Quantum fluctuations in quasi-one-dimensional superconductors

H. J. Schulz
Institut Laue-Langevin, BP 156X, 38042 Grenoble Cedex, France

C. Bourbonnais
Laboratoire de Physique des Solides, Université Paris-Sud, 91405 Orsay, France
(Received 26 October 1982)

A model for the low-temperature properties of quasi-one-dimensional superconductors, including quantum effects, is investigated. Both long-range Coulomb effects and scattering by nonmagnetic impurities enhance quantum effects. For strong quantum fluctuations the transition from a fluctuating to a long-range-ordered superconducting state obeys Bardeen-Cooper-Schrieffer-like thermodynamic relations. Application to the tetramethyltetraselenafulvalene-X $[(TMTSF)_2X]$ class of compounds is discussed. Our results also apply to other quasi-one-dimensional systems.

Since the discovery of superconductivity in the quasi-one-dimensional organic conductor tetramethyltetraselenafulvalene phosphorous hexafluoride $[(TMTSF)_2PF_6]$ (Ref. 1) considerable experimental effort has been devoted to this and related compounds.[2] Theoretically, there is by now a fairly complete picture of the properties of a one-dimensional (1D) interacting electron gas.[3] In such a system thermal and quantum fluctuations destroy long-range order (LRO), and only due to the finite interchain coupling LRO can exist in a *quasi*-1D system. The transition temperature T_c, where (three-dimensional) LRO sets in in a quasi-1D system, has been calculated by several authors.[4–6] However, so far very little is known on the behavior near T_c and in the ordered state. In the presence of some experimental results (to be discussed below) it is of interest to have a description of a quasi-1D superconductor in that temperature region. It is the purpose of this paper to give such a description.

Consider a square lattice (spacing d) of N weakly coupled 1D superconductors at temperatures well below the mean-field transition temperature T_c^0 of an individual chain. LRO is then destroyed by long-wavelength, low-energy fluctuations of the phase ϕ of the superconducting order parameter, whereas its amplitude Δ_0 is essentially constant. At low temperatures quantum effects are important, so we have to include in our description the momentum density conjugate to ϕ, namely, the density of Cooper pairs.[7] Coupling between chains is due to Josephson tunneling, so that the important phase fluctuations are described by the Hamiltonian

$$H=\sum_{m,n}\int dz\left[\frac{\pi_{mn}^2}{2\rho}+\frac{c}{2}\left(\frac{\partial\phi_{mn}}{\partial z}\right)^2-2\lambda_x\cos(\phi_{m+1,n}-\phi_{mn})-2\lambda_y\cos(\phi_{m,n+1}-\phi_{mn})\right] . \tag{1}$$

Here m and n number chains in the x and y directions, respectively, and ϕ_{mn}, π_{mn} are the phase and its conjugate momentum density on chain (m,n), respectively. The coefficient ρ is related to the electronic compressibility, and for weak electron-electron interactions one finds $\rho=1/2\pi v_F$, where v_F is the Fermi velocity (for the effect of long-range Coulomb interactions, see below). From microscopic theory one has $c=v_F/2\pi$ (Refs. 6 and 8) and $\lambda_j=t_j^2/\pi v_F$ $(j=x,y)$,[7,9] where $4t_j$ is the transverse bandwidth in a tight-binding picture. The amplitude of the order parameter only enters via the condition $T\ll\Delta_0$, necessary for the description of the system by Eq. (1).

For $\lambda_x=\lambda_y=0$ the order-parameter propagator is

$$\chi(q,\omega)=-i\int dt\,dz\,e^{i(\omega t-qz)}\Theta(t)\langle[e^{i\phi(z,t)},e^{-i\phi(0,0)}]\rangle$$
$$=-\frac{\alpha^2}{v}\left[\sin\pi\gamma\left(\frac{2\pi\alpha T}{v}\right)^{2\gamma-2}B\left(\frac{\gamma}{2}-is_+,1-\gamma\right)B\left(\frac{\gamma}{2}-is_-,1-\gamma\right)-\frac{\pi}{1-\gamma}\right] ,$$

where $v=\sqrt{c/\rho}$, $\gamma=1/4\pi\sqrt{c\rho}$, $s_{\pm}=(\omega \pm vq)/4\pi T$, $B(x,y)=\Gamma(x)\Gamma(y)/\Gamma(x+y)$, and α^{-1} is a short-wavelength cutoff. At $T=0$ one has $\chi \propto \omega^{2(\gamma-1)}$, reflecting the absence of LRO.[3] From the values for c and ρ derived above one finds $\gamma=\frac{1}{2}$, in agreement with microscopic results for weakly attractive short-range electron-electron interaction ($g_1<0$ in the language of Refs. 3). In that case it is known that the low-energy excitations of a single chain are indeed correctly described by a Hamiltonian of the form (1). On the other hand, for $g_1>0$ one finds $\gamma<1$,[3] and in the classical limit $\rho\rightarrow\infty$ one has $\gamma\rightarrow 0$. In the following we consider γ as given by microscopic calculations.[3]

For finite interchain coupling we expect superconducting LRO to develop at low temperatures, characterized by a finite expectation value $\langle e^{i\phi}\rangle$. To describe this situation we use a mean-field approximation for the interchain coupling,[6,10] leading to a 1D quantum sine-Gordon model

$$H=N\int dz\left[\frac{\pi^2}{2\rho}+\frac{c}{2}\left(\frac{\partial\phi}{\partial z}\right)^2-2|\psi|\cos\phi+\frac{|\psi|^2}{2(\lambda_x+\lambda_y)}\right]. \tag{2}$$

The order parameter $\psi=2(\lambda_x+\lambda_y)\langle e^{i\phi}\rangle$ has to be determined by minimizing the (free) energy. H can be mapped onto the massive Thirring model.[11] Using exact results for that model[12] we find that for $\gamma\leq 1$ superconducting LRO exists, i.e., at $T=0$, $\langle e^{i\phi}\rangle$ takes a finite value:

$$\langle e^{i\phi}\rangle=\frac{\pi}{2(2-\gamma)\cos(\pi\gamma/2)}\left[\frac{\pi}{2(2-\gamma)}\frac{\lambda}{\sin\pi\gamma}\right]^{\gamma/(2-2\gamma)} \quad (\gamma<1) \tag{3a}$$

$$=(2/\lambda)e^{-1/\lambda};\ [\lambda=4\pi\alpha^2(\lambda_x+\lambda_y)/v]\ \ (\gamma=1)\ , \tag{3b}$$

and the condensation energy is

$$E_c=-\frac{LNv}{2\alpha^2}\frac{1-\gamma}{2-\gamma}\tan\frac{\pi\gamma}{2}\left[\frac{\lambda\langle e^{i\phi}\rangle}{2\sin(\pi\gamma/2)}\right]^{2/(2-\gamma)}. \tag{4}$$

In the classical case $\gamma=0$, Eq. (3a) gives $\langle e^{i\phi}\rangle=\pi/4$ instead of unity, due to the inequivalent cutoffs of the sine-Gordon and Thirring models in that limit. Therefore Eq. (3a) is only valid for $\gamma>\lambda/4$. With increasing γ quantum fluctuations reduce $\langle e^{i\phi}\rangle$ from unity, and for weak coupling one has $\Delta(T)\equiv\Delta_0\langle e^{i\phi}\rangle << \Delta_0$. For $\gamma>1$ the quantum fluctuations completely destroy LRO.

Near T_c, $|\psi|$ is small, so that from Eq. (2) a Ginzburg-Landau-type energy functional can be derived by a perturbation expansion, assuming a slowly varying ψ:

$$F=\int d^3r\left[a|\psi|^2+\sum_{j=xyz}c_j\left|\frac{\partial\psi}{\partial j}\right|^2+b|\psi|^4\right],$$

$$a=[\chi(0,0)+\tfrac{1}{2}(\lambda_x+\lambda_y)^{-1}]/d^2\ ,$$

$$b=\frac{7\zeta(3)\pi\alpha^4}{2\gamma^3vT^2d^2}\left[\frac{2}{\zeta(3)}\right]^{1-\gamma}\left[\frac{v}{2\pi\alpha T}\right]^{4-4\gamma}, \tag{5}$$

$$c_z=\left[\frac{v}{4\pi T}\right]^2\left[\psi'\left(1-\frac{\gamma}{2}\right)-\psi'\left(\frac{\gamma}{2}\right)\right]\left[\chi(0,0)-\frac{\pi\alpha^2}{v}\right]\Big/d^2,$$

$$c_j=-\lambda_j[\chi(0,0)+\tfrac{1}{4}(\lambda_x+\lambda_y)^{-1}]/(\lambda_x+\lambda_y)\ .$$

The coefficient b is exact for $\gamma=0$, 1, and for intermediate values has been obtained from renormalization group arguments.[13] A functional like Eq. (5) can also be derived from a mean-field treatment of interchain coupling in microscopic models. The transition into the long-range ordered state occurs for $a=0$, giving

$$T_c=\frac{v}{2\pi\alpha}\left[\frac{\lambda}{4\pi}B^2\left(\frac{\gamma}{2},\frac{\gamma}{2}\right)\tan\frac{\pi\gamma}{2}\right]^{1/(2-2\gamma)} \quad (\gamma<1) \tag{6a}$$

$$=\frac{2ve^C}{\pi\alpha}e^{-1/\lambda}\ \ (\gamma=1)\ , \tag{6b}$$

where $C=0.577$. Though the full temperature dependence of $\Delta(T)$ cannot be calculated from the above, apart from the case $\gamma=1$, interpolating between the results of Eqs. (3) ($T=0$) and (6) ($T\approx T_c$) the curves shown in Fig. 1 for different values of γ can be obtained.

There is a jump in the specific heat at T_c: $\Delta C=Va'^2/2bT_c$. On the other hand, the specific heat of uncoupled chains is $C_n=V\pi T/3d^2v$. For $\gamma=1$ one then finds $\Delta C/C_n=12/7\zeta(3)\approx 1.43$, the same as in BCS theory. With γ decreasing, $\Delta C/C_n$ increases first (Fig. 2), due to the sharper initial increase of the ordering (Fig. 1); but below $\gamma\approx\frac{1}{2}$ the ratio decreases, due to the sharp increase of C_n. Combining Eqs. (4) and (6) we find $E_c=A(\gamma)T_cC_n(T_c)$, with $A(1)=0.75e^{-2C}\approx 0.24$. This numerical factor again agrees with BCS theory.

To check the consistency of our above calculation, we look at the Ginzburg critical temperature region,[14] defined by requiring that the first fluctuation correction to the specific heat should be comparable to ΔC,

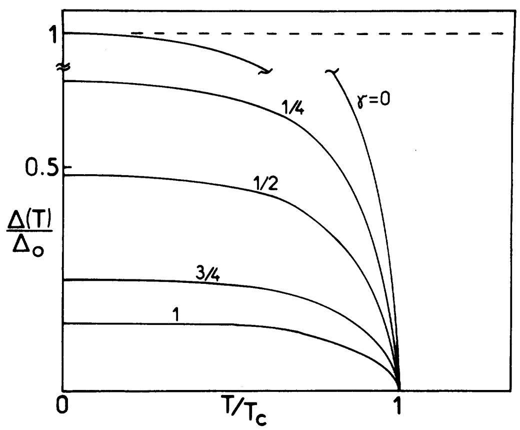

FIG. 1. Temperature dependence of the gap $\Delta(T) = \Delta_0\langle e^{i\phi}\rangle$ for different values of γ. $\lambda = 0.25$ for $\gamma = 1$ and $\lambda = 0.1$ othewise. The dashed line is the mean-field result.

i.e.,

$$\Delta t_c = (3/8\pi)^2 b^2 T_c^2/(a' c_x c_y c_z)$$

in units of T_c. From Eq. (5),

$$\Delta t_c = f(\gamma)\frac{(\lambda_x+\lambda_y)^2}{4\lambda_x\lambda_y}\left[1+\frac{\lambda}{2(1-\gamma)}\right]^2 . \quad (7)$$

For $\gamma \approx 1$ one has $f(\gamma) \approx 2(1-\gamma)^2$ or $\Delta t_c \approx 0.5\lambda^2$ if $\lambda_x = \lambda_y$. The general form of $f(\gamma)$ is shown in Fig. 2, exhibiting a relatively narrow critical region even for $\gamma = 0$ as long as $\lambda_x \approx \lambda_y$. On the other hand, the crossover temperature above which the transverse coherence length is smaller than d is given by

$$\Delta t^* = \frac{\lambda_j}{4(\lambda_x+\lambda_y)}\frac{1}{1-\gamma+\lambda/2} . \quad (8)$$

Thus, as long as $\gamma \approx 1$, one has $\Delta t^* >> \Delta t_c$, so that the continuum approximation used in Eq. (5) is well justified. It fails only for $\gamma \approx 0$, where $\Delta t^* \approx \Delta t_c$.

It is worthwhile emphasizing that in the case of strong quantum effects ($\gamma \approx 1$) the thermodynamic relations, including numerical factors, are those of BCS theory. The nature of the transition is, however, quite different: it occurs from a state of strongly developed short-range order on individual chains (with a strong depression of the density of states at the Fermi level, the "pseudogap"[15]) to a long-range ordered superconducting state. In spite of the strong fluctuations on individual chains, the widths of the transition, determined by the *critical three-dimensional* fluctuations, is quite small.

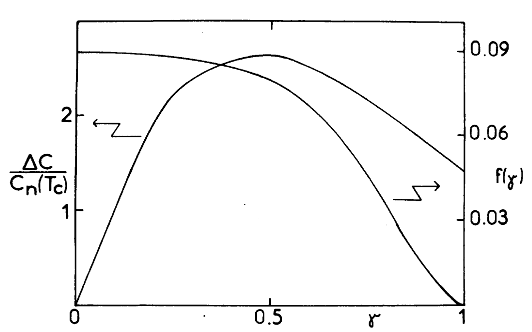

FIG. 2. Ratio $\Delta C/C_n(T_c)$ and the function $f(\gamma)$, parametrizing the critical width [Eq. (7)].

The long-range Coulomb interactions between the charge-density fluctuations can be included by an additional term

$$H_c = \frac{1}{2}\sum_{\substack{mm'\\nn'}}\int dz\,dz'\,\pi_{nm}(z)V(\vec r-\vec r\,')\pi_{m'n'}(z') \quad (9)$$

in the Hamiltonian (1), where $V(\vec r) = 4e^2/r$. For $\lambda = 0$, $\chi(q,\omega)$ remains diagonal in the chain indices, and H_c only changes γ:

$$\gamma = \frac{1}{4\pi A_\perp\sqrt{c\rho}}\int d^2k_\perp\left[1+\frac{\epsilon_\parallel}{\epsilon_\perp}\left(\frac{\omega_{\rm pl}}{vk_\perp}\right)^2\right]^{1/2} , \quad (10)$$

where $\omega_{\rm pl}$ is the longitudinal plasma frequency, $\epsilon_\parallel$, $\epsilon_\perp$ are the high-frequency dielectric constants parallel and perpendicular to the chains, and $A_\perp$ is the area of the Brillouin zone in the transverse directions. The correction factor in Eq. (10) can be quite large, thus decreasing the tendency to 3D ordering. Similar results are found in microscopic calculations.[16]

The exponent γ is also increased by scattering from *nonmagnetic* impurities. This decreases the coefficient c in Eq. (1),[8] and the effect is even stronger in a quasi-1D system.[17] Thus in the present model the superconducting transition can be suppressed by nonmagnetic impurities, in marked contrast to the usual BCS theory. Finally, $\chi(q,\omega)$ and especially γ are strongly magnetic field dependent,[3,18] and therefore a straightforward use of Eq. (5) for critical-field calculations seems not reasonable.

Let us now try to apply our model to the organic superconductors of the $(TMTSF)_2X$ class. First, current microscopic models[19] imply $\gamma \approx 1$. The band structure is described by[2] $v_F = 350$ meV d_z, $t_x = 10$ meV, $t_y = 0.3$ meV (d_z is the longitudinal lattice constant), giving $\lambda \approx 3.10^{-3}\alpha^2/d_z^2$. For nonretarded electron-electron interactions one has $\alpha = d_z$, leading to an extremely small T_c. However, if the retarded electron-phonon interaction is included,[19] α is increased. Choosing $\alpha = 8d_z$ we obtain $T_c \approx 2$ K, the order of magnitude of experimental T_c's. On the other hand, tunneling,[2] infrared,[2] and heat conductivity[2,20] measurements imply $T_c^0 \approx 10-15$ K, so that our model should apply. We are then able to explain some experimental findings: (i) The BCS-like thermodynamics of the transition[21] is expected in our model for $\gamma \approx 1$. (ii) In the presence of a large x-y anisotropy, instead of Eq. (7), one finds $\Delta t_c \approx 0.1\sqrt{\lambda}$ for $\gamma \approx 1$, explaining the small width of the transition.[21] (iii) The large sensitivity of the transition to nonmagnetic disorder: alloying on the level of some percent destroys the transition completely, whereas the precursor regime is much less affected.[22]

In conclusion, our calculations show that: (i) quantum fluctuations are important for the low-temperature properties of quasi-1D superconductors and especially may lead to BCS-like thermodynamics of the transition to a 3D superconducting state; (ii) long-range Coulomb interactions or scattering by impurities enhance quantum fluctuations; (iii) our results allow one to explain the transition in the $(TMTSF)_2X$ compounds as being one from a state of 1D fluctuations to a 3D superconducting state. A model given by Eq. (1) also applies to weakly coupled 1D charge-density wave (CDW)[23] or magnetic systems. In the CDW case, however, the large phonon effective mass[23] usually leads to $\gamma \ll 1$, i.e., the classical limit.

ACKNOWLEDGMENTS

The authors thank D. Jérome, K. Bechgaard, T. M. Rice, and J. Solyom for helpful discussions.

[1]D. Jérome *et al.*, J. Phys. (Paris) Lett. 41, L95 (1980).
[2](a) *Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, 1981* [Mol. Cryst. Liq. Cryst. 79, (1982)]; (b) D. Jérome and H. J. Schulz, Adv. Phys. 31, 299 (1982).
[3]J. Solyom, Adv. Phys. 28, 201 (1979); V. J. Emery, in *Highly Conducting One-Dimensional Solids*, edited by J. T. Devreese *et al.* (Plenum, New York, 1979), p. 247.
[4]L. P. Gorkov and I. E. Dzyaloshinskii, Zh. Eksp. Teor. Fiz. 67, 397 (1974) [Sov. Phys. JETP 40, 198 (1975)]; V. N. Prigodin and Yu.A. Firsov, *ibid.* 76, 1602 (1979) [*ibid.* 49, 813 (1979)].
[5]R. A. Klemm and H. Gutfreund, Phys. Rev. B 14, 1086 (1976); P. A. Lee *et al.*, *ibid.* 15, 2984 (1977).
[6]K. B. Efetov and A. I. Larkin, Zh. Eksp. Teor. Fiz. 66, 2219 (1974) [Sov. Phys. JETP 39, 1129 (1974)].
[7]P. W. Anderson, in *Lectures on the Many-Body Problem*, edited by E. R. Caianiello (Academic, New York, 1964), p. 113.
[8]For a similar calculation in three dimensions, see N. R. Werthamer, in *Superconductivity*, edited by R. D. Parks (Dekker, New York, 1969), p. 321.
[9]V. Ambegaokar and A. Baratoff, Phys. Rev. Lett. 10, 486 (1963); 11, 104 (1963).
[10]This approach gives good results in classical systems; see D. J. Scalapino *et al.*, Phys. Rev. B 11, 2042 (1975).
[11]S. Coleman, Phys. Rev. D 11, 2088 (1975).
[12]H. Bergknoff and H. B. Thacker, Phys. Rev. D 19, 3666 (1979).
[13]N. Menyhard, J. Phys. C 11, 2207 (1978).
[14]V. L. Ginzburg, Fiz. Tver. Tela (Leningrad) 2, 2031 (1960) [Sov. Phys. Solid State 2, 1824 (1960)].
[15]For a microscopic derivation, see Y. Suzumura, Prog. Theor. Phys. 63, 51 (1980).
[16]H. J. Schulz (unpublished).
[17]A. I. Larkin and V. I. Melnikov, Zh. Eksp. Teor. Fiz. 71, 2199 (1976) [Sov. Phys. JETP 44, 1159 (1976)].
[18]G. E. Gurgenishvili *et al.*, Zh. Eksp. Teor. Fiz. 73, 279 (1977) [Sov. Phys. JETP 46, 145 (1977)].
[19]S. Barisic and S. Brazovskii, in *Recent Developments in Condensed Matter Physics*, edited by J. T. Devreese (Plenum, New York, 1981), Vol. 1, p. 327; B. Horovitz *et al.*, Solid State Commun. 39, 541 (1981); V. J. Emery *et al.*, Phys. Rev. Lett. 48, 1039 (1982).
[20]D. Djurek *et al.*, J. Phys. C 15, L669 (1982).
[21]P. Garoche *et al.*, J. Phys. (Paris) Lett. 43, L147 (1982).
[22]K. Bechgaard *et al.*, in Ref. 2(a), p. 275; C. Coulon *et al.*, J. Phys. (Paris) 43, 1721 (1982).
[23]H. Fukuyama, J. Phys. Soc. Jpn. 41, 513 (1976).