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Phase diagram of quasi-2D BEDT-TTF conductors: effect of lattice type on magnetic properties

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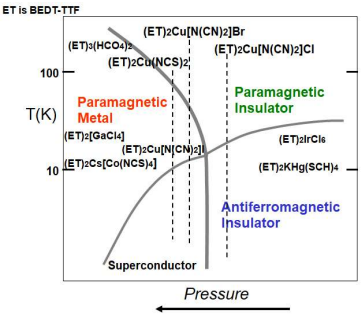
Introduction

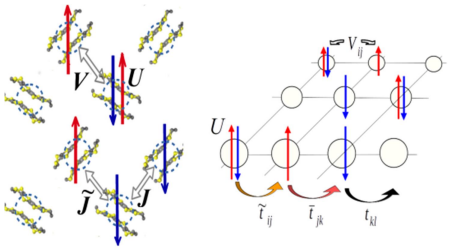
BEDT-TTF family of quasi-two-dimensional organic conductors exhibits large variety of ordered phases [1]. Due to the variety of packing types and lattice parameters of the compounds from the studied family, and the abundance of the experimental studies of the phase transitions in $(BEDT\text{-}TTF)_2X$ (BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene molecule, X denotes monovalent anion $Cu[N(CN)_2]Cl$, $Cu[N(CN)_2]Br$, $Cu[N(CN)_2]I$, $Cu(SCN)_2$, ICl_2, $AuBr_2$, AuI_2, Ibr_2, I_3) we are able to explain qualitative differences of behaviour for α- and κ- configurations with taking into account the realistic electronic density of states form and the correlated hopping of electrons [2].

Phase diagram for organic metals with BEDT-TTF molecule



The effective Hamiltonian of quasi-2D electronic subsystem

A peculiarity of BEDT-TTF family of organic conductors is a wide variety of electronic structures. For a quantitative description to be obtained, orientations of molecules in unit cell is to be taken into account as it causes substantial distinctions of intra- and inter-dimer electron transfer integrals [3]. However, local characteristics are somewhat more universal, in particular, on-site Coulomb repulsion described by the Hubbard U for all BEDT-TTF compounds varies from 0.7 eV to 1.3 eV. This range of U values can serve as a reference point for constructing a model of electronic subsystem and defines a suitable energy scale for this model. A conduction band is formed by the highest occupied molecular orbital (HOMO) [4]. Every dimer of BEDT-TTF molecules can be modeled as a lattice site [5] with one hole per site, analogously to the approach of papers [6, 7]. Energy band widths are comparable to the on-site Coulomb repulsion therefore it is necessary to take into account main factors, which change the bandwidth, namely the external pressure and correlated hopping of electrons.



Energy parameters of the model Hamiltonian. The left panel shows BEDT-TTF dimers with on-site Hubbard parameter U, inter-site repulsion V and exchange parameters J or $\tilde{J}$. In the right panel, different hopping integrals between the nearest neighboring sites are visualized. Only on-site and nearest-neighbors parameters are shown in this figure, though in the model the next-nearest-neighbor interactions are effectively taken into account as well

For description of electron correlation we generalize the effective Hamiltonian in configurational representation of works [6,7] by taking into account the inter-site Coulomb interaction:

$$H_{eff} = H_0 + H_1 + H_2 + H_{ex} + \tilde{H}_{ex},$$

where

$$H_0 = -\mu \sum_i \left(X_i^{\uparrow} + X_i^{\downarrow} + 2X_i^2\right) + U \sum_i X_i^2 + \frac{1}{2} N V_0 \kappa u^2$$

$$H_1 = \sum_{ij\sigma} t_{ij}(n) X_i^{\sigma 0} X_j^{0\sigma} + \sum_{ij\sigma} \tilde{t}_{ij}(n) X_i^{2\sigma} X_j^{\sigma 2},$$

$$H_2 = \frac{1}{2} \sum_{ij\sigma\sigma'} V(ij) \left(X_i^{\sigma} + 2X_i^2\right)\left(X_j^{\sigma'} + 2X_j^2\right),$$

$$H_{ex} = -\frac{1}{2} \sum_{ij\sigma} J(ij) \left(\left(X_i^{\sigma} + X_i^{\bar{\sigma}}\right)\left(X_j^{\sigma} + X_j^{\bar{\sigma}}\right) + X_i^{\bar{\sigma}} X_j^{\bar{\sigma}\sigma}\right),$$

$$\tilde{H}_{ex} = -\frac{1}{2} \sum_{ij\sigma} \tilde{J}(ij) \left(X_i^{\sigma} X_j^{\sigma} - X_i^{\sigma\bar{\sigma}} X_j^{\bar{\sigma}\sigma}\right).$$

In the above expressions X^{kl} are transition operators of site from state $|l\rangle$ to state $|k\rangle$ (Hubbard operators) in configurational representation. Terms of the Hamiltonian have the following meaning. H_0 describes electron subsystem in localization limit (μ is chemical potential, U is Coulomb repulsion of two electrons in the same site), first sum in H_1 describes electron hoppings in the plane of molecules between sites occupied with single electron and empty sites with hopping integral $t_{ij}(n)$ (these processes form the lower Hubbard subband), second sum describes hoppings between singly and doubly occupied sites with parameter $\tilde{t}_{ij}(n)$ (these processes form the upper Hubbard subband). H_2 describes inter-site Coulomb interactions. H_{ex} describes direct inter-site exchange between nearest neighbors, $\tilde{H}_{ex}$ describes effective exchange interaction within the plane with effective exchange integral $\tilde{J}(ij) = \frac{2t_{ij}(n)t_{jk}(n)}{\Delta}$, ($\tilde{t}_{ij}$ is the integral of hole-doublon pair creation at translation along the plane of molecules, $\Delta = U - V + zV(\langle X_i^0\rangle + \langle X_i^2\rangle)$ is the activation energy for the hole-doublon pair). In the proposed model, $\frac{t_{ij}(n)}{\Delta}$ is the small parameter and not $|t(ij)|/U$ as in the t-J model. Under the external pressure p, the band half-width $w = w_0(1 + \alpha u)$ is proportional to the relative strain $u = \frac{\Delta V}{V_0} \sim p$ (here $\alpha < 0$, V_0 is the unit volume, $w_0 = z|t_{ij}|$ is bare (unperturbed) half-bandwidth and z stands for the number of nearest neighbors to a site). Hopping integrals also depend on electron concentration due to correlated hopping of electrons which reduces the hopping probability for occupied sites. Therefore, translation processes are characterized by different hopping integrals $t_{ij}(n) = (1+\alpha u)(1-\tau_1 n)t_{ij}$ for holes and $\tilde{t}_{ij}(n)=(1+\alpha u)(1-\tau_1 n-2\tau_2)t_{ij}$ for doublons; $\tilde{t}_{ij}(n)=(1+\alpha u)(1-\tau_1 n-\tau_2)t_{ij}$ is parameter of the hopping of an electron between doublon and hole [8].

The energy spectrum and phase transitions

With use of the decoupling procedure [2, 8] in the Green function equation of motion method, the single-electron Green function has been obtained as

$$\left\langle\left\langle X_s^{0\uparrow} \middle| X_{s'}^{\uparrow 0}\right\rangle\right\rangle_{\vec{k}} = \frac{\left\langle X_s^0 + X_s^{\uparrow}\right\rangle}{2\pi}\left(\frac{A_{\vec{k}}^{\uparrow}}{E - E_1^{\uparrow}(\vec{k})} + \frac{B_{\vec{k}}^{\uparrow}}{E - E_2^{\uparrow}(\vec{k})}\right),$$

$$A_{\vec{k}}^{\uparrow} = \frac{1}{2}\left(1 - \frac{K^{\uparrow}}{\sqrt{\left(K^{\uparrow}\right)^2 + 4\alpha_s^{\prime\uparrow}\alpha_p^{\prime\uparrow}\left(t_{\vec{k}}^t\right)^2}}\right), \qquad B_{\vec{k}}^{\uparrow} = 1 - A_{\vec{k}}^{\uparrow}.$$

The energy spectrum describes two energy subbands

$$E_{1,2}^{\uparrow}(\vec{k}) = -\mu + \frac{1}{2}\sum_x \left(\alpha_x^{\uparrow} t_{\vec{k}}(n) + \beta_x^{\uparrow}(\vec{k}) - C_x^{\uparrow}\right) \mp \frac{1}{2}\sqrt{\left(K^{\uparrow}\right)^2 + 4\alpha_s^{\prime\uparrow}\alpha_p^{\prime\uparrow}\left(t_{\vec{k}}^t\right)^2},$$

where x denotes sites of p or s alternating 2D sublattices,

$$K^{\uparrow} = (\alpha_s^{\uparrow} - \alpha_p^{\uparrow}) t_{\vec{k}}(n) + \beta_s^{\uparrow} - \beta_p^{\uparrow} - C_s^{\uparrow} + C_p^{\uparrow},$$

$$C_x^{\uparrow} = z_1 J \lambda_x^{\uparrow} + \frac{1}{2} z_2 J' \lambda_x^{\prime\uparrow} + z_1 \tilde{J} \tilde{\lambda}_x^{\uparrow} + \frac{1}{2} z_2 \tilde{J}' \tilde{\lambda}_x^{\prime\uparrow}.$$

The antiferromagnetic order onset in the system is associated with the energy gap opening. Subband narrowing factors α_x^{σ} and $\alpha_x^{\prime\sigma}$ and parameters λ_x^{σ}, $\lambda_x^{\prime\sigma}$, $\tilde{\lambda}_x^{\sigma}$, $\tilde{\lambda}_x^{\prime\sigma}$ may be calculated with use of quasi-classical approach for averages of $\left\langle X_s^{\downarrow\uparrow} X_j^{\uparrow\downarrow}\right\rangle$ type, $\left\langle X_s^{\sigma}\right\rangle$ values being determined by the considered type of magnetic ordering. Spin-dependent subband center shifts $\beta_x^{\sigma}(\vec{k})$ are to be calculated self-consistently. For the antiferromagnetically ordered state, the system of equations for electron concentration and sublattice magnetization reads as

$$m = \frac{m}{4w}\int_{-w}^{w} d\varepsilon \left(f(E_1) + f(E_2)\right) - \frac{m(2-n)}{4w}\int_{-w}^{w} d\varepsilon \frac{L(\varepsilon)}{\sqrt{D}}\left(f(E_1) - f(E_2)\right),$$

$$n = \frac{2-n}{2wn}\int_{-w}^{w} d\varepsilon \left(f(E_1) + f(E_2)\right) - \frac{m^2(2-n)}{4w}\int_{-w}^{w} d\varepsilon \frac{L(\varepsilon)}{\sqrt{D}}\left(f(E_1) - f(E_2)\right),$$

here $\sqrt{D} = \sqrt{(K_z^{\sigma})^2 + 4\alpha_s^{\prime\sigma}\alpha_p^{\prime\sigma} g^2 \varepsilon^2}$, $f(E) = 1/\left(\exp\left(E/kT\right) + 1\right)$

$K^{\sigma} = \eta_{\sigma} m L$, and $L = \left(1 - \frac{n^2 - m^2}{(2-n)^2 - m^2}\right) I_k - \frac{4w(1-n)}{(2-n)^2 - m^2} + zJ_{eff}$, with the effective antiferromagnetic exchange integral

$$zJ_{eff} = z_1(J - \tilde{J}) + z_2(J' - \tilde{J}')/2 < 0,$$

where z_1 stands for the number of the nearest neighbors in same plane and z_2 – that in adjacent plane. For the case of checkerboard antiferromagnet:

$$\alpha_i^{\sigma} = \alpha_i^{\prime\sigma} = \frac{(2 - n + \eta_{\sigma}\eta_i m)^2 + n^2 - m^2}{(2 - n + \eta_{\sigma}\eta_i m)},$$

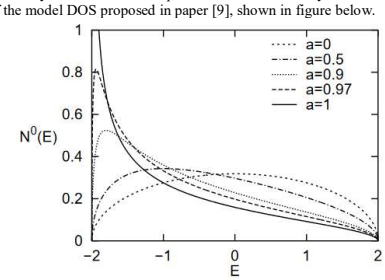
$$\beta_i^{\sigma} = \frac{w(n)(1-n)(n - \eta_{\sigma}\eta_i m)}{2 - n + \eta_{\sigma}\eta_i m},$$

$$\lambda_s^{\sigma} = \lambda_s^{\prime\sigma} = \tilde{\lambda}_p^{\sigma} = \tilde{\lambda}_p^{\prime\sigma} = \frac{n - \eta_{\sigma} m}{2} + \frac{1}{2}\cdot\frac{n^2 - m^2}{2 - n + \eta_{\sigma} m},$$

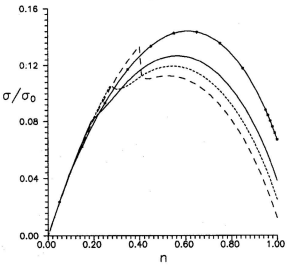
$$\lambda_p^{\sigma} = \lambda_p^{\prime\sigma} = \tilde{\lambda}_s^{\sigma} = \tilde{\lambda}_s^{\prime\sigma} = \frac{n + \eta_{\sigma} m}{2} + \frac{1}{2}\cdot\frac{n^2 - m^2}{2 - n + \eta_{\sigma} m},$$

with η_s=1 and η_p=–1.

To study the effect of the unperturbed electron density of state we make use of the model DOS proposed in paper [9], shown in figure below.

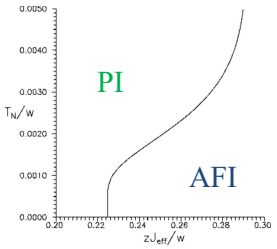


The static electrical conductivity, calculated within the present model, has peculiar concentration dependence, shown in the following figure. Of whole concentration interval $0<n<1$ modeled in our study, the quarter-filled (n=0.25) and half-filled (n=0.5) cases are relevant to BEDT-TTF family, however, possible sharp changes in conductance due to the onset of magnetic ordering can be visualized by the presented concentration dependences which suggest that the asymmetry of DOS inherent to 2D system and enhanced by the correlated dopping of electrons is responsible for dramatic differences of quarter-filled and half-filled systems behavior.

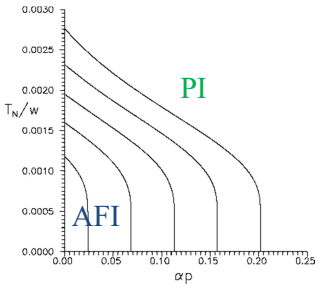


Concentration dependence of the static conductivity. Solid curve corresponds to asymmetry parameter a=0.3, a=0.5 for dashed-dotted curve, a=0.2 for short-dashed curve and a=0.1 for long-dashed curve.

The antiferromagnetic ordering is stable for values of the effective exchange parameter which exceed some critical value which depends on temperature and lattice type.



Dependence of Neel temperature on the effective exchange integral



Theoretical pressure-temperature phase diagram of the model. The shown AFI-PI phase boundaries correspond to values zJ_{eff}/w=0.27, 0.26, 0.25, 0.24, 0.23 (from up to down).

The pressure-induced transition from the low-temperature antiferromagnetic phase to the high-temperature paramagnetic insulator can be modeled within the present approach, as exemplified by the above phase diagram.

Conclusions

We use the model of electronic subsystem to describe both the stability of magnetically ordered phases in a number of $(BEDT\text{-}TTF)_2X$ compounds and the transition driven by temperature change or the external pressure application as the strong electron correlation effects. By applying a variant of the projection method in the Green function equation of motion approach we calculated the single-particle energy spectrum, sublattice magnetization in spin- and charge-ordered phases and the transition temperatures. These results allow us to interpret available experimental data and suggest new mechanisms for the magnetic ordering stabilization in $(BEDT\text{-}TTF)_2X$ compounds.

References

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