Similarities in electronic properties of organic charge-transfer solids and layered cobaltates

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Abstract

The apparently counterintuitive carrier concentration-dependent electronic properties of layered cobaltates have attracted wide interest. Here we point out that very similar carrier-concentration dependence has previously been noted in strongly correlated quasi-one dimensional (quasi-1D) organic charge-transfer solids. The normal states of both families can be understood, over the entire range of carrier concentration of interest, within the extended Hubbard Hamiltonian with significant intersite Coulomb interaction. As with the charge-transfer solids, superconductivity in the cobaltates appears to be limited to bandfilling of one-quarter. We point out further that there exist other families of correlated superconductors, such as spinels, where too strong correlations, geometric lattice frustration and bandfilling of one-quarter seem to be the essential features of the unconventional superconductors.

Key words: Strong correlations, Unconventional superconductors, Charge-transfer solids, Layered cobaltates
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1. Introduction

Twenty five years after the discovery of high Tc superconductivity (SC) in the cuprates, none of the proposed scenarios have led to a consistent mechanism of this phenomenon. It is now recognized that there exist many other superconductors in which electron-electron (e-e) interactions are repulsive. One approach to arriving at the theory of correlated-electron SC is to determine the common characteristics shared by different families of correlated-electron superconductors. Once such common features are determined, one could ask what the implications of these features are for the mechanism of SC. It is with this goal we report and explain the strong parallels between conducting organic charge-transfer solids (CTS) and layered cobaltates.

Both families have been compared individually to the cuprates. Resonating Valence Bond (RVB) theories of SC have in the past been proposed for both quasi-2D \( \kappa-(BEDT-TTF)_{2}X \) [1] and the layered hydrated cobaltate \( \text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}, x \sim 0.35 \) [2–4].

Our description here uses the carrier concentration \( \rho \), rather than the bandfilling. In the CTS, \( \rho \) is the charge per individual molecule. The charge carriers in the CTS occupy the highest molecular orbitals of the molecules, which act as single sites. The layered cobaltates, - \( \text{Na}_x\text{CoO}_2, \text{Li}_x\text{CoO}_2 \) and \( \text{K}_x\text{CoO}_2 \) - consist of \( \text{CoO}_2 \) layers separated by layers of alkali ions. The Co ions form a triangular lattice and have average charge \((4-x)^+\). The large crystal field splitting [5] leads to low-spin states for the Co-ions, and the \( \text{Co}^{3+} \) (\( \text{Co}^{4+} \)) ions are spinless (spin \( \frac{1}{2} \)) Trigonal distortion splits the \( t_{2g} \) \( d \)-orbitals on the Co ions further into two low-lying \( e'_g \) orbitals and a higher \( a_{1g} \) orbital, and photoemission studies of \( \text{Na}_x\text{CoO}_2 \) suggest that the charge carrying holes on the \( \text{Co}^{4+} \) ions occupy the \( a_{1g} \) orbitals only.
Note that the hole density $\rho = 1 - x$ here.

In both families $\rho$ can be tuned over wide ranges. We briefly describe the experimental observations, and then present a consistent theory of the systematic $\rho$-dependence in the two apparently unrelated families. Following this we point out that SC in the CTS and the cobaltates may be occurring at the same $\rho = 0.5$. Given the strong role of carrier concentration in both families, this cannot be a coincidence. There exist other inorganic materials where also SC is limited to the same $\rho$. A correct theory of correlated-electron SC should explain this shared feature.

2. Experimental Observations

In the quasi-1D CTS $\rho$ ranges from 0.5 to 1. The $\rho = 1$ materials are Mott-Hubbard semiconductors [8]. Experimental signatures of strong correlations in the $\rho < 1$ conductors are, (i) magnetic susceptibility $\chi(T)$ enhanced relative to the calculated Pauli susceptibility $\chi_P$, and (ii) 4$k_F$ instability. Structurally similar 1D conductors, with nearly identical molecular components and crystal structures, exhibit very different behavior. Thus $\chi(300K)/\chi_P$ is $\sim 20$ in MEM(TCNQ)$_2$, $\sim 3$ in TTF-TCNQ, and $\sim 1$ in HMTSF-TCNQ [9]. The 4$k_F$ transition temperature $T_{4k_F} = 335K$ in MEM(TCNQ)$_2$ [10], but considerably lower in TTF-TCNQ [11]. HMTSF-TCNQ shows no 4$k_F$ instability and only the “normal” 2$k_F$ instability [11]. These observations had led to various “large $U$” and “small $U$” Hubbard model-based theories with, however, no understanding why $U$ could be both large and small. More recently, the emphasis has been on the 4$k_F$ charge-ordering in 2:1 cationic CTS [12]. $\chi(T)$ in Na$_x$CoO$_2$ is strongly $x$-dependent. Early work [13] labeled $\chi(T)$ as “Pauli paramagnetic” for $x < 0.5$ (large $\rho$) and “Curie-Weiss” for $x > 0.5$ (small $\rho$). More recent works label the small $x$ (large $\rho$) materials as “weakly” (“strongly”) correlated, and put the boundary between these close to $x = 0.67$ instead of 0.5 [14]. Thermopower measurements give similar results. Early theories ascribed the $x$-dependence of the electronic behavior in Na$_x$CoO$_2$ to Na-ion potentials. Experiments [14] that have established identical $x$-dependence in Li$_x$CoO$_2$ with much smaller Li-ions and in the incommensurate misfit cobaltates show that the behavior is intrinsic to the CoO$_2$ layers. Weakly correlated behavior for systems with $\rho$ close to 1, - which for large enough $U$ would be a Mott-Hubbard semiconductor, - and strongly correlated behavior for small $\rho$, where the system is closest to being a band insulator with all Co-ions as spinless Co$^{3+}$, - are both counterintuitive. Weak correlation has sometimes been ascribed to greater mixing of $a_{1g}$ and $e_g$ orbitals, but it is not clear why such mixing should be $x$-dependent.

3. Theory

The problems in understanding the $\rho$-dependence arise from limiting discussions of e-e interactions to the simple Hubbard model, with the onsite repulsion $U$ as the only significant Coulomb interaction. The simple Hubbard model provides a good description of the ground state and the low energy spin excitations for $\rho = 1$, where the effects of longer range Coulomb interactions can be incorporated with an effective onsite interaction $U_{\text{eff}}$ (with only short range nearest neighbor (NN) repulsion $V$, $U_{\text{eff}} \approx U - V$.) This effective parametrization breaks down for $\rho \neq 1$. We demonstrate that the observed $\rho$-dependence in both CTS and cobaltates can be understood very well within the extended Hubbard Hamiltonian provided $U$ is finite and $V/U$ is nonnegligible.

We consider the Hamiltonian,

$$H = - \sum_{\langle i,j \rangle \sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} + V \sum_{\langle i,j \rangle} n_i n_j,$$

for both the CTS and the cobaltates. In the above $\langle ij \rangle$ imply NN, the Fermion operator $c_{i\sigma}^\dagger$ creates an electron or a hole with spin $\sigma$ ($\uparrow$ or $\downarrow$) on a CTS molecular site, and a hole in the triangular lattice of Co-ions in the layered cobaltates. All other terms have their usual meanings. In the following we express all energies in units of $|t|$. As discussed in Section 2, the susceptibility relative to the Pauli susceptibility is the most used measure of the degree of correlation. Since calculations of thermodynamic quantities can be done only with relatively small number of electrons, we choose to calculate the normalized probability of double occupancy in the ground state,

$$g(\rho) = \frac{\langle n_{i\uparrow} n_{i\downarrow} \rangle}{\langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle},$$

which can be calculated for much larger system size. Explicit calculations of $g$ [9] and susceptibility [15] indicate that small (large) $g$ is both necessary and sufficient for enhanced (unenhanced) susceptibility. The physical reason for this is that the reduction of Hubbard Hamiltonians to the Heisenberg spin Hamiltonian requires $g \to 0$, while large $g$ implies metallic behavior.

We have performed exact numerical calculations of $g(\rho)$. Our previous 1D calculations [9,15] were with different system sizes for different $\rho$. Substantive improvements in computer capabilities in the intervening years now allow us to vary $\rho$ keeping the same number of sites $N$. Our calculations are for periodic rings of $N = 16$. In Fig. 1 we have plotted $g(\rho)$ against $\rho$ for $U = 10$. 


Fig. 1. (Color online) Exact $g(\rho)$ versus $\rho$ for $U=10$, and $V=0$ (circles), 2 (diamonds) and 3 (triangles), for periodic ring of 16 sites. Lines are guides to the eye.

$V = 0$, 2 and 3. The value of $U$ chosen is realistic for CTS [8]. Although $\rho < 0.5$ systems do not exist here we have retained one such a point for comparison to the 2D calculations below. The key points of Fig. 1 are: (i) for $V = 0$ correlation effects are nearly independent of $\rho$, (ii) for $V \neq 0$, correlations are strongest for materials near $\rho = 0.5$, and (iii) materials with $\rho$ between $\sim 0.67$ - 0.9 should exhibit weakest correlations.

Our calculations in 2D are for six different finite periodic triangular lattices, with $N = 12$, 16, 18 and 20 (two different 16-site and 20-site lattices each can be constructed) [17]. Here we report results for the $N = 16$ and 20-site lattices shown in Fig. 2(a) and (b), respectively. The corresponding plots for $g(\rho)$, for the same $U$ and $V$ as in Fig. 1, are shown in Figs. 2(c) and (d), respectively. These $U$ and $V$ were arrived at from experiments [17,18]. Importantly, $\rho$-dependent $g(\rho)$ in either 1D or 2D is not found in the $U \rightarrow \infty$ limit, where $g \rightarrow 0$ for all $\rho$. Finite $U$ and $V$ are both required [15,17]. The natures of the plots for the two different lattice sizes are very similar: (a) $g(\rho)$ is nearly $\rho$-independent for $V = 0$, (b) is small for $\rho \leq \frac{1}{3}$ for $V \neq 0$, and (c) fairly large in the region $\rho > 0.4$ for significant $V$. In particular, $V$ decreases $g(\rho)$ in the region $\rho \leq \frac{1}{3}$ but enhances it for larger $\rho$, $\rho = \frac{1}{2}$ in the triangular lattice thus corresponds to $\rho = 0.5$ in 1D.

Fig. 2 predicts that 1D systems with $\rho = 0.5$ and realistic $V$ are the most strongly correlated, and the effective correlations decrease with increasing $\rho$, until about $\rho \sim 0.8$ beginning from where the effective correlations increase again. Precisely such a systematic $\rho$-dependent behavior is seen in the entire CTS family [15]. Among the three CTS mentioned above, (i) MEM(TCNQ)$_2$ exhibits very strongly correlated behavior because it is $\rho = 0.5$, where $g(\rho)$ is the smallest; (ii) TTF-TCNQ with intermediate $\rho = 0.59$ exhibits moderately strongly correlated behavior, with $g(\rho)$ still smaller than that at $\rho = 1$; (iii) the weakly correlated behavior of HMTSF-TCNQ with $\rho = 0.75$ is expected, since $g(\rho)$ here close to being largest (see Fig. 1). Recent discovery of 4$k_F$ charge ordering in the (TMTTF)$_2$X [12] and the accompanying theoretical discussions [16] are in agreement with these conclusions. Thus weakly and strongly correlated behavior can both emerge in spite of having the same $U$ and $V$.

Figs. 2(c) and (d) predict that correlation effects in the triangular lattice are strongest for $\rho \leq 0.33$ ($x > 0.67$), and that the boundary between strongly and moderately correlated regions occurs at $\rho \sim 0.3 - 0.4$. Asymmetry between $\rho = \frac{1}{3}$ and $\frac{2}{3}$ is predicted, with $\rho = \frac{2}{3}$ predicted to show weakly correlated behavior. In the $U \rightarrow \infty$ limit $\sqrt{3} \times \sqrt{3}$ charge-ordering is expected in both cases [4]. Our predictions are in strong agreement with observations in Na$_2$CoO$_2$, Li$_2$CoO$_2$ and the misfit cobaltates [14]. Here we have ignored the $e'_0$ orbitals. Elsewhere [17] we have shown that the two-band extended (but not simple) Hubbard Hamiltonian explains the weak $e'_0$ hole occupancy near $\rho = 0.67$, also in agreement with experiments [7].

5. Superconductivity

SC in correlated-electron superconductors invariably occurs over a narrow range of carrier concentration, and sometimes the superconducting substance is a line compound. The latter is true with superconducting CTS, which are 2:1 cationic compounds ($\rho = \frac{1}{2}$ hole carriers) or 1:2 anionic compounds ($\rho = \frac{1}{2}$...
electron carriers). We find this significant, given the strong \( \rho \)-dependence of the electronic behavior and the natural explanation of the same within the extended Hubbard model. Beyond this, superconducting CTS are quasi-2D with strong interstack interactions. Highest \( T_c \) is reached in the \( \kappa \)-(BEDT-TTF)\(_2\)X, in which the superconducting state is often proximate to an antiferromagnetic state. The \( \kappa \)-lattice is strongly dimerized, and the dimer unit cells form an anisotropic triangular lattice. Theoretical explanation of the antiferromagnetism requires that the dimer lattice be thought of as effective \( \rho = 1 \), with each dimer as a single site. This is what has led to the RVB theories of SC within the \( \rho = 1 \) Hubbard Hamiltonian on an anisotropic triangular lattice [1]. Within these models increasing pressure increases frustration as well as bandwidth, and SC appears at the interface of antiferromagnetism and metallicity. This idea, though attractive, is incorrect. There is no SC within the \( \rho = 1 \) Hubbard Hamiltonian for any \( U \) or anisotropy [20]. Importantly, there exist many CTS in which the superconducting transition is from an insulating state different from antiferromagnetism, or where the triangular lattice of monomers is not dimerized, which would also argue against any mechanism based on the \( \rho = 1 \) Hubbard Hamiltonian. The only common features between CTS superconductors are strong correlations, frustrated lattice of molecules, and \( \rho = 0.5 \).

The hole density in the superconducting hydrated cobaltate is more elusive. The original assumption that the Na-concentration determines the hole density also in the hydrated material has been found to be not true; some water molecules enter as \( \text{H}_2\text{O}^+ \), and the actual \( \rho \) in the superconductor is much smaller than the 0.65 that would be guessed from the Na-concentration. There have been several reports that SC occurs over a very narrow range of hole density, and that maximum \( T_c \) occurs at or very close to Co-ion valency 3.5+ [19], corresponding to \( \rho = 0.5 \).

The common features between all organic superconducting CTS and the cobaltates then appear to be strong correlations, geometric lattice frustration and \( \rho = \frac{1}{2} \). Yet another class of compounds that share these features are inorganic spinels \( \text{AB}_2\text{X}_4 \). The B sublattice forms a frustrated pyrochlore lattice and usually consists of transition metal cations with partially filled \( t_{2g} \) d-orbitals. Only four of the many spinel compounds are superconducting, of which three have effective carrier density \( \rho = 0.5 \): \( \text{LiTi}_2\text{O}_4 \), \( \text{CuRh}_2\text{S}_4 \), and \( \text{CuRh}_2\text{Se}_4 \). In \( \text{LiTi}_2\text{O}_4 \) there is one d-electron per two \( \text{Ti}^{3.5+} \) ions. The \( \text{Rh}^{3.5+} \) ions, like \( \text{Co}^{3.5+} \), are also \( \rho = 0.5 \).

Elsewhere we have shown that increased frustration within Eq. 1 leads to an antiferromagnetism-to-spin singlet charge-ordered transition in \( \rho = 0.5 \) [21], and that this same spin-singlet state can undergo transition to a superconducting state with further increase in frustration [22]. While further work on the proposed superconducting transition is required, the attractive features of this scenario are that the peculiar \( \rho \)-dependence of the above diverse materials are explained within Eq. 1, and the possibility exists that SC can be explained within a single plausible mechanism.

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