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κ-BEDT-TTF SALTS AS LAYERED CORRELATED ELECTRON SYSTEMS

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Abstract The κ-ET_2X compounds are classified as strongly correlated electron systems.The tight-binding approach for correlated electrons is presented. The anisotropic superconducting pairing interaction is constructed based on the symmetry of electronic transfer integral and superconducting characteristics are calculated. For superconducting and normal properties, a decisive role of internal degrees of freedom in ET-layers, particularly in the ET_2 dimers is shown. The nodes of superconducting order parameter are reasonable for description of low energy experiments: nonactivated temperature dependence of superconducting specific heat and NMR relaxation rate.

INTRODUCTION

In recent years, systematic NMR, electrodynamic, thermodynamic and transport measurements under pressure have given an opportunity to lead to an united knowledge about κ-ET_2X materials with a variety of properties. The importance of intraET Anderson-Hubbard like electron-electron correlations U_{ET} for a few layered ET-based material has been marked.[1,2,3,4] On the basis of the experimental data and theoretical estimates, the κ-ET_2X family is characterized by high-energy scale of $U_{ET} \sim$ 1eV, an intradimer hopping, t_{ra}, and a weak interdimer hopping, t_{er}, with emphasized internal degrees of freedom in ET-layers, particularly in the ET_2 dimers. We put a goal to investigate the manner in which the internal degree of freedom in the ET_2 plane can influence on normal electronic structure and superconducting condensate properties beyond discussion about the nature of the superconducting pairing mechanism.
In the present paper, κ-ET_2X are modelled as correlated electron systems, where the ET_2 dimers are considered as entities with two degenerated energy levels. Then the electronic structure of the dimerized ET_2 layer is calculated. Based on the electronic band symmetry, the anisotropic pairing interaction is constructed for κ-ET_2X

superconductors. In the frame of the realistic weak coupling limit for gapless superconductivity, characteristics of the superconducting condensate are evaluated.

THE CORRELATED NARROWING OF THE ENERGY BAND

Intradimer hopping, t_{ra}, is small compared to the intraET electron-electron correlations: $t_{ra} / U_{ET} << 1$. Therefore, the dimerized ET_2 layer can be represented by sites with degenerated energy levels, namely the doubly degenerated Hubbard model. According to the the diagrammatic technique developed for correlated electrons[5], one needs to prepare a ground state and at least one exited state. Since one hole spreads over a dimer/site, ET_2^+, with three electrons, it is easier to deal with in the hole representation than in the electron one. We employ the former for hole concentration , n, around 1.

Let's denote each of 16 multielectron eigenstates in a dimer of $ET_2 = ET_aET_b$ as $\langle ab \rangle$. Then the one-particle ground state is formed by 4-fold degenerated states $\langle \uparrow 0 \rangle$, $\langle \downarrow 0 \rangle$, $\langle 0 \uparrow \rangle$, $\langle 0 \downarrow \rangle$ with population, n_1, differentiated by spin projection and hole position in $(ET_aET_b)^+$. The nearest exited states are the $\langle 0\ 0 \rangle$, with a population, n_0. For correlated electron picture, instead of fermion operators one has to use the generalized Hubbard-Okubo operators[5] as $a_\sigma = X^{00}_{\sigma 0}$, $b_\sigma = X^{00}_{0\sigma}$: X^B_A transforms a dimer state from A to B. Average values of diagonalized X-operators are equal to populations of each eigen state: $\langle X^{00}_{00} \rangle = n_0$, $\langle X^{\sigma 0}_{\sigma 0} \rangle = \langle X^{0\sigma}_{0\sigma} \rangle = n_1$. Applying orthogonality of the X-operator basis and 4-fold degeneracy of the ground state, one can get the following system of equations for site occupations: $4n_1+n_0=1$ and $n_1 = n/4$. The so called correlation factor[5,6,7] is derived as

$$f = \langle \{ X^{\sigma 0}_{00} X^{00}_{\sigma 0} \} \rangle = \langle X^{00}_{00} \rangle + \langle X^{\sigma 0}_{\sigma 0} \rangle = n_0 + n_1 = \frac{4 - 3n}{4} \quad ,$$

which reflects filling of the correlated energy band by carrier number, n. Using the formalism given in Refs.5, we get the spectrum of one-particle excitations as follows:

$$\xi^{a,b}_{\vec{p}} = f\, t_{er}(\vec{p}) - \mu = \frac{4 - 3n}{4}\, t_{er}(\vec{p}) - \mu \,. \qquad (1)$$

The $t_{er}(p)$ refers to the bonding branch of spectrum of noncorrelated hole carriers in ET_2-layer and will be calculated in the next section. One can get the chemical potential from the following equation for the number of holes per site:

$$n_\sigma = \frac{n}{2} = 2f \sum_{\vec{p}, \omega_n} e^{i\delta}\, G^{00}_{\sigma 0}(\omega_n, \vec{p}) = 2f \sum_{\vec{p}} \vartheta(-\xi_{\vec{p}}) \quad . \qquad (2)$$

Here in the right-hand side the multiplier 2 is due to the a-b degeneracy of the spectrum (1). Assuming a rectangular (flat weighted) density of states with a half-bandwidth , w,

for noninteracting carriers, one can derive from Eq.(2) a dependence of the chemical potential on carrier concentration as

$$\mu = \frac{5n - 4}{4} w , \tag{3}$$

which reflects the correlated narrowing of the energy band.

THE TIGHT-BINDING ELECTRONIC STRUCTURE IN ET_2-LAYER

For the κ-ET_2X family, the internal degrees of freedom in the ET_2-layers are important: the dimeric nature of ET-molecules and two ET dimers per basic unit . Square lattice for ET_2 is assumed for simplicity while real arrangement has rhombic distortion. All of the interdimer hopping integrals are reasonably supposed to be the same and the t_1^{er} and $t2^{er}$ are ~0.1eV according to Ref.8 (the t_2^{er} is an azimuthal hopping integral in the crystal b direction). In reality, t_1^{er} is slightly splitted due to the non-symmetry of the dimer, as was shown by the extended Huckel HOMO calculation[8]. Then the secular eguation for the bonding branches of noncorrelated hole spectrum, $\varepsilon_{\vec{p}}$, of elementary excitations (antibonding branches of electron kind) is as follows:

$$\left| (t^{ra} - \varepsilon_{\vec{p}}) \delta_{ij} + H_{ij} \right| = 0 \quad , \tag{4}$$

where matrix elements , $H_{ij} = \langle \Psi_i \left| H^{int} \right| \Psi_j \rangle$, of the interdimer transfer Hamiltonian H^{int} are expressed via the Bloch functions, Ψ_i , of the i-th doubly degenerated energy state of the dimer pair as follows

$$H_{11,22} = t_2^{er} \left(\cos p_y \pm \frac{1}{2} \left(1 + \cos p_y + \cos p_x + \cos (p_y + p_x) \right) \right)$$

$$H_{12} = \frac{i}{2} t_2^{er} \left(\sin p_y + \sin p_x + \sin (p_y + p_x) \right) = H_{21}^{*}$$

Here we assummed the equal magnitudes of interdimer hopping integrals and all momenta are given in reduced units : $|p_x| = |p_y| = \pi$ on the respective Brillouine zone boundaries. From Eq. (4), one obtains a pair of hole bonding spectrum branches as

$$\varepsilon_{\vec{p}} = t^{ra} + t_{\vec{p}} \quad , \text{where} \quad t_{\vec{p}} = 2\, t_2^{er} \left\{ \cos p_y \pm 2 \left| \cos \frac{p_y}{2} \cos \frac{p_x}{2} \right| \right\} . \tag{5}$$

The derivation of the hole bonding branches (5) from the secular eguation (4) is justified if the energy difference, $2t_{ra}$, between the bonding and antibonding pairs exceeds the energy splitting of each bonding and/or antibonding energy branches. Applying the tight-binding method for correlated electrons[5] to the dimeric structure of ET_2 layer with a

finite magnitude of t_{ra} / U_{ET} after canonical transformation to natural bonding and antibonding orbitals, we have got a pair of bonding branches and a pair of antibonding branches of spectrum for correlated holes as follows[9]:

$$\xi_{\vec{p}} = \pm t_{ra} + (1+\frac{4t_{ra}}{U_{ET}}) f t_{\vec{p}} - \mu \qquad (6)$$

The noncorrelated branches (5) reproduce the detailes of the first prinsiples calculation [10], tight-binding method[11] or numerical simulation[12] of the κ-ET_2X band structure.

EFFECTIVE PAIRING INTERACTION AND SUPERCONDUCTIVITY IN ET_2-LAYER

A complex Fermi surface does not provide either constant pairing interaction or a constant energy gap, $\Delta(\vec{R})$ [13]. The anisotropy in the electronic transfer symmetry (1) ((5)) and (6) should be naturally reflected in the pairing interaction of which the anisotropy has an influence on the superconducting order parameter[14]. In the tight-binding approach, the symmetry of the Bloch functions, $\psi(\vec{R})$, and the symmetry of the Fermi surface dictate the symmetry of the superconducting order parameter[15] as follows

$$\Delta_{pp'} = \sum_{r\,r'} \exp\{i(\vec{p}\,'\vec{r}\,' - \vec{p}\,\vec{r})\} \int \psi^*(\vec{r} - \vec{R})\Delta(\vec{R})\psi(\vec{r}\,' - \vec{R})d\vec{R} \approx$$
$$\sum_{r} \exp\{i(\vec{p}\,' - \vec{p}\,)\,\vec{r})\} \int \Delta(\vec{R})\left|\psi(\vec{r} - \vec{R})\right|^2 d\vec{R}$$

This form and the pairing interaction $V_{pp'}$ depend on momenta difference of pairing fermions , namely $\Delta(\vec{p}-\vec{p}')$ and $V(\vec{p}-\vec{p}')$, for weak overlapping of wave functions.
One can see that around the Fermi surface the variable part of the dispersion law (6) is mainly $\xi_{\vec{p}} \approx 2f\,t_{er}\cos p_y$, and is determined by the lower branch of bonding hole spectrum (the upper antibonding branch of electronic spectrum). Then the effective pairing interaction can be expressed as follows

$$V(\vec{p}-\vec{p}') = 2V \sum_{\alpha=x,y,z} \cos(p_\alpha - p_\alpha') = \frac{2V}{(2^{n/2})^2 f^2 t_{er}^2} \xi_{\vec{p}}\xi_{\vec{p}'} + \begin{pmatrix} \text{terms odd} \\ \text{in } p,p' \end{pmatrix} . \qquad (7)$$

Here V is the amplitude of arbitrary attractive interaction, z is the coordination number for ET_2-dimer in plane (z=6 for our model), and correlation factor f=1/4 (the κ-ET_2X salt case is n=1) . The attractive interaction (7) can be due to some mechanism other than the electron-phonon one.

Eliashberg had noted that superconducting theory does not have to be based on noncorrelated band spectrum and Green's functions of noncorrelated electrons[16]. Starting from correlated Green's functions , we have calculated the superconducting "gap" and transition temperature. The resultant formulae are

$$\Delta(\varepsilon) = \varepsilon\,\Delta = \varepsilon\sqrt{\left(\frac{\rho V \omega_c^2}{2^z f^5 t_{er}^2}\right)^2 - 1}\quad \vartheta(\omega_c^2 - \varepsilon^2) \tag{8}$$

with a condensation energy of

$$-\omega_c^2\left(\frac{2^{z-1} f^5 t_{er}^2}{\rho V \omega_c^2} + \frac{\rho V \omega_c^2}{2^{z+1} f^5 t_{er}^2} - 1\right)\ , \tag{9}$$

and $$T_c = \frac{\sqrt{3}}{\pi}\,\omega_c\sqrt{1 - \frac{2^z f^5 t_{er}^2}{\rho V \omega_c^2}}\ . \tag{10}$$

In Eqs. (8)-(10) ω_c and ρ denotes the cut-off energy and the normal electronic density of states at the Fermi surface, respectively.

CONCLUDING REMARKS

From the spectrum (6), we can get for correlated carriers in the κ-ET_2X the chemical potential as $\mu=(1/4 - 3t^{ra}/U_{ET})w$ that means quarter narrowing of the noncorrelated energy bands (5) as in the strongly correlated limit, $t^{ra} / U_{ET} = 0$ (c.f. Eq. (3) at n=1). So, the actual bandwidth is 4-fold smaller for the reason of particle correlations. For realistic difference in nonazimuthal interdimer hopping integrals $\Delta t \equiv \Delta t_1^{er}$ in Eqs. (5) and (6), one can extend the expression for t_p^- to

$$t_p^- = 2\left\{\pm t_2^{er}\cos p_y \pm 2\, t_1^{er}\left|\cos\frac{p_y}{2}\right|\left[\left(1+\frac{1}{4}\frac{\Delta t}{t_1^{er}}\right)\cos^2\frac{p_x}{2} + \left(\frac{\Delta t}{2t_1^{er}}\right)^2\right]^{\frac{1}{2}}\right\}. \tag{11}$$

Here the sign "+" in the first term stands for antibonding and the sign "− " for bonding kind of electronic branches. The interdimer hopping , t_{er}, increases under pressure. As can be seen in equations (8), (9), (10) for the superconducting condensate, it leads to decrease of condensation energy and T_c in the proposed model of κ-ET_2X superconducting salts. The opposite tendency occurs with increase of lattice parameters or expansion of the basic unit. These are in agreement with empirical conclusions.

Moreover, stronger dimerizition associated with decrease of interdimer hopping integral, ter, and increase of density of states, ρ, lead to enhancement of superconducting

condensate. Because of presence of nodes in the superconducting gap given by Eq.(8), the present approach is reasonable for description of the low energy experiments such as NMR[17,18,19] and electronic specific heat [20]in the superconducting state.
The present study can be useful and applicable to other organic materials with dimeric structure, e. g. to BETS compounds [21].

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