

Nodeless d -wave superconductivity in a quasi-one-dimensional organic superconductor under anion order

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We propose a mechanism of nodeless d -wave superconductivity in a quasi-one-dimensional organic superconductor under anion order. It is shown that a split of the Fermi surfaces due to the anion order eliminates the line nodes of a d -wave gap function on the Fermi surfaces, and a small finite energy gap appears in the quasiparticle excitations of superconductivity. We discuss that temperature dependences of thermal conductivity and the NMR relaxation rate observed in a quasi-one-dimensional organic superconductor $(\text{TMTSF})_2\text{ClO}_4$ can be explained consistently by the small energy gap.

Anisotropy of a superconducting gap in organic superconductors is an important subject, since it is closely related to the pairing mechanism. In particular, a mechanism of an anisotropic superconductivity by pairing interactions mediated by antiferromagnetic (AF) fluctuations was proposed by Emery in the quasi-one-dimensional (Q1D) superconductors $(\text{TMTSF})_2X$,¹ and has been studied by many authors, because of the proximity to the spin-density wave. For example, it was shown that the phase diagrams and line nodes are semiquantitatively reproduced by this mechanism in a microscopic calculation.² At present, however, there is not any experimental evidence that clarifies the origin of the pairing interactions in those compounds.

For this subject, an NMR experiment was made in a Q1D superconductor $(\text{TMTSF})_2\text{ClO}_4$ by Takigawa *et al.*³ In their data, the nuclear relaxation rate T_1^{-1} did not exhibit a coherence peak (Hebel-Slichter peak) just below the superconducting transition temperature T_c , and it was proportional to T^3 at lower temperatures. These results suggest that the superconducting gap function is anisotropic and has line nodes on the Fermi surface. By calculating the relaxation rate, Hasegawa and Fukuyama proposed two possibilities, singlet pairing with the gap function $\Delta(\mathbf{k}) \sim \cos(k_y) + C$ (where $C \ll 1$) and triplet pairing with $\Delta(\mathbf{k}) \sim \sin(k_y)$.⁴ Here, we choose the x axis in the direction of the highly conductive chain, i.e., the a axis, and the y axis in the direction of the b axis.

However, recently Belin and Behnia observed a temperature dependence of thermal conductivity which indicates the nodeless gap.⁵ It may appear to contradict the NMR data at low temperatures, but as they pointed out, the NMR experiment was made only for $T \gtrsim 0.6T_c$, which may not be sufficiently low to determine the power of T . On the other hand, the absence of the peak of T_1^{-1} just below T_c still suggests an anisotropic superconductivity. Hence, they argued the possibility of the triplet superconductivity with a gap function $\Delta(\mathbf{k}) \sim \sin(k_y)$, which is anisotropic, but is finite over the whole open Fermi surfaces.

For this triplet pairing, the Hebel-Slichter peak is much smaller than that for the s -wave pairing since the coherence factor is canceled in the momentum integral which gives the relaxation rate. However, in a theoretical prediction,⁴ it does

not seem to be small enough to explain the experimental data in which the peak is not seen at all. Further, although the NMR experiment was not made at low temperatures, a tendency of $T_1^{-1} \propto T^3$ was seen above $0.6T_c$. Thus, if we believe the NMR data at the present, it is plausible that an anisotropic gap function which gives a quasiparticle density of states similar to that given by a gap function with line nodes develops at least for $T \gtrsim 0.6T_c$.

In addition to the inexplicability in the NMR data, the following two points are not clarified in explanations based on the triplet pairing: (1) The triplet pairing seems to contradict that the proximity to the antiferromagnetism may favor the d -wave superconductivity. (2) There has not been observation of a reentrant superconducting phase, which is expected if a sufficiently high field is reached experimentally,^{6,7} although the high critical field⁸ can be explained by the triplet pairing.

In this paper, we propose a mechanism of nodeless d -wave superconductivity which could explain the behaviors mentioned above, which appear to be inconsistent with each other. First, we assume pairing interactions mediated by the AF fluctuations. In the absence of anion order, the line nodes are obtained near $k_y = \pm \pi/2$, as in a result of a microscopic calculation.² When anion order occurs, the lattice periodicity changes in the b direction, and the Brillouin zone becomes half in the k_y direction. Since the degeneracies are removed by potentials due to the anions, which are staggered in the b direction, the Fermi surfaces split at the new zone boundary, near which the line nodes are situated. Hence, the line nodes are eliminated for appropriate parameters.

Recently, Yoshino *et al.* estimated the staggered potentials due to the anion order $E_g \approx 0.083t$ from their experimental data of magnetoresistance,⁹ where t denotes the hopping energy along the chain. We will show below that the value of E_g is, as an order of magnitude, large enough to eliminate the nodes of the d -wave superconducting gap near $k_y = \pm \pi/2$.

We start with a two-dimensional tight-binding Hamiltonian

$$H = - \sum_{i,j,\sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \sum_{i,\sigma} \epsilon_i \sigma_{i\sigma}^\dagger c_{i\sigma} + \sum_{i,j} V_{ij} c_{i\uparrow}^\dagger c_{i\downarrow}^\dagger c_{j\downarrow} c_{j\uparrow}, \quad (1)$$

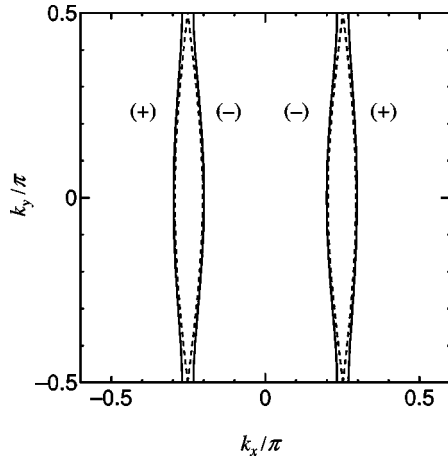


FIG. 1. Fermi surfaces of the (+) and (-) electron bands for 1/4 filling, when $t'=0.1$. Solid and broken lines show those for $E_g=0.083$ and $E_g=0$, respectively.

with effective interactions V_{ij} . We define two subchains A and B, and site energies $\epsilon_i=E_g$ and $-E_g$ for $i \in A$ and $i \in B$, respectively. The hopping energies t_{ij} are assumed to be zero unless the sites i and j are nearest neighbor. For the nearest-neighbor sites, $t_{ij}=t$ when i and j are on the same chain, while $t_{ij}=t'$ when i and j are on different subchains. We use units with $t=1$.

The bilinear terms of the Hamiltonian are diagonalized by the transformations

$$\alpha_{k,\sigma} = \sum_{s=+,-} u_{\alpha s} c_{k,\sigma}^{(s)} \quad (2)$$

with $\alpha=a,b$ and $s=+,-$, where we define $a_{i,\sigma}=c_{i,\sigma}$ for $i \in A$ and $b_{j,\sigma}=c_{j,\sigma}$ for $j \in B$. We obtain

$$u_{a+} = -u_{b-} = u(k_y) = \left[\frac{1}{2} \left(1 + \frac{E_g}{E_y} \right) \right]^{1/2}, \quad (3)$$

$$u_{a-} = u_{b+} = v(k_y) = \left[\frac{1}{2} (1 - E_g/E_y) \right]^{1/2},$$

and the dispersion relations of the (s) electron bands

$$\epsilon^{(s)}(\mathbf{k}) = -2t \cos(k_x) - sE_y(k_y), \quad (4)$$

where $E_y = \sqrt{\epsilon_y^2 + E_g^2}$ and $\epsilon_y = -2t' \cos(k_y)$. These forms of the dispersion relations were used by Yoshino *et al.* to explain their experimental results.⁹ The Fermi surfaces are modified by the staggered potential as shown in Fig. 1. In particular, the Fermi surfaces split at the boundary of the new Brillouin zone ($k_y = \pm \pi/2$).

We write the Fourier transformation of V_{ij} as

$$V(\mathbf{q}) = V_0(q_x) + V_1(\mathbf{q}) \quad (5)$$

with intrachain and interchain interactions V_0 and V_1 , respectively. Since the spin fluctuations are enhanced by the Fermi surface nesting with nesting vector $\mathbf{q}_m \approx (\pm \pi, \pm \pi/2)$, which is equivalent to $\mathbf{q}_m \approx (0, \pm \pi/2)$ in the presence of the anion order, the spin susceptibility $\chi(\mathbf{q}, \omega)$ peaks at $\mathbf{q} = \mathbf{q}_m$. The peak width is very small in the p_x direction, while it is broad in the p_y direction.² Therefore, the

effective interactions due to the exchange of the spin fluctuations are of long range in the a direction, but of short range in the b direction.¹⁰ Thus, we take interactions up to those between nearest-neighbor chains

$$V_1(\mathbf{q}) = -v_1(q_x) \cos(q_y). \quad (6)$$

The functions $V_0(q_x)$ and $v_1(q_x)$ have very sharp peaks at $q_x = \pm \pi/2$, reflecting the behavior of $\chi(\mathbf{q}, \omega)$.

Here, we make a simplification that the peak widths of $V_0(q_x)$ and $v_1(q_x)$ are similar, which is qualitatively justified when $t'/t \ll 1$. Further, in order to express the sharp peak, we employ Lorentzian form

$$f(q_x) = \sum_{q_{mx} = \pm \pi/2} \frac{1}{(q_x - q_{mx})^2 + q_0^2}, \quad (7)$$

and put $V_0(q_x) = g_0 f(q_x)$ and $v_1(q_x) = g_1 f(q_x)$.

Since the peaks are situated at the nesting vectors which connect the (+) and (-) electron bands, the peak width corresponds to the width of the area near the Fermi surfaces in which the pairing interactions are efficient. Therefore, we can assume that important contributions to the superconductivity mainly come from the pairing of electrons near the Fermi surfaces as in the standard weak-coupling theory. Hence, we can put $\langle c_{-\mathbf{k}\downarrow}^{(\pm)\dagger} c_{\mathbf{k}\uparrow}^{(\mp)\dagger} \rangle = 0$ when E_g and t' are not too small, since \mathbf{k} and $-\mathbf{k}$ cannot be near the Fermi surfaces of (\mp) and (\pm) electron bands, respectively, at the same time. This approximation is appropriate qualitatively when $E_g \gg k_B T$, and the experimental result $E_g = 0.083t$ in (TMTSF)₂ClO₄ satisfies this condition.

Hence, we obtain a gap equation

$$\Delta^{(s)}(\mathbf{k}) = -\frac{2}{N} \sum_{\mathbf{k}'s'} V^{(ss')}(\mathbf{k}, \mathbf{k}') W^{(s')}(\mathbf{k}') \Delta^{(s')}(\mathbf{k}'), \quad (8)$$

where we define

$$W^{(s')}(\mathbf{k}') = \frac{1}{2E^{(s')}(\mathbf{k}')} \tanh \left(\frac{E^{(s')}(\mathbf{k}')}{2k_B T} \right), \quad (9)$$

$$E^{(s')}(\mathbf{k}') = \sqrt{[\epsilon^{(s')}(\mathbf{k}')]^2 + [\Delta^{(s')}(\mathbf{k}')]^2}.$$

The effective pairing interactions $V^{(ss')}$ are obtained as

$$\begin{aligned} V^{(++)}(\mathbf{k}, \mathbf{k}') &= V^{(--)}(\mathbf{k}, \mathbf{k}') \\ &= \frac{1}{2} \left[V_0(\mathbf{k} - \mathbf{k}') \left(1 + \frac{E_g^2}{E_y E_y'} \right) \right. \\ &\quad \left. + V_1(\mathbf{k} - \mathbf{k}') \frac{|\epsilon_y \epsilon_y'|}{E_y E_y'} \right], \end{aligned} \quad (10)$$

$$\begin{aligned} V^{(+-)}(\mathbf{k}, \mathbf{k}') &= V^{(-+)}(\mathbf{k}, \mathbf{k}') \\ &= \frac{1}{2} \left[V_0(\mathbf{k} - \mathbf{k}') \left(1 - \frac{E_g^2}{E_y E_y'} \right) \right. \\ &\quad \left. - V_1(\mathbf{k} - \mathbf{k}') \frac{|\epsilon_y \epsilon_y'|}{E_y E_y'} \right], \end{aligned}$$

where $E'_y = E_y(k'_y)$ and $\epsilon'_y = \epsilon_y(k'_y)$.

Since the contributions from the electrons near the Fermi surfaces are dominant as we discussed above, we replace the effective pairing interactions with those on the Fermi surfaces. Further, for the sharp peak of the pairing interactions, we introduce an effective cutoff energy ω_c . Thus, we rewrite the right-hand side of Eq. (8) as

$$-\int_{-\pi/2}^{\pi/2} \frac{dk_y}{\pi} \rho^{(s')}(0, k'_y) \int_{-\omega_c}^{\omega_c} d\epsilon W^{(s')}(k'_x, k'_y) \times K^{(ss')}(k_y, k'_y) \Delta^{(s')}(k'_y), \quad (11)$$

where we define

$$K^{(ss')}(k_y, k'_y) \equiv V^{(ss')}((k_x, k_y), (k_{Fx}^{(s')}(k'_y), k'_y)) + V^{(ss')}((k_x, k_y), (-k_{Fx}^{(s')}(k'_y), k'_y)), \quad (12)$$

$$\Delta^{(s)}(k_y) \equiv \Delta^{(s)}(\pm k_{Fx}^{(s)}(k_y), k_y).$$

Here, the function $k_{Fx}^{(s)}(k_y) > 0$ gives the value of k_x on the Fermi surface of the (s) electron band at k_y . The function $\rho^{(s)}(0, k_y)$ expresses the density of states at $\epsilon=0$ and k_y of the (s) electron band of $k_x > 0$, which is calculated as $\rho^{(s)}(0, k_y) = 1/[4\pi t \sin[k_{Fx}^{(s)}(k_y)]]$.

Therefore, in the limit of $T \rightarrow T_c$, we obtain the linearized gap equations in a form of eigenvalue equations

$$\lambda \Delta^{(s)}(k_y) = - \sum_{s'=\pm} \int_{-\pi/2}^{\pi/2} \frac{dk'_y}{\pi} \rho(0, k'_y) \times K^{(ss')}(k_y, k'_y) \Delta^{(s')}(k'_y), \quad (13)$$

where $\lambda = 1/\ln(2e^\gamma \omega_c / \pi k_B T)$ with the Euler constant $\gamma = 0.57721 \dots$. The eigen solution which belongs to the maximum positive eigenvalue gives the momentum dependence of the gap function near $T = T_c$.

We solve Eq. (13) numerically for $E_g = 0, 0.083$, and 0.2 , when $t' = 0.1$. The chemical potential μ is adjusted so that the filling of holes $n = 1/4$. Since it was found in a microscopic calculation² that the range of the interaction are over 30 sites along the chain, and that interchain interactions are much weaker than intrachain interactions, we use the parameters $q_0/\pi = 0.01$ and $g_0/g_1 = 5$ as an example. The qualitative result that we will show below is not very sensitive to the values of these parameters.

Figure 2 shows the numerical result of $\Delta^{(s)}(k_y)$, where the normalization constant $\bar{\Delta}$ is defined by

$$\bar{\Delta} = \left[\int_{-\pi/2}^{\pi/2} \frac{dk_y}{\pi} |\Delta(k_y)|^2 \right]^{1/2}, \quad (14)$$

which must increase as temperature decreases. When $E_g = 0$, the result in the absence of anion order is reproduced. We have usual d -wave superconductivity with line nodes at $k_y \approx \pm \pi/2$ (dotted lines). The gap functions $\Delta^{(+)}$ and $\Delta^{(-)}$ have opposite signs equivalently to that $\Delta(|k_y| \leq \pi/2) > 0$ and $\Delta(\pi/2 \leq |k_y| < \pi) < 0$, which corresponds to the pairing with $\Delta(\mathbf{k}) \sim \cos(k_y)$ in a more simplified model. When E_g

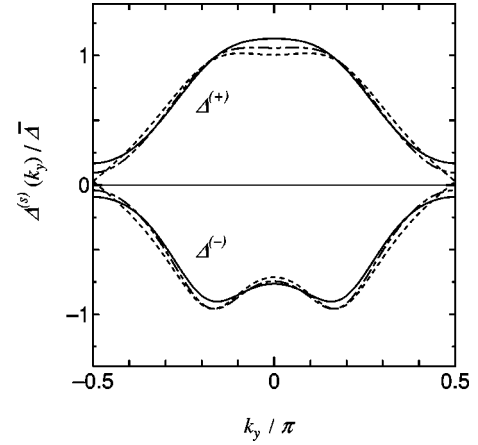


FIG. 2. The gap functions on the Fermi surfaces. The solid, dotted broken, and dotted lines show the solutions for $E_g = 0.2, 0.083$, and 0 , respectively.

$\neq 0$, we find that the line nodes vanish but the gap functions $\Delta^{(+)}$ and $\Delta^{(-)}$ still have opposite signs. The magnitudes $|\Delta^{(\pm)}|$ take minimum values at the zone boundary, and it is found that the minimum values increase with E_g .

Figures 3 and 4 show the densities of states near the Fermi level for $E_g = 0$ and 0.2 , respectively. It is found that the energy gap opens when $E_g \neq 0$, but except for the small energy gap near $E = 0$ the behavior of the density of states is very similar to that for $E_g = 0$.

The eigenvalue λ can be regarded as an effective dimensionless coupling constant. The value of $\lambda t/g_0$ is estimated to be 29.9, 25.1, and 14.8, for $E_g = 0, 0.083t$, and $0.2t$, respectively. One could make an estimation of T_c if the values of g_0/t and ω_c are given, but in practice since an effect of self-energy renormalization, especially that from the pseudo gap, is very strong,² we need a more careful treatment for a quantitative discussion.

In conclusion, we propose a mechanism of a nodeless d -wave superconductivity under the anion order. The momentum dependence of the gap function is calculated in a model with pairing interactions mediated by the AF fluctuations. It is found that the line nodes are located near the boundary of the half Brillouin zone in the absence of the

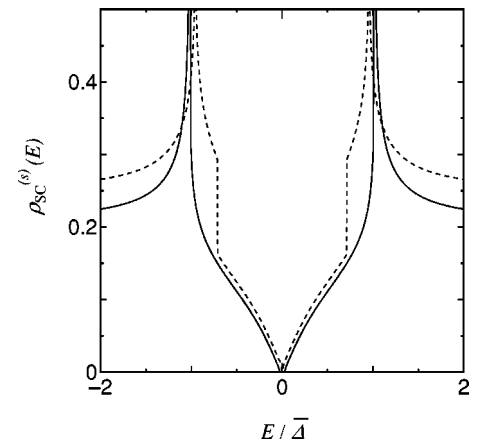


FIG. 3. Density of states near the Fermi level, when $E_g = 0$. Solid and broken lines show the results for the (+) and (-) electron bands, respectively.

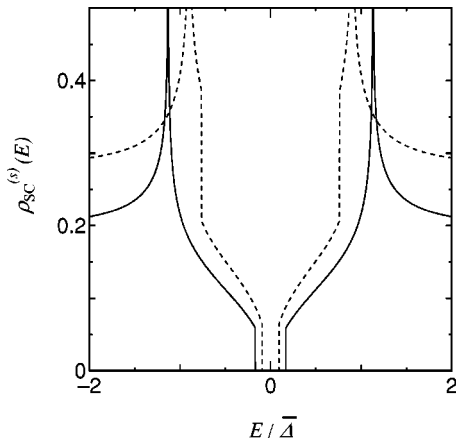


FIG. 4. Density of states near the Fermi level, when $E_g=0.2$. Solid and broken lines show the results for the (+) and (-) electron bands, respectively.

anion order, and because of their locations, the line nodes vanish in the presence of the anion order.

Thus, the energy gap of the quasiparticle excitations of superconductivity becomes finite as shown in Fig. 4. Such a small energy gap would not be observed very well in experiments at high temperatures near T_c . Since the behavior of

the density of states is very similar to that for $E_g=0$ except for the small energy gap, and the gap function changes its sign depending on $s = \pm$, temperature dependences near T_c of observed quantities are expected to be similar to those for the d -wave gap function with line nodes. In particular, it is expected that a Hebel-Slichter peak does not occur just below T_c and a tendency of $T_1^{-1} \propto T^3$ is observed near and below T_c , in NMR relaxation rate.

On the other hand, we could expect behaviors of a full gap superconductivity for low temperatures. As temperature decreases, the superconducting gap develops, and finally the temperature becomes smaller than the finite energy gap. For such low temperatures, the electronic thermal conductivity should become vanishingly small.

These behaviors may explain the recent experimental results of the thermal conductivity and the NMR relaxation rate in $(\text{TMTSF})_2\text{ClO}_4$ consistently. However, quantitative confirmation by fitting the experimental data seems to be difficult, because detailed information on the pairing interactions, such as those in momentum, frequency, and temperature dependences, is needed for this purpose. In the future, observation of the Knight shift may clarify whether the pairing is singlet or triplet.¹¹

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¹⁰The term "long range" in this paper means that the range of the interaction is much larger than the lattice constant, but does not mean a dependence like $1/r$.

¹¹In a review article by Bourbonnais and Jerome [*cond-mat/9903101*, in *Proceedings of ICSM'98* (Elsevier, New York, in press)], possibility of d -wave superconductivity in the presence of the anion order is mentioned.