Conductivity, Superconductivity, and the Peierls Instability*

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(Received 18 June 1973)

We investigate the properties of a one-dimensional model of the electron-phonon system which exhibits the Peierls instability. The instability tends to suppress BCS pairing, and the resulting Peierls state below the structural transformation is semiconducting. Results of the conductivity calculation compare favorably with recent measurements on most samples of tetrathiofulvalinium tetracyanoquinodimethane but cannot explain the extraordinary conductivity peaks found in a few samples.

Recently, the synthesis of the highly conducting organic solid tetrathiofulvalinium tetracyanoquinodimethane (TTF-TCNQ) was reported by two groups.[1,2] The temperature dependence of the conductivity is metallike above 60 K and insulatorlike below. The Johns Hopkins group[1] found the maximum conductivity (at 66 K) to be 1.47 $\times 10^4/\Omega$ cm. Coleman *et al.*[2] observed some seventy crystals which have similar behavior. However, three of their crystals had much larger conductivity peaks near 60 K ($>10^6/\Omega$ cm).

The two groups pointed out that a possible explanation of the low-temperature insulating phase is the Peierls instability[3] in one dimension. At room temperature the crystal structure of TTF-TCNQ is monoclinic,[4] with parallel chains of TTF (electron donor) and TCNQ (electron acceptor). Because of the very small interchain overlaps, electrons are confined to the one-dimensional TCNQ chains and holes to the TTF chains.

Several explanations have been given for the extraordinary conductivity peaks of Coleman *et al.* The experimenters themselves[2] explain the extraordinary peaks in terms of superconducting fluctuations due to BCS electron-electron pairing[5] via the Peierls soft phonon. They suggest that suppression of the Peierls transition could lead to a stable high-temperature superconductor.[2,6] Bardeen[7] has suggested that the peaks are the result of fluctuations of a different kind of superconducting state arising from a one-dimensional model proposed by Fröhlich.[8] In this theory, although the chains distort as suggested by Peierls, a superconducting current-carrying state could be constructed in which the electrons move with the lattice distortion.

We have calculated the properties of a one-dimensional electron-phonon system. In this note we discuss the nature of the results with particular regard to the following questions: (1) the possibility of BCS pairing above the Peierls instability, (2) the current response of the Peierls state, and (3) the fluctuation conductivity above the transition.

We adopt the Hamiltonian for a one-dimensional coupled electron-phonon system, neglecting direct electron-electron interaction. Arguments have been given for small electron-electron interactions in TTF-TCNQ[9]; the inclusion of a strong interaction would tend to suppress the Peierls instability and favor a magnetic state at low temperature, in disagreement with experiments. The calculations have been performed in both the effective-mass and tight-binding limits (with only slight numerical differences). The interaction is

$$H_{ep}=\sum_{kqG} g(k, q+G)a_k^\dagger a_{k+q+G}(b_{-q}+b_q^+), \qquad (1)$$

where G is a reciprocal-lattice vector, a and b are operators for electrons and phonons, respectively, and a sum over spins is understood. The Peierls instability may be regarded as arising from the softening of the phonon with wave vector $q\sim 2k_{\rm F}\equiv q_0$, which is due to the enhanced Kohn effect[10] in one dimension. The Peierls transition temperature $T_{\rm P}$ is the point at which the q_0 phonon frequency first reaches zero as the temperature is lowered. Just above the transition, the random-phase-approximation (RPA) calculation of the phonon Green's function yields (for $q=q_0+p$, $p<k_{\rm F}$, $\omega<T$)[11]

$$[D(q_0+p,\omega)]^{-1}=-\omega^2+\lambda\Omega^2\left(\epsilon+\xi^2p^2-\frac{i\pi\omega}{8T}\right), \qquad (2)$$

where Ω is the unrenormalized phonon frequency, $\lambda\sim N(0)g^2/\Omega$, and the coherence length $\xi\sim v_{\rm F}/T$. Above $T_{\rm P}$, $\epsilon\simeq(T-T_{\rm P})/T_{\rm P}$; while in the critical region and below $T_{\rm P}$, ϵ decreases to zero monotonically as T decreases as a result of the strong effect of fluctuations in one dimension. Equation (2) is the time-dependent Ginzburg-Landau equation for a fluctuation into the Peierls state. Although the coefficients are the same as those for the superconducting case, (2) differs in that it does not lead to a contribution to the current, and in the presence of a finite electron-impurity scattering rate $1/\tau$, the transition temperature is lowered according to $\epsilon \to \tilde{\epsilon} = \epsilon + \pi/8\tau T$.

The BCS-type superconducting transition temperature T_c is determined by the temperature at which the binding of the Cooper pair ($k\uparrow$ and $-k\downarrow$) due to phonon-mediated attraction occurs. Just above the Peierls transition, the attraction between electrons comes mainly from the soft phonons near q_0. The condition for a singular solution of the Cooper-pair t matrix is

$$1 = T\sum_{p,\omega} g^2 D(q_0+p,\omega)G(q_0+p,E+\omega)G(-q_0-p,-E-\omega), \tag{3}$$

where D is given by Eq. (2) and G is the electron Green's function. E is set equal to zero *after* the energy summation.

Examination of Eq. (3) yields three reasons why soft phonons tend to destroy rather than enhance BCS pairing:

(1) Lowering the phonon frequency ω would raise T_c only if $\omega > T_c$. If $\omega < T_c$, then these phonons do not provide attraction for electrons to form a Cooper pair. This is a very general result valid for all kinds of materials. To show this, we evaluate Eq. (3) by using bare electron Green's functions and the phonon Green's function of Eq. (2), neglecting the damping term. We obtain an electronic term

$$1 = g^2\int_{-\pi}^{\pi}\frac{dp}{2\pi}\,\frac{\tanh(\mathcal{E}_p/2T_c)}{2\mathcal{E}_p}\,\frac{1}{\omega_p^{\,2}-\mathcal{E}_p^{\,2}} + \cdots, \tag{4}$$

where $\mathcal{E}$ is the electron energy, ω_p is the renormalized frequency of the q_0+p phonon. The function $\tanh(\mathcal{E}/2T_c)/2\mathcal{E}$ is approximately constant for $|\mathcal{E}| < 2T_c$ and $1/2|\mathcal{E}|$ outside. If $\omega_p > 2T_c$, the phonons provide attraction for the Cooper instability as usual. If $\omega_p < 2T_c$, elementary integration shows that Eq. (4) cannot be satisfied. That is, phonons of frequencies comparable to or less than T_c tend to destroy Cooper pairing.

(2) If the soft-phonon fluctuation contribution to the electron self-energy is included, the electron Green's function becomes

$$G^{-1}(k,\omega) = \omega - \mathcal{E}_k - \delta^2/(\omega + \mathcal{E}_k + i4T\epsilon^{1/2}), \tag{5}$$

with the fluctuation gap $\delta = \pi^{1/2}T/\epsilon^{1/4}$. The major effect on Eq. (4) is to replace $\mathcal{E}_p$ by $(\mathcal{E}_p^{\,2}+\delta^2)^{1/2}$ which further reduces T_c.

(3) Thermal occupation of phonons also tend to destroy BCS pairing.[12] Although this effect is small in ordinary solids, it does also provide a depairing mechanism for soft phonons.[13] If this term is evaluated for the soft phonons, neglecting the damping, it goes like $(T - T_\mathrm{P})^{-3/2}$. Rice and Strässler[14] have suggested that this large term suppresses superconductivity. However, if the phonon damping term is included as in Eq. (2), the thermal phonon term is much reduced, being dominated by the damping term rather than by the soft-frequency contribution $(T - T_\mathrm{P})^{-3/2}$. Thus while this term helps to suppress BCS superconductivity, its effect is not as decisive as those given in the first two reasons.

We consider now the description of the system below T_P. The equations of motion involve a correlation function of the a's and b's which, above T_P, is dominated by the interaction of the electrons with the soft phonons. Below the Peierls instability one is led to introduce an order parameter δ proportional to the displacement of alternate TCNQ molecules in a chain which represents the "condensation" of a macroscopic number of phonons into the $q_0 = \pi/a$ state, in analogy to Gor'kov's treatment for the superconductor. Thus

$$g_q\langle Ta_{k+q+G}(b_{-q}+b_q^{\dagger})a_k^{\dagger}\rangle \Rightarrow g\langle b_{-q_0}+b_{q_0}^{\dagger}\rangle\langle Ta_{k\pm q_0}a_k^{\dagger}\rangle = \delta G(k,k\pm q_0), \tag{6}$$

where

$$\delta \equiv g\langle b_{-q_0}+b_{q_0}^{\dagger}\rangle = (g^2/\Omega^2)\textstyle\sum_k G(k,k+q_0), \tag{7}$$

and $G(k,k+q_0)$ is an "anomalous" propagator which represents *diagonal* long-range order, in contrast to the superconducting state.[15]

Although (6) is the natural factorization which reflects the Peierls instability, other choices, leading to a supercurrent, are conceivable. The only decomposition we have found that leads to the possibility of a supercurrent is the conventional BCS one, which is suppressed by the Peierls instability. In addition, (6) results in a transition temperature whose scale is set by the Fermi energy[16] (rather than the smaller phonon energy): $T_\mathrm{P} \sim \epsilon_\mathrm{F}\exp(-1/\lambda)$, and which is of the correct order of the transition temperature for TTF-TCNQ.[1,2]

Explicit evaluation of the current response, including the anomalous propagator in the Peierls state, confirms the absence of a supercurrent. Although the expression for the electromagnetic response is similar to that of the BCS superconductor, the coherence factor has the opposite sign and thus leads to an insulator behavior.

In the region $T_P < T < 2T_P$, the fluctuation conductivity is obtained by expanding in powers of the soft phonon. The resulting diagrams shown in Fig. 1 are similar to those above the superconducting transition[17] with several crucial differences which correspond to the difference between the superconducting state and the Peierls state. First, the contribution of Fig. 1(c), the analog of the Aslamazov-Larkin[18] diagram, vanishes to leading order in general, and is identically zero if there is particle-hole symmetry and $q_0 = \pi/a$. Since the contribution of this diagram is related to the coupling of the electric field to the time-dependent Ginzburg-Landau equation (2) describing the soft mode, the absence of the Aslamazov-Larkin diagram is related to the fact that the characteristic charge of the fluctuating electron-hole pair described by (2) is zero, rather than $2e$ as for a superconductor. Second, the contribution to the conductivity of Fig. 1(b) is negative, in contrast to the superconducting case, and corresponds directly to the cancelation of the coherence factor below the transition as mentioned previously. Thus, the contributions from both fluctuation terms, Figs. 1(a) and 1(b), reduce the conductivity.

In the limit of small scattering ($\tau T_P \gg 1$), we obtain the simple approximation for the conductivity,

$$\sigma = 2\sigma_0/(1+e^{\delta/T}), \tag{8}$$

where σ_0 is the metallic conductivity in the absence of the phase transition. Equation (8) is also valid above T_P, where δ^2 is related to the density of soft phonons. Equation (8) is compared with experimental data in Fig. 2. We have used $\sigma_0(T) = \sigma_0(300)[(T/300)^2 + R]^{-1}$, where R is the contribution of impurity scattering, and the T^2 dependence is taken from experiment.[1]

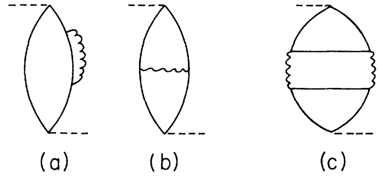

FIG. 1. Fluctuation contributions to the conductivity. Solid lines, electrons; wavy lines, soft phonons; dashed lines, external vertices.

Other properties of the system have been calculated, including the dielectric constant, ultrasonic attenuation, spin susceptibility, and thermopower. Details will be presented elsewhere. Here we merely note that all properties are consistent with a transition to a semiconducting state below T_P. Of particular interest is the ultrasonic attenuation, which we predict should have an appreciable peak just below the transition for clean enough samples. This is analogous to the conductivity behavior of the BCS superconductor with paramagnetic impurities.[19] On the other hand, the conductivity of the Peierls state is similar to the ultrasonic attenuation in the BCS system. These phenomena are indicative of the characteristic signature of the coherence factors of the Peierls state. One final consequence of the model is that T_P increases strongly with uniaxial compression. We estimate that 10 kbar should increase T_P by a large fraction,[20] thus causing a big change in conductivity at a fixed temperature.[21]

We wish to thank Professor B. T. Matthias, Professor J. Bardeen, Professor W. Kohn, and

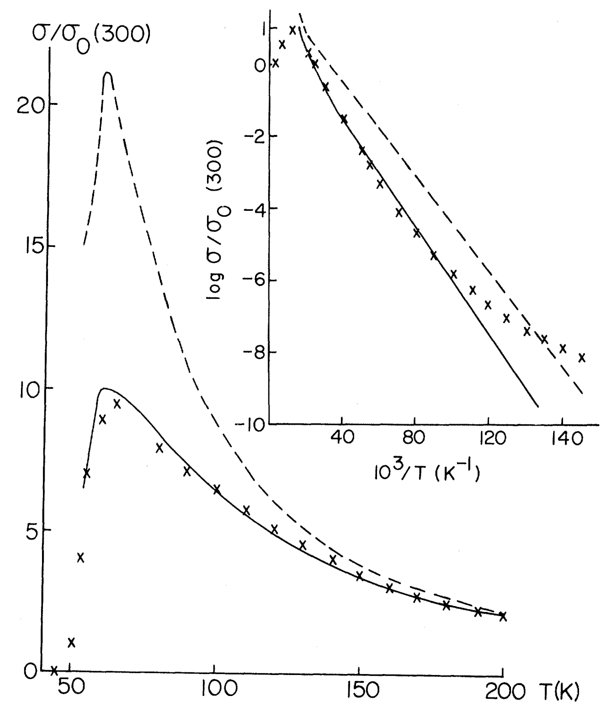

FIG. 2. High-temperature conductivity data of Ref. 2 compared with Eq. (7). Crosses, experiment; solid line, theory with $R = 0.05$; dashed line, theory with $R = 0$; and $\epsilon_c = 0.01$ defined as in Ref. 17. Inset: Low-temperature conductivity data of Ref. 1 with $\delta/T_P = 2.9$.

Professor H. Suhl for helpful conversations.

*Research supported by the National Science Foundation under Grants No. GP-28997 and No. GH-37719.

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[1]J. Ferraris, D. O. Cowan, V. Walatka, Jr., and J. H. Perlstein, J. Amer. Chem. Soc. 95, 948 (1973); A. N. Bloch, J. P. Ferraris, D. O. Cowan, and T. O. Poehler, to be published.

[2]L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, Solid State Commun. 12, 1125 (1973).

[3]R. E. Peierls, *Quantum Theory of Solids* (Oxford Univ. Press, Oxford, England, 1953), p. 108.

[4]T. E. Phillips, T. J. Kristenmacher, J. P. Ferraris, and D. O. Cowan, Chem. Commun. 14, 471 (1973).

[5]J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).

[6]*The New York Times*, 25 March 1973, p. 43; Phys. Today 26, No. 5, 17 (1973).

[7]J. Bardeen, to be published.

[8]H. Fröhlich, Proc. Roy. Soc., London, Ser. A 223, 296 (1954).

[9]A. J. Epstein, S. Etemad, A. F. Garito, and A. J. Heeger, Phys. Rev. 25, 952 (1972); J. G. Vegter, J. Kommandeur, and P. A. Fedders, Phys. Rev. B 1, 2929 (1973).

[10]W. Kohn, Phys. Rev. Lett. 2, 393 (1959).

[11]For simplicity, we have adopted the commensurate case of one electron per molecule, where $q_0 = \pi/a$. Our results will not be changed qualitatively for the noncommensurate case with q_0 close to π/a.

[12]J. Appel, Phys. Rev. Lett. 21, 1164 (1968).

[13]P. B. Allen, Solid State Commun. 12, 379 (1973).

[14]M. J. Rice and S. Strässler, to be published. We wish to thank Professor D. Scalapino for bringing it to our notice.

[15]W. Kohn and D. Sherrington, Rev. Mod. Phys. 42, 1 (1970).

[16]C. G. Kuper, Proc. Roy. Soc., London Ser. A 227, 214 (1955).

[17]B. R. Patton, Phys. Rev. Lett. 27, 1273 (1971).

[18]L. G. Aslamazov and A. I. Larkin, Fiz. Tverd. Tela 10, 1104 (1968) [Sov. Phys. Solid State 10, 875 (1968)].

[19]A. Griffin and V. Ambegaokar, in *Proceedings of the Ninth International Conference on Low Temperature Physics, Columbus, Ohio, 1964*, edited by J. G. Daunt *et al.* (Plenum, New York, 1965), p. 524.

[20]Preliminary measurements by B. T. Matthias, A. Lawson, and D. Johnston indicate such a big change in T_P with pressure.

[21]R. B. Aust, G. A. Samara, and H. G. Drickamer, J. Chem. Phys. 41, 2003 (1964).

Temperature Independence of Positron Trapping by Vacancies in Gold*

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(Received 27 April 1973)

Experimental data are presented which indicate that the trapping rate of positrons per unit vacancy concentration in gold is temperature independent.

The temperature dependence of positron trapping by vacancies in gold has been directly measured. The results show that below 0°C the positron trapping rate per unit vacancy concentration is independent of temperature. From the same data, but less directly, it appears likely that temperature independence continues up to at least 650°C.

The importance of this result arises from the increasing use of positron trapping to determine vacancy-formation energies E_v in metals.[1] The temperature dependence of trapping must be known if E_v is to be evaluated with an accuracy of better than about 10%.

The method was to fix the concentration of vacancies in gold, by quenching, and then to measure the positron lifetime at nitrogen and ice temperatures. The gold foil, of 99.99% purity from Johnson and Matthey, $0.4\times 0.6\times 0.010$ in.[3], was prepared by annealing for 4 h at 950°C in air and slowly cooling over about 12 h to room temperature. It was then etched. These pieces were clamped at each end in a light frame and quenched from 650°C by plunging them end first into water. The quenching rate was observed to be about 0.5×10^4 °C per second for the first 125° while the foil was still in air and about 3×10^4 °C per second thereafter in water. After quenching, these specimens were etched for a few minutes at room temperature and placed immediately in the apparatus which cycled them between ice temperature and 100°K. The few minutes at room temperature and the several hours at ice temperature and below during data collection should result in no significant annealing of monovacancies.[2] The change in positron lifetime between two fixed