of freedom are described by a spin-$\frac{1}{2}$ Heisenberg model on a square lattice. The Hamiltonian is

$$H=J\sum_{\langle \mathbf{ij}\rangle} \boldsymbol{S}_{\mathbf{i}}\cdot\boldsymbol{S}_{\mathbf{j}}, \tag{4}$$

where $\boldsymbol{S}_{\mathbf{i}}$ denotes a spin operator on site $\mathbf{i}$, and the sum $\langle \mathbf{ij}\rangle$ runs over pairs of next-nearest-neighbor lattice sites in the original square lattice.

We now calculate the singlet-triplet splitting from fourth-order perturbation theory. If $|\Psi_0\rangle$ is an eigenstate of $H_0=V\Sigma_{\langle ij\rangle}n_in_j$ then a perturbation $H_1=H-H_0$, which has no effect to third order, shifts the energy by

$$\Delta E_0^{(4)}=\sum_{\{m,n,p\}\neq 0}\frac{\langle\Psi_0|H_1|\Psi_m\rangle\langle\Psi_m|H_1|\Psi_n\rangle\langle\Psi_n|H_1|\Psi_p\rangle\langle\Psi_p|H_1|\Psi_0\rangle}{(E_0^{(0)}-E_m)(E_0^{(0)}-E_n)(E_0^{(0)}-E_p)}, \tag{5}$$

where the intermediate states labeled by $\{m,n,p\}\neq 0$ are not degenerate with $|\Psi_0\rangle$. The following process involving exchange of electrons around a plaquette will contribute to a shift in the energy of the ground state. For the triplet states it can be represented as

$$\left|\begin{matrix}\uparrow & o\\ o & \uparrow\end{matrix}\right\rangle \rightarrow \left|\begin{matrix}o & \uparrow\\ o & \uparrow\end{matrix}\right\rangle \rightarrow \left|\begin{matrix}o & \uparrow\\ \uparrow & o\end{matrix}\right\rangle \rightarrow \left|\begin{matrix}\uparrow & \uparrow\\ o & o\end{matrix}\right\rangle \rightarrow \left|\begin{matrix}\uparrow & o\\ o & \uparrow\end{matrix}\right\rangle. \tag{6}$$

The first, second, and fourth matrix elements are t and the third is $-t$. The intermediate states have energy $3V$, $4V$, and $3V$, respectively. (Note one needs to take into account the interaction with the neighbors not shown in the above representation.) There are eight distinct ways of doing this exchange: at the first step there are four choices and at the third step there are two choices. Thus, the expression (5) implies that the triplet is increased in energy by $2t^4/9V^3$.

A similar process for the singlet is

$$\left|\begin{matrix}\uparrow & o\\ o & \downarrow\end{matrix}\right\rangle \rightarrow \left|\begin{matrix}o & \uparrow\\ o & \downarrow\end{matrix}\right\rangle \rightarrow \left|\begin{matrix}o & \uparrow\\ \downarrow & o\end{matrix}\right\rangle \rightarrow \left|\begin{matrix}\downarrow & \uparrow\\ o & o\end{matrix}\right\rangle \rightarrow \left|\begin{matrix}\downarrow & o\\ o & \uparrow\end{matrix}\right\rangle. \tag{7}$$

Thus, for the singlet this fourth-order process brings one back to the singlet wave function with a sign change and so the energy shift is opposite to that of the triplet. Hence, we arrive at Eq. (3) for the difference in energy between the singlet and triplet.

It should be pointed out that there are also fourth-order processes of the form $|0\rangle\rightarrow|n\rangle\rightarrow|0\rangle\rightarrow|p\rangle\rightarrow|0\rangle$ that will produce a decrease in the ground state energy. However, because they produce the same shift for the singlet and triplet states we neglect them here. Our value of J is consistent with a recent calculation[41] of the effective exchange interaction in the charge-ordered phase of the extended Hubbard model on a ladder when that result is rescaled to allow for different excitation energies of the intermediate states. For the ladder, the energies of the intermediate states are all $2V$. Thus the ladder exchange is larger than for the square lattice by a factor of 9/2.

We now consider whether this possible explanation for the origin of antiferromagnetism in the θ type materials is quantitatively reasonable. Roughly, it predicts that the value of J will be some fraction of t, typical values of t from Table I are of the order of 500–1000 K for the materials with insulating ground states.[43] θ-$(C_1TET\text{-}TTF)_2Br$ is an insulator with a charge gap of 600 meV and a value[43] of t of about 60 meV.[17] Since the charge gap is $3V$ for $t \ll V$ this gives $V\sim 200$ meV. Using $J=4t^4/9V^3$ gives $J\sim 10$ K, which is in reasonable agreement with the observed value[17] of 6 K. We do not make quantitative comparisons of Eq. (3) for other materials because they are not so clearly in the regime $t \ll V$, required for its validity. For example, for θ-$(BEDT\text{-}TTF)_2Cu_2(CN)[N(CN)_2]_2$ Hückel calculations give $t\sim 80$ meV and the measured charge gap[27] is about 200 meV. This is inconsistent with the fact that the charge gap would be $3V$ if $t \ll V$.

V. SLAVE-BOSON THEORY FOR THE SU(N) VERSION OF THE EXTENDED HUBBARD MODEL WITH $U\rightarrow\infty$

We consider the SU(N) generalization of the Hamiltonian (2) for which the spin index, σ, runs from 1 to N, and consider $1/N$ as a small expansion parameter assuming that N is large. Slave-boson fields are introduced to allow treatment of the no double occupancy constraint required by the $U\rightarrow\infty$ limit. The effective action for the slave-boson fields can be expanded in powers of $1/N$. The mean-field solution corresponds to the Gutzwiller approximation and is exact in the $N\rightarrow\infty$ limit.[44,45] This approach has been used to study other strongly correlated models such as the Kondo model for magnetic impurities[44,46] in metals, the Hubbard model,[45] the Hubbard-Holstein model,[47] and the Anderson[48] and Kondo lattices.[49] It has also been used to analyze the phase diagram of two-dimensional t-J model,[50–52] and extended Hubbard model at one-half filling.[53] It is convenient to describe the projected Hilbert space associated with the Hamiltonian (2), using the slave-boson representation.[46,54,55] The electron creation operator is replaced by $c^\dagger_{i\sigma}=f^\dagger_{i\sigma}b_i$, where the spinless charged boson operator, b_i, is introduced to keep track of the empty sites, and $f^\dagger_{i\sigma}$ is a fermion operator carrying spin. In order to preserve the anticommutation relation for the electrons the new operators must satisfy the local constraint

$$f^\dagger_{i\sigma}f_{i\sigma}+b^\dagger_i b_i=N/2. \tag{8}$$

For $N=2$ it reduces to the condition that either an electron or a boson can occupy each lattice site at all times.

Following Kotliar and Liu,[50] we write the partition function in the coherent state path integral representation:

$$Z=\int Db^\dagger Db\, Df^\dagger Df\, D\lambda\, \exp\left(-\int_0^\beta L(\tau)d\tau\right), \tag{9}$$

where the Lagrangian at imaginary time τ is given by

$$\begin{aligned}L(\tau)=&\sum_i f^\dagger_{i\sigma}(\partial_\tau-\mu)f_{i\sigma}+b^\dagger_i\partial b_i-\frac{1}{N}\sum_{ij}T_{ij}(f^\dagger_{i\sigma}f_{j\sigma}b^\dagger_j b_i\\ &+\text{H.c.})+\frac{1}{N}\sum_{ij}V_{ij}f^\dagger_{i\sigma}f_{i\sigma}f^\dagger_{j\sigma'}f_{j\sigma'}\\ &+\sum_i i\lambda_i(f^\dagger_{i\sigma}f_{i\sigma}+b^\dagger_i b_i-N/2),\end{aligned} \tag{10}$$

$\beta=1/(k_BT)$ at temperature T, and we have used the fact that $c^\dagger_{i\sigma}c_{i\sigma}=f^\dagger_{i\sigma}f_{i\sigma}$. λ_i is a static Lagrange multiplier enforcing the constraint (8). A sum from 1 to N is assumed whenever a repeated σ index appears in the equations. The $1/N$ factors are introduced so that the Lagrangian is proportional to N. $T_{ij}=t$, if i and j are nearest neighbors, $T_{ij}=t'$ if i and j are next-nearest neighbors sitting along *one* of the diagonals of the square lattice, and $T_{ij}=0$ otherwise. $V_{ij}=V$ if i and j are nearest neighbors and is zero otherwise. μ is the chemical potential, which is fixed to give the average number of electrons per site, $n=\langle f^\dagger_{i\sigma}f_{i\sigma}\rangle$. The conservation of the charge, $q=N/2$, is a consequence of a local U(1) symmetry because

under the local gauge transformation: $b_i \to b_i e^{i\theta_i(\tau)}$, $f_{i\sigma} \to f_{i\sigma} e^{i\theta_i(\tau)}$, and $\lambda_i \to \lambda_i - \partial_\tau \theta_i(\tau)$, $L(\tau)$ remains the same. To avoid possible infrared divergences it is convenient to choose the radial gauge where the boson amplitude becomes a real number, $r_i = |b_i|$, and λ_i becomes a dynamical field: $\lambda_i(\tau)$. We introduce these fields in expression (10), and we use the relation $f^\dagger_{i\sigma} f_{i\sigma} = N/2 - b^\dagger_i b_i$ to replace one pair of fermion operators in the V term so that we are left with a quadratic Lagrangian in the fermionic Grassmann variables. After integrating out the fermions, the effective Lagrangian for the boson fields becomes

$$L(\tau) = \sum_i \left(r_i(\tau)[\partial_\tau + i\lambda(\tau)] r_i(\tau) - i\lambda_i(\tau)\frac{N}{2} \right) - NTr \ln\left\{ \left[\partial_\tau - \mu + i\lambda_i(\tau) + \frac{1}{N}\sum_l V_{il}\left(\frac{N}{2} - r_l(\tau) r_l(\tau) \right) \right] \delta_{ij} - \frac{1}{N} r_i(\tau) T_{ij} r_j(\tau) \right\}. \quad (11)$$

A. Mean-field solution

The mean-field (MF) solution of the model is obtained by assuming that the boson fields are spatially homogeneous and time independent: $r_i(\tau) = b$ and $i\lambda_i(\tau) = \lambda$. The resulting free energy ($F = -k_B T \ln Z$) is

$$F^{\mathrm{MF}}(b,\lambda) = -\frac{N}{\beta}\sum_{\mathbf{k},\omega_n} \ln(\epsilon_{\mathbf{k}} - i\omega_n) + \lambda\left(b^2 - \frac{N}{2} \right), \quad (12)$$

where $\omega_n = (2n+1)\pi T$ is a fermion Matsubara frequency. The mean-field eigenenergies are

$$\epsilon_{\mathbf{k}} = \frac{-tb^2}{N} T_{\mathbf{k}} + \lambda - \mu + 4V\frac{n}{N} \quad (13)$$

with $T_{\mathbf{k}} = 2[\cos(k_x) + \cos(k_y) + (t'/t)\cos(k_x + k_y)]$ being the Fourier transform of T_{ij} in units of the nearest-neighbor hopping t.

Minimization of the free energy (12) with respect to b and λ gives

$$b^2 = N/2 - n, \quad \lambda = \sum_{\mathbf{k}} f(\epsilon_{\mathbf{k}})(tT_{\mathbf{k}} + 4V). \quad (14)$$

μ is adjusted to give the correct electron filling, $n = N\Sigma_{\mathbf{k}} f(\epsilon_{\mathbf{k}})$, where $f(\epsilon)$ is the Fermi-Dirac distribution function.

The mean-field solution describes a renormalized Fermi liquid. The renormalization of the band is controlled by b^2, and the band is shifted from its bare position by λ. The overall effect of the nearest-neighbor Coulomb interaction, V, at the mean-field level, reduces to a constant shift in the chemical potential. In the case of a one-quarter-filled band ($n = 1/2$) the bandwidth is reduced to half its bare value. The effective mass measured in magnetic oscillation experiments will then be increased by a factor of $m^*/m = 1/b^2 = 2$. Note that this is much smaller than the effective mass enhancements that occur in materials described by the Hubbard model on the anisotropic triangular lattice at one-half filling.[7] Therefore, for $N \to \infty$ the one-quarter filled t-V model behaves as a Fermi liquid with effective masses that are twice the bare ones. In the next subsection we consider the effect of the leading 1/N corrections.

B. Fluctuations about the mean-field solution

We now consider how as V/t is increased, the Fermi-liquid phase resulting from the mean-field solution becomes unstable to charge ordering. The analysis is similar to the treatment of instabilities in the doped Hubbard model by Tandon *et al.*[56] We write the boson fields in terms of the static mean-field solution, (b,λ), and the dynamic fluctuating parts: $r_i(\tau) = b + b\,\delta r_i(\tau)$, and $i\lambda_i(\tau) = \lambda + i\,\delta\lambda_i(\tau)$. Physically, $\delta r_i(\tau)$ is related to local fluctuations in the charge density. We substitute these expressions in Eq. (11), introducing the Fourier transforms of $\delta r_i(\tau)$ and $\lambda_i(\tau)$, and, expanding to second order in the boson fields, we obtain the effective action

$$S = F^{\mathrm{MF}} + S^{(2)}, \quad (15)$$

where the part of the action due to fluctuations in the boson fields is

$$S^{(2)} = \frac{1}{2\beta}\sum_{\mathbf{q},\nu_n} [\,\delta r(-\mathbf{q},-\nu_n)\,\delta\lambda(-\mathbf{q},-\nu_n)] \begin{pmatrix} \Gamma_{rr} & \Gamma_{r\lambda} \\ \Gamma_{\lambda r} & \Gamma_{\lambda\lambda} \end{pmatrix} \times \begin{pmatrix} \delta r(\mathbf{q},\nu_n) \\ \delta\lambda(\mathbf{q},\nu_n) \end{pmatrix}, \quad (16)$$

where $\nu_n = n\pi T$ is a boson Matsubara frequency. The elements of the $\hat{\Gamma}(\mathbf{q},\nu_n)$ matrix are

$$\Gamma_{rr}(\mathbf{q},\nu_n) = N\left[\frac{2b^2\lambda}{N} - \frac{2b^2 t}{N}\sum_{\mathbf{k}} \left(T_{\mathbf{k}-\mathbf{q}} + \frac{V}{t}V_{\mathbf{k}} \right) f(\epsilon_{\mathbf{k}}) + \sum_{\mathbf{k}} \frac{f(\epsilon_{\mathbf{k}+\mathbf{q}}) - f(\epsilon_{\mathbf{k}})}{\epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{k}} - i\nu_n} \left(\frac{b^2 t}{N}(T_{\mathbf{k}} + T_{\mathbf{k}+\mathbf{q}}) + \frac{2b^2 V}{N} V_{\mathbf{q}} \right)^2 \right],$$

$$\Gamma_{r\lambda}(\mathbf{q},\nu_n) = \Gamma_{\lambda r}(\mathbf{q},\nu_n) = N\left[\frac{i2b^2}{N} + i\sum_{\mathbf{k}} \frac{f(\epsilon_{\mathbf{k}+\mathbf{q}}) - f(\epsilon_{\mathbf{k}})}{\epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{k}} - i\nu_n} \times \left(\frac{-tb^2}{N}(T_{\mathbf{k}} + T_{\mathbf{k}+\mathbf{q}}) - \frac{2b^2 V}{N} V_{\mathbf{q}} \right) \right],$$

$$\Gamma_{\lambda\lambda}(\mathbf{q},\nu_n) = -N\sum_{\mathbf{k}} \frac{f(\epsilon_{\mathbf{k}+\mathbf{q}}) - f(\epsilon_{\mathbf{k}})}{\epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{k}} - i\nu_n}, \quad (17)$$

where $V_{\mathbf{k}} = 2[\cos(k_x) + \cos(k_y)]$ is the Fourier transform of V_{ij}. Note that $\Gamma_{\lambda\lambda}$ is the Lindhard function describing density-density fluctuations in the renormalized band structure. Since b^2 is of order N [compare Eq. (14)], the expres-

sions above show explicitly how the propagators of the boson fields $\hat{D}(\mathbf{q},\nu_n)=\hat{\Gamma}^{-1}(\mathbf{q},\nu_n)$ are of order O($1/N$), as they should.

C. Charge-ordering instability

The condition for the stability of the Fermi liquid phase is that the quadratic form (16) is always positive. Then fluctuations in the charge density will increase the free energy. Since $\Gamma_{\lambda\lambda}>0$ this is ensured if $\det\hat{\Gamma}(\mathbf{q},\nu)>0$ for all wave vectors $\mathbf{q}$ and frequency ν. In order to find the critical value of V/t, which we shall denote $(V/t)_c$, at which the system becomes unstable towards static charge ordering, we wish to find a $\mathbf{q}$ for which at some value of V/t, $\det\Gamma=\Gamma_{rr}\Gamma_{\lambda\lambda}-\Gamma_{\lambda r}\Gamma_{r\lambda}=0$, at $\nu=0$. This condition reduces to

$$\left(\frac{b^2t}{N}\sum_{\mathbf{k}} f(\epsilon_{\mathbf{k}})[T_{\mathbf{k}-\mathbf{q}}-T_{\mathbf{k}}+(V/t)_cV_{\mathbf{k}}]+\frac{4t(V/t)_cb^4}{N^2}(1-V_{\mathbf{q}})\right.$$
$$\left.-\frac{2t(V/t)_cb^2}{N}\right)\sum_{\mathbf{k}}\frac{f(\epsilon_{\mathbf{k}+\mathbf{q}})-f(\epsilon_{\mathbf{k}})}{\epsilon_{\mathbf{k}+\mathbf{q}}-\epsilon_{\mathbf{k}}}$$
$$-\frac{2b^4t}{N^2}\sum_{\mathbf{k}}\frac{f(\epsilon_{\mathbf{k}+\mathbf{q}})-f(\epsilon_{\mathbf{k}})}{\epsilon_{\mathbf{k}+\mathbf{q}}-\epsilon_{\mathbf{k}}}(T_{\mathbf{k}}+T_{\mathbf{k}+\mathbf{q}})+2\frac{b^4}{N^2}=0, \tag{18}$$

where λ and b^2 are the solution to the mean-field equations.

We now concentrate on the case $\mathbf{q}=(\pi,\pi)$, which is relevant to the formation of a charge-ordered state at one-quarter filling in the θ-type materials (see Fig. 3). For the square lattice case ($t'=0$), $\epsilon_{\mathbf{k}+\mathbf{q}}=-\epsilon_{\mathbf{k}}$, and Eq. (18) reduces to

$$\left[\left(1-\frac{(V/t)_c}{2}\right)\int_{-b^2W/2}^{b^2W/2}d\epsilon\rho_\sigma(\epsilon)\epsilon f(\epsilon)+t(V/t)_c\right.$$
$$\left.\times\left(10\frac{b^4}{N^2}-\frac{b^2}{N}\right)\right]\int_{-b^2W/2}^{b^2W/2}d\epsilon\frac{\rho_\sigma(\epsilon)f(\epsilon)}{\epsilon}+\frac{b^4}{N^2}=0, \tag{19}$$

where $\rho_\sigma(\epsilon)$ is the density of states at the Fermi surface per spin channel of the renormalized metal and W is the bare bandwidth of the metal.

Before solving this equation numerically for the density of states of the band structure, some insight can be gained by considering the case of a constant density of states. Taking a density of states of the form $\rho_\sigma(\epsilon)=1/b^2W$, if $-b^2W/2\leqslant\epsilon\leqslant b^2W/2$ and 0 otherwise, Eq. (19) can be simplified further. For this case, the critical ratio $(V/t)_c$, at which (π,π) charge ordering occurs for a given electron band filling, n, is

$$(V/t)_c=\frac{\dfrac{-4(N/2-n)^2}{N}-2n(n/N-1)\ln(1-2n/N)}{\left[n(1-n/N)+\dfrac{10(N/2-n)}{N}-1\right]\ln(1-2n/N)}. \tag{20}$$

For $N=2$, $(V/t)_c$ diverges at $n=0$, $n=1$, and $n=0.899$. While the divergence at $n=0$ appears because it is not possible to have charge ordering when there is no charge in the lattice, the divergence at $n=1$ is a consequence of the condition that there can be, at most, one electron at each lattice site: a charge-ordered state of alternating singly and doubly occupied sites would cost infinite energy to be formed. The divergence at $n=0.899$ is nontrivial and presumably is a consequence of the finding made by Tandon *et al.*[56] that close to one-half filling, $n\geqslant 0.88$, the $1/N$ fluctuations drive the $U\to\infty$ Hubbard model into phase separation. Hence, the creation of a charge-ordered state is forbidden by the breakdown of periodicity in the charge distribution of the lattice. At one-quarter filling ($n=1/2$), Eq. (20) gives $(V/t)_c=0.78$. This can be compared with the value of $(V/t)_c=0.69$ obtained from solving Eq. (19), with the actual density of states for the square lattice.

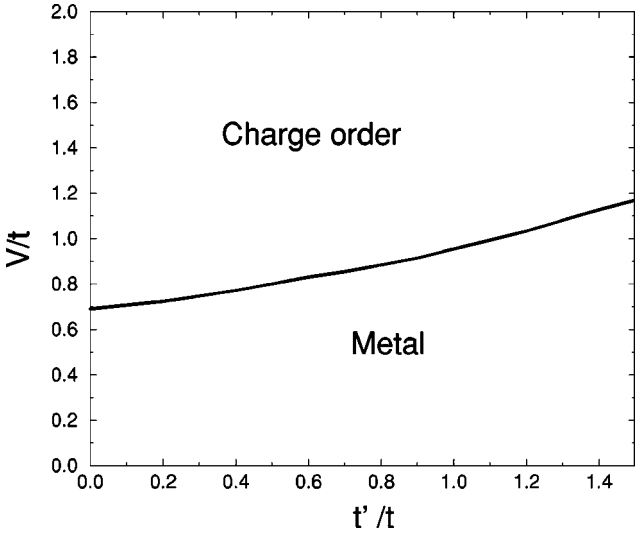

FIG. 4. Phase diagram for the SU(N) version of the t-t'-V model at quarter filling and zero temperature, to leading order in $1/N$ with $N=2$. This shows that the diagonal hopping t' (t_c in Fig. 1) has little effect on the critical value of V/t at which the metallic phase becomes unstable to the charge ordering shown in Fig. 3.

It is interesting to compare our results with DMRG calculations on the two-leg ladder by Vojta, Hübsch, and Noack[41] in the $U\to\infty$ limit. They find an insulating state for any value of V/t. At $V/t\approx 2$ a transition from a homogeneous insulating state to an insulator with charge ordering takes place. Slave-boson theory would predict a Mott insulating phase with no charge ordering for $V/t=0$ with $t_\perp/t_\parallel>1$, where $t_\perp$ is the hopping amplitude along the rungs and $t_\parallel$ along the chains. This is because for this case only the bonding band of the ladder is filled and it is exactly half-filled, so $b^2=0$. However, an extension of the approach presented here is needed to make a detailed comparison with the full phase diagram of the two-leg ladder.

D. Effect of the diagonal hopping

We can include the effect of a next-nearest-neighbor hopping integral in the analysis presented above. We have solved Eq. (18), for different values of the t'/t ratio. Figure 4 shows how the critical value, $(V/t)_c$, increases as the ratio t'/t is increased. The critical value changes from 0.68 for the

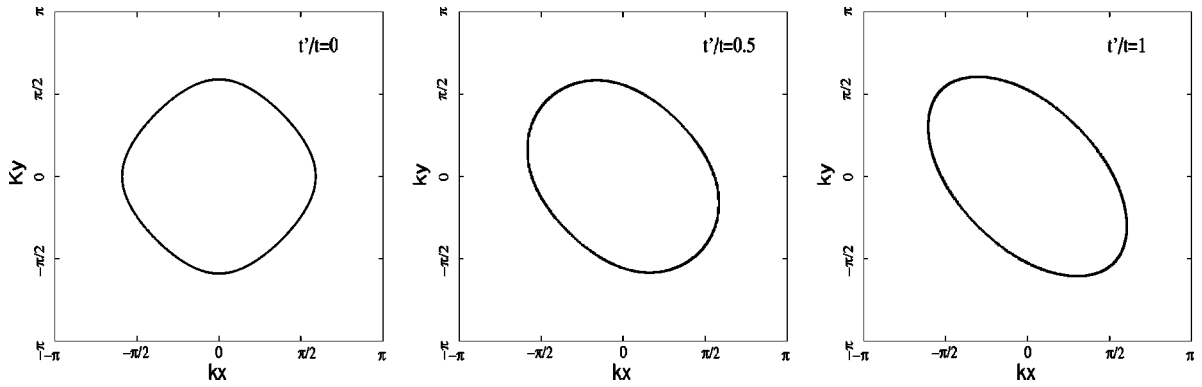

FIG. 5. Evolution of the Fermi surface for an anisotropic triangular lattice as the ratio between the next-nearest-neighbor and the nearest neighbors hoppings, t'/t, is varied. The band is kept at one-quarter filling for all three cases.

square lattice to $(V/t)_c \approx 0.95$ for the triangular lattice ($t'/t = 1$). This can be understood if we plot the Fermi surfaces for different ratios of the hopping integrals for fixed band filling: $n = 1/2$ (see Fig. 5). While for the square lattice case, $t'/t = 0$, the Fermi surface shows some remnants of the perfect nesting property present at one-half filling, it gradually elongates along the $k_y = -k_x$ direction becoming elliptical as t'/t is increased.[57] This effect makes it even harder to connect two points at the Fermi surface by the wave vector $\mathbf{q} = (\pi, \pi)$. The phase diagram in Fig. 4, also shows that it is possible to go from the metallic phase to the charge-ordered state by varying either the t'/t or V/t ratios. Because the dependence of $(V/t)_c$ on t'/t is weak we conclude that the ratio V/t plays a more important role than t'/t in driving the metal-insulator transition, within the large-N approach used here. Hence, as a first approximation we are justified in neglecting the effect of the diagonal hopping, as was done in Sec. IV.

Mori[34] found that the Coulomb repulsion V varied little with the angle θ between the donor molecules (see Fig. 2). This is because V scales roughly with the inverse of the distance between the molecules. In contrast the hopping integrals t_p and t_c depend strongly on θ. t_p varies by about a factor of 5 as θ varies from 100° to 140°. This is because the overlap integral depends exponentially on the distance between the molecules. Hence, the main effect of varying θ is to change the bandwidth. This is what will be driving the metal-insulator transition.

For θ-$(\mathrm{BEDT\text{-}TTF})_2\mathrm{Cu}_2(\mathrm{CN})[\mathrm{N}(\mathrm{CN})_2]_2$ the measured charge gap[27] is about 200 meV, suggesting that V is of the order of 100 meV. Assuming that V does not vary much between materials (for the reasons just given) the above calculations suggest that the critical value of the hopping integral t is about 100 meV. This is consistent[43] with the values in Table I; i.e., it is quite possible that the materials listed there are close to the metal-insulator transition, as is observed experimentally. We acknowledge that if we take the values of $V \approx 2-3$ eV calculated from quantum chemistry (see Sec. III), slave-boson theory would predict that the materials would be located far from the quantum critical point, well into the insulating phase. The theory presented here would then be unable to explain the phase diagram of the θ-type materials. However, the quantum chemistry estimates for V are calculated for isolated pairs of molecules rather than for an infinite system, for which screening may significantly reduce the value of V.

VI. RELEVANCE TO β''-$(\mathrm{BEDT\text{-}TTF})_2\mathrm{SF}_5Y\mathrm{SO}_3$

The family β''-$(\mathrm{BEDT\text{-}TTF})_2\mathrm{SF}_5Y\mathrm{SO}_3$ has been studied[14] with $Y = \mathrm{CH}_2\mathrm{CF}_2$, CH_2, CHF. The first material is superconducting with a transition temperature of 5.2 K. $Y = \mathrm{CH}_2$ is insulating with a charge gap of 56 meV and evidence for charge ordering is found in the fact that alternate molecules have the bond length and phonon frequency associated with the central carbon double bond different.[58] The charges are estimated to be $+0.6e$ and $+0.4e$ where e is the electronic charge. Below room temperature the spin susceptibility decreases monotonically, consistent with a spin gap of 8 meV. $Y = \mathrm{CHF}$ is a bad metal and may undergo a metal-semiconductor transition below 10 K. It is estimated that alternate molecules have charges of $+0.47e$ and $+0.53e$. A recent experimental study[59] estimated charges of $+0.43e$ and $+0.57e$ in $Y = \mathrm{CH}_2\mathrm{CF}_2$. The Fermi surface of the metallic phase of $Y = \mathrm{CH}_2\mathrm{CF}_2$ has been mapped out using angular-dependent magnetoresistance and magnetic oscillations.[60] However, the metallic phase differs significantly from a conventional Fermi liquid. First, in contrast to most BEDT-TTF metals,[6] even at a temperature as low as 14 K no Drude peak is present in optical conductivity.[61] Second, anomalous properties of the magnetoresistance were recently interpreted in terms of a magnetic-field-induced superconductor-insulator transition.[62] The temperature dependence of the penetration depth in the superconducting phase was recently found to vary as T^3 at low temperatures.[63] This is inconsistent with an s-wave state, but also deviates significantly from the linear temperature dependence expected for a d-wave state.

The arrangement of the BEDT-TTF molecules within a layer of the family β''-$(\mathrm{BEDT\text{-}TTF})_2\mathrm{SF}_5Y\mathrm{SO}_3$ are shown in Fig. 6. Table II lists values of the hopping integrals calculated in the Hückel approximation. Note that generally the diagonal terms a and a' are smaller than the vertical and horizontal terms. Hence, as a first approximation the system can be described by an anisotropic square lattice. However, we note that the main difference between the hopping param-

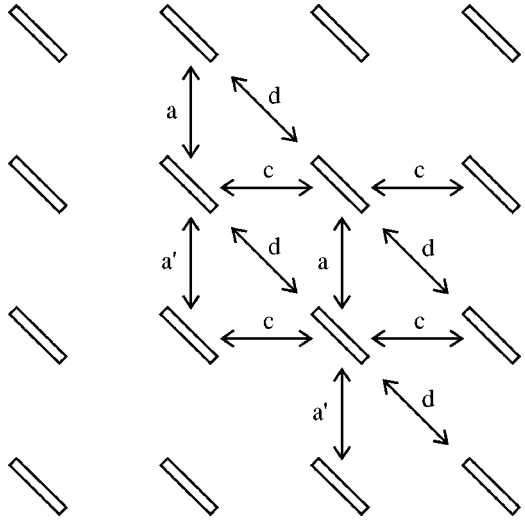

FIG. 6. Arrangement of the BEDT-TTF molecules within a layer for the β''-(BEDT-TTF)$_2$SF$_5$*Y*SO$_3$ family of molecular crystals. Typical values of the hopping integrals are given in Table II. In some of the materials the unit cell is larger and so the hopping integrals can have two values.

eters for the three different anions in Table II is that the diagonal terms a and a' vary significantly as the anion is changed. We see from Fig. 4 that the corresponding variations in t'/t are large enough to change the proximity to the charge-ordering instability and may lead to the three different ground states for these materials.

VII. CONCLUSIONS

In summary, we have argued that the essential physics of the electronic and magnetic properties of layered molecular crystals of the θ type can be captured by an extended Hubbard model on the square lattice and at one-quarter filling. For large Coulomb repulsion ($V \gg t$) between nearest neighbors, the ground state is a charge-ordered insulator. Antiferromagnetic interactions arise due to a novel fourth-order exchange process. A slave-boson treatment was given of the SU(N) generalization of the model. It was found that for sufficiently small V/t the metallic phase was stable against charge ordering.

We briefly mention the relation of this work to a recent paper of Mazumdar, Clay, and Campbell.[21] They have studied the extended Hubbard model at one-quarter filling on an anisotropic square lattice and discuss its relevance to a wide range of organic compounds, but not those considered here. They argue that in the real materials the nearest-neighbor Coulomb repulsion is smaller than the critical value necessary to form the charge-ordered state considered here. Coupling to phonons produces an insulating phase with a different kind of charge order (a bond-order wave). X-ray scattering experiments that can resolve the charge on individual molecules (due to different bond lengths) should be able to distinguish these two different ground states. There is controversy about whether nuclear magnetic resonance measurements can distinguish these two charge orderings.[64] The charge distribution observed[14] for β''-(BEDT-TTF)$_2$SF$_5$CH$_2$SO$_3$ is consistent with charge ordering considered here.

TABLE II. Hopping integrals in Fig. 6 for the family β''-(BEDT-TTF)$_2$SF$_5$*Y*SO$_3$ calculated by the extended Hückel method in Ref. 14. At low temperatures the materials are a superconductor, a bad metal, and a charge-ordered insulator, respectively.

Y	c (meV)	d (meV)	a (meV)	a' (meV)
CH_2CF_2	260	140	120	55
CHF	260	130	35, 86	95, 100
CH_2	260	120	85	12

We acknowledge that the actual θ-type materials are more complicated than the simplest Hubbard model considered here. For example, along the diagonals of the square lattice (corresponding to the vertical direction in Fig. 1) there is also Coulomb repulsion. In fact, Mori[34] finds the corresponding V to be larger than along the horizontal and vertical directions. Seo[18] has shown how the latter can lead to competition between different charge ordered states [i.e., those associated with wave vector (π,π) and $(0,\pi)$]. Also, x-ray scattering suggests that in (BEDT-TTF)$_2$RbM(SCN)$_4$ (M=Co,Zn) there is a structural transition associated with the charge ordering and that this changes the electronic structure in the insulating phase.[30] However, our view is that the t-V model on the square lattice captures the essential physics and first we need to understand it, before studying models with more complicated band structures.

Three outstanding questions concerning the t-V model at one-quarter filling need to be answered.

(i) Is there superconductivity in the model? The idea that proximity to a quantum critical point increases the tendency towards superconducting instabilities is supported by recent experiments on heavy-fermion materials.[65] It was first shown by Scalapino, Loh, and Hirsch[66] that proximity to a spin-density wave or charge-density wave transition can lead to d-wave superconductivity. In a future publication we plan to investigate whether charge fluctuations near the charge-ordering transition can produce superconductivity.[67–69]

(ii) Are charge ordering, the charge gap, and antiferromagnetism destroyed at the same critical value of V/t? In Sec. IV it was shown that for large V/t the ground state has a charge gap, charge ordering, and antiferromagnetism. In Sec. V it was shown that, for V/t less than a critical value, the metallic phase is stable, at least in the large-N limit. It is quite possible that the above three properties disappear at different values of V/t. For the case of the one-quarter-filled extended Hubbard model on a ladder, numerical calculations found that the charge ordering disappeared below a nonzero value of V/t, but the charge gap did not.[41] This unusual result may be an artifact of the one-dimensionality of the ladder. For the square lattice, this issue will probably be only resolved by careful numerical work.

(iii) Does non-Fermi-liquid behavior occur in the metallic phase near the quantum critical point? This is generally expected[70] and is observed in heavy-fermion materials.[71] Slave-boson theory has been used to show that in the doped

Hubbard model near a charge instability the quasiparticle scattering becomes singular leading to anomalous metallic properties.[72]

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