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Peierls–Fröhlich instability and superconductivity in linear chain crystals

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Abstract. The transition to insulating or superconducting states in linear chain systems is discussed in relation to the recently observed paraconductivity in TTF–TCNQ crystals. A relation between T_c, the Peierls transition temperature T_p, and the electron–phonon coupling strength is derived using the RPA and a simplified form of the strong coupling equation for T_c. It is argued that in principle one can have either $T_p > T_c$ or $T_c > T_p$.

Coleman *et al* (1973) found a huge anomaly in the electrical conductivity of the charge-transfer salt TTF–TCNQ around 60 K, indicating a tendency towards superconductivity at $T_c \approx 58$ K with one-dimensional critical fluctuations leading to strong paraconductivity above this temperature. They attributed the sudden drop in conductivity below 60 K to the Peierls instability in a one-dimensional system, and interpreted the high T_c as resulting from the phonon softening associated with this instability.

Fröhlich (1954) suggested that this instability would lead to superconductivity in one-dimensional systems, but his theory preceded the BCS theory and ignored Cooper pairing, so that it could not be applied in its original form. It was later suggested (Weger 1964) that the Peierls–Fröhlich instability could be responsible in part for the high T_c of some intermetallic compounds like Nb_3Sn (A-15 compounds) which are characterized by a linear chain structure. An experimentally observed instability at $q = 0$ (martensitic transition) was invoked by Labbe and Friedel (1966) and Barisic (1971) for the high T_c of such materials, but their theory ignored the fact that some compounds, like Nb_3Al, have the same linear structure and equally high T_c, but do not show the $q = 0$ instability.

The Peierls–Fröhlich instability is associated with the Kohn anomaly in the phonon spectrum at $q = 2p_F$. It was pointed out by Alfanasev and Kagan (1963) that in a one-dimensional system this anomaly leads to a sharp minimum in the phonon spectrum. The phonon spectrum in the neighbourhood of $q = 2p_F$ was calculated in some detail in a previous paper (Horovitz *et al* 1972) for $T = 0$. It was shown that the frequency ω vanishes in the neighbourhood of $q = 2p_F$ and two phonon branches were found in this region. Two branches in the phonon spectrum were previously observed by Shirane and Axe (1967) by neutron diffraction measurements on Nb_3Sn, but it is not clear whether these are the ones predicted theoretically.

In the present note we discuss the relation between the phonon softening above the

Peierls–Fröhlich transition and superconductivity. We adopt a very simple picture of free electrons with a Fermi surface consisting of two parallel planes coupled to phonons. Using the random phase approximation and a simplified form of the strong coupling equation for T_c, we derive a connection between T_c, the Peierls transition temperature T_p and the electron phonon coupling strength. We then argue that in principle one can have either $T_p > T_c$ or $T_p < T_c$.

We start from an effective Fröhlich hamiltonian

$$H = \sum_p \epsilon_p c_p^+ c_p + \sum \omega_q^0 a_q^+ a_q + \sum_{p,q} g_q(a_q + a_{-q}^+) c_{p+q}^+ c_p, \tag{1}$$

where a_q, c_p are the phonon and electron destruction operators and g_q is the electron–phonon coupling constant. It is assumed that the long range effects of the electron–electron interaction are already included in ϵ_p, ω_q^0 and g_q. The coupling constant is characterized by a dimensionless parameter s_q defined by

$$g_q^2 = \frac{\pi^3 \omega_q^0}{\beta m p_F} s_q, \tag{2}$$

where β is related to the electron density by $n = \frac{1}{2}\beta(p_F/\pi)^3$. The phonon spectrum is obtained from the poles of the phonon Green function

$$D(q, \omega) = \frac{2\omega_q^0}{\omega^2 - \omega_q^{0\,2} - 2\omega_q^0 \Pi(q, \omega) + i\delta} \qquad \delta = +0 \tag{3}$$

where $\Pi(q, \omega)$ is the retarded phonon self-energy, which in the RPA is given by

$$\prod(q, \omega) = \frac{s_q \omega_q^0 p_F}{4m} \int_{-\infty}^{\infty} \frac{n_p - n_{p+q}}{\omega + \epsilon_p - \epsilon_{p+q} + i\delta} \mathrm{d}p, \tag{4}$$

where

$$n_p = \left[\exp\left(\frac{p^2 - p_F^2}{2mkT}\right) + 1\right]^{-1}. \tag{5}$$

The detailed behaviour of the phonon spectrum in the vicinity of $q = 2p_F$ at finite temperatures and the validity of the approximation will be discussed elsewhere. Here we are only interested in the solutions $\omega = 0$, which signal the onset of the Peierls instability. When the temperature is lowered, these solutions occur first at $q = 2p_F$. Assuming that $T \ll T_F$ (the Fermi temperature) one can replace the exponent in equation (5) by a term linear in p. Approximating, subsequently, the expression for n_p by an inclined step function with the correct slope at p_F, we find

$$\begin{aligned} \operatorname{Re}\prod(2p_F, 0) &= \frac{s\omega^0}{4}\left[\ln\left(\frac{\tau}{2}\right) - 1\right], \\ \operatorname{Im}\prod(2p_F, 0) &= 0, \end{aligned} \tag{6}$$

where $\tau = T/T_F$. We dropped the momentum index of s and ω^0 meaning their values at $q = 2p_F$. The denominator of equation (3) vanishes for $q = 2p_F$ at $\omega = 0$ if

$$1 + \frac{s}{2}\left[\ln\left(\frac{\tau}{2}\right) - 1\right] = 0. \tag{7}$$

This defines the transition temperature to the Peierls instability

$$T_\mathrm{p} = 2T_\mathrm{F} \exp\left(1 - \frac{2}{s}\right). \tag{8}$$

Note that this expression holds as long as $T_\mathrm{p} \ll T_\mathrm{F}$. See also Kuper (1955).

Let us now consider the transition to the superconducting state. This is mainly determined by the parameter λ which characterises the electron–phonon interaction and is defined by (McMillan 1968)

$$\lambda = 2\int_0^\infty \frac{1}{\omega}\,\alpha^2(\omega)\,F(\omega)\,\mathrm{d}\omega, \tag{9}$$

where

$$\alpha^2(\omega)\,F(\omega) = \int \frac{\mathrm{d}^2 p}{v_\mathrm{F}} \int \frac{\mathrm{d}^2 p'}{(2\pi)^3 v'_\mathrm{F}}\, g^2_{p-p'}\, B(p - p'; \omega) \Big/ \int \frac{\mathrm{d}^2 p}{v_\mathrm{F}}. \tag{10}$$

Here $B(q, \omega)$ is the phonon spectral density distribution, v_F is the Fermi velocity and the integrals extend over the Fermi surface. Assuming that phonon momentum components perpendicular to the chains have a negligible coupling to the electrons, we are left with $p - p' = 2p_\mathrm{F}$ in equation (10). In view of equations (2), (9) and (10), we get

$$\lambda = \frac{s\omega^0}{4} \int_0^\infty \frac{B(2p_\mathrm{F}, \omega)}{\omega}\,\mathrm{d}\omega. \tag{11}$$

The ω^{-1}-moment of the spectral distribution function is simply $D(q, 0)/2$ and thus, on account of equation (3), we find

$$\int_0^\infty \frac{B(2p_\mathrm{F}, \omega)\,\mathrm{d}\omega}{\omega} = \frac{1}{\omega^0 + 2\Pi(2p_\mathrm{F}, 0)}. \tag{12}$$

With equation (6) and (11), we get

$$\lambda = \frac{s}{4}\left[1 - \frac{s}{2} + \frac{s}{2}\ln\left(\frac{\tau}{2}\right)\right]^{-1}. \tag{13}$$

In contrast to the usual case, this λ depends critically on T and diverges at $T = T_p$. We shall use the strong coupling expression for the transition temperature T_c, ignoring the effect of the Coulomb pseudopotential in order to avoid unnecessary complications in our crude picture, (McMillan 1968)

$$T_\mathrm{c} = \theta \exp\left(-\frac{1 + \lambda}{\lambda}\right). \tag{14}$$

The expression on the RHS depends on T, and T_c will be determined as the temperature for which this expression is equal to T_c. The parameter θ is a temperature characterizing the phonon energies and is usually taken to be of the order of the Debye temperature. In our case θ may depend on T, reflecting the softening of the phonons as one approaches T_p. But even if one ignores this dependence, the value of $\theta_\mathrm{D} = 90$ K found in TTF–TCNQ is too low to give $T_\mathrm{c} \simeq 60$ K with equation (14). To meet this difficulty, Coleman *et al* assume the formation of small polarons and argue that in this limit the exponent in equation (14) should be replaced by $(-1/\lambda)$. We propose another possibility. Appel and Kohn (1971) showed that in narrow band superconductors the dominant contribution to the phonon-exchange vertex comes from processes in which the two electrons which form a Cooper pair sit on the same atom, or in the present case, on the same molecule. It is plausible to assume that such intramolecular correlations are governed by the optical (rather than the acoustic) phonons. The energies of these phonons are determined by the molecular vibrations and the characteristic temperatures may be much higher than θ_D. Optical phonons may also lead to a Peierls–Fröhlich instability which could involve a transition from $(TCNQ)^-$ $(TCNQ)^-$ $(TCNQ)^-$... chains to $(TCNQ)^0$ $(TCNQ)^{--}$ $(TCNQ)^0$ $(TCNQ)^{--}$... chains (though this is not the only possibility). It is thus possible that the transitions to the superconducting or the insulating state are both governed by the optical phonon frequencies. With optical phonon temperatures the parameter θ may reflect considerable softening with respect to the original value and may still be high enough to account for the observed T_c. Apart from this possible reduction we assume that θ does not depend on T. This would be the case if, for example, the characteristic temperature would be determined by $\langle\omega\rangle$, where the average is taken over the normalized distribution function $(\omega/\omega^0)B(2p_F, \omega)$. As the frequency approaches zero with decreasing T, the phonon energy broadens and the spectral function B becomes asymmetric around the peak with a longer tail towards high ω. This results in a very weak dependence of $\langle\omega\rangle$ on T.

Solving equation (14) for T_c we get, in view of equation (13),

$$T_c = 2T_F \exp\left\{-\frac{4}{3s} + \frac{1}{3}\left[\ln\left(\frac{\theta}{2T_F}\right) + 1\right]\right\}. \tag{15}$$

In figure 1 we plot T_p (equation 8) as a function of s for T_F given by $E_F = 0{\cdot}2$ eV which corresponds to TTF–TCNQ (curve A). In our case $T_p = 60$ K which leads to $s = 0{\cdot}375$.

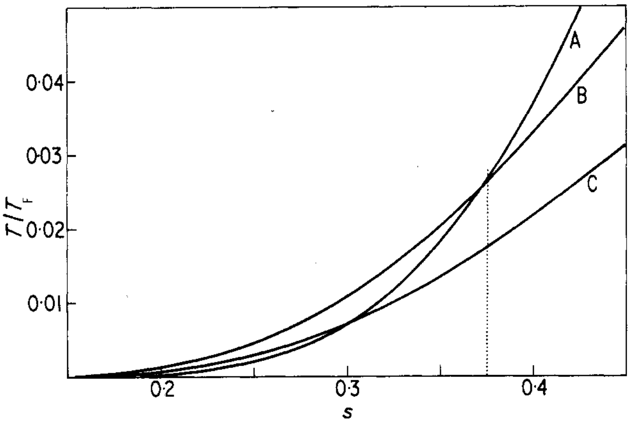

Figure 1. T_p (curve A) and T_c (curves B and C) for two values of $\theta/2T_F$ as function of the coupling parameter s. The dotted vertical line indicates the s-value for TTF–TCNQ. B, $\theta/2T_F = 0{\cdot}035$; C, $\theta/2T_F = 0{\cdot}01$.

This value of s is used to find the value of θ from equation (15) for $T_c = 58$ K. We then plot T_c as a function of s for this θ (curve B) and find that there is a critical value s_c above which $T_p > T_c$ and below which $T_c > T_p$. This critical value depends on θ and is lowered when θ decreases, as illustrated by curve C.

If the picture presented here is correct, it seems that there is no *apriori* reason for T_c to be lower than T_p. It is clear from figure 1 that if the parameter s could be slightly reduced without effecting θ one would get $T_c > T_p$. It follows from general thermodynamic arguments that in this case the onset of superconductivity should suppress (or, at least lower the temperature of) the Peierls–Fröhlich transition. Such an effect apparently occurs in the A-15 compounds (Testardi 1971, Weger and Goldberg 1973).

Let us conclude with several remarks concerning the similarity with the A-15 compounds mentioned by Coleman *et al.* Some of these compounds possess a martensitic transformation to a tetragonal state, which is attributed to the $m_l = \pm 2$ states of the d band (Weger and Goldberg 1973) (more precisely to the d_{xy} states on chains in the z direction). A high T_c is observed also in materials which do not undergo this transformation, such as Nb_3Al and $Nb_3Al_{0 \cdot 8}Ge_{0 \cdot 2}$. Thus, the instability associated with the $m_l = \pm 2$ sub-bands need not be connected with high T_c. However, theoretical considerations indicate that the $m_1 = 0$ sub-band should possess a planar Fermi surface with $k_F \approx \pi/a$ (Weger 1970). Positron annihilation measurements seem to support this conclusion for V_3Si, at least (Berko and Weger 1970, 1972). Additional support to this picture comes from the observed enhancement of the relaxation rate above T_c in NMR measurements on Nb_3Al, V_3Si and other A-15 compounds (Ehrenfreund *et al* 1971). This enhancement has been attributed to quasi one-dimensional fluctuations (Weger *et al* 1972). A tendency towards the Peierls–Fröhlich instability with $q \approx 2p_F$ in the $m_l = 0$ band may contribute to the high T_c in these compounds. Curve C in figure 1 corresponds to a value of $\theta/2T_F$ appropriate for the $m_l = 0$ band in V_3Si (the Fermi energy measured from the bottom of this band is 2·7 eV (Weger and Goldberg 1973) and we take $\theta = 300$ K). In this case the parameter s derived from the observed T_c turns out to be about 0·2 and for this s one gets $T_c > T_p$. We could have also taken θ from the frequency of the optical phonon of Γ_2 or Γ'_{12} symmetry, which has been estimated (Klein and Birman 1970) to be of the order of 200 K, without effecting the results in an essential way.

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Note added in proof. Since this paper has been submitted, the large conductivity peak reported by Coleman *et al* (1973) has not been confirmed by other groups, and the presence of superconducting fluctuations has been seriously questioned (Ferraris *et al* 1973). The point that the present note tries to make is that if superconductivity is at all possible in materials like TTF–TCNQ at reasonably high temperatures, it requires strong coupling of the conduction electrons to the intra-molecular vibrations, such as those of the CN bonds ($\omega_0 = 2200$–$2300\ \mathrm{cm}^{-1}$), and that a strong degree of electron–phonon coupling ($s \approx 0{\cdot}3$) is not unreasonable. It is easy to see that the coupling strength is given by Horovitz *et al* 1972)

$$s \approx |\psi\,(\mathrm{bond})|^2\,(\partial R/\partial n)^2 M\omega_0^2 n(E_F)$$

where ψ(bond) is the value of the wavefunction of the conduction electron at the relevant bond; $\partial R/\partial n$ is the change in bond length as one electron is added to the bond; $M\omega_0^2$ is the force constant of the bond, and $n(E_F)$ is the electronic density of states. For CN bonds in TCNQ, $|\psi(\mathrm{bond})|^2 \approx \frac{1}{8}$, $\partial R/\partial n \approx 0{\cdot}05$ Å, $M\omega_0^2 \approx 10^5\ \mathrm{dyne/cm}^{-1}$, $n(E_F) \approx 4\ \mathrm{eV}^{-1}$ per molecule; thus s is indeed of order 0·3. The vibrations of the four CN groups form four normal modes of A_{1g}, B_{1g}, B_{2u}, B_{3u} symmetry; the first couples directly to the conduction electrons, the third couples when $\pi \to \pi^*$ admixture is allowed. Similar considerations apply to the vibrations of the other bonds (such as C=C, CS). This coupling pulls the frequency of the bond vibrations down, and broadens them due to a finite lifetime. (The $\Pi(q, \omega)$ term in (3); see also Horovitz *et al* 1972, 1974.) Thus, observation of the bond frequencies in TTF–TCNQ as function of temperature should provide a direct, unambiguous test of the mechanism proposed in this note.

From the theoretical aspect, this note points out that in the RPA, the temperatures of the Peierls transition (lattice transformation) and superconductivity are close together for reasonable values of the parameters $[T_c/T_p = (\omega_0/eT_p)^{1/3}$, from (8), (15)], but do not coincide. Bychkov *et al* (1966) point out using a Parquet diagram expansion that these two temperatures coincide. Experimental evidence on A15 compounds, which are quasi-one-dimensional systems (Weger and Goldberg 1973) indicates that these two temperatures are close, but do not coincide. Thus this aspect requires further study.

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