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THE PHASE DIAGRAM OF 2:1 CATIONIC ORGANIC CHARGE TRANSFER SALTS

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ABSTRACT

We propose a new theoretical approach, stressing the role of Coulomb interactions and band-filling effects, to describe the phase diagram of the 2:1 cationic organic charge transfer salts, including those exhibiting field induced spin density wave (FISDW) behavior. We predict three distinct nonsuperconducting phases.

INTRODUCTION

When magnetic fields (H) are applied at low temperatures ($\sim 5^\circ K$) to the superconducting (TMTSF)$_2$X salts [1], superconductivity first gives way to a "metallic" state, albeit with possible unusual properties. Then for fields $H > H_f$ ($\sim$ 5 Tesla) a cascade of transitions to semimetallic SDW phases (as deduced from NMR data [2]) is observed. The explanations of this FISDW phenomenon involve the gradual "one dimensionalization" of the anisotropic 2-D Fermi surface due to the magnetic field, and an accompanying *sequence* of nesting instabilities [3-5]. Within these "standard" theories, the phase at very high fields is expected to be a commensurate, large gap SDW semiconductor. These theories thus fail to account for the recent observation in the perchlorate salt (X = ClO$_4$) of the VFHT [6,7], where for H > 17 Tesla it is found the transition temperature T_{SDW} begins to *decrease* with field, and actually goes to zero for H $\cong$ 25-30 Tesla. At present, there exists only one "nonstandard" [8] theoretical approach that explains the VFHT. Importantly, within this approach, the VHF phase is predicted to be metallic; experimentally, however, the material exhibits high resistivity, activated conductivity, vanishing Hall signal and diamagnetism, all characteristics of a semiconductor or a semimetal. Thus it appears that, despite its successes [8], the "nonstandard" approach is incomplete.

In the present article we argue that an anisotropic, quasi-2-D extended Hubbard Hamiltonian, in which both nearest-neighbor Coulomb interactions and the quarter-filled nature of the organic stacks are incorporated [9], not only explains the VHFT but also unifies the theoretical understanding of the pressure and magnetic field dependence of the phases of many other families of structurally similar 2:1 cationic organic charge transfer salts, including the TMTTF, BEDT-TTF, DM   and MDT-TTF

materials. We show that the model predicts three different *non*superconducting phases, depending on the extent of the anisotropy. Further, pressure, magnetic field or any other effects that change the *effective* anisotropy can drive transitions among the phases. The FISDW behavior can be included as in the original theories, and it has been suggested [10] that the same model can provide a mechanism for the superconductivity seen in some of these systems.

THEORETICAL MODEL AND NUMERICAL RESULTS

We consider the sing.e-band, anisotropic, quasi-2D extended Hubbard model,

$$H = -\sum_{i,\sigma}(t_x c_{i,\sigma}^\dagger c_{i+x,\sigma} + t_y c_{i,\sigma}^\dagger c_{i+y,\sigma} + h.c.) + U\sum_i n_{i\uparrow}n_{i\downarrow} + \sum_i (V_x n_i n_{i+x} + V_y n_i n_{i+y}), \qquad (1)$$

on a rectangular lattice, but realistic lattice structures can be incorporated later. The operators and parameters in (1) have their standard interpretations; the $x-$axis is chosen as the stacking axis. The implicit parameter ρ, the number of holes per site on the organic stack, is very significant, and is fixed at 0.5 (quarter-filling). Numerical calculations are then performed for various anisotropies ($0 < t_y/t_x < 1, 0 < V_y/V_x < 1$) to determine the dominant broken symmetry.

Before presenting our numerical results, we indicate our physical arguments suggesting the possibility of three distinct phases for the ground state of the Hamiltonian (1) for $\rho = 0.5$. In the 1-D limit $t_y = 0 = V_y$, it is known that the SDW, which is a continuous broken symmetry, can never occur as a distinct phase with long-range order. Indeed, the dominant broken symmetry, for small enough V_x (relative to U) is the *bond order wave* (BOW) in which the order parameter is the bond order (charge transfer); given any coupling at all to the lattice, this leads to either a Peierls (weak coupling) or a spin-Peierls (SP) (strong coupling) phase.[9,11] In the isotropic case ($V_y = V_x, t_y = t_x$), it is known for $\rho = 1$ that the BOW does *not* occur [10], and that the SDW dominates (as it can in a 2-D ground state). Intuitively, we expect the relative suppression of the BOW to occur even for t_y considerably less than t_x, and for $\rho = 0.5$ as well as for $\rho = 1$. However, while for $\rho = 1$ the SDW becomes progressively *stronger* with increasing t_y, for $\rho = 0.5$ (and $V \neq 0$), a *spin frustration* can occur, destroying the SDW. This is sketched in Fig. 1, which for simplicity depicts the large U limit. These considerations lead us to expect three distinct possible ground states for the Hamiltonian in Eq. (1): (i) a SP (BOW) phase, for $t_y < t_{y_1}$; (ii) a SDW phase (including FIDSW effects), for $t_{y_2} < t_y < t_{y_1}$; and (iii) a "spin frustrated" (SF, presumably metallic) phase, for $t_y > t_{y_2}$. We expect distinct boundaries between these regions.

To provide partial quantitative support for our qualitative considerations, we study the ($x - x$ component of the) bond order and the spin-density "structure factors",

$$\chi_{BOW}(\vec{q}) = \frac{1}{N}\sum_{i,j} e^{i\vec{q}\cdot(\vec{r}_i - \vec{r}_j)}(\langle B_{i,i+x}B_{j,j+x}\rangle - \langle B_{i,i+x}\rangle\langle B_{j,j+x}\rangle), \qquad (2a)$$

where $B_{i,i+x} = \sum_\sigma(c_{i,\sigma}^\dagger c_{i+x,\sigma} + h.c.)$, and

$$\chi_{SDW}(\vec{q}) = \frac{1}{N}\sum_{i,j} e^{i\vec{q}\cdot(\vec{r}_i - \vec{r}_j)}\langle [n_{i+l,\uparrow} - n_{i+l,\downarrow}][n_{i,\uparrow} - n_{i,\downarrow}]\rangle, \qquad (2b)$$

as functions of anisotropy. In the 1-D limit, we carried out quantum Monte Carlo (QMC) simulations for a chain of 128 atoms at temperature T $= 1/32$ in units of t_x; for $t_x = 0.2$ eV, 'his corresponds to $70°K$, higher than temperatures of interest in FISDW but reasonably close to typical organic SP

t_y	$\chi_{BOW}(q_x)$ $U=3$, $V_x=1$			$\chi_{SDW}(q_x)$ $U=3$, $V_x=1$			$\chi_{SDW}(q_x)$ $U=0$, $V_x=0$		
	$q_x=0$	$q_x=\pi/2$	$q_x=\pi$	$q_x=0$	$q_x=\pi/2$	$q_x=\pi$	$q_x=0$	$q_x=\pi/2$	$q_x=\pi$
0.0	0.2050	0.7078	0.2163	0.0008	0.6643	0.4721	0.1163	0.4957	0.5000
0.5	0.2699	0.6981	0.2829	0.0222	0.7422	0.4582	0.3010	0.4750	0.5000
0.8	0.6146	0.9474	0.6146	0.2696	0.6307	0.4968	0.4000	0.4825	0.5000
1.0	0.9041	1.0066	0.8073	0.3099	0.5638	0.4941	0.4418	0.5000	0.5000

Table 1: Structure factors versus q_x for various values of t_y. Columns 2–4 are χ_{BOW} for $U=3$, $V_x=1$; columns 5–7 are χ_{SDW} for $U=3$, $V_x=1$; columns 8–10 are χ_{SDW} for $U=0$, $V_x=0$; all units $t_x=1$.
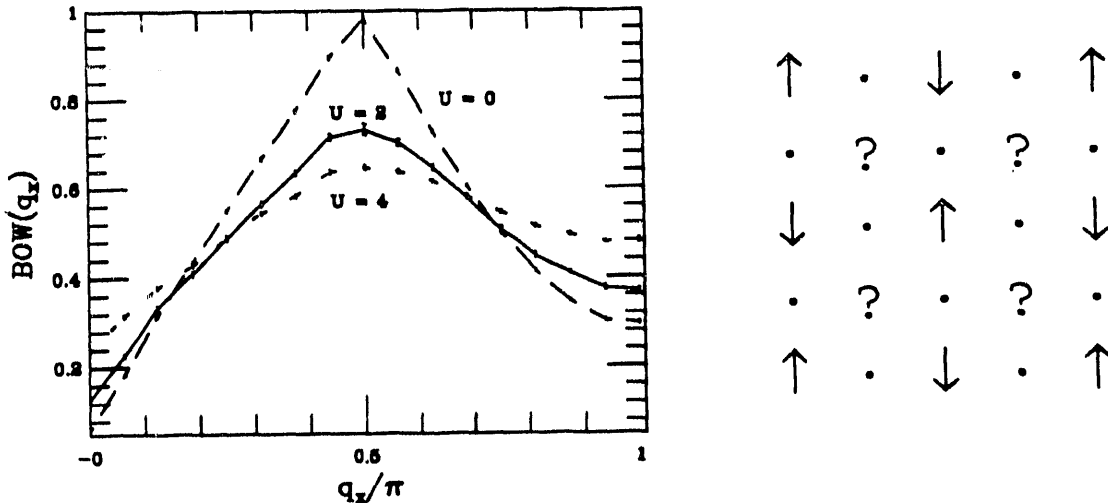

Fig. 1 (left). A small section of a 2-D lattice showing a spin configuration at 1/4-filling; note that the antiferromagnetic couplings in the $\vec{x}$, $\vec{y}$ and $\vec{x}+\vec{y}$ directions lead to frustration on the sites labeled '?'.
Fig. 2 (right). χ_{BOW} for the 1-D Hubbard Model from a QMC calculation with N=128, $T = t_x/32$, and $U/t_x=0,2$, and 4.

temperatures. As seen in Fig. 2, the $\chi_{BOW}(q)$ peaks at $2k_F$ for values of U in the weak to intermediate coupling range. Although (unlike the case for $\rho = 1$) for $\rho = 0.5$ the Coulomb interaction *suppresses* the BOW monotonically, a logarithmic divergence always exists [11], suggesting that a $2k_F$ BOW instability will occur for any finite electron-lattice coupling. For 2D lattices, except in the case $\rho = 1$, similar QMC simulations are not possible because of the well-known "negative sign" problem. We have therefore done exact calculations for a 4 x 4 rectangular lattice. Finite size scaling is not possible currently; thus for comparison we use the $U = V_x = V_y = 0$ case, for which analytical results are available. For brevity we present results only for $U = 3$ and $V_x = 1$ (in units of $t_x = 1$) and always with $V_y/V_x = t_y/t_x$. Finally, we present here results for $q_y = \pi$ only, as correlation functions along (q_x, π) direction are the most relevant for describing SP or SDW transitions in 2D. [10] As seen in Table 1, the $q_x = \pi/2$) BOW is gradually weakened as t_y increases. In an infinite system we expect the reduction in the amplitude of the BOW with increasing t_y to be faster. As Table 1 also shows, the amplitude of the $q_x = \pi/2$) SDW, enhanced by the Coulomb interactions, first increases with t_y, but then peaks and actually decreases, indicating the frustration discussed above and sketched in Fig. 1.

COMPARISON TO EXPERIMENT AND DISCUSSION

Clearly our 2-D results are on systems of such small size that no *quantitative* comparison to experiment is fruitful; for instance, in our calculations the SDW is enhanced until a fairly large value of t_y is reached, only beyond which the SDW amplitude begins to decrease. We focus thus on the *qualitative*

the behavior of different classes of 2:1 materials.

(i) TMTTF salts. These are known to be the most 1-D in character. With some exceptions ((TMTTF)$_2$Br, for example) a low temperature SP phase is the norm. Under pressure, the SP phase gives way to a SDW in (TMTTF)$_2$PF$_6$, with T_{SDW} initially increasing with pressure and then exhibiting a maximum and decreasing [12]. Our approach explains this, since pressure increases t_y, first taking the system from the $t_y < t_{y_1}$ region to the $t_{y_1} < t_y < t_{y_2}$ region and then finally into the spin frustration regime.

(ii) TMTSF salts. These are the materials in which FISDW and VFHT are seen. The effect of the magnetic field is opposite to that of pressure; H $\neq$ 0 makes the system more one dimensional and takes it from the frustrated $t_y > t_{y_2}$ region to the $t_{y_1} < t_y < t_{y_2}$ region. However, in the VHFT region, transition to the $t_y < t_{y_1}$ "phase" is expected; thus we predict a SP phase, separated by a distinct boundary, from the "high" temperature phase at large H.[13] The SP phase will have all the characteristics of a semiconductor, including diamagnetism. Also, within our model FISDW should not necessarily be limited to superconducting TMTSF salts [8], although the experimental conditions under which the FISDW might appear are not clear, since application of *both* pressure and magnetic field may be necessary to be in the right regime.

(iii) BEDT-TTF and MDT-TTF salts. These materials are the most strongly 2-D and are thus likely in the $t_y > t_{y_2}$ region where no SDW is expected. However, the crystal structures of these materials can vary from salt to salt, and sometimes several modifications are known even with the same anion. This is especially true for the MDT-TTF salts with asymmetric cations. Nakamura *et al.* have recently shown that (MDT-TTF)$_2$Au(CN)$_2$ exhibits a SDW below 20°K, but the SDW state is easily suppressed by application of pressure [14]. Although this is *opposite* to the effect seen in (TMTTF)$_2$PF$_6$, within our approach it can be explained by assuming that at ambient pressure (MDT-TTF)$_2$Au(CN)$_2$ is in the $t_{y_1} < t_y < t_{y_2}$ region, so that pressure can take it into the SF regime.

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