Thermodynamics of field-induced spin-density-wave states in Bechgaard salts

Kazumi Maki
Department of Physics, University of Southern California, Los Angeles, California 90089-0484
(Received 23 September 1985; revised manuscript received 23 October 1985)

Assuming that the spin-density-wave (SDW) state in a high magnetic field (e.g., $H>10$ T) in a typical Bechgaard salt such as di-tetramethyltetraselenafulvalene perchlorate $(TMTSF)_2ClO_4$, has the **Q** vector proposed by Gor'kov and Lebed, we construct the Gor'kov equation for Green functions in the SDW state. We find the thermodynamics of this SDW state (Gor'kov-Lebed state) is equivalent to that of a Bardeen-Cooper-Schrieffer superconductor. Furthermore, we obtain a simple expression of the magnetization in the SDW, which is compared with experimental data of $(TMTSF)_2ClO_4$.

I. INTRODUCTION

The di-tetramethyltetraselenafulvalene $[(TMTSF)_2X]$ family of organic charge-transfer salts (Bechgaard salts) exhibit a number of phase transitions at low temperatures.[1] Perhaps the most intriguing is a series of field-induced spin-density-wave (SDW) transitions first observed in $(TMTSF)_2PF_6$ under pressure.[2] It is later confirmed[3,4] in R-$(TMTSF)_2ClO_4$ (slowly cooled) that a series of SDW transitions are induced at low temperatures when a high magnetic field is applied along the c^* direction.

Recently, Gor'kov and Lebed[5] (GL) have shown that the SDW transitions are intrinsic to the quasi-two-dimensional systems with the quasiparticle energy given by

$$\epsilon(\mathbf{p})=v_F(|p_x|-p_F)-2t_b\cos(b^*p_y)-2t_b'\cos(2b^*p_y)-2t_c\cos(c^*p_z) \qquad (1)$$

when a magnetic field is applied in the c^* direction. In particular, GL consider the SDW with wave vector $(2p_F,\pi/b^*,\pi/c^*)$, and study the SDW instability within mean-field approximation, and find that the transition temperature is given by

$$T_c(H)=1.14E_c\exp[-\lambda(\alpha)^{-1}] \qquad (2)$$

with $\lambda(\alpha)=\lambda J_0^2(\alpha)$, where $\alpha=2t_b'/b^*v_FeH$, $J_0(z)$ is the Bessel function, and E_c is a cutoff energy. Furthermore, λ is estimated[5] to be $\lambda\simeq0.1$. This approach is later generalized for more general SDW wave vectors by Héritier *et al.*[6] On the other hand, at $T=0$ K, Yamaji[7] has shown within mean-field theory that SDW state has lower energy than the normal state. Héritier *et al.*[6] neglected the third term (the second-nearest-neighbor hopping term) in Eq. (1), which plays the crucial role in the GL theory.[5] Furthermore, almost nothing is known about the SDW in the intermediate-temperature regions ($0<T<T_c$).

The object of this paper is to study the thermodynamics of the GL state at all temperatures ($0\le T\le T_c$). In spite of generalization by Héritier *et al.*,[6] we believe that the GL state is the most stable[8] in the high-field region (e.g., $H>10$ T). Furthermore, the GL state is the simplest among the field-induced SDW's.

In Sec. II we construct the Gor'kov equation for Green functions in the SDW state, which is solved exactly in the limit $J_0(\alpha)\gg J_1(\alpha),J_2(\alpha)$—where $J_n(a)$ are the Bessel functions and α has been defined below Eq. (2). For appropriate parameters of $(TMTSF)_2ClO_4$, we find that the above condition is satisfied for $H\ge10$ T. The thermodynamics of the SDW is determined in Sec. III. We compare these results with a recent experiment on $T_c(H)$ and magnetization in $(TMTSF)_2ClO_4$ in Sec. IV.

II. GOR'KOV EQUATION

Assuming that the quasiparticle spectrum of a Bechgaard salt is given by Eq. (1), we write the Gor'kov equation[9] as follows:

$$[i\omega-\epsilon(\mathbf{p}-e\mathbf{A})-\mu H]G_\omega(x,x')+\Delta(x)F_\omega(x,x')=\delta(x-x')\ ,$$
$$[i\omega-\epsilon(\mathbf{p}+\mathbf{Q}-e\mathbf{A})+\mu H]F_\omega(x,x')+\Delta^*(x)G_\omega(x,x')=0\ , \qquad (3)$$

where $G_\omega(x,x')$ and $F_\omega(x,x')$ are the Fourier transform of the thermal Green functions with ω the Matsubara frequency defined by

$$G_\uparrow(x,x')=-i\langle T[\psi_\uparrow(x)\psi_\uparrow^\dagger(x')]\rangle\ ,$$
$$F_\uparrow(x,x')=\langle T[\psi_\downarrow(x)\psi_\uparrow^\dagger(x')]e^{i\mathbf{Q}\cdot\mathbf{x}}\rangle\ . \qquad (4)$$

We can write a similar set of equations for $G_\downarrow(x,x')$ and $F_\downarrow(x,x')$, where μH in Eq. (3) is replaced by $-\mu H$.

Furthermore, the self-consistency equation is given by

$$\Delta^*(x)=\lambda N_0^{-1}T\sum_\omega F_\omega(x,x)\ , \qquad (5)$$

where N_0 is the density of states at the Fermi surface.

Hereafter, following Gor'kov and Lebed,[5] we take

$$\mathbf{Q}=(2p_F,\pi/b^*,\pi/c^*) \qquad (6)$$

and

$$\mathbf{A}=(0,Hx,0)\ . \qquad (7)$$

Then substituting

$$G_\omega(x,x')=g(x,x')\exp\left[\frac{2it_b}{v_F}\int_{x'}^{x}dx''\cos[b^*(p_y-eA_y)]+\frac{2it_b'}{v_F}\int_{x'}^{x}dx''\cos[2b^*(p_y-eA_y)]\right.$$
$$\left.+i[2t_c\cos(c^*p_z)+\mu H](x-x')v_F^{-1}\right] \tag{8}$$

and

$$F_\omega(x,x')=f(x,x')=\exp\left[\frac{2it_b}{v_F}\int_{x'}^{x}dx''\cos[b^*(p_y-eA_y)]\right.$$
$$-\frac{2it_b'}{v_F}\left[\int_0^x dx''\cos[2b^*(p_y-eA_y)]+\int_0^{x'}dx''\cos[2b^*(p_y-eA_y)]\right]$$
$$\left.+i[2t_c\cos(c^*p_z)+\mu H](x-x')v_F^{-1}\right] \tag{9}$$

into Eq. (3), we obtain

$$\left[i\omega+iv_F\frac{d}{dx}\right]g(x,x')+\tilde{\Delta}(x)f(x,x')=\delta(x-x')\ ,$$
$$\left[i\omega-iv_F\frac{d}{dx}\right]f(x,x')+\tilde{\Delta}^*(x)g(x,x')=0\ , \tag{10}$$

where

$$\tilde{\Delta}(x)=\Delta(x)\exp\left[\frac{4it_{b'}}{v_F}\int_0^x dx''\cos[2b^*(p_y-eA_y)]\right]$$
$$=\Delta(x)e^{i\alpha\sin(kx_0)}\left[\sum_{n=-\infty}^{\infty}J_n(\alpha)e^{ink(x-x_0)}\right]\ , \tag{11}$$

where

$$\alpha=2t_b'/b^*v_FeH\ ,$$
$$k=2b^*eH,\ \text{and}\ x_0=p_y/eH \tag{12}$$

and $J_n(z)$ is the Bessel function.

In the following we limit ourselves to the limit where

$$J_0(\alpha)>J_1(\alpha)\gg J_2(\alpha),J_3(\alpha),\ldots \tag{13}$$

which is realized when $H\geq 2t_b'/b^*v_Fe$. In this limit we can take $\Delta(x)=C$ independent of position without loss of generality, which corresponds to the Gor'kov-Lebed state.[5] Then we obtain

$$\tilde{\Delta}(x)=e^{i\alpha\sin(kx_0)}[\Delta_0+i\Delta_1\sin k(x-x_0)]\ , \tag{14}$$

where

$$\Delta_0=CJ_0(\alpha)$$

and

$$\Delta_1=CJ_1(\alpha)\ . \tag{15}$$

Then Eq. (10) is recast as

$$\left[i\omega+iv_F\sigma_3\frac{d}{dx}+\Delta_0\sigma_1+2\Delta_1\sigma_2\sin[k(x-x_0)]\right]\tilde{g}=\hat{1}\delta(x-x')\ , \tag{16}$$

where

$$\tilde{g}=\begin{bmatrix}g_\uparrow(x,x') & f_\downarrow(x,x')\\ f_\uparrow(x,x') & g_\downarrow(x,x')\end{bmatrix} \tag{17}$$

and σ_i are Pauli spin operators. Here we restored the spin indices explicitly. Furthermore, we eliminate the phase of $\tilde{\Delta}(x)$ by redefining f by $e^{-i\alpha\sin(kx_0)}f$, although this phase factor has to be reinserted in the gap equation (5).

Before solving Eq. (16), we shall consider the quasiparticle energy spectrum, which is obtained from

$$\left[E_n+iv_F\sigma_3\frac{d}{dx}+\Delta_0\sigma_1+2\Delta_1\sigma_2\sin[k(x-x_0)]\right]\psi_n=0\ , \tag{18}$$

where

$$\psi_n=\begin{bmatrix}u_n(x)\\ v_n(x)\end{bmatrix} \tag{19}$$

and E_n is the energy eigenvalue.

Then the Green functions are constructed in terms of eigenwave functions and eigenvalues E_n as

$$g(x,x')=\sum_n(i\omega-E_n)^{-1}u_n(x)u_n^\dagger(x')\ ,$$
$$f(x,x')=\sum_n(i\omega-E_n)^{-1}v_n(x)u_n^\dagger(x')\ , \tag{20}$$

for example.

In the limit $\Delta_1/\Delta_0\ll 1$, Eq. (18) is solved in terms of the plane-wave solutions:

$$\psi_p(x)=\begin{bmatrix}u_p\\ v_p\end{bmatrix}(2\pi)^{-1/2}e^{ipx} \tag{21}$$

as

$$E=\pm E_p=\pm(\xi_p^2+\Delta_0^2)^{1/2}\ ,$$
$$u_p=[\tfrac{1}{2}(1+\xi/E)]^{1/2},\ v_p=-[\tfrac{1}{2}(1-\xi/E)]^{1/2}\ , \tag{22}$$

where

$$\xi = \xi_p = v_F p \; . \tag{23}$$

The last term in Eq. (18) allows the mixing of ψ_p and $\psi_{p\pm k}$ with $k = 2b^* eH$. Then this mixing causes a splitting of the continuous energy band for $E > 0$ into two bands at $\xi = \pm 2 v_F b^* eH = \pm \zeta$ with a small energy gap of $|\Delta_1|$. This leads to the orbital quantization in SDW's; the SDW transforms the open orbits of quasiparticles into closed orbits in the SDW.[10] However, in the limit $|\Delta_1/\Delta_0| \ll 1$, the effects of small gap on the thermodynamics of the spin-density wave is certainly negligible.

The Green functions are readily found in this limit as

$$\begin{aligned} g(x,x') &= -(2\pi)^{-1} \int dp (i\omega + \xi)(\omega^2 + E^2)^{-1} e^{ip(x-x')} \; , \\ f(x,x') &= -(2\pi)^{-1} \int dp \, \Delta_0 e^{-i\alpha \sin(kx_0)} \\ &\quad \times (\omega^2 + E^2)^{-1} e^{ip(x-x')} \; , \end{aligned} \tag{24}$$

where E and ξ have been defined in Eqs. (22) and (23).

Then the gap equation (5) reduces to

$$C = \lambda \Sigma T \sum_\omega \int d\xi \, \Delta_0 \langle e^{-i\alpha \sin(kx_0)} \rangle (\omega^2 + E^2)^{-1} \; , \tag{25}$$

which is rewritten as

$$1 = \lambda(\alpha) T \sum_\omega \int d\xi (\omega^2 + E^2)^{-1} \; , \tag{26}$$

and $\lambda(\alpha)$ has been already defined after Eq. (2). Here $\langle \; \rangle$ means the average over p_y.

III. THERMODYNAMICS

Since Eq. (26) is the same as the Bardeen-Cooper-Schrieffer (BCS) gap equation[9] for a superconductor, the thermodynamics is identical to a BCS superconductor. First, the transition temperature $T_c(H)$ is given by the Gor'kov-Lebed[5] expression (2), where E_c is the cutoff energy. Furthermore, the energy gap in the vicinity of T_c and at $T = 0$ K is given by

$$\Delta(H,T) \simeq \begin{cases} \pi T_c(H) [8/7\zeta(3)]^{1/2} (1 - T/T_c)^{1/2} , & (27) \\ \dfrac{\pi}{\gamma} T_c(H) \; , & (28) \end{cases}$$

respectively, where $\zeta(3) = 1.202\ldots$ is the zeta function and γ is the Euler constant.

Similarly, the free energy is given by

$$\Delta F = F_{\mathrm{SDW}} - F_n = \begin{cases} -N_0 \dfrac{(2\pi T_c)^2}{7\zeta(3)} (1 - T/T_c)^2 \quad \text{for } T \simeq T_c & (29) \\ N_0 \left[\frac{1}{3}(\pi T)^2 - \dfrac{\Delta^2}{2} - \left[2\pi \Delta^3 T \right]^{1/2} \left[1 + \dfrac{15}{8} \dfrac{T}{\Delta} \right] e^{-\Delta/T} \right] \quad \text{for } T \ll T_c \; . & (30) \end{cases}$$

For example, the specific heat in the SDW state is the same as a BCS superconductor. Furthermore, the excess magnetization associated with the SDW is given by

$$\begin{aligned} M &= -\frac{\partial}{\partial H} (\Delta F) \\ &= -N_0 \Delta^2(H,T) [2\alpha J_0'(\alpha) / \lambda J_0^3(\alpha) H] \; , \end{aligned} \tag{31}$$

where $J_0'(z) = (d/dz) J_0(z)$.

The excess magnetization is always positive and decreases like H^{-3} as the magnetic field is increased. This magnetization may be considered to be due to canting of the SDW, since it is proportional to Δ^2. In particular, in the vicinity of the transition temperature and at $T = 0$ K, Eq. (31) reduces to

$$M = \begin{cases} -N_0 \dfrac{2(2\pi)^2}{7\zeta(3)} (T_c - T) T_c [2\alpha J_0'(\alpha)/\lambda J_0^3(\alpha) H] \; , & (32) \\ -N_0 \Delta^2 [2\alpha J_0'(\alpha) / \lambda J_0^3(\alpha) H] \; , & (33) \end{cases}$$

respectively.

Indeed the magnetization[11] recently observed in $(\mathrm{TMTFS})_2\mathrm{ClO}_4$ at 22 mK for $H \geq 10$ T is described quite well by Eq. (33), if we assume that we are already in the region of $\alpha \ll 1$. Furthermore, the temperature dependence of the magnetization in the third peak[11] appears to be proportional to Δ^2, although the third SDW is certainly not the GL state. We believe, however, that M is proportional to Δ^2, in general, as in the GL state. Furthermore, the observed transition temperature for $H > 10$ T is described quite well[8] by Eq. (2).

IV. CONCLUDING REMARKS

Limiting ourselves to the special type of SDW state proposed by Gor'kov and Lebed,[5] we have obtained the Green functions describing the quasiparticles in SDW's. We find that Green functions have identical structures as in a BCS superconductor, if we neglect a small energy gap due to the orbital quantization. In this limit the thermodynamics is identical to that of a BCS superconductor. We obtain also a simple expression for the magnetization.

When $J_1(\alpha) \gtrsim J_0(\alpha)$ the present SDW becomes certainly unstable. If we identify the phase transition at $H \simeq 8$ T, with this transition we will have $t_b' = 0.716 b v_F eH \simeq 10$ K, which appears to be quite reasonable. Analysis of the SDW when $J_1(\alpha) \gtrsim J_0(\alpha)$ will be reported in a future publication.

ACKNOWLEDGMENTS

I would like to thank Liang Chen and Attila Virosztek for useful discussions. Particular thanks go to Attila Virosztek, who corrected some errors in the early version. I would like to thank also Dr. D. Jérome for sending me publications on the present subject. I have greatly benefitted from discussions with Dr. K. Yamaji on related subjects. The present work is supported in part by the National Science Foundation under Grant No. DMR-82-14525.

[1]For reviews, see R. L. Greene and P. M. Chaikin, Physica **126B**, 431 (1984); D. Jérome, Philos. Trans. R. Soc. London, Ser. A **314**, 69 (1985).

[2]J. F. Kwak, J. E. Schirber, R. L. Greene, and E. M. Engler, Phys. Rev. Lett. **46**, 1296 (1981); J. F. Kwak, Mol. Cryst. Liq. Cryst. **79**, 111 (1982); J. Phys. (Paris) Colloq. **44**, C3-839 (1983).

[3]K. Kajimura, H. Tokumoto, M. Tokumoto, K. Murata, T. Ukachi, H. Anzai, T. Ishiguro, and G. Saito, J. Phys. (Paris) Colloq. **44**, C3-1059 (1983).

[4]T. Takahashi, D. Jérome, and K. Bechgaard, J. Phys. (Paris) Colloq. **44**, C3-805 (1983); L. J. Azevedo, J. M. Williams, and S. J. Compton, Phys. Rev. B **28**, 6600 (1983).

[5]L. P. Gor'kov and A. G. Lebed, J. Phys. (Paris) Lett. **45**, L433 (1984).

[6]M. Héritier, G. Montambaux, and P. Lederer, J. Phys. (Paris) Lett. **45**, L943 (1984).

[7]K. Yamaji, J. Phys. Soc. Jpn. **54**, 1034 (1985); Synth. Metals **13**, 29 (1986).

[8]Liang Chen and K. Maki (unpublished).

[9]See, for example, A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinskii, *Methods of Quantum Field Theory in Statistical Physics* (Dover, New York, 1975).

[10]A. Virosztek, Liang Chen, and K. Maki (unpublished).

[11]N. J. Naughton, J. S. Brooks, L. Y. Chiang, R. V. Chamberlin, and P. M. Chaikin, Phys. Rev. Lett. **55**, 969 (1985).