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SUPERCONDUCTING FLUCTUATIONS IN ONE-DIMENSIONAL ORGANIC SOLIDS*

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It is suggested that the superconducting fluctuations observed by Coleman *et al.* just above the Peierls soft mode instability in psuedo one-dimensional organic solids is a reflection of Fröhlich's one-dimensional model in which superconductivity arises from a coupling of the electrons with moving lattice waves rather than from a BCS type pairing.

COLEMAN *et al.*[1] have observed an extraordinary increase in conductivity just above the Peierls soft mode instability in an organic solid in which the conduction is primarily along chains of molecules in essentially one dimension. They attribute the increase to paraconductivity from superconducting fluctuations above T_c using the usual pairing model of superconductivity. We agree that the evidence for paraconductivity is very strong, but suggest that the origin of the superconductivity is accounted for by Fröhlich's one-dimensional model,[2] presented in 1954, based on strong coupling between electrons and lattice vibrations, rather than the pairing model. In Fröhlich's model, the macroscopic occupation which gives rise to the superconducting properties is that of a travelling lattice wave rather than the common mometum of the pairs. There are no pairs in Fröhlich's picture.

Fröhlich's model was regarded as an interesting mathematical model without real physical significance. Aside from the fact that it applied only to one-dimensional systems, the model did not seem to give properties corresponding to known metallic superconductors. For one thing, according to the model the energy gap and transition temperature should be roughly the same as phonon energies; while in usual superconductors the gap, 2Δ, is much smaller than $k_B\theta_D$. It is remarkable that nearly twenty years later, there seems to have been found a counterpart of Fröhlich's model in nature.

In the system studied by Coleman *et al.* the molecules in the chains are free radicals with one electron per molecule available for conduction. If there is a uniform spacing between molecules, there are just enough electrons to fill half of the states in the first one-dimensional Brillouin zone, with boundaries at $\pm \pi/a$, where a is the spacing between molecules. The Peierls instability is a lattice distortion of period $2a$ so as to give gaps at the Fermi surface, or at $k_F = \pm \pi/2a$. The organic system is designed to minimize the repulsive Coulomb interaction between electrons; and we shall follow Fröhlich in taking a simple free electron model and neglect any interaction between electrons. In this simple model, there is metallic conduction at high temperatures which changes to semiconducting or insulating as the temperature drops below the critical temperature, T_c, where the double period distortion sets in.

Fröhlich suggested that the model would exhibit superconducting properties if the lattice distrotion moves with the electrons when the electrons are displaced in k-space so as to give a current flow. The energy gaps then move with the Fermi surface and are fixed relative to it. At low temperatures, only the states below the gap are occupied. There is a consequent decrease in the energy of the electrons at the expense

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of the energy required to distort the lattice. Fröhlich found that at $T = 0°\,K$ and with no current flow, there is an energy gap

$$2\Delta = 16E_F e^{-1/\lambda}, \qquad (1)$$

where λ is an interaction parameter. This is of the same form as the expression for the gap in the pairing theory, with the Fermi energy E_F replacing the phonon cut-off $k_B\theta_D$. When the whole coupled system is displaced in k-space to give a current flow with velocity v_s, the lower band is completely occupied, giving a supercurrent flow $j_s = nev_s$. Thus at $T = 0°\,K$, $n_s = n$.

If $E(k)$ is the energy of the electron in a frame moving with the electrons, the energy in the rest frame of the crystal is $E(k) + \hbar k v_s$. Thus when $\hbar k v_s$ becomes greater than Δ, it becomes favorable for electrons to be scattered back to the next higher band, decreasing the current and the free energy. With increasing v_s, the gap will then begin to decrease and will eventually go to zero. As in usual pairing superconductors, there will be a critical velocity for maximum supercurrent flow.

Kuper[3] calculated the free energy at finite temperatures, and thus the temperature, T_c, at which there is a second-order transition to the metallic phase:

$$k_B T_c = 0.57\Delta_0 . \qquad (2)$$

Here Δ_0 is the gap parameter at $T = 0°\,K$. He did not calculate n_s as a function of temperature. Presumably one would find near T_c a Ginzburg–Landau type equation for $|\psi|^2 = n_s/n$, with the only difference from the usual theory being in the values of the parameters. One would expect that there would be paraconductivity above T_c from fluctuations in n_{sq}, the superfluid density for a velocity $mv_s = \hbar q$. The relaxation time, τ_q, for such fluctuations could be determined from a time-dependent version of the Ginzburg–Landau equation. One would expect to find that the paraconductivity would have the same temperature dependence as for one-dimensional metallic systems,

$$(\sigma - \sigma_n)/\sigma_n \sim (T - T_c)^{-3/2} . \qquad (3)$$

Coleman *et al.* find only paraconductivity, not superconductivity below T_c. Presumably the moving lattice waves that carry the electrons are not metastable, but relax to give a static lattice distortion and an insulating phase. It might be possible to observe superconducting phenomena below T_c at high frequencies. The explanation of the paraconductivity in terms of Fröhlich's model may account for the fact that very perfect crystals are required to observe the phenomenon. It would be necessary to have the relaxation time for the lattice waves from other possible mechanisms longer than the τ_q associated with fluctuation paraconductivity.

It is obvious that much more experimental and theoretical work will have to be done to find out what is really going on and to determine the relevant parameters. One should use a tight binding model rather than the almost free felectron model used by Fröhlich and effects of electron–electron interactions should be considered. Since the band gaps are small compared with the band widths, this should change only the values of some of the numerical factors. It appears that Coleman *et al.* have found experimental evidence not only for superconducting phenomena at high temperatures, but also for a new mechanism for superconductivity, one predicted long ago by Fröhlich.

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On suggère que les fluctuations supraconductrices observées par Coleman *et al.* juste au-dessus de l'instabilité du mode mou de Peierls dans des solides organiques et pseudo-uni-dimensionels sont une réflexion du modèle uni-dimensionell de Fröhlich où la supraconductivité résulte d'un couplage des électrons avec des ondes de réseau mouvantes au lieu d'une formation des paires du type B.C.S.