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ORGANIC CONDUCTORS - METALS WITH A SHORT MEAN FREE PATH

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Abstract At ambient temperature the organic conductors have a mean free path of the order of a lattice constant. In this temperature range the magnetic susceptibility is enhanced over its Pauli value and the resistivity obeys a T^2-law just like at lower T where the conductivity is metallic. We describe a theory based on a quadratic electron-phonon coupling which accounts for these features.

INTRODUCTION

The magnetic susceptibility χ of TTF-TCNQ and other organic metals increases from a value corresponding to the Pauli susceptibility at about 80 K by a factor of 2 at 300 K[1]. At this temperature χ saturates and there is even indication that it begins to decrease. A systematic survey[2] indicates that this is a general property of organic metals which have a large mean free path ($\ell \gg b$, b being the lattice constant) at low temperature and a small one ($\ell \simeq b$) at room temperature. A particular feature of the spin susceptibility is its pressure dependence[3] in contrast to the normal case when depends only weakly on pressure. This general behaviour of χ has also been observed in the recently synthesized perylene compounds[4] and in a series of TMTTF-compounds reported at this meeting[5].

In the same temperature range the resistivity follows approximately a T^2-law and like χ it is strongly pressure dependent. This T^2-behavior is observed at constant pressure. At constant volume the temperature dependence is more complicated[6]. However, there is evidence that the phonon frequency increases strongly with temperature ($\Delta\omega/\omega \simeq 20\%$ between 60 K and 300 K) at constant volume,

but is approximately temperature independent at constant pressure[7,8]. We therefore feel that the constant pressure data reflect better the requirement that the phonon frequencies in the Hamiltonian are constant .

We have already pointed out that in these materials one goes from a region in which $\ell >> b$ just above the Peierls transition to $\ell \simeq b$ at room temperature. The conductivity mechanism changes from metallic to hopping conductivity between these two regions. Nevertheless, we find the same T^2-law with approximately the same coefficient in the low temperature and the high temperature range, although the mechanisms are entirely different. This property and the associated enhancement in the magnetic susceptibility are unique and unexpected features of organic metals in the low mean free path region.

It was suggested that the enhancement of the spin susceptibility is a result of a large Coulomb repulsion U between two electrons on the same molecule[9]. The problem with this explanation is that for values of U required to increase χ by a factor of 2 over its Pauli value, χ_o does not increase with T, but is roughly constant. In addition, the "big U" approach has not been successful in explaining the transport properties of organic metals. It has been often claimed that the $4k_F$-reflections are an indication of a large Coulomb interaction[10], however, it has been shown[11] that this phenomenon can also be understood on the basis of a rather small value of U. On the other hand, the strong pressure dependence of χ and of thetransport properties is an empirical indication of the dominance of the electron-phonon interaction. Thus we assume that the electronic properties of organic metals are determined predominantly by the electron-phonon interaction. In addition we assume that the normal electron-phonon interaction, which is linear in the phonon operators is small and that the main interaction is quadratic in the phonon operators, and is largely with librons, which possess a low frequency and a strong quadratic coupling with the

electrons. This assumption leads immediately to the T^2-law of the resistivity in the metallic region and is the essence of the previously developed "libron theory" of transport[12]. However, this theory is not sufficient to explain why the T^2-behaviour continues into the range where $\ell \simeq b$, where from the Boltzman treatment we would expect a saturation of the resistivity.

In the present paper we present a theory which treats χ and ρ within the same framework, based on the quaratic electron-phonon interaction and which accounts for the behaviour of these properties as one passes from the metallic to the hopping regime.

THE MAGNETIC SUSCEPTIBILITY

We have previously related the enhancement of the magnetic susceptibility to the band narrowing and increase in the density of states resulting from the electron-phonon interaction. We have considered both linear[13] and quadratic[14] coupling. The main difference between linear and quadratic coupling is that in the first case, in a one-dimensional system, there is always formation of a bound polaron. This difference is demonstrated in fig. 1. The dotted line Aq_o^2 is the elastic energy, the dashed line is the energy of the electron due to the distortion q_o, and the full line is the total energy. In the linear case there is a minimum at a negative energy and such a potential well, however small, will always trap an electron in one-dimension. For quadratic coupling Aq_o is replaced by Aq_o^2 and, as long as $A < B$, there is no self-trapping. However, provided that the localization is weak we can apply a formalism similar to the small polaron approach and find, also for quadratic coupling, temperature dependent band narrowing but without polaron binding.

We start from the Hamiltonian of tightly bound electrons coupled to Einstein phonons

$$H = -\Sigma J C_n^{+} C_{n+\delta} + \hbar\omega\Sigma(a_n^{+}a_n + \tfrac{1}{2}) + \Sigma g^{(2)}(n+m)\, C_m^{+} C_m (a_n^{+} + a_n)^2, \quad (1)$$

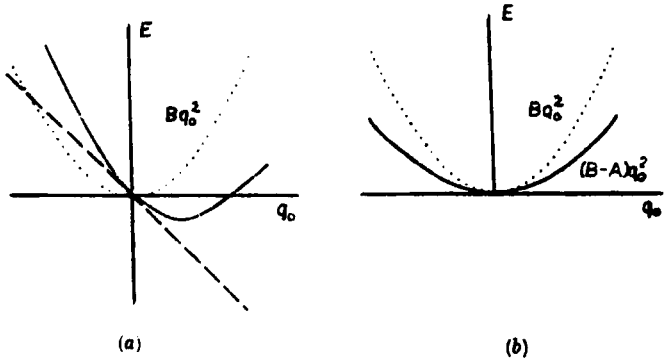

FIGURE 1 Energy as a function of lattice distortion for (a) linear and (b) quadratic electron-phonon coupling.

where a_n, C_n are the phonon and electron operators respectively, $4J$ is the bandwidth, ω the phonon frequency and $g^{(2)}(n+m)$ - the quadratic coupling strength of an electron on site m to a distortion of site n. To eliminate the electron-phonon term we perform a unitary transformation $H^T = e^{-S} H e^{-S}$, where

$$S = \Sigma \frac{1}{2} \Gamma (n+m) C_m^+ C_m (a_n^2 - a_n^{+2}). \tag{2}$$

The resulting Hamiltonian is

$$H^T = \Sigma_n [(\frac{\hbar\omega}{2})^2 + \hbar\omega \Sigma_m g^{(2)}(n+m) C_m^+ C_m]^{\frac{1}{2}} (a_n^+ a_n + a_n a_n^+) +$$

$$+ \Sigma (-J) C_n^+ C_{n+\delta} \exp[-\frac{1}{2} \Sigma_m (\Gamma(m+n) - \Gamma(m+n+\delta))(a_m^2 - a_m^{+2})] \tag{3}$$

$\Gamma(n)$ is determined by a complicated transcendental equation. To lowest order $\Gamma(n) = g^{(2)}(n)/\hbar\omega$. The first term contains the free phonon Hamiltonian, and contributions to the electron and phonon self-energies. The second term leads to band narrowing which is represented by an effective transfer integral J_{eff} obtained by ther-

mally averaging the exponential. The deviation from the thermal average contributes to the life time in a band state. The thermal average can be calculated rigorously only when the electron-phonon interaction is local. In this case one finds that the band width decreases with temperature as a power unlike the exponential decrease. For an extended interaction we expand the exponential and calculate the average with respect to the free phonon Hamiltonian. When the temperature is not too high (compared to $\hbar\omega$), we obtain

$$J_{eff} = J[1 - \frac{1}{2} \sum_q \frac{|g^{(2)}(q)|^2}{\hbar\omega} (1-\cos qb)((N_{ph}+1)^2 + N_{ph}^2)], \quad (4)$$

where N_{ph} is the phonon occupation number. In the same approximation, the life-time in a band state is

$$\frac{\hbar}{\tau} = 4\pi \sum_q |g^2(q)|^2 (1+2N_{ph})^2 N(\epsilon_F), \quad (5)$$

where $N(\epsilon_F)$ is the bare density of states at the Fermi level. The band picture becomes invalid at a certain temperature when the bandwidth is comparable to the inverse lifetime. About this temperature there is a transition from the band picture to localized states. In fig. 2 we plot the bandwidth and h/τ in units of $\hbar\omega$ for typical parameters of TTF-TCNQ. The parameter $\pi N(\epsilon_F)\Sigma|g^{(2)}(q)|^2/\hbar\omega$ is equal to 0.16 for the solid lines and 0.22 for the dashed lines. Curves 1 and 2 correspond to $J/\hbar\omega = 4$, curves 3 and 4 to $J/\hbar\omega = 2$. We find that the band picture is valid up to temperatures of twice the phonon energy.

In this temperature range $N(\epsilon_F) \propto J_{eff}^{-1}$, and since $\chi = 2\mu N(\epsilon_F)$, we can relate the temperature and pressure behaviour of χ, to that of J_{eff}. This in turn can be related to the mean free path $\ell = \ell(T,P)$[15].

At higher temperatures the quadratic electron-phonon interaction is greater than the bandwidth and the potential resembles a statically disordered potential in which all the states are locali-

zed and the electrons propagate by hopping. In this region we expect that the susceptibility should show a Curie like behaviour. Experimentally, there is an indication of a transition to such behaviour above 300 K[1].

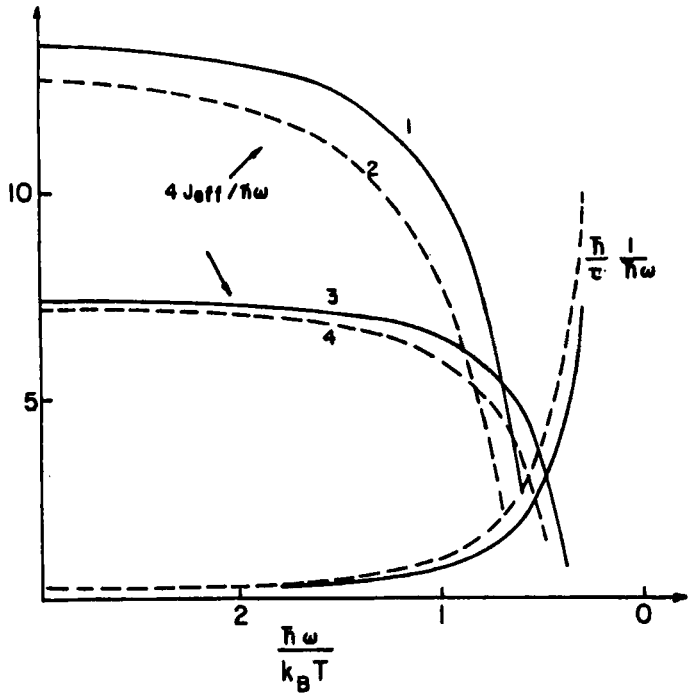

FIGURE 2 The bandwidth and the inverse lifetime in a band state for typical parameters (see text).

We wish to point out an additional feature of the quadratic vs. linear electron-phonon coupling, which shows up when interaction with several phonon branches is considered. It was shown previously[16] that when $g^{(2)}_{\mu_1\mu_2}$ is diagonal in the phonon branch index the contribution of all phonon modes to the electron self-energy is additive and therefore large, while the frequency shift of each

phonon mode is small. In organic metals there are three translations, three rotation and several internal modes all of which are coupled strongly to the electrons. Moreover, it was shown[17] that $g^{(2)}$ is indeed approximately diagonal inthe phonon modes. Thus we can have a strong band narrowing without a lattice instability, in contrast to the case of the linear coupling where a strong electron-phonon interaction always leads to a lattice instability.

THE RESISTIVITY

We shall characterize the transport properties in the different temperature regions by an effective scattering time τ defined so that $D = b^2/\tau$, where D is the diffusion constant. The mobility is given by $\mu = eD/\epsilon_F$, when $\epsilon_F > k_BT$, and by $\mu = eD/k_BT$, when $k_BT > \epsilon_F$. In the metallic region the scattering rate is obtained from "libron theory"[12]. For comparison, we write it in the form

$$\left(\frac{1}{\tau}\right)_{LT} \simeq \frac{1}{\hbar}\frac{J^4}{\Gamma^2}\frac{1}{J}\left(\frac{1}{k_BT}\right)^2, \tag{6}$$

where, as before, J is the transfer integral and Γ is the dimensionless electron-phonon coupling parameter related to the Frohlich constant by $\Gamma = g^{(2)}/h\omega$.

At higher temperature whenthe mean free path becomes smaller, we describe transport by a simple model of tunnelling between two square wells whose relative height is modulated by the thermal lattice fluctuations. Let the energy difference be $\Delta E(t) = \Delta E_o \sin(\omega t)$, where ω is the phonon frequency, and for our case of quadratic interaction $\Delta E_o = A(\Delta R)^2$, where $(\Delta R)^2 = k_BT/M\omega^2$. The electron can tunnel between the wells when $\Delta E(t) < J$, that is when $\omega t < J/\Delta E$. The probability that tunnelling will occur within a time 2t is given by $(J2t/\hbar)^2 = (2J^2/\Delta E_o\hbar\omega)^2$, and the tunnelling rate is

$$\left(\frac{1}{\tau}\right)_{DT} \simeq \frac{1}{\hbar}\frac{J^4}{\Gamma^2}\frac{1}{\hbar\omega}\left(\frac{1}{k_BT}\right)^2, \tag{7}$$

where DT denotes direct tunnelling, and Γ is related to the coupling parameter by $\Gamma = A/M\omega^2$.

At still higher temperatures, phonon assisted tunnelling should become important. The hopping rate for this process can be obtained from the second term in eq. 3 at high temperature when the states are localized[14]. When the interaction is local the hopping rate is given by

$$\left(\frac{1}{\tau}\right)_{PT} \simeq \frac{J^2}{2\hbar}\frac{1}{k_B T}\frac{\pi}{\sinh \Gamma\,(\sinh^2 \Gamma + 1)^{\frac{1}{2}}} \qquad (8)$$

where PT denotes "polaron theory". We have a different T-dependence, but now $k_B T > \varepsilon_F$, so that $\mu = D/k_B T$, and the resistivity is still proportional to T^2. Thus all the three mechanisms have the same temperature behaviour. In addition, since J and $\hbar\omega$ are of the same order and Γ is of order unity, the three expressions lead to the same form for the resistivity $\rho = BT^2$, with approximately the same coefficient B. This explains why one finds the same T-dependence of ρ when one goes from the range $\ell \gg b$ to $\ell \simeq b$.

DISCUSSION

We have considered the change in behaviour when the mean free path decreases and becomes of the order of the lattice constant. Experimentally, the most striking manifestation of this changeover is the enhancement of the magnetic susceptibility and a change from Pauli to Curie behaviour. A crossover from a T-law of resistivity to a T^2-law was previously predicted[18] at a temperature where $1/\tau \simeq \omega$, i.e. when $\ell \simeq (v_F/v_S)b$. In organic metals this occurs between 40K and 100K, but no such anomaly is observed in this region. In particular, in $(TMTSF)_2PF_6$ the T^2-law is obeyed very well above and below this temperature range. A recent computer simulation[19] indicates that a crossover from itinerant to localized state, simi-

lar to that predicted in ref. 18 occurs in a one-dimensional electron-phonon system when $1/\tau \approx 20\omega$, namely, at significantly higher temperatures.

The main point of our discussion is that the quadratic electron-phonon interaction provides a consistent explanation for both the transport and magnetic properties. It explains the smooth transition in the temperature behaviour of the resistivity from the metallic to the hopping regime and accounts for the enhancement of the magnetic susceptibility due to a phonon induced band narrowing. It should be pointed out that in ordinary metals the electron-phonon interaction does not affect the susceptibility. The reason is that the electron-phonon interaction modifies the electronic spectrum in a region of order $\hbar\omega$ around ϵ_F, much smaller than the bandwidth. The shifting of the down-spin spectrum relative to the up-spin spectrum caused by an external magnetic field is not affected by this modification and consequently the susceptibility is unchanged. In the present case $\hbar\omega$ as well as the scattering rate are comparable to the bandwidth and therefore the entire band "feeds" the electron-phonon interaction.

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