Theory of the High Field Phase in (TMTSF)₂ClO₄

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We theoretically study the high field phase in the quasi-one-dimensional organic conductor, (TMTSF)₂ClO₄, under the anion ordering, where the new phase diagram of the magnetic field and temperature is reported in the recent magnetization and transport measurements. We obtain the first order transition between the spin density wave states, which explains the experiment. [organic conductors, (TMTSF)₂ClO₄, anion ordering, phase diagram, spin density wave]

1. Introduction

The field induced spin density wave (FISDW) transition is known to occur at low temperatures ($T \sim$ a few K) and above the threshold field ($H \sim$ a few T) in (TMTSF)₂X.^{1,2)} This FISDW phenomenon is due to the quasi-one-dimensionality of a pair of open sheet like-Fermi surfaces (FS's) of (TMTSF)₂X and is described by the so-called standard theory.¹⁾ The successive FISDW transition is characterized by changing the SDW wave number $Q_x = 2k_F + N\delta$ ($k_F = \pi/4a$; the Fermi wave number, N ; integer and $\delta = eaH/\hbar c$) along the most conducting direction (k_x axis). The corresponding subphases have different N values. In high field limit ($H > 10$ T) the FISDW with $Q_x = 2k_F$ and $Q_y = \pi/b$, that is, the $N = 0$ state is realized where the H -dependent transition temperature $T_{SDW}(H)$ tends to saturate to 12 K. These features are observed in X=PF₆.

When in X=ClO₄ the anion ordering (AO) occurs at $T_{AO}=24$ K, whose vector is $\mathbf{Q}_{AO} = (0, \pi/b)$, the FS becomes two pairs of parallel open sheets, which is shown in Fig. 1. The successive transitions are observed even in this FS situation and the H - T phase diagram is much different from the one in the absence of the AO.³⁾ Lebed' and Bak⁴⁾ and Osada et al.⁵⁾ attempted to analyze the FISDW in X=ClO₄ by introducing the effect of the AO. The SDW nesting vector used by Lebed' and Bak is $\mathbf{Q}_{SDW} = (2k_F, \pi/b)$ as shown in Fig. 1. The most stable vector $\mathbf{Q}$ which Osada et al. found by examining the spin susceptibility is slightly shifted from the optimal $\mathbf{Q}_{SDW}$ in the standard theory. Certain features of the FISDW in X=ClO₄, namely, the suppression of the even- N phase have been explained by their approaches but the predicted oscillatory boundary is not observed.

McKernan et al.⁶⁾ present a new H - T phase diagram of X=ClO₄ by the magnetization and transport measurements (see Fig.4 in Ref. 6). They show that the region above 20 T and below 5.5 K is occupied by yet another new kinds of the SDW subphases; SDW₁ (20 T < H < 28 T and 0.5 K < T < 3.5 K) and SDW₂ (20 T < H < 28 T and 3.5 K < T < 5.5 K and H > 28 T and 0.5 K < T < 5.5 K). In their new H - T phase diagram, there are a first order transition line from the SDW₁ phase to the SDW₂

phase at 20 T < H < 28 T and 0.5 K < T < 3.5 K and a second order transition line of the SDW₂ at $H > 15$ T occurring almost H -independently at $T = 5.5$ K. It has been suggested that the SDW state in the high field region ($H > 15$ T) is not the FISDW state with $N = 0$, namely, a nesting state with $\mathbf{Q}_{SDW}$.

Fig. 1. Bold lines denote the FS. The nesting vectors $\mathbf{Q}_{SDW} = (2k_F, \pi/b)$, $\mathbf{Q}_{SDW}^- = (2k_F^-, \pi/2b)$ and $\mathbf{Q}_{SDW}^+ = (2k_F^+, \pi/2b)$.

The purpose of this paper is to investigate the high field phase in ClO₄ in the presence of the AO. In particular, we examine other possible SDW nesting vectors which have not been analyzed in this system. We focus on $\mathbf{Q}_{SDW}^-$ and $\mathbf{Q}_{SDW}^+$ in Fig. 1, because we will see that the SDW nesting vector $\mathbf{Q}_{SDW}^\pm$ become a more appropriate nesting as the AO potential V increases. It is well known^{1,2)} that $\mathbf{Q}_{SDW}$ is not a perfect nesting vector for the band structure of ClO₄ described by the tight binding model: $\epsilon(k_x, k_y) = -2t_a \cos ak_x - 2t_b \cos bk_y$ (transfer integrals ratio $t_a : t_b \approx 1 : 0.1$). By adding the AO potential V , the band structure is represented by two bands: $\epsilon^\pm(k_x, k_y) = -2t_a \cos ak_x \pm \sqrt{4t_b^2 \cos^2 bk_y + V^2}$, yielding the FS shown in Fig. 1. Even in this FS case, $\mathbf{Q}_{SDW}$ is still imperfect (see Fig. 1). From Fig.1, we can see that $\mathbf{Q}_{SDW}^\pm$ is a good nesting vector so as to choose $Q_y = \pi/2b$ in stead of $Q_y = \pi/b$ thought before,^{4,5)} because $\epsilon^\pm(k_x, k_y)$ can be fitted by cosine bands

and its first Brillouin zone along the k_y axis is restricted by $-\pi/2b \leq k_y \leq \pi/2b$. Even if there is a solution with $Q = Q_{\text{SDW}}^-$ or Q_{SDW}^+ , only the upper or lower band is mixed by Q_{SDW}^- or Q_{SDW}^+ so that only a pair of the FS's disappears (still metallic), whereas by Q_{SDW} both of the upper band and lower band are mixed each other so that two pairs of the FS's simultaneously disappear (insulating). Thus, the SDW condensation energy gained by Q_{SDW}^- or Q_{SDW}^+ will be worse than that by Q_{SDW} . However, if the nestings by Q_{SDW}^- and Q_{SDW}^+ are considered at the same time, two pairs of the FS's disappear (insulating) so that this state can gain the comparable energy as the Q_{SDW} nesting state. Thus, we expect that a Q_{SDW} nesting state and a coexistent state of Q_{SDW}^- and Q_{SDW}^+ nestings compete at high field. McKernan et al.⁶⁾ already have intuitively suggested this idea.

2. Formulation

Let us study the standard model with the AO potential V and seek self-consistent solutions at $T = 0$ in the mean field approximation. The Hamiltonian is $\hat{H} = \hat{K} + \hat{V} + \hat{H}_{\text{int}}$, where $\hat{K} = \sum_{i,j,\sigma} t_{i,j} C_{i,\sigma}^\dagger C_{j,\sigma} - \mu_B H \sum_{i,\sigma} \sigma n_{i,\sigma} = \sum_{\mathbf{k},\sigma} C_{\mathbf{k},\sigma}^\dagger \epsilon(\mathbf{k},\sigma) C_{\mathbf{k},\sigma}$, $\hat{V} = V \sum_{i,\sigma} \cos \mathbf{Q}_{\text{AO}} \cdot \mathbf{r}_i C_{i,\sigma}^\dagger C_{i,\sigma}$ and $\hat{H}_{\text{int}} = U \sum_i n_{i,\uparrow} n_{i,\downarrow}$. In the above $\sigma = \uparrow, \downarrow$, $n_{i,\sigma} = C_{i,\sigma}^\dagger C_{i,\sigma}$, $C_{i,\sigma}^\dagger$ is the creation operator of σ spin electron at i site, and $\epsilon(\mathbf{k},\sigma) = -2t_a \cos ak_x - 2t_b \cos bk_y - \mu_B H \sigma$, where μ_B is the Bohr magneton. By taking the Landau gauge $\mathbf{A} = (Hy, 0, 0)$, we write $\hat{K}$ as $\hat{H}_p = \sum_{\mathbf{k}', n, m, \sigma} \{-2t_a (\cos a(k'_x + n\delta)) - \mu_B H \sigma\} C^\dagger(k'_x + n\delta, k'_y + \frac{m\pi}{b}, \sigma) C(k'_x + n\delta, k'_y + \frac{m\pi}{b}, \sigma) + \{-t_b \exp(ik'_y + im\pi) C^\dagger(k'_x + n\delta, k'_y + \frac{m\pi}{b}, \sigma) C(k'_x + (n+1)\delta, k'_y + \frac{m\pi}{b}, \sigma) + h.c.\}$, where $\delta = (\phi/\phi_0)(2\pi/a)$, $\phi = abH$ is the flux passing through a unit cell and $\phi_0 = 2\pi\hbar c/e$ is a unit flux. The interaction term $\hat{H}_{\text{int}}$ is treated in mean field approximation as, $\hat{H}_M = \sum_{\mathbf{Q}} M(\mathbf{Q}) \sum_{\mathbf{k}', n, m, \sigma} \{C^\dagger(k'_x + n\delta, k'_y + \frac{m\pi}{b}, \sigma) C(k'_x - Q_x + n\delta, k'_y + \frac{m\pi}{b}, \sigma) + h.c.\}$. The self-consistent equation for $M(\mathbf{Q})$ is given by $M(\mathbf{Q}) = -U/N_s \sum_{\mathbf{k}', n, m} \langle C^\dagger(k'_x + n\delta, k'_y + \frac{m\pi}{b}, \downarrow) C(k'_x - Q_x + n\delta, k'_y - Q_y + \frac{m\pi}{b}, \uparrow) \rangle$, where N_s is the total site number and $M(\mathbf{Q})$ is assumed to be real.^{1,2)} In the above equations, the region of $\mathbf{k}'$ is in the magnetic Brillouin zone in the presence of V , i.e. $k_F < k'_x < k_F + \delta$ and $0 < k'_y < \pi/b$, n is integer and $m = 0, 1$. We take $t_a = 2843$ K, $t_b = 335$ K, $U = 8200$ K, $a \approx 3.6$ Å and $b \approx 7.7$ Å. Lebed' and Bak⁴⁾ and Osada et al.⁵⁾ took the value $V \sim 50$ K. Note, however, that V may not be of the order of T_{AO} , because the AO is not driven by the FS instability. Experimentally, Yoshino et al. estimate that V is of the order of t_b from the angular dependent magnetoresistance measurement.⁷⁾ We take here $V = 580$ K as the order of t_b .

When ϕ/ϕ_0 is a rational number, namely, $\phi/\phi_0 = p/q$ with p and q being mutually prime number, the matrix size of $\hat{H}_p$ is q . By diagonalizing $\hat{H}_p + \hat{V} + \hat{H}_M$ under the self-consistent condition, for various possible ordered states we can calculate the ground state energy per site $E(H, M) = (1/N_s) \{\sum_{i=1}^{N_s} \epsilon_i + 2N_s/U \sum_{\mathbf{Q}} M(\mathbf{Q})^2\}$, where ϵ_i is one electron eigenvalue and N_s is total electron number. Having seen that there are the new optimal

nesting vectors for $Q_y = \pi/2b$ in addition to $Q_y = \pi/b$, which is known before, we study for $H = 240, 189$ and 156 T ($\phi/\phi_0 = 1/60, 1/76$ and $1/92$) to see which states are more stable. We find both self-consistent solutions for $M(Q_x, \pi/b)$ and $M(Q_x, \pi/2b)$.

3. Result

As for $M(Q_x, \pi/b)$, in the case of the single SDW solution, the SDW wave number Q_x which minimizes the energy of the system is $2k_F$ for all H as shown at Fig. 2(a). This wave vector leads to the simultaneous disappearance of two pairs of the FS's so that there is little nesting chance for other additional SDW wave vector to appear. In fact, we tried to find the self-consistent solution starting with both $M(2k_F, \pi/b)$ and $M(2k_F - \delta, \pi/b)$ finite and only obtain either $M(2k_F, \pi/b)$ or $M(2k_F - \delta, \pi/b)$ where the other becomes zero.

Fig. 2. The solution $M(Q_x, \pi/b)$ in (a) and $M(Q_x, \pi/2b)$ in (b) are indicated by dots, $\circ$, $\square$ and $\diamond$, when $H = 240, 189$ and 156 T. The horizontal axis is $Q_x = 2k_F + N\delta$.

As for $M(Q_x, \pi/2b)$ where two order parameter solutions for $Q_x > 2k_F$ and $Q_x < 2k_F$ is allowed, Q_x 's in which the energy of the system has minima are found to be $2k_F \pm 3\delta$, $2k_F \pm 4\delta$ and $2k_F \pm 5\delta$ when $H = 240, 189$ and 156 T, respectively. The resulting $M(Q_x, \pi/2b)$ is shown in Fig. 2(b). Those solutions are due to the nesting vector $Q_{\text{SDW}}^\pm$ in Fig. 1. Since by Q_{SDW}^+ and Q_{SDW}^- two pairs of the FS's disappear, $M(2k_F^+, \pi/2b)$ and $M(2k_F^-, \pi/2b)$ can coexist. When we suppose a single SDW solution, for example, $M(2k_F - 3\delta, \pi/2b)$ and try to calculate self-consistently, the convergent value is the same within a numerical accuracy as the results of one of the coexistent solutions such as $M(2k_F - 3\delta, \pi/2b)$ in Fig. 2(b). We also look for the solution, with three order parameters $M(2k_F, \pi/b)$ and $M(2k_F^\pm, \pi/2b)$. We seek the self-consistent solution by iteration and find that three order parameters do not exist at the same time. This can be understood as follows; for example, as two pairs of the FS's disappear when there is $M(2k_F, \pi/b)$, there is little nesting chance by other vector such as Q_{SDW}^+ or Q_{SDW}^- .

The solutions, $M(2k_F, \pi/b)$ and $M(2k_F^\pm, \pi/2b)$ monotonically increase as H increases. This is due to the optimization of the nesting by the magnetic field, seen already in the standard theory of the FISDW.^{1,2)}

The calculated energy $E(H, M)$ as a function of H

are shown in Fig. 3. The energy $E(H, M)$ is for $M \equiv M(2k_F, \pi/b)$ shown at Fig. 2(a) and $E(H, M^- + M^+)$ and $E(H, M^-)$ are for $M^- \equiv M(2k_F^-, \pi/2b)$ and $M^+ \equiv M(2k_F^+, \pi/2b)$ shown at Fig. 2(b). Comparing $E(H, M^-)$ and $E(H, M^- + M^+)$ in Fig. 3 we can see that $E(H, M^- + M^+)$ has always lower energy than $E(H, M^-)$. This reason is that the coexistent state of M^- and M^+ gains the SDW condensation energy both from the Q_{SDW}^- and Q_{SDW}^+ nesting, whereas the M^- state from only the Q_{SDW}^- nesting. For the higher field $E(H, M)$ become lower than $E(H, M^- + M^+)$ with occurring the energy crossing at H_c shown at Fig. 3. This may correspond to the experimentally observed first order transition from the SDW₁ to the SDW₂ when $H = 28$ T and $T = 0.5$ K. The energy crossing is due to the different H -dependence between M and $M^\pm$. At high field, the M state is more stable than the coexistent state of M^+ and M^- . We consider that the stabilized $M(2k_F, \pi/b)$ state in our result at the high field corresponds to the $M(2k_F, \pi/b)$ state, because Q_{SDW} nearly coincide with $Q = (2k_F, \pi/b)$, which gives the largest $\chi_0(Q)$ in Osada et al.⁵⁾ (Since $2\tilde{k}_F - 2k_F = 2\Delta/\hbar v_F \ll (1/p)(2\pi/a)$, we cannot analyze $M(2k_F, \pi/b)$).

Fig. 3. The energy $E(H, M)$, $E(H, M^- + M^+)$ and $E(H, M^-)$ is denoted by $\circ$, $\square$ and $\diamond$ as a function of H .

4. Discussion

From the above result at $T = 0$ we will consider the free energy $F(H, T, M)$ at finite temperatures by taking account of the temperature dependence of the order parameters as that in the BCS theory. When T increases, the order parameter $M(Q, T)$ decreases, and at the critical temperature (T_c), $M(Q, T_c)$ becomes zero. Since $M(Q_{SDW}, 0)$, $M(Q_{SDW}^+, 0)$ and $M(Q_{SDW}^-, 0)$ are different as seen in Fig. 2, T_c 's (T_c^0 , T_c^+ and T_c^-) are not the same, namely, $T_c^0 > T_c^- > T_c^+$ as $M(Q_{SDW}, 0) > M(Q_{SDW}^-, 0) > M(Q_{SDW}^+, 0)$. If the temperature will increase, as $M^+ = 0$ when $T = T_c^+$, there will be no energy gain due to M^+ . Thus, we expect the followings; (1) At H_1 in Fig. 3, $E(H_1, M^+ + M^-) < E(H_1, M) < E(H_1, M^-)$ when $T = 0$ but, upon increasing T , when $T \simeq T_c^+$, M^+ becomes nearly zero, $F(H_1, T, M^+ + M^-) \simeq F(H_1, T, M^-) > F(H_1, T, M)$. Thus, a first order transition is expected from the SDW₁

to the SDW₂ at the transition temperature ($T_{SDW}^1(H_1)$). (2) At H_2 in Fig. 3, when $T = 0$, $E(H_2, M) < E(H_2, M^+ + M^-) < E(H_2, M^-)$. Since M^+ and M^- are expected to decrease faster than M as temperature increases, $F(H_2, T, M)$ will stay the lowest one, thus, no transition will be expected. (3) At $H_1 < H < H_c$, similar to (1), however, $T_{SDW}^1(H)$ is smaller than $T_{SDW}^1(H_1)$, because the energy difference of $E(H, M^+ + M^-)$ and $E(H, M)$ is smaller than that of $E(H_1, M^+ + M^-)$ and $E(H_1, M)$. (4) Finally, at $H = H_c$, $T_{SDW}^1(H_c) = 0$. From these, we obtain that $T_{SDW}^1(H)$ monotonically increases upon decreasing H , beginning from $T_{SDW}^1(H_c) = 0$. We show an expected first order transition line in the H - T phase diagram at Fig. 4. This line is in good agreement with a first order transition line in McKernan's phase diagram.⁶⁾

Fig. 4. The schematic H - T phase diagram.

5. Conclusion

By comparing the energies for various possible FSDW states under the AO we have found a new FSDW state with $Q = (2k_F^-, \pi/2b)$ stabilized over the known state with $Q = (2k_F, \pi/b)$. We demonstrate at $T = 0$ a first order transition between the SDW₁ phase and SDW₂ phase to exist upon varying H , which we suggest the observed first order transition by McKernan et al.⁶⁾ We identify that the SDW₁ phase ($H < 28$ T) is a state in which $M(2k_F^-, \pi/2b)$ and $M(2k_F^+, \pi/2b)$ coexist and the SDW₂ phase ($H > 28$ T) is a state characterized by $M(2k_F, \pi/b)$. We discuss the observed anomalous first order transition line based on our result at $T = 0$.

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