

# Electronic Structure, Insulator–Metal Transition and Superconductivity in $\kappa$ -ET<sub>2</sub>X Salts

V. A. Ivanov,<sup>1\*</sup> E.A. Ugolkova,<sup>1</sup> M. Ye. Zhuravlev<sup>1</sup> and T. Hakiöglu<sup>2</sup>

<sup>1</sup>N. S. Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, 31 Leninskii prospect, Moscow 117 907, Russia

<sup>2</sup>Department of Physics, Bilkent University, Ankara 06533, Turkey

The electronic structure and superconductivity of layered organic materials based on the bis(ethylenedithio)tetrathiafulvalene molecule (BEDT-TTF, hereafter ET) with essential intra-ET correlations of electrons are analysed. Taking into account the Fermi surface topology, the superconducting electronic density of states (DOS) is calculated for a realistic model of  $\kappa$ -ET<sub>2</sub>X salts. A d-symmetry of the superconducting order parameter is obtained and a relation is found between its nodes on the Fermi surface and the superconducting phase characteristics. The results are in agreement with the measured non-activated temperature dependences of the superconducting specific heat and NMR relaxation rate of central <sup>13</sup>C atoms in ET. © 1998 John Wiley & Sons, Ltd.

KEYWORDS organic conductors; electron correlations; dielectric–metal transition; superconductivity; Fermi surface

## INTRODUCTION

Condensed organics have constituted a branch of condensed matter science since the discovery of conductivity<sup>1,2</sup> and superconductivity<sup>3</sup> in organic matter. The electron donor ET molecule can form a wide class of salts,<sup>4</sup> the most attractive for fundamental science and applications being the  $\kappa$ -ET<sub>2</sub>X family. Despite the similarity in electronic and crystal structures and the same carrier concentration of half a hole per ET molecule, the  $\kappa$ -ET<sub>2</sub>X family includes semiconductors, normal metals and superconductors with critical superconducting temperatures as high as  $T_c \approx 13$  K. Its crystal

motif is made by ET<sub>2</sub><sup>+</sup> dimers arranged in a crossed dimer manner in ET layers, separated by alternating polymerized X<sup>-</sup> anion sheets with a sheet periodicity of about 15 Å. The ET<sub>2</sub> dimers are fixed at lattice plane sites in a near-triangular configuration. The elementary cell is  $a$ -by- $\sqrt{3}a$  rectangular and includes two ET<sub>2</sub> dimers (hereafter the lattice constant  $a = 1$ ). The intermolecular distance within an ET<sub>2</sub> dimer is 3.2 Å, while the separation between neighbouring ET<sub>2</sub> dimers is about 8 Å.

In this work the analysis of the normal and superconducting phases of  $\kappa$ -ET<sub>2</sub>X salts is based on the assumption that their properties are governed by the scale of  $U_{ET} \geq 1$  eV (intra-ET electron–electron repulsion),  $t_0 \approx 0.2$  eV (intra-ET<sub>2</sub> carrier hopping),  $t_{1,2,3} \approx 0.1$  eV (inter-ET<sub>2</sub> carrier hopping between nearest molecules of neighbouring dimers)<sup>5,6</sup> and  $\tau \approx 3 \times 10^{-4}$  eV (interlayer hopping). The dispersion relations are presented in Section 2 for a realistic  $\kappa$ -ET<sub>2</sub>X lattice symmetry. On the basis of the Hubbard model with two ET<sub>2</sub><sup>+</sup> sites per unit cell, the insulating state is obtained for the  $\kappa$ -ET<sub>2</sub>X family and a phase

\* Correspondence to: V. A. Ivanov, N. S. Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, 31 Leninskii Prospect, Moscow 117 907, Russia

Contract grant sponsor: Russian Foundation for Basic Researches

Contract grant number: 98-03-32670a

Contract grant sponsor: Russian Ministry of Science and Technologies (Russian–Turkish Project)

transition to metal is observed in Section 3. Besides the discussion about the nature of the superconducting mechanism, the anisotropic pairing of different symmetries is studied within the BCS approximation in Section 4. In Section 5 the relation between the superconducting electronic DOS and the topology of the Fermi surface is discussed. In Section 6 it is shown that nodes of the superconducting order parameter are responsible for the description of such quantities as the non-activated superconducting specific heat and  $^{13}\text{C}$  NMR.

### TIGHT-BINDING ELECTRONIC ENERGY DISPERSIONS

In the tight-binding approach<sup>7</sup> for a triangular lattice the electronic energy dispersion relations are of the form  $E_p^\pm = \pm t_0 + \varepsilon_p$ , where

$$\varepsilon_p = t_2 \cos p_y \pm \cos(p_y/2) \sqrt{t_1^2 + t_3^2 + 2t_1 t_3 \cos(\sqrt{3}p_x)} \quad 1$$

In the limiting case of completely isotropic hopping ( $t_{1,2,3} \equiv t$ ) the dispersions of Eqn. 1 are

$$\varepsilon_p/t = \varepsilon_p^\pm = \cos p_y \pm 2 \cos(p_y/2) \cos(\sqrt{3}p_x/2) \quad 2$$

Around the  $\Gamma$ -point of the Brillouin zone (BZ) the energy dispersion relations of Eqn. 2 become

$$\varepsilon_p^+ = 3 - 3p^2/4$$

$$\varepsilon_p^- = -1 + (3p_x^2 - p_y^2)/4$$

To consider non-zero energy dispersion along the  $c$ -direction, we need to take into account the essential  $\text{ET}_2$  layers shown in Fig. 1. Assuming a small interlayer carrier hopping  $\tau$  along the  $c$ -axis ( $t_{1,2,3} \equiv t$ ), we can obtain the general energy dispersion relations as

$$\omega_p^{1,2} = \varepsilon_p^\pm \pm \frac{\tau}{t} \cos \frac{p_z c}{2} \sqrt{3 + 2\varepsilon_p^\pm}$$

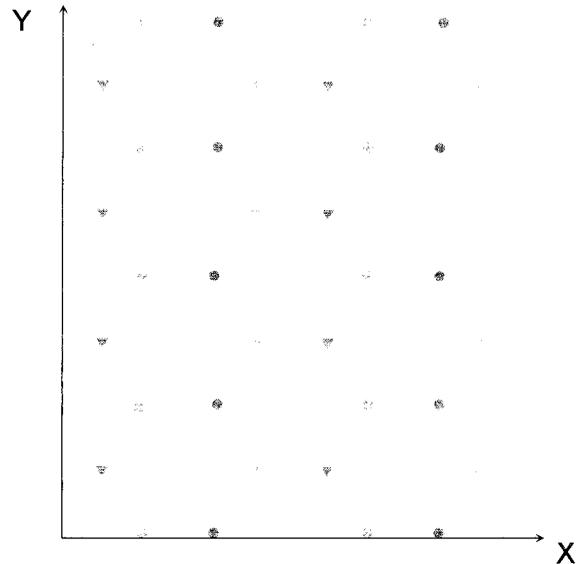
$$\omega_p^{3,4} = \varepsilon_p^\pm \pm \frac{\tau}{t} \cos \frac{p_z c}{2} \sqrt{3 + 2\varepsilon_p^\mp}$$

These carrier energy dispersions are different from cited ones such as  $\varepsilon = \varepsilon_p^\pm + t_\perp \cos(p_z c)$ . It is easily seen from Eqn. 3 that the effective carrier hopping  $t_\perp = \sim \cos(p_z c/2)/\cos(p_z c)$  increases with increasing interlayer separation  $c$ , in agreement with experimental visualization.<sup>8</sup> The Fermi surface corresponding to the spectral branches (Eqn. 3) of electronic energies has a corrugated topology, in contrast with the conventional two-dimensional Fermi surface derived on the basis of the energy dispersion relations of Eqn. 2<sup>7</sup> with neglect of the interlayer hopping  $\tau$ .

### INSULATOR-METAL PHASE TRANSITION

The  $\kappa\text{-ET}_2\text{X}$  insulating problem can be described in the frame of the half-filled Hubbard model with two  $\text{ET}_2^+$  sites per unit cell in the  $\text{ET}_2$  lattice. We employ the  $X$ -operator technique of Refs. 5, 6, 9 and 10 for generalized Hubbard<sup>11</sup>-Okubo<sup>12</sup> operators  $X_A^B = |B\rangle\langle A|$  projecting multielectron A states of the crystal cell  $\mathbf{r}$  to B states. Then the local,  $\mathbf{r} = \mathbf{r}'$ , Green function acquires the form

$$D_{\alpha\beta}^0(\mathbf{r}t, \mathbf{r}'t') = \delta_{\mathbf{r},\mathbf{r}'} G_{\alpha}^0(\mathbf{r}t, \mathbf{r}'t') \langle [X_{\alpha} X_{-\alpha}]_{\pm} \rangle_0$$



3 Fig. 1. Scheme of crystal structure of neighbouring  $\text{ET}_2$  layers: inverted triangles,  $\text{ET}_2$  dimers of one layer; circles, projection of  $\text{ET}_2$  dimers of neighbouring layer

In the Matsubara  $\omega$ -representation it can be rewritten as

$$D_{\alpha(B A)}^0(\omega_n) = f_\alpha G_{\alpha(B A)}^0(\omega_n) = \frac{f_\alpha}{-i\omega_n + \varepsilon_A - \varepsilon_B} \quad 4$$

where the subscripts  $\alpha(B A)$  denote the transitions  $A \rightarrow B$  in the discrete spectrum of the non-perturbative Hamiltonian  $H_0$  and the correlation factor<sup>9,10,13–15</sup>

$$f_\alpha = \langle [X_\alpha X_{-\alpha}]_{\pm} \rangle_0 = \langle X_A^A \rangle \pm \langle X_B^B \rangle = n_A \pm n_B$$

is determined by the Boltzmann populations  $n_{A,B}$  of the  $H_0$  eigenstates A and B with expansions of the Fermi operators given by

$$a_\sigma = \sum_{\alpha(B A)} g_\alpha X_\alpha \quad 5$$

according to the tight-binding approach for correlated electrons,<sup>11,12</sup> the band spectra should be derived from the equation

$$\begin{aligned} \sum_\alpha g_\alpha^2 D_\alpha^0(\omega_n) &= \frac{\sum g_\alpha^2 f_\alpha}{-i\omega_n - \varepsilon} + \frac{\sum g_\alpha^2 f_\alpha}{-i\omega_n + \varepsilon} \quad 6 \\ &= -\frac{1}{t\varepsilon_p^\pm}. \end{aligned}$$

Then one can get from Eqn.6 the correlated antibonding branches

$$\xi_p^\pm = (t_2/2) \left[ \varepsilon_p^\pm \pm \sqrt{(\varepsilon_p^\pm)^2 + (2\varepsilon/t_2)^2} \right]. \quad 7$$

From the tight-binding correlated bands, Eqn.7, it follows that intra-dimer electron interactions are responsible for the insulating gap, i.e.  $\Delta = \xi^+(\min \varepsilon_p^+) - \xi^-(\max \varepsilon_p^+)$ . Taking into account the energy ranges  $-1 < \varepsilon_p^+ < 3$  and  $-3/2 < \varepsilon_p^- < 1$  of uncorrelated carriers in Eqn.2 and the dispersion relations of Eqn.7, one can evaluate the band gap as

$$\begin{aligned} \Delta &= \left[ \sqrt{9 + (2\varepsilon/t_2)^2} \right. \\ &\quad \left. + \sqrt{(3/2)^2 + (2\varepsilon/t_2)^2} - 9/2 \right] t_2/2. \quad 8 \end{aligned}$$

With the assumptions  $\varepsilon = U_{ET_2}/2 \approx t_0 \approx 0.2$  eV and  $t_2 \approx 0.1$  eV the magnitude of this band gap is in agreement with the measured activation energy  $E_g = \Delta/2 \approx 10^2$  meV in  $\kappa$ -ET<sub>2</sub>X semiconductors.<sup>16,17</sup>

A metallic dimerised ET<sub>2</sub> layer in  $\kappa$ -ET<sub>2</sub>X can be represented by a lattice of sites  $ET_2 \equiv ET_a ET_b$  with degenerate energy levels of orbitals ‘a’ and ‘b’, namely the doubly degenerate Hubbard model with a hole concentration  $n$  of around unity.<sup>5</sup> The ground state and polar populations are  $\langle X_{00}^{00} \rangle = n_0$  and  $\langle X_{0\sigma}^{00} \rangle = \langle X_{0\sigma}^{0\sigma} \rangle = n_1$  respectively. The completeness relation for the fourfold degenerate ground state yields the concentrations  $n_0 \approx 1 - n$  and  $n_1 \approx n/4$ . The desired spectrum of one-particle excitations follows from the pole of the Green function as

$$\xi_p^{a,b} = f\varepsilon_p - \mu = (1 - 3n/4)\varepsilon_p - \mu \quad 9$$

where  $\varepsilon_p$  refers to the dispersion from Eqn. 1, 2 or 3.

In the general case of  $k$ -fold degeneracy of the GS in the unperturbed Hamiltonian  $H_0$  the Mott–Hubbard phase transition is governed by singularities of the two-particle vertex  $\Gamma_{ab}$  for small momentum transfer.<sup>18</sup> One can derive the critical point of the insulator–metal phase transition as<sup>19</sup>

$$\begin{aligned} \left( \frac{t_2}{\varepsilon} \right)_{\text{crit}} &= \left( \frac{t_2}{U_{ET_2}/2} \right)_{\text{crit}} \\ &= \frac{4\pi}{\sqrt[4]{3\sqrt{15}\pi^2 + 64}} = 0.66. \quad 10 \end{aligned}$$

(Note that for a square ET<sub>2</sub> lattice the phase transition critical point is 0.43.<sup>6</sup>)

In terms of the conducting bandwidths  $W_U$  and the dimer band splitting  $\Delta E = 2t_0$ , it is known that the empirical ratio  $W_U/\Delta E = 1.1–1.2$ <sup>20</sup> separates  $\kappa$ -ET<sub>2</sub>X insulators from metallic  $\kappa$ -ET<sub>2</sub>X compounds. Taking into account the antibonding bandwidth  $4.5t_2$ , the empirical relation can be considered as  $t_2/t_0 = 0.48–0.54$ , which agrees fairly well with the calculated phase critical point of Eqn.10,  $(t_2/t_0)_{\text{crit}} = 0.66$  ( $U_{ET_2} \approx 2t_0$ ). We can conclude, for example, that  $\kappa$ -ET<sub>2</sub>Cu[N(CN)]<sub>2</sub>Cl with the characteristic ratio  $t_2/t_0 = 0.32$ <sup>20</sup> should be an insulator near the insulator–metal phase boundary. Recently it was reported that  $\kappa$ -ET<sub>2</sub>Cu[N(CN)]<sub>2</sub>Cl insulator undergoes the

phase transition to metal under a moderate hydrostatic pressure of 30 MPa.<sup>21</sup>

In conclusion of this section we estimate the influence of intra-dimer phonons on the effective Hubbard energy for the simplest exactly solvable model of the dimer with electron hopping correlated by phonons:

$$\begin{aligned}
 H = & \omega b^+ b + \lambda(b^+ + b)(n_1 + n_2) \\
 & - [t_0 + \tilde{t}_0(b^+ + b)] \sum_{\sigma} (c_{1\sigma}^+ c_{2\sigma} + \text{h.c.}) \\
 & + U \sum_{i=1,2} n_{i\uparrow} n_{i\downarrow}
 \end{aligned} \quad 11$$

To obtain the effective Hubbard interaction in the dimer, one should determine the ground state energies for one and two electrons in a dimer. Using the one-electron basis for the wavefunction in the case of one electron, the wave function of the dimer has the form

$$\Psi = [f_1(b^+)c_1^+ + f_2(b^+)c_1^+] |0\rangle^{\text{el}} \otimes |0\rangle^{\text{ph}}$$

In this electron basis the Schrödinger equation takes the matrix form

$$\begin{aligned}
 H_{\text{el-ph}} F &= \begin{pmatrix} \omega b^+ b + \lambda(b^+ + b) & -[t_0 + \tilde{t}_0(b^+ + b)] \\ -[t_0 + \tilde{t}_0(b^+ + b)] & \omega b^+ b + \lambda(b^+ + b) \end{pmatrix} \\
 &\times \begin{pmatrix} f_1(b^+) |0\rangle \\ f_2(b^+) |0\rangle \end{pmatrix} = E \begin{pmatrix} f_1(b^+) |0\rangle \\ f_2(b^+) |0\rangle \end{pmatrix}
 \end{aligned} \quad 12$$

The system of equations can be diagonalised into bonding and antibonding orbitals

$$\begin{aligned}
 f_a &= [f_1(b^+) + f_2(b^+)]/\sqrt{2} \\
 f_b &= [f_1(b^+) - f_2(b^+)]/\sqrt{2}
 \end{aligned}$$

The corresponding branches of the spectrum are

$$\begin{aligned}
 E_n^{(1,b)} &= \omega n - \frac{(\lambda - \tilde{t}_0)^2}{\omega} - t_0 \\
 E_n^{(1,a)} &= \omega n - \frac{(\lambda + \tilde{t}_0)^2}{\omega} - t_0
 \end{aligned} \quad 13$$

Depending on the values of the parameters of the electron–phonon interaction, either of the branches can be the lower one:  $E_n^{(1,b)} < E_n^{(1,a)}$  if  $t_0 > 2g\tilde{t}_0/\omega$ . The similar problem for two electrons in a dimer can be solved exactly for finite intra-ET electron correlations,  $U_{\text{ET}} = \infty$ . In this case the electron basis is reduced to two functions and the wavefunction of the dimer can be chosen as

$$\Psi = [c_{1\uparrow}^+ c_{2\downarrow}^+ f_1(b^+) + c_{2\uparrow}^+ c_{1\downarrow}^+ f_2(b^+)] |0\rangle^{\text{el}} \otimes |0\rangle^{\text{ph}}$$

Then the doubly degenerated spectrum is

$$E_n^{(2)} = \omega n - \frac{4\lambda^2}{\omega} \quad 14$$

Thus

$$\begin{aligned}
 U_{\text{ET}_2}^{\text{eff}} &= 2t_0 + \frac{2\tilde{t}_0^2}{\omega} - \frac{2\lambda^2 + 4\lambda\tilde{t}_0}{\omega} \\
 &\text{for } t_0 < 2\lambda\tilde{t}_0/\omega
 \end{aligned}$$

and

$$\begin{aligned}
 \tilde{U}_{\text{ET}_2}^{\text{eff}} &= -2t_0 - \frac{2\lambda^2}{\omega} + \frac{2\tilde{t}_0^2 + 4\lambda\tilde{t}_0}{\omega} \\
 &\text{for } t_0 > 2\lambda\tilde{t}_0/\omega
 \end{aligned}$$

These expressions can be positive as well as negative. We assume the realistic case  $U_{\text{ET}_2}^{\text{eff}} > 0$ .

---

## SUPERCONDUCTING PAIRING IN ET<sub>2</sub> LAYER MODEL

---

As can be seen from Eqn. 9, 1 or 2, band structure effects are important when the Fermi surface is near the BZ (this is the case for the  $\kappa$ -ET<sub>2</sub>X family), where the influence of the crystal potential is strong.

Experiments imply that, in  $\kappa$ -ET<sub>2</sub>X superconductors, anisotropic singlet d-type pairing with nodes of the order parameter given by  $\Delta_d(\mathbf{p}) \propto \cos p_x - \cos p_y$  (so called  $d_{x^2-y^2}$ -pairing) or another one ( $d_{xy}$ ) occurs at the Fermi surface. They are also consistent with anisotropic singlet s\*-pairing with nodes  $\Delta_s(\mathbf{p}) \propto \cos p_x + \cos p_y$  without a sign change or minimum of the gap on the Fermi surface, but in the same direction in the BZ

as in the case of d-pairing. To determine the type of Cooper pairing, we start from correlated Green functions to apply the formalism.<sup>22</sup>

Here we assume a triangular ET<sub>2</sub> lattice and express the Fermi operators via  $X$ -operators in the effective pairing Hamiltonian. For a particular triangular lattice with a single-point basis of the  $\kappa$ -ET<sub>2</sub>X model the general form of attractive interaction between fermions, namely

$$V(\mathbf{p} - \mathbf{p}') = 2V \left( \cos(p_y - p'_y) + \cos \frac{\sqrt{3}(p_x - p'_x) + p_y - p'_y}{2} + \cos \frac{\sqrt{3}(p_x - p'_x) - (p_y - p'_y)}{2} \right), \quad 15$$

conserves a symmetry of elementary excitation dispersions (Eqn.2) irrespective of the superconducting pairing mechanism. Its expansion over the basis functions of irreducible representations of the point symmetry group of the triangular lattice is

$$V(\mathbf{p} - \mathbf{p}') = 2V \sum_{i=1}^6 \eta_i(\mathbf{p}) \eta_i(\mathbf{p}'), \quad 16$$

where

$$\begin{aligned} \eta_1(\mathbf{p}) &= \frac{1}{\sqrt{3}} \left( \cos p_y + 2 \cos \frac{p_y}{2} \cos \frac{\sqrt{3}p_x}{2} \right) \\ \eta_2(\mathbf{p}) &= \frac{2}{\sqrt{6}} \left( \cos p_y - \cos \frac{p_y}{2} \cos \frac{\sqrt{3}p_x}{2} \right) \\ \eta_3(\mathbf{p}) &= \sqrt{2} \sin \frac{p_y}{2} \sin \frac{\sqrt{3}p_x}{2} \\ \eta_4(\mathbf{p}) &= \frac{1}{\sqrt{3}} \left( \sin p_y + 2 \sin \frac{p_y}{2} \cos \frac{\sqrt{3}p_x}{2} \right) \\ \eta_5(\mathbf{p}) &= \frac{2}{\sqrt{6}} \left( \sin p_y - \sin \frac{p_y}{2} \cos \frac{\sqrt{3}p_x}{2} \right) \\ \eta_6(\mathbf{p}) &= \sqrt{2} \cos \frac{p_y}{2} \sin \frac{\sqrt{3}p_x}{2} \end{aligned}$$

Here the basis functions  $\eta_1(\mathbf{p})$ ,  $\eta_2(\mathbf{p})$  and  $\eta_3(\mathbf{p})$  describe respectively anisotropic singlet  $s^*$ -pairing,  $d_{x^2-y^2}$ -pairing and  $d_{xy}$ -pairing. The basis functions  $\eta_{4,5,6}(\mathbf{p})$  are linear combinations of the basis functions for the two-dimensional representation corresponding to triplet p-pairing.

From the standard BCS equation for the superconducting order parameter, i.e.

$$\Delta(\mathbf{p}) = \sum_{i=1}^6 \Delta_i \eta_i(\mathbf{p}),$$

we obtain the following equation for  $T_c$ :

$$\left| \delta_{ij} - 2V \sum_{\mathbf{p}, \alpha = \pm} \frac{\tanh(\xi_{\mathbf{p}}^{\alpha}/2T_c)}{2\xi_{\mathbf{p}}^{\alpha}} \Delta_j \eta_i(\mathbf{p}) \eta_j(\mathbf{p}) \right| = 0. \quad 17$$

Because the oddness of the integrals in Eqn.17 with respect to the momentum  $p_y$ , only superconducting pairing of  $\eta_1(\mathbf{p})$  with  $\eta_2(\mathbf{p})$  and of  $\eta_4(\mathbf{p})$  with  $\eta_5(\mathbf{p})$  can be allowed. In Eqn.17 the anisotropic singlet pairings of the d- and  $s^*$ -type break down to one-dimensional  $d_{xy}$ -pairing and mixed( $s^* + d_{x^2-y^2}$ )-pairing. Knight shift measurements<sup>23,24</sup> indicate only a singlet form of electron pairing in  $\kappa$ -ET<sub>2</sub>X superconductors.

Applying the logarithmic approximation, one can get that for  $d_{xy}$ -pairing the superconducting critical temperature  $T_c$  satisfies an equation of the form

$$1 = (2V/f)F_{33} \ln(\omega_c f/2T_c) \quad 18$$

with a cut-off energy parameter  $\omega_c$ . Recalling that the correlation factor  $f = \frac{1}{3}$ , it immediately follows that the corresponding coupling constant is  $\lambda_{xy} = 8VF_{33}(1.47)$ , where  $F_{33}(1.47) = 2.09/\pi^2$  for a realistic value of  $\mu/f = -0.415$ . The superconducting critical temperature for the order parameter of mixed symmetry  $s^* + d_{x^2-y^2}$  is specified by the quadratic equation

$$\begin{vmatrix} 1 - 8VF_{11} \ln(\omega_c/8T_c) & -8VF_{12} \ln(\omega_c/8T_c) \\ -8VF_{12} \ln(\omega_c/8T_c) & 1 - 8VF_{22} \ln(\omega_c/8T_c) \end{vmatrix} = 0, \quad 19$$

where  $F_{ij}$  are expressed via values of elliptic integrals of the first, second and third kinds:  $F_{11}(1.47) = 1.60/\pi^2$ ,  $F_{22}(1.47) = 0.36/\pi^2$  and  $F_{12}(1.47) = -0.48/\pi^2$ . Then the mixed symmetry coupling constants are evaluated as  $\lambda_{d_{x^2-y^2}+s^*} =$

$8VF_{1,2}$ , with  $F_1 = 1.76/\pi^2$  and  $F_2 = 0.20/\pi^2$ . That is, both coupling constants are smaller in magnitude than the coupling constant for superconducting  $d_{xy}$ -pairing. Hence it follows that the superconducting order parameter of the  $d_{xy}$ -wave symmetry is preferable for the  $\kappa$ -ET<sub>2</sub>X superconductor model under consideration.

For an effective pairing interaction  $V = 0.022$ , made dimensionless by the inter-dimer hopping integral  $t$ , the ratio of superconducting critical temperatures of interest is  $T_c^{d_{xy}}/T_c^{s^* + d_{x^2-y^2}} = 1.65$ . With the same  $V$  value and assuming that the cut-off energy parameter  $\omega_c$  is equal to the inter-dimer hopping integral, i.e.  $\omega_c = t \approx 0.1$  eV, in the logarithmic approximation, we can estimate the superconducting transition temperature  $T_c$  as 10 K for  $d_{xy}$ -wave pairing. This value is a reasonable magnitude for  $\kappa$ -ET<sub>2</sub>X superconductors.

---

### SUPERCONDUCTING ELECTRONIC DENSITY OF STATES

---

For the energy range  $E > 0$  the electronic density of states (DOS) in the superconducting phase of principal interest is defined by

$$\rho_s^\pm(E) = \frac{\sqrt{3}}{4\pi^2} \int_{-\pi}^{\pi} dp_y \int_{-\pi/\sqrt{3}}^{\pi/\sqrt{3}} dp_x \times \delta[E - \sqrt{(\xi_p^\pm)^2 + \Delta_p^2}] \quad 20$$

with the order parameter  $\Delta_p = \Delta_0 \sin(p_y/2) \sin(\sqrt{3}p_x/2)$  and one-particle energies given by Eqn. 9.

The magnitude of  $\Delta_p$  is small in the neighbourhood of four nodes on the Fermi surface inside the first BZ near the straight lines  $p_x = 0$ ,  $p_y = 0$ . In Eqn. 20 let us expand the  $\xi_p$  and  $\Delta_p$  magnitudes in terms of variations from the values at the nodes of the order parameter  $\Delta_p = 0$  on the Fermi surface  $\mu(p_x, p_y)$ . One finds that close to the node  $p_x = 0$ ,  $p_y = 2 \cos^{-1}(\sqrt{3}/4 + \mu/2ft - 1/2)$  on the electron section  $\xi_p^+ = 0$  of the Fermi surface the DOS is

$$\rho_s^+(E) = \frac{E}{2\pi\Delta_0 ft \sin^2(p_y/2)[2 \cos(p_y/2) + 1]} = \beta_+ E \quad 21$$

In a similar manner, close to the node  $p_y = 0$ ,  $p_x = (2/\sqrt{3}) \cos^{-1}(1/2 - \mu/2ft)$  on the hole section  $\xi_p^- = 0$  of the Fermi surface the DOS is

$$\rho_s^-(E) = \frac{E}{2\pi\Delta_0 ft \sin^2(\sqrt{3}p_x/2)} = \beta_- E \quad 22$$

Within the conventional isotropic superconducting gap of s-type the DOS is equal to zero. As one would expect, Eqns. 21 and 22 show that for an anisotropic  $d_{xy}$ -order parameter the superconducting electronic DOS is linearly proportional to the energy near the nodes on the Fermi surface. It is significant that the Fermi surface portions with different curvatures contribute different coefficients,  $\beta_-/\beta_+ \approx 3$ , for the calculated value of  $\mu/ft = -0.415$ .

---

### CHARACTERISTICS OF ANISOTROPIC SUPERCONDUCTING PHASE

---

The superconducting electronic DOS obtained in the previous section makes it possible to derive the temperature dependences of the electronic specific heat and spin–lattice relaxation time of conduction electrons in the ET<sub>2</sub> plane. The linear dependences (Eqns. 21 and 22) of DOS on energy in the superconducting condensate lead to a quadratic temperature dependence of the electronic specific heat, namely

$$\begin{aligned} C_s &= 2 \sum_{\mathbf{p}, \delta} \xi_p^\alpha \frac{\partial N_F}{\partial T} \\ &= 2 \int_0^\infty (\beta_+ + \beta_-) E^2 \left( \frac{\partial N_F}{\partial T} \right) dE \\ &= 9(\beta_+ + \beta_-) \zeta(3) T^2 \\ &= 10.8(\beta_+ + \beta_-) T^2 \quad 23 \end{aligned}$$

for a unit cell of the ET<sub>2</sub> layer. Here  $\zeta(3)$  is the Riemann  $\zeta$ -function. Putting into Eqn. 23 the reasonable parameters  $t = 0.12$  eV,  $\Delta_0 = (2.5-3.5)T_c^{25,26}$  and  $T_c = 10$  K for  $\kappa$ -ET<sub>2</sub>X salts, we obtain the superconducting specific heat per mole as  $C_m = \alpha T^2$ , where the coefficient  $\alpha = 10.8N_A(\beta_+ + \beta_-)k_B^3/2$  ( $N_A$  is Avogadro's number and  $k_B$  is Boltzmann's constant) can vary

between 1.59 and 2.23 mJ K<sup>-3</sup> mol<sup>-1</sup>. Such  $\alpha$  values are in agreement with the results of measurements in Ref. 27, where the experimental magnitude of  $\alpha$  has been estimated as 2.2 and less than 3.53 mJ K<sup>-3</sup> mol<sup>-1</sup> respectively for superconductors  $\kappa$ -ET<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br with  $T_c = 11.6$  K and  $\kappa$ -(ET)<sub>2</sub>Cu(NCS)<sub>2</sub> with  $T_c = 10$  K.

In the ET molecule centre the <sup>13</sup>C nuclear magnetic momentum damps out through the conduction electrons under NMR conditions. The corresponding spin-lattice relaxation rate  $R = 1/T_1$  is defined in the superconducting phase by the relation<sup>28</sup>

$$\frac{R_s}{R_n} = \frac{2}{T} \int_0^w \frac{(\beta_+ + \beta_-)^2 E^2}{[\rho(\mu)]^2} \times \frac{\exp(E/T)}{[\exp(E/T) + 1][\exp((E + \nu)/T) + 1]} dE \quad 24$$

where  $\nu$  is the frequency of the oscillating magnetic field,  $\rho$  denotes the normal DOS on the Fermi level and  $w$  is the cut-off energy for the linearly energy-dependent superconducting DOS. When it is considered that radio frequency  $\nu \approx 10$  MHz  $\sim 10^{-4}$  K, at lower temperatures  $T \ll w$  we can calculate the result

$$\frac{R_s}{R_n} = \frac{2T^2 \beta^2 \xi(2)}{\rho^2(\mu)} \left( 1 - \frac{\nu}{T} \frac{\ln 2}{\xi(2)} \right) \quad 25$$

For the normal phase,  $R_n \sim T$  in accordance with the Korringa law; as a consequence, we find that for the superconducting phase the spin-lattice relaxation rate has a cubic low-temperature dependence of the form  $R_s \sim T^3$ .

Electron-electron correlations influence the coefficients  $\beta_+$  and  $\beta_-$  in Eqns. 21–24 via the factor  $f = \frac{1}{4}$  and the renormalised chemical potential. The derived temperature dependence in Eqn. 25 differs from the activated dependence  $R_s \sim \exp(-\Delta/T)$  at low temperatures in superconductors with s-pairing and it has been observed in  $\kappa$ -ET<sub>2</sub>X salts<sup>29–31</sup> at  $T \ll T_c$ .

## CONCLUDING REMARKS

An analytical formulation of the electronic structure in one-dimensional organic compounds has allowed us to analyse various phenomena with

a prediction of several effects. The  $\kappa$ -ET<sub>2</sub>X salts can be firstly modelled as a correlated electron system with doubly degenerate sites in the triangular ET<sub>2</sub> layer, where ET<sub>2</sub> dimers are considered as entities with two degenerate energy levels. Strong electron correlations renormalise the hopping integrals and chemical potential owing to the correlation factor  $f = 1 - 3n/4$  in Eqn. 9 and lead to correlated narrowing of the carrier energy band in the paramagnetic state. Also from Eqn. 9 it follows that the magnetic breakdown gap between the closed and open portions of the Fermi surface is  $\xi_p^+ - \xi_p^- = 2f \cos(p_{y0}/2) |t_1 - t_3| \approx |t_1 - t_3|/4 \approx 4$  meV (at the Fermi momentum  $p_{y0} \approx 2\pi/3$ ) for a realistic difference of non-azimuthal hopping integrals  $t_{1,3}$ . This gap value is in agreement with the experimental magnitude in Refs. 32–35.

Close to the nodes of the superconducting order parameter on the Fermi sections the superconducting DOS (Eqns. 21 and 22) is proportional to the excitation energy. As a result, the number of elementary excitations has a power dependence on temperature. Because of this, the superconducting specific heat is quadratic with respect to temperature (Eqn. 23) and the spin-lattice <sup>13</sup>C relaxation rate is cubic (Eqn. 25) at low temperature.

The calculated cubic temperature dependence of the spin-lattice relaxation rate (Eqn. 25) due to conduction electrons is in agreement with experiments<sup>29–31</sup> on nuclear magnetic spins of central carbon isotopes in ET at low temperatures  $T \ll T_c$ . The absence of the Hebel-Slichter peak at  $T \leq T_c$  can be explained by Maleyev scenario  $U_{ET} \gg t_{1,2,3}$ .<sup>36</sup>

The correlation factor  $f = 1 - 3n/4$  ( $n = 1$  is the number of holes per dimer) affects the superconducting condensate properties. In Ref. 20, according to ESR signals, a Cu<sup>2+</sup> concentration change has been measured in the anion layer of  $\kappa$ -ET<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub>  $\equiv \kappa$ -ET<sub>2</sub><sup>1-x</sup>Cu<sub>2-x</sub><sup>+</sup>Cu<sub>x</sub><sup>2+</sup>(CN<sup>-</sup>)<sub>3</sub>. An increase in paramagnetic Cu<sup>2+</sup> ions decreases the concentration  $1 - x$  of hole carriers in the ET<sub>2</sub> layer and leads to an increase in the correlation factor  $f$  and a decrease in  $T_c$  according to Eqns. 18 and 19.

In the normal phase the factor  $f$  renormalises the dispersion relations of Eqn. 9 for correlated carriers. This suggests a fourfold narrowing of the energy band with a possible difference in optical and cyclotron electron masses<sup>37–39</sup> and decrease

in the cross-section of hole orbits in  $\kappa$ -ET<sub>2</sub>Cu [N(CN)<sub>2</sub>]Br.<sup>40</sup>

---

### ACKNOWLEDGEMENT

---

The support for this work from the Russian Foundation for Basic Researches (Grant No. 98-03-3270a) and the Russian Ministry of Science and Technologies (Russian–Turkish Project) is acknowledged.

---

### REFERENCES

---

- H. Akamatsu and H. Inokuchi, *J. Chem. Phys.*, 1950, **18**, 810–811.
- H. Akamatsu, H. Inokuchi and Y. Matsunaga, *Nature*, 1954, **173**, 168–170.
- D. Jerome, A. Mazaud, M. Ribault and K. Bechgaard, *J. Phys. Lett.*, 1980, **41**, L95–L97.
- T. Ishiguro and K. Yamaji, *Organic Superconductors*, Springer, Berlin, 1990.
- V. Ivanov and K. Kanoda, *Physica C*, 1996, **268**, 205–215.
- V. A. Ivanov, *Physica C*, 1996, **271**, 127–132.
- V. Ivanov, K. Yakushi and E. Ugolkova, *Physica C*, 1997, **275**, 26–36.
- J. Wosnitzer, G. Goll, D. Beckmann, S. Wanka, D. Schweitzer, W. Strunz, *J. Phys. I France*, 1996, **6**, 1597–1608.
- V. A. Ivanov, in A. Narlikar (ed.) *Studies on High-T<sub>c</sub> Superconductors*, Vol. 11, Nova Science, New York, 1993, pp. 331–351.
- V. A. Ivanov, *J. Phys.: Condens. Matter*, 1994, **6**, 2065–2075.
- J. Hubbard, *Proc. R. Soc. A.*, 1965, **285**, 542–560.
- S. Okubo, *Prog. Theor. Phys.*, 1962, **27**, 949–960.
- S. Nakajima, M. Sato and Y. Murayama, *J. Phys. Soc. Jpn.*, 1991, **61**, 2333–2347.
- Y. Murayama and S. Nakajima, *J. Phys. Soc. Jpn.*, 1991, **61**, 4265–4273.
- Y. Murayama, V. A. Ivanov and S. Nakajima, *Phys. Lett. A.*, 1996, **211**, 181–186.
- J. M. Williams, A. M. Kini, H. H. Wang, K. D. Carlson, U. Geiser, L. K. Montgomery, G. J. Pyrka, D. M. Watkins, J. M. Kommers, S. J. Boryschuk, A. V. S. Crouch and W. K. Kwok, *Inorg. Chem*, 1990, **29**, 3272–3274.
- H. Sato, T. Sasaki and N. Toyota, *Physica C.*, 1991, **185–189**, 2679–2680.
- R. O. Zaitsev and V. A. Ivanov, *Sov. Phys.–Solid State*, 1985, **27**, 2147–2158.
- V. Ivanov and Y. Murayama, in S. Nakajima and M. Nurakami (eds.) *Advances in Superconductivity IX*, Springer, Tokyo, 1997, p. 315.
- T. Komatsu and G. Saito, *Mol. Cryst. Liq. Cryst.*, 1996, **285**, 51–56.
- H. Ito, T. Ishiguro, M. Kubota and G. Saito, *J. Phys. Soc. Jpn*, 1996, **65**, 2987–2993.
- L. P. Gor'kov, *Sov. Phys.–JETP*, 1958, **7**, 505–516.
- D. Jerome, in J.-P. Farges (ed.) *Organic Conductors*, Marcel Dekker, New York, 1994, pp. 405–494.
- K. Kanoda, *Kotai Butsuri (Jpn. Solid State Phys.)*, 1995, **30**, 84–89.
- M. Dressel, O. Klein, G. Gruner, K. D. Karlson, H. H. Wang and J. M. Williams, *Phys. Rev. B*, 1994, **50**, 13,603–13,615.
- M. Lang, N. Toyota, T. Sasaki and H. Sato, *Phys. Rev. Lett*, 1992, **69**, 1443–1446.
- Y. Nakazawa and K. Kanoda, *Phys. Rev. B*, 1997, **55**, 8670–8680; *Physica C*, 1997, **282–287**, 1897–1898.
- R. D. Parks (ed.), *Superconductivity*, Plenum, New York, 1981.
- S. M. de Soto, C. P. Slichter, A. M. Kini, H. H. Wang, U. Geiser and J. M. Williams, *Phys. Rev. B*, 1995, **52**, 10,364–10,368.
- H. Mayaffre, P. Wzietek, D. Jerome, C. Lenoir and P. Batail, *Phys. Rev. Lett.*, 1995, **75**, 4122–4125.
- K. Kanoda, K. Miyagawa, A. Kawamoto and Y. Nakazawa, *Phys. Rev. B*, 1996, **54**, 76–79.
- T. Sasaki, H. Sato and N. Toyota, *Physica. C*, 1991, **185–189**, 2687–2688.
- C.-P. Heidman, H. Müller, K. Biberacher, K. Neumaier, Ch. Probst, K. Andres, A. Jansen and W. Joss, *Synth. Met.*, 1991, **41–43**, 2029–2032.
- J. Wosnitzer, G. W. Crabtree, H. H. Wang, U. Geiser, J. M. Williams and K. D. Carlson, *Phys. Rev. B*, 1992, **5**, 3018–3025.
- J. Caulfield, J. Singleton, F. L. Pratt, M. Doport, W. Lubczynski, W. Hayes, M. Kurmoto, P. Day, P. T. J. Hendriks, J. A. A. J. Perenboom, *Synth. Met.*, 1993, **61**, 63–70.
- S. V. Maleyev, A. G. Yashenkin, D. N. Aristov, *Phys. Rev. B*, 1994, **50**, 13825–13828.
- A. Ugawa, G. Ojima, K. Yakushi and H. Kuroda, *Phys. Rev. B*, 1988, **38**, 5122–5125.
- J. Caulfield, W. Lubczynski, F. L. Pratt, J. Singleton, D. K. Y. Ko, W. Hayes, M. Kurmoo and P. Day, *J. Phys.: Condens. Matter*, 1994, **6**, 2911–2924.
- F. L. Pratt, J. Singleton, M. Kurmoto, *et al.*, in G. Saito and S. Kagoshima (eds.) *The Physics and Chemistry of Organic Superconductors*, Springer, Berlin, 1990, pp. 200–203.
- M. V. Kartsovnik, G. Yu. Logvenov, H. Ito, T. Ishiguro and G. Saito, *Phys. Rev. B*, 1995, **52**, 15,715–15,718.