Possible Triplet Electron Pairing and an Anisotropic Spin Susceptibility in Organic Superconductors (TMTSF)$_2$X

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We argue that (TMTSF)$_2$PF$_6$ compound under pressure is likely a triplet superconductor with a vector order parameter $\mathbf{d}(\mathbf{k}) \equiv (d_a(\mathbf{k}) \neq 0, d_c(\mathbf{k}) = 0, d_d(\mathbf{k}) = 0); |d_a(\mathbf{k})| > |d_d(\mathbf{k})|$. It corresponds to an anisotropic spin susceptibility at $T = 0$: $\chi' = \chi_0$, where $\chi_0$ is its value in a metallic phase. The spin quantization axis, $z$, is parallel to the so-called $b'$-axis. We show that the suggested order parameter explains why the upper critical field along the $b'$-axis exceeds all paramagnetic limiting fields, including that for a nonuniform superconducting state, whereas the upper critical field along the $a$-axis ($a \perp b'$) is limited by the Pauli paramagnetic effects [I. J. Lee, M. J. Naughton, G. M. Danner and P. M. Chaikin, Phys. Rev. Lett. 78, 3555 (1997)]. The triplet order parameter is in agreement with the recent Knight shift measurements by I. J. Lee et al. as well as with the early results on a destruction of superconductivity by nonmagnetic impurities and on the absence of the Hebel-Slichter peak in the NMR relaxation rate.

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Quasi-one-dimensional (Q1D) organic compounds (TMTSF)$_2$X ($X = $ PF$_6$, ClO$_4$, etc.) have been intensively investigated since the discovery of superconductivity$^{1-2}$ in the first organic superconductor (TMTSF)$_2$PF$_6$. From the beginning, it was clear that their properties are unusual. It was found$^{3-5}$ that superconductivity in (TMTSF)$_2$X ($X = $ PF$_6$, ClO$_4$) is destroyed by nonmagnetic impurities. This was interpreted in terms of a possible triplet pairing of electrons$^6$. Another unusual feature, the absence of the Hebel-Slichter peak in the $1/T_1$ NMR data in (TMTSF)$_2$X ($X = $ PF$_6$, ClO$_4$)$^{10,11,12}$, was prescribed$^{13}$ to the existence of zeros of a superconducting order parameter on the Q1D Fermi surfaces (FS). As was stressed$^{13}$, the early experiments$^{3-8,10,11}$ provided information only about an orbital part of the order parameter and could not distinguish between some triplet and singlet pairings$^{2,13}$.

To reveal triplet superconductivity, experimental tests which probe a spin part of an order parameter are essential. Among them, are: a surviving of triplet superconductivity in Q1D case$^{14-17}$ at magnetic fields higher than both the upper orbital critical field and the Clogston paramagnetic limit$^{18}$, observation of spin-wave excitations$^{15}$, the Knight shift measurements$^{12}$ and some others. Nowadays, interest in a possible triplet pairing has been renewed due to remarkable measurements of the upper critical fields (which are sensitive to a spin part of the order parameter) in (TMTSF)$_2$ClO$_4$ and in (TMTSF)$_2$PF$_6$ at $P \approx 6$ kbar by Naughton, Lee, Chaikin and Danner$^{19-21}$ and due to the theoretical analysis$^{16}$ of these experiments. The experimental fields along $b'$-axis (which are 3 times bigger$^{20,21}$ than the Clogston paramagnetic limit) were shown$^{16}$ to be even bigger than the paramagnetic limit$^{16,22}$ for the Larkin-Ovchinnikov-Fulde-Ferrell (LOFF) phase$^{23}$. Therefore, measurements$^{19-21}$ were interpreted$^{16,19-21}$ in term of triplet superconductivity. Recently, Lee et al.$^{12}$ have found no change of the Knight shift for $H || b'$ in a superconducting phase of (TMTSF)$_2$PF$_6$ at $P \approx 6$ kbar. This is consistent with the results$^{16,19-21}$ and strongly supports the triplet scenario$^{16,19-21}$ of superconductivity.

The goals of our paper are: 1) To calculate the paramagnetic limited field along $b'$-axis, $H_{b'}^c$, for the LOFF phase in a Q1D superconductor, taking account of both the paramagnetic$^{16}$ and orbital destructive effects against superconductivity. (We show that the calculated value of $H_{b'}^c$ is 4-5 times less than the experimental fields$^{20,21}$ in (TMTSF)$_2$PF$_6$); 2) To demonstrate that the value of $H_{b'}^c$ becomes consistent with$^{20,21}$ if we switch off the paramagnetic effects. (These indicate that an electron spin susceptibility along $b'$-axis, $\chi_{b'}$, at $T = 0$ is equal to its value in a metallic state, $\chi_0$, which is a distinct feature of triplet superconductivity$^{21,27}$); 3) To stress that the experimental critical fields$^{20,21}$ along the conducting chains (i.e., along $a$-axis), $H_{a}^c$, are strongly paramagnetically limited and thus the corresponding electron spin susceptibility $\chi_a \ll \chi_0$ at $T = 0$; 4) To show that the above described properties are naturally explained within the framework of a triplet superconductivity scenario with the following vector order parameter frozen into the crystalline lattice (i.e., the case of strong spin-orbit coupling$^{27}$):

$$\mathbf{d}(\mathbf{k}) = (d_a(\mathbf{k}) \neq 0, d_c(\mathbf{k}) = 0, d_d(\mathbf{k}) = 0); \ |d_a(\mathbf{k})| > |d_d(\mathbf{k})| \quad (1)$$

corresponding to the BCS-pair's wave function

$$\Psi(\mathbf{k}) = [-d_a(\mathbf{k}) + id_d(\mathbf{k})] | \uparrow \uparrow \rangle + [d_a(\mathbf{k}) + id_d(\mathbf{k})] | \downarrow \downarrow \rangle \quad (2)$$

and to the anisotropic spin susceptibility at $T = 0$:

$$\chi_{b'} = \chi_0 , \ \chi_a \ll \chi_0 \quad (3)$$

where $| \uparrow \rangle (| \downarrow \rangle )$ stands for a spin-up (spin-down) electron with respect to the quantization axis $z || b'$ [$a(x) \perp b'(x) \perp c'(y)$], the momentum $\mathbf{k}$ defines the position on the FS, $x$ is the easy axis for a spin direction in a spin-density-wave (SDW) phase of (TMTSF)$_2$PF$_6$. Thus, one may expect that the order parameter (1) is the most stable since it corresponds to the BCS pairs (2) only with $S_{b'} \equiv S_a = \pm 1$. At the end of the paper, we discuss some consequences of a
group theory classification of the possible triplet phases, including the most probable orbital part of the order parameter and a possibility to break the time reversal symmetry.

Q1D electron spectrum corresponds to two open sheets of the FS\cite{1,2}:

\[ \epsilon^\pm(p) = \pm v_F (p_a \mp p_F) - 2t_0 \cos(p_b b) - 2t_c \cos(p_c c), \]

where \( \pm \) stands for the right (left) sheet of the FS; \( v_F = t_a a/\sqrt{2} \) and \( p_F \) are the Fermi velocity and Fermi momentum, respectively; \( t_a \approx 1600 \, K, \) \( t_c \approx 200 \, K \) and \( t_c \approx 5 \, K; \) \( (\lambda = 1). \)

Singlet \( (S = 0) \) and triplet \( (S = 1) \) phases are characterized by the following wave functions of the BCS pair's\cite{27}:

\[ \psi_S(k, r) = (\mid \uparrow \downarrow \rangle - \mid \downarrow \uparrow \rangle) \psi(k, r), \quad S = 0; \quad (5) \]

\[ \psi_S(k, r) = \mid \uparrow \uparrow \rangle \langle \uparrow \downarrow |d_S(k, r) + id_T(k, r)| + \mid \downarrow \downarrow \rangle \langle \downarrow \uparrow |d_S(k, r) + id_T(k, r)|, \quad S = 1. \quad (6) \]

In Eqs. (5,6), \( S \) is the total spin of the BCS pair, \( r \) is its coordinate of a center of masses; \( \psi_S(k, r) = \psi_S(-k, r), \) \( d(k, r) = -d(-k, r). \)

At \( H \to 0, \) \( \psi(k, r) \) and \( d(k, r) \) do not depend on \( r. \) Electron spin susceptibility tensor, \( \chi_{ij}, \) at \( T = 0 \) for a singlet phase is \( \chi_{1,1} = 0 \) whereas for a triplet phase is given by\cite{27}:

\[ \chi_{ij} \equiv \chi_0 \left( \delta_{i,j} - \frac{d^*_T(k) d_T(k)}{d^*_S(k) d_S(k)} \right) \quad (7) \]

where \( \delta_{i,j} = 1 \) if \( i = j \) and \( \delta_{i,j} = 0 \) if \( i \neq j; \) \( \langle d(k)^2 \rangle_k = 1, \) \( \langle \ldots \rangle_k \) means an averaging over the FS. Here, we consider only unitary triplet phases\cite{27} (i.e., \( d_S(k) d^*_T(k) = d^*_S(k) d_T(k) \)).

At first we consider the case \( H \parallel b'(z). \) In singlet phase (5), superconductivity is destroyed by paramagnetic effects in arbitrary directed magnetic field. In a triplet phase (6), as it follows from Eq. (7), \( d_{ij}(k) \equiv d_{ij}(k) \) component is responsible for the deviation of the spin susceptibility \( \chi_{ij} \equiv \chi_{zz} \) from \( \chi_0). \)

If \( d_{ij}(k) \neq 0 \) there exist two related phenomena: the paramagnetic destructive mechanism against superconductivity and a change of the Knight shift at \( T < T_c(H). \) Let us calculate the upper critical field for \( H \parallel b'. \) By using a common approach\cite{28} to the upper critical field of a clean superconductor\cite{29} with open electron orbits and with one-component order parameter, it is possible to prove that Eq. (5) of Ref. \cite{28}:

\[ \Delta(x) = \frac{g}{2} \sqrt{2\pi T \Delta x} \int_{|x-x_1|>d} \frac{2\pi T d x_1}{\sqrt{2\pi T |x-x_1|}} J_0 \left( \frac{2\alpha B H(x-x_1) \Delta_S}{v_F} \right) \times J_0 \left( 2 \alpha \left( \frac{2\pi T \Delta x}{2v_F} \right) \right) \Delta(x_1), \quad (8) \]

is extended to a singlet phase \( \psi_S(k, r) \equiv f(k) \Delta(x) \) as well as to the triplet phases \( d_1(k, r) \equiv (d_a = 1, d_c = 0, d_{ij} = 0) f(k) \Delta(x) \) and \( d_2(k, r) \equiv (d_a = 0, d_c = 0, d_{ij} = 1) f(k) \Delta(x). \) Here, \( \left< |f(k)|^2 \right>_k = 1; \) \( g \) is an effective electron interaction constant, \( d \) is a cutoff distance; \( \alpha = \sqrt{x_0}/t_a, \) \( \omega_c = e v_F H c / \gamma; \) \( \lambda = 4 \epsilon_c / \omega_c; \) \( \mu_B \) is a Bohr magneton, \( e \) and \( c \) are the electron charge and the velocity of light, correspondingly; \( \Delta_S = 0 \) for \( d_1 \)-triplet phase. By solving Eq. (8) numerically for \( S_a = 1, \alpha = 0.17, \) \( |dH^{b'}/dT|_{Tc} \approx 2 \, T/K, \)

\( v_F = 10^5 \, cm/sec, \) \( t_c \approx 3K, \) \( T_c(0) = 1.14 \, K, \) \( c^* = 13.6 \, A \) (see Refs. \cite{1,2,19,21,29}) we found that the calculated value of the paramagnetic limited critical field, \( H^{b'}_{\text{cr}} \approx 1.3 - 1.4 \, T, \) is 4.5 times less than the experimental one\cite{20,21,23} (see Fig. \ref{Fig3}).

A similar analysis for \( d_2 \)-triplet phase (which is not paramagnetically limited) shows that superconductivity survives at \( H^{b'}_{\text{cr}} \approx 6 \, T \) and \( T \approx 0.26 - 0.26 \, K \) in qualitative agreement with experiments\cite{20,21} (see Fig. \ref{Fig3}). On the basis of the calculation of \( H^{b'}_{\text{cr}} \) and \( H^{b'}_{\text{cr}}, \) we can conclude that \( |d_S(k)| \neq |d_T(k)| = 0 \) in Eq. (7) and thus \( \chi_{zz} \equiv \chi_{zz} \equiv 0. \) Note that the recent Knight shift measurements\cite{12} are also in favor of \( \chi_{zz} < \chi_0 \) below \( T_c(H). \)

If we consider the case \( H \parallel a(x) \) then \( d_a \equiv d_{zz} \)-component of the order parameter (6) is responsible for the destructive paramagnetic effects against superconductivity and for the change of the Knight shift at \( T < T_c(H). \) Let us calculate the critical field for \( H \parallel a \) in the \( d_1(k) \equiv (d_a \neq 0, d_c = 0, d_{ij} = 0) \) triplet phase (which is paramagnetically limited). The corresponding linearized gap equation can be obtained from the common Eq. (5) of Ref. \cite{28}:

\[ \Delta(x) = \frac{g}{2} \int_{|x-x_1|>d} \frac{2\pi d x_1}{\sqrt{2\pi T |x-x_1|}} J_0 \left( \frac{2\pi T \Delta x}{2v_F} \right) \times J_0 \left( 2 \alpha \left( \frac{2\pi T \Delta x}{2v_F} \right) \right) \Delta(x_1), \quad (9) \]

where \( \gamma = t_a a / (2t_u b) \) Numerical solution of Eq. (9) (with the same values of parameters as Eq. (8)) shows that the best fitting of the data\cite{20,21} at \( H \leq 1.5 \, T \) (see Fig. \ref{Fig3}) corresponds to \( S_a \approx 0.9 \) (i.e., \( d_a = 0.9, \chi_{zz} \approx 0.2 \chi_0 < \chi_0) \) and \( |dH^{b'}/dT|_{Tc} \approx 8 \, T/K. \) The latter is in good agreement with the experimental slopes\cite{20,21} \( |dH^{b'}/dT|_{Tc} \approx 2 \, T/K \) since the value of \( t_c/t_a \approx 8.5 \) is known\cite{29}. Note that the accuracy of our calculations does not allow us to distinguish between the triplet phases with \( d_a = 0 \) and \( |d_a| > |d_c|. \)

Summarizing, our analysis of the experimental critical fields\cite{20,21} measured in (TMTSF)_2PF_6 at \( P \approx 6 \, kbar \) has shown that paramagnetic destructive effects against superconductivity do not affect \( H^{b'} \) whereas \( H^{a} \) is paramagnetically limited at \( H \leq 1.5 \, T. \) These are naturally explained within a triplet scenario of superconductivity\cite{10,16,19,21} with the triplet order parameter (1). We suggest to measure the Knight shift along the \( a \)-axis at \( H \leq 1.5 \, T \) and \( T < T_c(H) \) to prove the order parameter (1). Note that temperature dependence of the critical field along \( a \)-axis, \( H^{a}(T), \) changes drastically\cite{20,21} at \( H \geq 1.5 \, T. \) We speculate that at \( H \geq 1.5 \, T \) there may appear a triplet phase with \( d(k) \perp H, \) which minimizes the magnetic contribution to the free energy\cite{30}. Nevertheless, we cannot completely exclude another possibility - the appearance of the LOFF state at \( H \geq 1.5 \, T \) for \( H \parallel a. \) Note that our theoretical analysis of the critical fields is based on the the Fermi-liquid picture\cite{29} proved at \( P \approx 6 \, kbar \) in (TMTSF)_2PF_6. At higher
pressures, $P \approx 9.8 \text{ kbar}$, the behavior of $(\text{TMTSF})_2\text{PF}_6$ may deviate from the Fermi liquid one\textsuperscript{31}. At the end of the paper, we would like to make a few comments based on symmetry arguments. We classify the possible triplet phases in the case of strong spin-orbit coupling for orthorhombic ($D_{2h}$) and triclinic ($C_{1}$) point group symmetries (see Table I), where the matrix order parameter $\hat{\Delta}(k) = d_z(k)\tau_z$, $(\hat{\tau}_z = i\sigma_x\sigma_y; \hat{\sigma}_i$ are the Pauli matrices). As it seen from Table I, there are no degenerated orbital states, thus a time reversal symmetry is broken only if a nonunitary triplet phase appears\textsuperscript{27}. In our particular case, this happens when $d_y(k)d_x^*(k) \neq d_x^*(k)d_y(k)$. Using the expression for a gap in a quasi-particle spectrum\textsuperscript{27}, $\delta(k) = |d(k)|$ (the unitary case), it is possible to make sure that there are no generic phases with the lines of zeros on the FS in accordance with a common theorem\textsuperscript{32}. This is in agreement with the experimental data\textsuperscript{26,33} which seem to be in favor of fully gapped FS and against the existence of isolated zeros on the FS\textsuperscript{32}. Therefore, we speculate that the orbital part of the order parameter is likely $d_y(k) \sim d_y(k) \sim sgn(k_y)$ which corresponds to a fully gapped Q1D sheets of the FS. From Table I it is possible to conclude that, for a triclinic space group of $(\text{TMTSF})_2\text{PF}_6$, the most generic case is $d_y \neq 0$, $d_x \neq 0$ and $d_0 \neq 0$. However, it is known\textsuperscript{12,34} that the spin dependent interactions in a SDW phase of $(\text{TMTSF})_2\text{PF}_6$ (which has a common boundary with the superconducting phase) result in an alignment of spins along $b'$-axis. Therefore, it is natural to expect the form (1) for the superconducting order parameter corresponding to the absence of the BCS pairs with $\Delta_y = 0$ (see Eq. (2)).

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\begin{table}[h]
\centering
\begin{tabular}{ |c|c|c| }
\hline
Group & Representation & Order parameter $\Delta(k)$ \\
\hline
$D_{2h}$ & $A_{1u}$ & $Ak_\tau + Bk_y\tau_y + Ck_z\tau_z$ \\
 & $B_{1u}$ & $Ak_\tau + Bk_y\tau_x$ \\
 & $B_{2u}$ & $Ak_\tau + Bk_z\tau_x$ \\
 & $B_{3u}$ & $Ak_\tau + Bk_y\tau_y$ \\
\hline
$C_i$ & $A_u$ & $Ak_\tau + Bk_y\tau_y + Ck_z\tau_z + Dk_y\tau_x$
& & $+ Fk_\tau + Gk_\tau + Hk_y\tau_y + Ik_\tau_y$ \\
\hline
\end{tabular}
\caption{Triplet order parameter $\hat{\Delta}(k)$ for $D_{2h}$ and $C_i$ groups. (A-I are constants)}
\end{table}

[1] D. Jerome and H. J. Schultz, Adv. Phys. 4, 299 (1982).
[2] T. Ishiguro, K. Yamaji and G. Saito, Organic Superconductors (Second Edition, Springer-Verlag, Heidelberg, 1998).
[3] M.-Y. Choi et al., Phys. Rev. B 25, 6208 (1982).
[4] R. L. Green et al., Molec. Crystals.-Liq. Crystals 79, 183 (1982).
[5] S. Bouffard et al., J. Phys. C15, 2951 (1982).
[6] S. Tomic et al., J. Phys. J. Phys. 44, C3-1075 (1983).
[7] C. Coulon et al., J. Phys. (Paris) 43, 1721 (1982).
[8] F. Tsobnang et al., Phys. Rev. B 49, 15110 (1994).
[9] A. A. Abrikosov, J. Low Temp. Phys. 53, 359 (1983).
[10] M. Takigawa et al., J. Phys. Soc. Jpn. 56, 873 (1987).
[11] K. Hiruma, Master Thesis, Gakushuin University, Tokyo, Japan (1998).
[12] I. J. Lee et al., preprint cond-mat/0001332.
[13] Y. Hasegawa and H. Fukuyama, J. Phys. Soc. Jpn. 56, 877 (1987).
[14] A. G. Lebed, Pis’ma Zh. Eksp. Teor. Fiz. 44, 89 (1986) [JETP Lett. 44, 114 (1986)].
[15] L. N. Burlachkov et al., Europhys. Lett. 4, 941 (1987).
[16] A. G. Lebed, Phys. Rev. B 59, R721 (1999).
[17] N. Dupuis et al., Phys. Rev. Lett. 70, 2613 (1993).
[18] A. M. Clogston, Phys. Rev. B 46, 643 (1985); B. S. Chandrasekhar, Appl. Phys. Lett. 9, 266 (1962).
[19] I. J. Lee et al., Synth. Metals 70, 747 (1995); Appl. Supercond. 2, 753 (1994).
[20] M. J. Naughton et al., Synth. Metals 85, 1481 (1997).
[21] I. J. Lee et al., Phys. Rev. Lett. 78, 3555 (1997).
[22] The paramagnetic limiting field in Q1D case\textsuperscript{16} differs from the Clogston limit\textsuperscript{18} due to the possibility of the LOFF state formation\textsuperscript{23}.
[23] A. I. Larkin and Yu. V. Ovchinnikov, Zh. Eksp. Teor. Fiz. 47, 1136 (1964) [Sov. Phys. JETP 20, 762 (1965)]; P. Fulde and R. Ferrell, Phys. Rev. 135A, 550 (1964).
[24] The other effects which can increase the paramagnetic limits seem to be weak. Indeed, spin-orbital scattering is not significant\textsuperscript{20,21,25}; the specific heat jump is close to its weak coupling BCS value\textsuperscript{26}.
[25] L. P. Gor’kov and D. Jerome, J. Phys. (Paris) Lett. 46, L643 (1985).
[26] P. Garinge et al., J. Phys. (Paris) Lett. 43, L147 (1982).
[27] V. P. Mineev and K. V. Samokhin, Introduction to Unconventional Superconductivity (Gordon and Breach, Amsterdam, 1999); M. Sigrist and K. Ueda, Rev. Mod. Phys. 63, 239 (1991).
[28] A. G. Lebed, J. of Superconductivity 12, 453 (1999).
[29] I. J. Lee and M. J. Naughton, Phys. Rev. B 58, R13343 (1998).
[30] K. Machida et al., J. Superconductivity 12, 557 (1999).
[31] G. M. Danner and P. M. Chaikin, Phys. Rev. Lett. 18, 4690 (1995).
[32] G. E. Volovik and L. P. Gor’kov, Zh. Eksp. Teor. Fiz. 88, 1412 (1985) [Sov. Phys. JETP 61, 843 (1985)]; E. I. Blount, Phys. Rev. B 32, 2935 (1985).
[33] S. Belin and K. Behnia, Phys. Rev. Lett. 79, 2125 (1997).
[34] J. M. Delrieu et al., J. Phys. (Paris) 47, 839 (1986); L. P. Le et al., Europhys. Lett. 15, 547 (1991).
FIG. 1. Circles stand for the critical magnetic fields along $b'$-axis: open circles show experimental curve$^{20,21}$, a full circle corresponds to the calculated paramagnetically limited value of $H_{b}'$ at $T = 0$ in a singlet superconductor whereas crossed circles show the calculated non-paramagnetically limited critical fields $H_{b}'(T)$ for a triplet order parameter (1). Triangles stand for the experimental critical fields$^{20,21}$ along $a$-axis, $H_{a}'(T)$, ($a \perp b'$). In the inset, the experimental values$^{20,21}$ of $H_{b}'(T)$ are shown in comparison with the calculated paramagnetically limited field (full line) for a triplet order parameter (1) (see the text).