Unconventional spin density wave in Bechgaard salt (TMTSF)$_2$NO$_3$

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Among many Bechgaard salts, (TMTSF)$_2$NO$_3$ exhibits very anomalous low temperature properties. Unlike conventional spin density wave (SDW), (TMTSF)$_2$NO$_3$ undergoes the SDW transition at $T_C \approx 9.5$ K and the low temperature quasiparticle excitations are gapless. Also, it is known that (TMTSF)$_2$NO$_3$ does not exhibit superconductivity even under pressure, while FISDW is found in (TMTSF)$_2$NO$_3$ only for $P = 8.5$ kbar and $B > 20$ T. Here we shall show that both the angle dependent magnetoresistance data and the nonlinear Hall resistance of (TMTSF)$_2$NO$_3$ at ambient pressure are interpreted satisfactory in terms of unconventional spin density wave (USDW). Based on these facts, we propose a new phase diagram for Bechgaards salts.

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I. INTRODUCTION

(TM)SF$_2$X are quasi one dimensional molecular conductors, known as Bechgaard salts, where TMTSF denotes tetramethyltetraselenafullvalene and $X$ is an inorganic anion with various possible symmetries: spherical (octahedral) ($X$=PF$_6$, AsF$_6$...), tetrahedral ($X$=ClO$_4$, ReO$_4$...), or triangular (NO$_3$). The well known are their very complex (pressure, magnetic field, temperature) phase diagrams with a variety of electronic ground states: (conventional) spin density wave (SDW), field induced SDW (FISDW), superconductivity (triplet, unconventional), unconventional spin density wave (USDW). The observation of superconductivity in the (TMTSF)$_2$X series requires the use of high pressure, with the exception of (TMTSF)$_2$ClO$_4$, which is superconducting under ambient pressure, and (TMTSF)$_2$NO$_3$, which never becomes a superconductor even under pressure.

NO$_3$ anions are in an orientational disorder at ambient pressure and for $T > 45$ K. The anion ordering (AO) transition takes place at $T_{AO} \approx 45$ K, with wave vector $q = (1/2, 0, 0)$. Contrary to AO in most other salts, $q$ has the nonzero component parallel to the most conducting direction. The SDW state develops below $T_C \approx 9.5$ K. From the resistivity data very small activation energy was obtained, of order of $10^{-3}$ eV, but the curvature of the log $R$ vs. $1/T$ plot indicated that the ground state should be considered as semimetalic, rather than semiconducting.

The phase diagram of Bechgaard salts under pressure is interpreted in terms of the standard model, where the approximate nesting of the quasi-one dimensional Fermi surface (i.e. the imperfect nesting), and the repulsive Coulomb interaction between electrons are the crucial ingredients. The applied pressure increases the 2-dimensionality of Bechgaard salts through the increase of the imperfect nesting term. However, the standard model does not yet describe neither the triplet superconductivity nor USDW.

UDW is a density wave, whose gap function depends on the wavevector, vanishes on certain subsets of the Fermi surface, allowing for low energy excitations. The average of the gap function over the Fermi surface is zero, causing the lack of periodic modulation of the charge and/or spin density. As noted by Nersesyan et al. (Refs. 13 and 14), the quasiparticle spectrum in UDW is quantized in a magnetic field. This Landau quantization gives rise to the spectacular angle dependent magnetoresistance (ADM) and giant Nernst effect. As we shall see later both the angle dependent magnetoresistance and the nonlinear Hall resistance of (TMTSF)$_2$NO$_3$ are described nicely in terms of USDW. We note that an earlier attempt to describe the magnetoresistance of (TMTSF)$_2$NO$_3$ in terms of conventional SDW with a large imperfect nesting might not be the most appropriate model since it cannot describe the details of the resis-
tance quantitatively. We also propose the revision of the generally accepted phase diagram, taking into account the identification of USDW state in several Bechgaard compounds. 

II. IDENTIFICATION OF USDW

Here we summarize briefly what is known about unconventional density wave. The unconventional density wave is a kind of density wave, where the quasiparticle energy gap vanishes along lines on the Fermi surface. In the present instance we can assume 

\[ \Delta(k) \sim \cos b k \text{ or } \sin b k \]

as in earlier analysis of UCDW in \( \alpha-\text{(ET)}_2\text{KHg(SCN)}_4 \). Then the quasiparticle Green function is given by

\[ G^{-1}(k, \omega) = \omega - \eta(k) - i \xi(k) - \Delta(k) \]

where \( \eta(k) \) is the kinetic energy of electrons measured from the Fermi energy in the normal state, \( \xi(k) \equiv v(k_n - k_F) \) and \( \Delta(k) = \Delta \cos b k \). Here, \( v \) denotes the Fermi velocity in the chain (a) direction, which is the order parameter for unconventional SDW, and \( b \) is the lattice constant.

Then in a magnetic field \( B \) in the \( b' - c^* \) plane with angle \( \theta \) from the \( c^* \) axis the quasiparticle energy changes into

\[ E_x^\pm = \pm \sqrt{2} \frac{eB}{|b|} \cos \theta \Delta \]

with \( n = 0,1,2,... \) Here we have neglected \( \eta(k) \) for simplicity. Also in the following we assume \( b = 7.567 \text{ Å} \) and \( v = 3 \times 10^5 \text{ m/s} \). Eq. (3) is the consequence of the Landau quantization of the quasiparticle spectrum in UDW, or the Nersesyan effect.

Then the conductivity tensor is constructed as

\[ \sigma_{xx} = \sigma_1 + 2C_1 \text{sech}^2(x_1/2) + \cdots \]

\[ \sigma_{yy} = \sigma_2 + 2C_2 \text{sech}^2(x_1/2) + \cdots \]

\[ \sigma_{xy} = \sigma_3 n(B,T) B \cos \theta \]

with

\[ n(T,B) = n_0 [1 + 2(1 - \tanh(x_1/2)) + \cdots] \]

where \( x_1 = E_1/k_B T \) and we have assumed that \( x_1 \gg 1 \). Also, we have assumed that \( \sigma_1, \sigma_2, \sigma_3, C_1 \) and \( C_2 \) are weakly dependent on \( T \) and \( B \). Then from Eqs. (4)–(6) we can construct the resistivity tensor as

\[ R_{xx}(B, \theta) = \frac{R_0}{1 - D_1 \tanh^2(x_1/2)} \]

FIG. 1: (Color online) The angular dependence of the normalized resistance \( R(B, \theta)/R_0 \) at \( T = 4.2 \text{ K} \) (full lines: experimental data; dashed lines: fits to the theory). Magnetic field is rotated in \( b' - c^* \) plane, and \( \theta = 0^\circ \) corresponds to \( B || c^* \). Data are from Ref. 17 \((B \geq 8 \text{ T})\) and Ref. 21 \((B = 6 \text{ T})\).

In Fig. 1 we show our fitting of the angle dependent magnetoresistance data for \( \text{(TMTSF)}_2\text{NO}_3 \) at \( T = 4.2 \text{ K} \) for a variety of magnetic field. From this fitting we obtain USDW order parameter \( \Delta = 6.3 \text{ K} \) and \( D_1 = 0.93 \). As is readily seen the fitting is excellent except for the bumpy structures. These should come from the imperfect nesting term as discussed in Refs. 8, 21 and 22. Also we note \( D_1 \approx 2C_1/(1 + 2C_1) \) indicating that \( C_1 \approx 7.1 \); therefore \( \sigma_{xx} \) is dominated by the \( n = 1 \) excitations.

In Fig. 2 we show \( R_{xy} \) fitted by Eq. (6); again we obtain reasonable fitting with \( D_2 \approx 80 \text{ T} \). Figure 3 shows temperature dependence of the parameter \( D_2 \), along with temperature dependence of the resistance \( R_{xx} \). There appears to be a slight change of the parameter \( D_2 \) across \( T^* \approx T_C/3 = 3 \text{ K} \): for \( T \geq 3 \text{ K} \) it follows temperature dependence of resistance \( R_{xx} \), while for lower temperature it is nearly constant. It signals the possible occurrence of yet another phase transition at \( 3 \text{ K} \) – as in \( \text{(TMTSF)}_2\text{PF}_6 \), in agreement with several other suggestions.

III. THE NEW PHASE DIAGRAM OF BECHGAARD SALTS

Recently, one of us proposed phase diagram for Bechgaard salts with octahedral (centrosymmetric) anion like \( \text{PF}_6 \) which exhibit metallic behaviour down to the SDW transition at \( T_C \approx 12 \text{ K} \) (see Ref. 16). The salts
with non-centrosymmetric anions undergo the AO transition and become insulating at ambient pressure, except for \( X = \text{ClO}_4 \) and \( \text{NO}_3 \). Here, we propose an extension/revision of the phase diagram (see Fig. 4). As indicated in Fig. 4 (TMTSF)\(_2\)PF\(_6\) at ambient pressure undergoes yet another transition around \( T^* \approx T_C/3 \approx 4\,\text{K} \). The drastic change in the quasi-particle spectrum through \( T^* \) has been interpreted as appearance of SDW+USDW.\(^{20}\) Further, from the angle dependent magnetoresistance of (TMTSF)\(_2\)PF\(_6\) and (TMTSF)\(_2\)ReO\(_4\) for \( P > 8\,\text{kbar} \) the existence of USDW in the high pressure range is inferred.\(^{22}\) Then, it is customarily to put (TMTSF)\(_2\)ClO\(_4\) at ambient pressure around \( P \approx 8\,\text{kbar} \) in Fig. 4 where transition from metallic state to superconducting one takes place. In this way we may understand the superconductivity at ambient pressure. Similarly, we may put (TMTSF)\(_2\)NO\(_3\) at ambient pressure around \( P \approx 8\,\text{kbar} \), since the transition from metallic state to density wave state takes place at \( T_C \approx 9.5\,\text{K} \). The further behaviour of \( T_C \) vs. pressure is based on the experiments, which have shown that \( T_C \) is gradually suppressed under increasing pressure.\(^{23}\) Then is the absence of superconductivity, and appearance of FISDW only at high pressure and high magnetic fields (\( P \geq 8\,\text{kbar}, B > 20\,\text{T} \)) very surprising.

We think that the lack of inversion symmetry in \( \text{NO}_3 \) is at the heart of the absence of superconductivity and FISDW (for low pressure, \( P < 8.5\,\text{kbar} \)) in (TMTSF)\(_2\)NO\(_3\). For example P.W.Anderson\(^{29}\) speculated that the triplet superconductor cannot exist in a crystal without inversion symmetry. Also the nature of superconductivity in CePt\(_3\)Si, the crystal without inversion symmetry, is hotly discussed in the current literature.\(^{30,31}\) The inversion symmetry breaking is usually characterized by \( E_{ch} \) the chiral symmetry breaking term or the Rashba term.\(^{31,32,33}\) Both the absence of the triplet superconductivity (for \( T_{SC} < 1\,\text{K} \)) and the appearance of FISDW for \( B > 20\,\text{T} \) suggest \( 2\,\text{K} < |E_{ch}| < 10\,\text{K} \). Also this \( E_{ch} \) appears to be consistent with \( T_{AO} \approx 45\,\text{K} \) (\( T_{AO} \gg E_{ch} \))\(^{34}\) We believe that further study of the electronic properties of (TMTSF)\(_2\)NO\(_3\) is of great interest.

### IV. CONCLUDING REMARKS

We have shown that the anomalous low temperature behaviour of ADMR and Hall resistance of the Bechgaard salt (TMTSF)\(_2\)NO\(_3\) could be interpreted in terms of unconventional spin density wave, indicating that the...
absence of FISDW for conductivity and partial suppression of FISDW (i.e. the absence of superconductivity). Both the absence of superconductivity and partial suppression of FISDW (i.e. the absence of superconductors which exhibit USDW under ambient pressure.) We have also proposed possible explanation about the absence of superconductivity. Both the absence of superconductivity and partial suppression of FISDW (i.e. the absence of FISDW for $P < 8$ kbar, $B < 20$ T) are due to the inversion symmetry breaking associated with the NO$_3$ anion ordering. The details on this will be published elsewhere.\cite{24}

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