Upper critical field $H_{c2}$ in Bechgaard salts $(TMTSF)_2PF_6$

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Abstract. – The symmetry of the superconducting order parameter in Bechgaard salts is still unknown, though the triplet pairing is well established by NMR data and large upper critical field $H_{c2}(0) \sim 5$ Tesla for both $\vec{H} \parallel a$ and $\vec{H} \parallel b'$. Here we examine the upper critical field of a few candidate superconductors within the standard formalism. The present analysis suggests strongly chiral f-wave superconductor somewhat similar to the one in Sr$_2$RuO$_4$ is the most likely candidate.

Introduction. – The Bechgaard salts (TMTSF)$_2$PF$_6$ is the first organic superconductor discovered in 1980 [1]. For a long time the superconductivity is believed to be conventional s-wave [2]. Recently the symmetry of the superconducting energy gap becomes the central issue [3, 4]. The upper critical field at $T = 0K$, $H_{c2} \sim 5$ Tesla for both $\vec{H} \parallel a$ and $\vec{H} \parallel b'$ for both (TMTSF)$_2$PF$_6$ [5] and (TMTSF)$_2$ClO$_4$ [6] are clearly beyond the Pauli limit [7, 8] indicating the triplet pairing. More recently the NMR data from (TMTSF)$_2$PF$_6$ [9] indicates clearly the triplet pairing. Therefore the candidates for the superconductivity in Bechgaard salts are more likely within p-wave and f-wave superconductors. In the following we shall examine the upper critical field of these superconductors following the standard method initiated by Gor’kov [10] and extended by Luk’yanchuk and Mineev [11] for unconventional superconductors. Also we take the quasiparticle energy in the normal state as in the standard model for Bechgaard salts [2]

$$\xi(k) = v(|k_a| - k_F) - 2v_b \cos bk - 2v_c \cos ck$$

(1)

with $v : v_b : v_c \sim 1 : 1/10 : 1/300$ and $v_b = \sqrt{2}t_b b$ and $v_c = \sqrt{2}t_c c$. There are earlier analysis of $H_{c2}$ of Bechgaard salts starting from the one dimensional models [12, 13]. However, those models predict diverging $H_{c2}(T)$ for $T \rightarrow 0K$ or the reentrance behaviour, which have not been observed in the experiments [5, 6]. Also, the quasilinear T dependence of $H_{c2}(T)$ in both (TMTSF)$_2$PF$_6$ and (TMTSF)$_2$ClO$_4$ is very unusual. Among the models we have considered,
Fig. 1 – $|\Delta(\vec{k})|$ of chiral f-wave and chiral $f'$-wave SC are sketched in a) and b) respectively.

The chiral $f'$-wave superconductor with $\Delta(\vec{k}) \sim \left( \frac{1}{\sqrt{2}} sgn(k_a) + i \sin \chi_2 \right) \cos \chi_2$, looks most promising, where $\chi_1 = \tilde{b} \cdot \vec{k}$ and $\chi_2 = \tilde{c} \cdot \vec{k}$ where $\tilde{b}$ and $\tilde{c}$ are crystal vectors.

Also if the superconductor belongs to one of the nodal superconductors [14] and if nodes lay parallel to $\vec{k}_c$ within the two sheets of the Fermi surface, the angle dependent nuclear spin relaxation rate $T_{11}^{-1}$ in a magnetic field rotated within the $b' - c^*$ plane will tell the nodal directions.

Before proceeding, we show $|\Delta(\vec{k})|$ os two chiral f-wave superconductors in Fig.1a) and b), where $|\Delta(k)| \sim \left[ (1 + \cos 2\chi_1)(1 - \frac{1}{2} \cos 2\chi_2) \right]^{\frac{1}{2}}$ and $|\Delta(k)| \sim \left[ (1 + \cos 2\chi_2)(1 - \frac{1}{2} \cos 2\chi_2) \right]^{\frac{1}{2}}$ for chiral $f_1$ and chiral $f_2$ respectively.

Upper critical field for $\vec{H} \parallel \vec{b}'$. – In the following we neglect the spin component of $\bar{\Delta}(\vec{k})$. Most likely the equal spin pairing is realised in Bechgaard salts as in Sr$_2$RuO$_4$ [4]. In this case the spin component is characterised by a unit vector $\hat{d}$. Also $\hat{d}$ is most likely oriented parallel to $\vec{c}^\ast$. Let’s assume $\hat{d} \parallel \vec{c}^\ast$, though $H_{c2}(T)$ is independent of $\hat{d}$ as long as the spin orbit interaction is negligible. Experimental data from both UPt$_3$ and Sr$_2$RuO$_4$ indicate that the spin-orbit interactions in these systems are not negligible but extremely small [15]. We consider a variety of triplet superconductors (see Fig.1):

A. Simple p-wave SC: $\bar{\Delta}(k) \sim sgn(k_a)$. Following [16] the upper critical field is determined by

$$- \ln t = \int_0^\infty \frac{du}{\sinh u} (1 - K_1)$$

(2)

$$-C \ln t = \int_0^\infty \frac{du}{\sinh u} (C - K_2)$$

(3)

where

$$K_1 = \langle e^{-\alpha u^2} + \frac{\alpha^2 u^2}{1 + 2 C \rho^2 u^4 s^4} \rangle$$

(4)
Fig. 2 - Normalised $H_c^2(t)$ and $C(t)$ for $\vec{H} \parallel \vec{b}'$ are shown in a) and b) respectively. Here solid, dashed and dotted lines are chiral f’-wave, chiral p-wave and simple p-wave respectively.

$$K_2 = \langle e^{-\rho u^2}|s|^2 \left( \frac{1}{6} \rho^2 u^4 s^4 + C \left( 1 - 8 \rho u^2 |s|^2 + 12 \rho^2 u^4 |s|^4 - \frac{16}{3} \rho^3 u^6 |s|^6 + \frac{2}{3} \rho^4 u^8 |s|^8 \right) \right) \rangle (5)$$

and $t = \frac{T_c}{T_c} \rho = \frac{v_a v_c e H_c^2(T)}{2(2\pi T_c)^2}$, $s = \frac{1}{\sqrt{2}} \text{sgn}(k_a) + i \sin \chi_2$, $\chi_2 = \vec{c} \cdot \vec{k}$ and $\langle \ldots \rangle$ means average over $\chi_2$. Here $v_a, v_c$ are the Fermi velocities parallel to the a axis and the c axis respectively.

Here we assumed that $\Delta(\vec{r})$ is given by [16]

$$\Delta(\vec{r}) \sim (1 + C(a^+)^4)$$

and $t = \frac{T_c}{T_c} \rho = \frac{v_a v_c e H_c^2(T)}{2(2\pi T_c)^2}$ is the Abrikosov state [17] and $a^+ = \frac{1}{\sqrt{2} e H_a} (-i \partial_z - \partial_x + 2 i e H z)$ is the raising operator.

Then in the vicinity of $t \rightarrow 1$ we find

$$\rho = \frac{v_a v_c e H_c^2(0)}{2 (2\pi T_c)^2} = 0.1583$$

and $C = -0.031$. From these we obtain

$$\Delta(\vec{r}) \sim (s + C s^* (a^+)^2)$$

Both $\rho(t)$ and $C(t)$ are evaluated numerically and shown in Fig. 2a) and b) respectively. Here $\rho(t) = t^2 \rho(t) = v_a v_c e H_c^2(0) / 2(2\pi T_c)^2$.

B. Chiral p-wave SC: $\Delta(k) = 1/\sqrt{2} \text{sgn}(k_a) + i \sin(\chi_2)$. Here $1/\sqrt{2} \text{sgn}(k_a) + i \sin(\chi_2)$ is the analogue of $e^{i\phi}$ in the 3D systems in the quasi 1D system. For a chiral state the Abrikosov function is written as [18]
where $s = \frac{1}{\chi_2} \text{sgn}(k_a) + \iota \sin(\chi_2)$. Then we obtained eq. 3 with

$$K_1 = \langle e^{-\rho u^2}|s|^2 \rangle \left( |s|^2 - 2C|s|^4 \right)$$  \hspace{1cm} (10)

$$K_2 = \langle e^{-\rho u^2}|s|^2 \rangle \left( -|s|^4 + C|s|^2 \left( 1 - 4\rho u^2|s|^2 + 2\rho^2u^4|s|^4 \right) \right)$$  \hspace{1cm} (11)

and the same expressions for $t$, $\rho$, etc.

For $t \rightarrow 1$ we find $C = 1 - \sqrt{1.5} = -0.2247$ and $\rho = 0.3838(-\ln t)$.

On the other hand, for $t \rightarrow 0$ we obtain $C = -0.3660$ and $\rho_0 = 0.27343$.

From these we obtain $h(0) = 0.71324$. We obtain $\rho(t)$ and $C(t)$ numerically. They are shown in Fig. 2a) and b) respectively.

C. Chiral f-wave SC: $\hat\Delta(k) \sim \tilde{d}s \cos \chi_1$. $H_{c2}(t)$ is determined from eq. 3 where now:

$$K_1 = \langle (1 + \cos 2\chi_1) e^{-\rho u^2}|s|^2 \rangle \left( |s|^2 - 2\rho u^2|s|^4 \right)$$  \hspace{1cm} (12)

$$K_2 = \langle (1 + \cos 2\chi_1) e^{-\rho u^2}|s|^2 \rangle \left( -\rho u^2|s|^4 + C|s|^2 \left( 1 - 4\rho u^2|s|^2 + 2\rho^2u^4|s|^4 \right) \right)$$  \hspace{1cm} (13)

Here now $\langle \dots \rangle$ means the average over both $\chi_1$ and $\chi_2$. Then it is easy to see that the chiral f-wave SC has the same $H_{c2}(t)$ and $C(t)$ as the chiral p-wave SC, since the variable $\chi_1$ is readily integrated out.

D. Chiral f’-wave SC: $\hat\Delta(k) \sim \tilde{d}s \cos \chi_2$. Now we have a set of equations similar to the chiral f-wave except $1 + \cos 2\chi_1$ in both eqs. 3 has to be replaced by $\frac{1}{3}(1 + \cos 2\chi_1)$. Then we obtain for $t \rightarrow 1$ $C = -0.2247$ and $\rho = 0.5181(-\ln t)$. On the other hand, for $t \rightarrow 0$ we find $C = -0.3660$ and $\rho_0 = 0.3734$.

We show $\rho_0$ and $C(t)$ of the chiral f’-wave in Fig. 2a) and b) respectively.

Note that $C(t)$ is the same for three chiral states (chiral p-wave, chiral f-wave and chiral f’-wave) as well as chiral p-wave studied in [18].

Therefore for the magnetic field $\vec{H} \parallel \vec{b'}$, the chiral f’-wave have the largest $H_{c2}(t)$ if we assume $T_c$ and $v$, $v_c$ are the same. Also $H_{c2}(t)$ of these states are closest to the observation.

Upper critical field for $\vec{H} \parallel \vec{a}$.

A. Simple p-wave SC: $\Delta(\vec{k}) = \text{sgn}(k_a)$. The equation for $H_{c2}(t)$ is given by [16] and can be written as in eq. 3 with

$$K_1 = \langle e^{-\rho u^2}|s|^2 \rangle \left( 1 + 2C\rho^2u^4|s|^4 \right)$$  \hspace{1cm} (14)

$$K_2 = \langle e^{-\rho u^2}|s|^2 \rangle \left( \rho^2 u^4|s|^4 + C \left( 1 - 8\rho u^2|s|^2 + 12\rho^2u^4|s|^4 \right) \right)$$  \hspace{1cm} (15)

where $t = \frac{T_c}{T'}$, $\rho = \frac{\nu_0\nu_HH_{c2}(t)}{2(2\pi T)^2}$ and $s = \sin\chi_1 + \iota \sin\chi_2$ with $\chi_1 = \tilde{b}k$ and $\chi_2 = \tilde{c}k$.

Then for $t \rightarrow 1$, we find $C = -\frac{93}{265} \rho$ and $\rho = \frac{2}{T_c(3\beta)}(-\ln t) = 0.2377(-\ln t)$. While for $t \rightarrow 0$ $C = \frac{3}{2\beta_0} - \sqrt{\left( \frac{3}{2\beta_0} \right)^2 + \frac{1}{12}} = -0.0170129$ and $\rho_0 = \frac{\nu_0\nu_HH_{c2}(0)}{2(2\pi T)^2} = \frac{1}{4\gamma} \exp |\alpha_0 + 2C\beta_0| = 0.1751209$, where $\alpha_0 = -\langle |\ln s|^2 \rangle = 0.220051$ and $\beta_0 = -\langle \frac{s^4}{|s|^4} \rangle = \frac{4}{3} - 1 = 0.1700$. From these we obtain $h(0) = 0.73673$.

Both $h(t)$ and $C(t)$ are evaluated numerically and we show them in Fig. 3a) and b) respectively.
B. Chiral p-wave SC: \( \Delta(k) \sim \left( \frac{1}{\sqrt{2}} \text{sgn}(k_a) + i \sin \chi_2 \right) \). Now \( H_{c2}(t) \) is determined by a similar set of equations as in sec. 1.B. In particular we find for \( t \to 1 \) \( C = -0.027735 \) and \( \rho = 0.212598 (\ln t) \) while for \( t \to 0 \) \( C = -0.067684 \) and \( \rho_0 = 0.139672 \). We obtain \( h(0) = 0.6566 \). We show \( h(t) \) and \( C(t) \) in Fig. 3 a) and b) respectively.

C. Chiral f-wave SC: \( \hat{\Delta}(k) \sim \hat{\Delta}_s \cos \chi_1 \). Again we use a similar set of equations as those discussed in sec. 1.C, we find for \( t \to 1 \) \( C = -0.0356236 \) and \( \rho = 0.2744495 (\ln t) \) while for \( t \to 0 \) \( C = 0.1920 \) and \( \rho_0 = 0.6997 \). Both \( h(t) \) and \( C(t) \) are evaluated numerically and shown in Fig. 3 a) and b).

D. Chiral f'-wave SC: \( \hat{\Delta}(k) \sim \hat{\Delta}_f \cos \chi_2 \). Now we find for \( t \to 1 \) \( C = -0.05 \) and \( \rho = -0.2910 (\ln t) \), while for \( t \to 0 \) \( C = -0.1019 \) and \( \rho_0 = 0.2090 \).

We have shown again \( h(t) \) and \( C(t) \) in Fig. 3 a) and b) respectively.

Comparing these results with \( H_{c2}(T) \) from (TMTSF)$_2$PF$_6$ and (TMTSF)$_2$ClO$_4$ [4, 5], we can conclude both \( \vec{H} \parallel \vec{a} \) and \( \vec{H} \parallel \vec{b} \) the chiral f'-wave SC is most consistent with experimental data. In particular these states have relatively large \( h(0) \) (see Table I). On the other hand almost the same \( H_{c2}(0) \) for \( \vec{H} \parallel \vec{b} \) and \( \vec{H} \parallel \vec{a} \) has to be still accounted.

Nodal lines in \( \Delta(\vec{k}) \). - We have seen that from the temperature dependence of \( H_{c2}(T) \), we deduce the chiral f-wave and chiral f' are the most favourable. They have nodal lines on the Fermi surface (i.e. the \( \chi_1 - \chi_2 \) plane), the chiral f-wave SC at \( \chi_1 = \pm \frac{\pi}{2} \), while chiral f'-wave SC at \( \chi_2 = \pm \frac{\pi}{2} \).

These nodal lines may be detected if the nuclear spin relaxation rate is measured in a magnetic field rotated within the \( b - c^* \) plane.

Following the standard procedure given in [14] the quasiparticle density of states in the vortex state for \( T \ll T_c \) and \( E = 0 \) is given by

\[
N \left( 0, \vec{H} \right) = \frac{2}{\pi^2} \varepsilon^2 \sqrt{\varepsilon H} \left( 1 + \cos \theta^2 \sin \chi_{10}^2 \right)^{\frac{1}{2}}
\]

(16)
where $\chi_{10}$ is the position of the nodal line on the $\chi_{10}$ axis. So for the chiral f-wave SC we find $\chi_{10} = \frac{\pi}{2}$ and $N \left( \chi_{10}, \vec{H} \right)$ exhibits the simple angular dependence. On the other hand when nodal lines are on the $\chi_{2}$ axis, the $\theta$ dependence will be too small to see. Finally this gives

$$T^{-1}_1 \left( \vec{H} \right) / T_N^{-1} = \left( \frac{2}{\pi^2} \right)^2 \vec{v}^2 \left( eH \right) (1 + \cos^2 \theta)$$

(17)

for the chiral f-wave SC.

We show the $\theta$ dependence of $T^{-1}_1$ in Fig. for a few candidates. The chiral f-wave SC has the strongest $\theta$ dependence (solid line) while the chiral h-wave SC (dashed line) and the chiral p-wave SC (dotted line) have a similar $\theta$ dependence.

Concluding remarks. – We have computed the upper critical field of Bechgaard salts for a variety of model superconductors with the standard microscopic theory. We find: a) Assuming all these superconductors have the same $T_c$, the chiral $f'$-wave SC ($\Delta(\vec{k}) \sim \left( \frac{1}{\sqrt{2}} \text{sgn}(K_a) + i \sin \chi_2 \right) \cos \chi_2$) appears to be the most favourable with largest $H_{c2}$'s for both $\vec{H} \parallel b'$ and $\vec{H} \parallel a$; b) however, none of these states exhibit the quasi T linear dependence of $H_{c2}(T)$ as observed in [4]; c) Also the present theory predicts $H_{c2}(0) \sim (v v_c)^{-1}$ and $(v_b v_c)^{-1}$ for $\vec{H} \parallel b'$ and $\vec{H} \parallel a$ respectively. This means $H_{c2}(0)$ for $\vec{H} \parallel a$ is about 5 time larger than the one for $\vec{H} \parallel b'$ contrary to observation; d) from $H_{c2}(0) \sim 5T$ and $T_c = 1.5K$ we can extract $V^2 = \vec{v} v_c \sim 1.5 \times 10^4 \text{cms}^{-1}$, consistent with the known values of $v$, $v_c$.

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REFERENCES

[1] Jerome D., Mazard A., Ribault M. and Bechgaard K., J. Phys (France) Lett, 41 (1980) L95
[2] Ishihuro T., Yamaji K. and Saito G., Organic Superconductors, Springer-Verlag (Berlin 1999)
[3] Sigrist M. and Ueda K., Rev. Mod. Phys., 63 (1991) 239
[4] Maki K., Haas S., Parker and Won H., Chinese J. Phys, 43 (2005) 532
Fig. 4 - The angle dependent nuclear spin relaxation rate for a few nodal superconductors is shown. (Chiral f-wave, chiral h-wave and chiral p-wave are represented in solid, dashed and dotted lines.)

[5] Lee I.J., Chaikin P.M. and Naughton M.J., Phys. Rev. B, 63 (2002) R180502
[6] Oh J.I. and Naughton M.J., Phys. Rev. Lett., 92 (2004) 067001
[7] Clogston A.M., Phys. Rev. Lett., 9 (1967) 266
[8] Chandrasekhar B.S., Appl. Phys. Lett., 1 (1962) 7
[9] Lee I.J., Brown S.E., Clark W.G., Strouse M.J., Naughton M.J., Kang W. and Chaikin P.M., Phys. Rev. Lett., 88 (2002) 017004
[10] Gor’kov L.P., Soviet Phys. JETP, 10 (1960) 59
[11] Luk’yanchuk I. and Mineev V.P., Soviet Phys. JETP, 66 (1987) 1168
[12] Lebed A.G., JETP Lett, 44 (1986) 114
[13] Depuis N., Mantambaux G. and Sa de Melo C.A.R., Phys. Rev. Lett., 70 (1993) 2613
[14] Won H., Haas S., Parker D., Telang S., Vanyolos A. and Maki K., Lectures on the Physics of Highly Correlated Electron Systems IX, AIP Conference Proceedings 789 (Melville 2005)
[15] Maki K., Haas S., Parker D. and Won H., cond-mat/0504635, (2005)
[16] Won H. and Maki K., Europhys. Lett., 30 (1995) 421 Phys. Rev. B, 53 (1996) 5927
[17] Abrikosov A.A., Soviet Phys. JETP, 5 (1957) 1174
[18] Wang G.F. and Maki K., Europhys. Lett., 45 (1999) 71