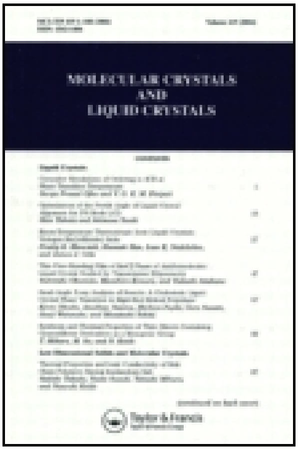

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Possibility of Coexistence of Spin Density Wave and Superconductivity in Organic Conductor $(TMTSF)_2PF_6$

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POSSIBILITY OF COEXISTENCE OF SPIN DENSITY WAVE AND SUPERCONDUCTIVITY IN ORGANIC CONDUCTOR $(TMTSF)_2PF_6$

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A theory for the coexistence problem of the spin density wave (SDW) and superconductivity (SC) in highly anisotropic materials is presented. On the basis of a simplified electronic band model a Hartree-Fock approximation is applied. It is concluded that SDW is precluded when SC developes at a higher temperature. When the SDW onset temperature is higher than that of SC, these long range orders generally coexist unless two orders interchange by a first order phase transition. Discussions on possible phase diagrams for $(TMTSF)_2PF_6$ under pressure are given.

INTRODUCTION

Newly synthesized organic conducting salts[1] $(TMTSF)_2X$ (tetramethyltetraselenafulvalene, $X = PF_6$, ClO_4, AsF_6, SbF_6 and TaF_6) attract much attention recently. They are reported to be extremely anisotropic materials and so called quasi-one dimensional conductors. They exhibit a metal=semiconductor (MS) transition at ambient pressure. In $(TMTSF)_2PF_6$, which is studied most extensively from experimental side, the pressure induced superconductivity ($P = 12$ k bar) is observed at $T = 1.1$ K[2]. Recently it is found that the superconductivity ($T_c \simeq 1.1$ K) persists down to $P = 6.5$ k bar and the MS transition ($T_{MS} \sim 6$K) is found[3] slightly above T_c. Susceptibility measurement[4] unambiguously show that the spin density wave (SDW) causes the MS transition.

The purpose of this paper[5] is to investigate the interplay between superconductivity (SC) and SDW. Previously[6] we have considered the SDW superconductivity exhibited by ternary rare earth compounds in which rare earth atoms have permanent magnetic moments and align antiferromagnetically at a temperature lower than T_c. The present conductor $(TMTSF)_2PF_6$ is quite different in the points that there is no permanent magnetic moments, the magnetic electrons should be itinerant in nature and the electronic band structure is very anisotropic. Therefore we must take account the two long range orders (SDW and SC) in the same footing. This situation is rather similar to the cases of A-15 type compounds[7] and layered type transition-metal dichalcogenides[8] where the conduction electrons play two roles of the charge density wave (CDW) and SC states.

Here following Bilbro and McMillan[7] we take a three dimensional anisotropic electron band model rather than purely mathematical one-dimensional interacting electron model[9]. Because several experiments[10] strongly indicate that $(TMTSF)_2PF_6$ is a multi-dimensional system.

MODEL HAMILTONIAN AND MEAN FIELD APPROXIMATION

We devide the momentum space in the Fermi surface into two region 1 and 2. In the region 1 the Fermi surface satisfies a certain nesting condition which allows the SDW gap formation. In the remaining region of the Fermi surface, denoted as the region 2, the SC energy gap is allowed to open. The model Hamiltonian in the mean field approximation is given by

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{SDW} + \mathcal{H}_{BCS} \tag{2.1}$$

$$\mathcal{H}_0 = \sum_k \sum_\sigma \epsilon_k C^+_{k\sigma} C_{k\sigma} \tag{2.2}$$

$$\mathcal{H}_{SDW} = -\sum_{k\in \text{region 1}} \sum_\sigma (\sigma M C^+_{k\sigma} C_{k+Q\sigma} + h.c.) \tag{2.3}$$

$$\mathcal{H}_{BCS} = -\sum_k (\Delta C^+_{k\uparrow} C^+_{-k\downarrow} + h.c.)\,. \tag{2.4}$$

The self-consistent equations for the sublattice magnetization M of the SDW state and the superconducting order parameter Δ are given by

$$M = \frac{I}{2} \sum_{k\in \text{region 1}} \sum_\sigma \sigma \langle C^+_{k\sigma} C_{k+Q\sigma} \rangle \tag{2.5}$$

and

$$\Delta = g \sum_{k} \langle C_{-k\downarrow} C_{k\uparrow} \rangle \tag{2.6}$$

where I is the exchange integral and g is the effective attractive BCS interaction.

Utilizing the thermal Green functions such as $\langle\langle C_{k\uparrow}; C^{+}_{k\uparrow}\rangle\rangle$, $\langle\langle C^{+}_{-k\downarrow}; C^{+}_{k\uparrow}\rangle\rangle$, $\langle\langle C_{k+Q\downarrow}; C^{+}_{k\uparrow}\rangle\rangle$ and $\langle\langle C^{+}_{-k-Q\downarrow}; C^{+}_{k\uparrow}\rangle\rangle$ to diagonalize eq.(2.1). The solution yields the following self-consistent equations:

$$\ln\frac{T}{T_{s0}} = 2\pi T \sum_{\omega_n \geq 0} \left[\frac{1}{2M} \left(\frac{M+\Delta}{\sqrt{\omega_n^2 + (M+\Delta)^2}} + \frac{M-\Delta}{\sqrt{\omega_n^2 + (M-\Delta)^2}} \right) - \frac{1}{\omega_n} \right] \tag{2.7}$$

and

$$\ln\frac{T}{T_{c0}} = \frac{N_1(0)}{N(0)} 2\pi T \sum_{\omega_n \geq 0} \left[\frac{1}{2\Delta} \left(\frac{\Delta+M}{\sqrt{\omega_n^2 + (\Delta+M)^2}} + \frac{\Delta-M}{\sqrt{\omega_n^2 + (\Delta-M)^2}} \right) - \frac{1}{\omega_n} \right]$$

$$+ \frac{N_2(0)}{N(0)} 2\pi T \sum_{\omega_n \geq 0} \left(\frac{1}{\sqrt{\omega_n^2 + \Delta^2}} - \frac{1}{\omega_n} \right) \tag{2.8}$$

where $N_1(0)$ $(N_2(0))$ is the density of states for the region 1 (region 2) at the Fermi energy, and $N(0)$ is the total density of states. $T_{s0}(T_{c0})$ is the onset temperature of SDW (SC) without SC (SDW).

FREE ENERGY AND ORDER PARAMETER EXPANSION

In order to discuss the phase stability and interplay between SDW and SC, we need the free energy $F(g.I)$ in the presence of two order parameters. We start with the following mathematical identity:

$$F(g,I) = F(0,0) + \int_0^g \frac{\partial F(g',I)}{\partial g'} dg' + \int_0^I \frac{\partial F(0,I')}{\partial I'} dI' . \tag{3.1}$$

Using the self-consistent eqs. (2.7) and (2.8), we evaluate the integrations as

$$\delta F(\Delta, M) = F(\Delta, M) - F(0,0)$$

$$= N(0)\Delta^2 \ln\frac{T}{T_{c0}} + N_1(0) M^2 \ln\frac{T}{T_{s0}}$$

$$-2N_1(0)\pi T\sum_{n=0}^{\infty}\left\{\sqrt{\omega_n^2+(\Delta+M)^2}+\sqrt{\omega_n^2+(\Delta-M)^2}-2\omega_n-\frac{\Delta^2+M^2}{\omega_n}\right\}$$

$$-4N_2(0)\pi T\sum_{n=0}^{\infty}\left\{\sqrt{\omega_n^2+\Delta^2}-\omega_n-\frac{\Delta^2}{2\omega_n}\right\} \qquad (3.2)$$

In order to understand the nature of the phase transition at the superconducting onset temperature T_c in the presence of SDW, we examine the free energy difference $\delta F(\Delta,M)$ near T_c by expanding it in terms of power of Δ. From eq.(3.2) $\delta F(\Delta,M)$ is expanded to the forth order of Δ as

$$\delta F(\Delta,M)=N(0)\Delta^2\ln\frac{T}{T_c}+\frac{1}{2}\beta_1 N(0)\Delta^4+F(0,M)$$

$$F(0,M)=N_1(0)M^2\ln\frac{T_c}{T_{s0}}-4N_1(0)\pi T_c\sum_{n=0}^{\infty}\left(\sqrt{\omega_n^2+M^2}-\omega_n-\frac{M^2}{2\omega_n}\right) \qquad (3.3)$$

where

$$\beta_1(M)=\frac{N_2(0)}{N(0)}2\pi T_c\sum_{n=0}^{\infty}\frac{1}{\omega_n^3}+\frac{N_1(0)}{N(0)}2\pi T_c\sum_{n=0}^{\infty}\frac{\omega_n^2(\omega_n^2-4M^2)}{(\omega_n^2+M^2)^{7/2}} \qquad (3.4)$$

When $T_c \ll T_{s0}$, the condition for $\beta_1(M)<0$, which means a first order phase transition at $T=T_c$, is approximately given by

$$\frac{N_1(0)}{N_2(0)} > 2\left(\frac{T_{s0}}{T_c}\right)^2 \qquad (3.5)$$

The second order transition at T_c may be realized when T_c/T_{s0} becomes small.

ONSET TEMPERATURES OF SDW AND SC STATES

Let us now calculate the onset temperatures of the SC and SDW states. First we consider the case $T_{c0} > T_{s0}$. At $T=T_{s0}$ eqs. (2.7) and (2.8) are rewritten as

$$\frac{1}{IN_1(0)}=2\pi T_{s0}\sum_{0\le\omega_n<E_B}\frac{\omega_n^2}{[\omega_n^2+\Delta^2(T_{s0})]^{3/2}} \qquad (4.1)$$

$$\frac{1}{gN(0)}=2\pi T_{s0}\sum_{0\le\omega_n<\omega_D}\frac{1}{\sqrt{\omega_n^2+\Delta^2(T_{s0})}} \qquad (4.2)$$

where we have put $M = 0$ and $T \to T_{s0}$. $E_B(\omega_D)$ is the energy cut-off for SDW (SC). In the weak coupling approximation ($\Delta \ll \omega_D$) eqs. (3.1) and (3.2) give

$$\left[\frac{\Delta(T_{s0})}{2\pi T_{s0}}\right]^2 \sum_{n=0}^{\infty} \frac{1}{\left[(n+\frac{1}{2})^2 + \left(\frac{\Delta(T_{s0})}{2\pi T_{s0}}\right)^2\right]^{3/2}} = \ln\frac{T_{s0}}{T_{c0}} \quad (4.3)$$

This is not satisfied for $T_{s0} < T_{c0}$. The SDW is never realized once the SC appears at a higher temperature. Therefore the two long orders never coexist in the case.

Let us consider the case $T_{c0} < T_{s0}$. The superconducting transition temperature T_c in the presence of the SDW is generally lower than T_{c0} . When a second order phase transition occurs at T_c , we take $\Delta \to 0$ limit in eqs.(2.7) and (2.8), that is,

$$\ln\frac{T_c}{T_{c0}} = \frac{N_1(0)}{N(0)} \sum_{n=0}^{\infty} \left\{ \frac{1}{\left[(n+\frac{1}{2})^2 + \left(\frac{M(T_c)}{2\pi T_c}\right)^2\right]^{1/2}} - \frac{1}{n+\frac{1}{2}} \right\} \quad (4.4)$$

which determines T_c implicitly . In the weak coupling approximation ($M \ll E_B$) T_c is approximately given by

$$T_c/T_{c0} = \left(T_{c0}/T_{s0}\right)^{N_1(0)/N_2(0)} \quad (4.5)$$

We depict the curves of T_c/T_{c0} vs T_{c0}/T_{s0} calculated numerically in Fig.1. Note that if the portion

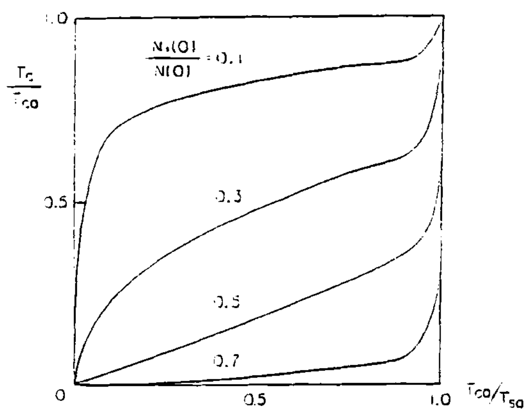


FIGURE 1 The depression of the superconducting transition temperature T_c as a function of T_{c0}/T_{s0} , which is calculated numerically by using eq. (4.4).

$(N_1(0)/N(0)$ of the region 1 of the SDW on the Fermi surface is large enough, then the SC is strongly suppressed. Therefore in highly anisotropic materials satisfying such criterion the SC is hard to exist and rapidly diminishes as T_{s0} rises.

PHASE DIAGRAM AND TEMPERATURE DEPENDENCE OF THE ORDER PARAMETERS

Before going into details of numerical calculations of the free energy, we give a simple argument about the ground state at $T=0$. The ground state energies of each phases; SC, SDW and SC + SDW are given by $E_{SC} = -\frac{1}{2}N(0)\Delta_0^2$, $E_{SDW} = -\frac{1}{2}N_1(0)M_0^2$ and $E_c = -\frac{1}{2}N(0)\Delta^2(0) - \frac{1}{2}N_1(0)M^2(0)$ respectively, where $\Delta_0(M_0)$ is the SC (SDW) order parameter at $T=0$ without SDW (SC). Since we have assumed that the SC is stable state at $T=0$, possible phases are limited to the following two cases; SC coexisted with SDW and SC without SDW. We compare these energies, that is,

$$E_{SC} - E_c = -\frac{1}{2}N(0)M_0^2\left\{\frac{T_{c0}}{T_{s0}}\left(1-\frac{\Delta^2(0)}{\Delta_0^2}\right) - \frac{N_1(0)}{N(0)}\frac{M^2(0)}{M_0^2}\right\}. \tag{5.1}$$

This implies if

$$\frac{N_1(0)}{N(0)}\left(\frac{M(0)}{M_0}\right)^2 > \left(\frac{T_{c0}}{T_{s0}}\right)^2\left(1-\frac{\Delta^2(0)}{\Delta_0^2}\right), \tag{5.2}$$

then the coexisting phase is more stable than SC without SDW. We display the condition (5.2) in the plane T_{c0}/T_{s0} vs $N_1(0)/N(0)$ in Fig.2.

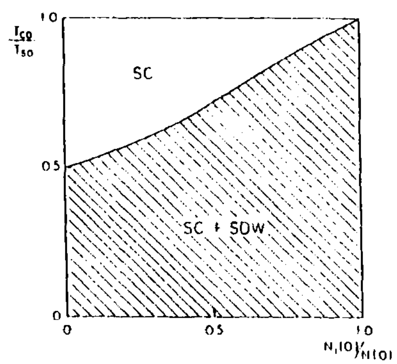
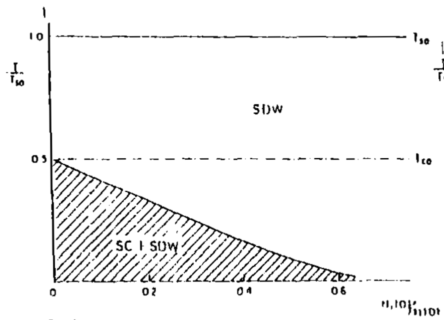


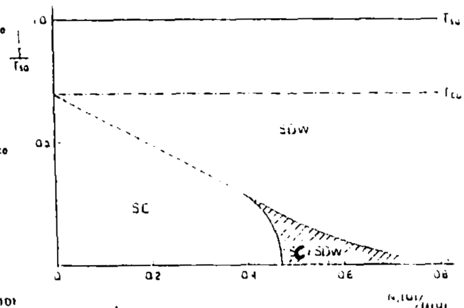
FIGURE 2 The phase diagram in the ground state $(T=0)$. The hatched region indicates the coexistence of superconducting state and SDW.

In order to determine phase diagrams at finite temperatures we must solve eqs. (2.7) and (2.8) and evaluate the free energy eq.(3.2).

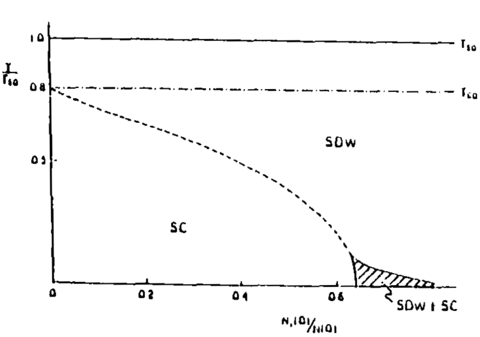
Some of phase diagrams for T/T_{s0} vs $N_1(0)/N(0)$ are shown in Figs. 3a ~ 3c. When $T_{c0}/T_{s0} = 0.5$ (Fig.3a), the stable SDW phase at high temperatures persists down to $T = 0$ coexisting with SC. The second order phase transition takes place at $T = T_c$. When $T_{c0}/T_{s0} = 0.7$ (Fig.3b) and $N_1(0)/N(0) < 0.4$, a first order transition line characterizes the phase change from SDW to SC. This line splits into two second order lines above $N_1(0)/N(0) > 0.4$. The coexistence is limited within a narrow temperature region for $0.4 \leq N_1(0)/N(0) < 0.47$. This is also the case for $T_{c0}/T_{s0} = 0.8$ (Fig.3c) except that the first order line extends up to $N_1(0)/N(0) = 0.64$. The temperature dependence of two order parameters is depicted in Figs. 4a ~ 4c.



3a

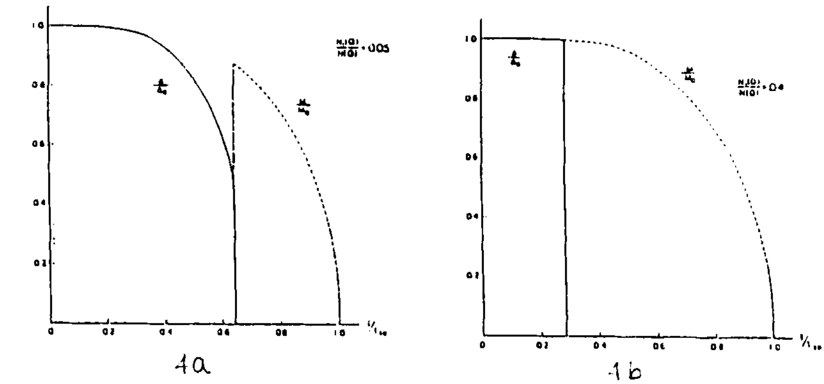


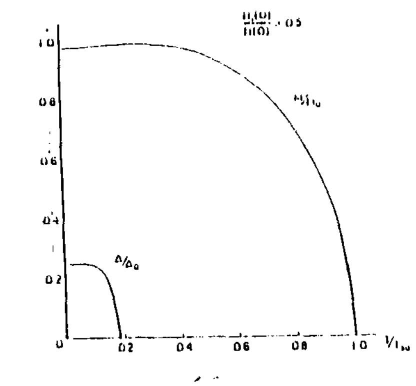
3b



3c

FIGURES 3a~3c The phase diagram: T/T_{s0} vs $N_1(0)/N(0)$. The dotted line indicates the first order phase transition from SDW to SC. The hatched region is the coexisting phase.





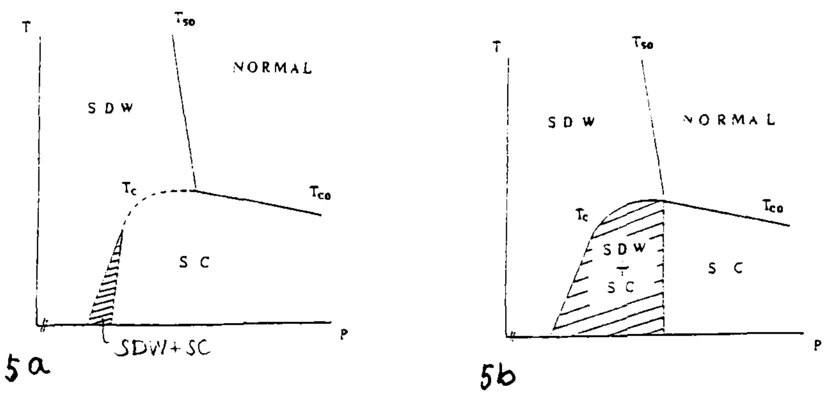
FIGURES 4a~4c The temperature variation of two order parameters M and Δ when $T_{c0}/T_{s0} = 0.7$.

CONCLUSIONS AND DISCUSSIONS

We have discussed the competition of the two long range orders of the SDW and SC states on the basis of a simplified anisotropic electron band model and Hartree-Fock approximation, and shown that the SC state precludes appearence of the SDW state when $T_{c0} > T_{s0}$. When $T_{c0} < T_{s0}$, there are two possibilities of the phase transitions from SDW to SC. Namely when the first order transition takes place, the two orders simply interchange at $T = T_c$. When the second order transition characterizes the change at $T = T_c$, two orders generally coexist below T_c down to $T = 0$. However depending on the values of $N_1(0)/N(0)$ and T_{c0}/T_{s0} , there is the case that the coexistence is limited within a narrow temperature region.

<u>Comments on experiments of $(TMTSF)_2PF_6$</u>

We now consider the organic superconductor $(TMTSF)_2PF_6$ under pressure. The anisotropic electronic band model we employ is expected to be applicable to it because several experiments[10] strongly indicate multi-dimensionality of the electronic structure of $(TMTSF)_2PF_6$. Therefore our conclusions obtained here should be checked experimentally. Namely (i) when SC appears at a high temperature T_{c0} , SDW is arrested by SC and never appears at lower temperature region. (ii) When SDW appears at a high temperature T_{s0} , then it may be possible to observe SC at lower temperatures under the condition that T_{s0} is not much higher than T_{c0} , otherwise the superconducting onset temperature T_c becomes extremely low and practically it is impossible to see SC. In the case that SC does appear at T_c lower than T_{s0} , and if the phase transition is of the second order, then two long range orders SDW and SC coexist in general. If the first order transition characterizes this transition at T_c , then two orders simply interchange, below which only SC persists and SDW disappears abruptly. We depict our conclusions in Figs. 5a and 5b schematically, which are expected to be applicable for $(TMTSF)_2X$ $(X = PF_6$, AsF_6, SbF_6 and $TaF_6)$ under pressure. The condition to determine the type of the phase transition at $T = T_c$ depends on the two parameters of our model, that is, $N_1(0)/N(0)$ and T_{c0}/T_{s0} . Therefore the present theory may be checked by varying lattice constant, that is, by applying pressure on $(TMTSF)_2PF_6$ or by changing the anion molecule X in $(TMTSF)_2X$.



FIGURES 5a and 5b Schematic figures of possible phase diagrams in temperature vs pressure for $(TMTSF)_2PF_6$ under pressure.

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