

Temperature dependence of the metallic conductivity of tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ)

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(Received 5 January 1977)

The interaction of electrons with librational modes is proposed as the basic mechanism responsible for the observed temperature behavior of the resistivity in tetrathiafulvalene-tetracyanoquinodimethane. This mechanism also gives a reasonable estimate of the relaxation time.

One of the puzzling properties of the linear chain compound tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) is the temperature behavior of the metallic conductivity above the Peierls transition. The basic feature of this behavior, which attracted most of the attention in the early stages of study in this field, is the appearance of giant conductivity peaks in the neighborhood of this transition. These peaks have been a subject of a strong controversy.^{1,2} At a rather early stage it was realized by Groff *et al.*,³ that the resistivity can be expressed as $\rho = \rho_0 + \rho_1 T^n$, with $n \approx 2.3$. By now, this form of temperature dependence, with $n \geq 2$, over a wide range of temperature and pressure, is well established.⁴⁻⁶ The value of ρ_0 varies widely between crystals grown in different laboratories, while the values of ρ_1, n are similar for nearly all crystals grown by many groups.

Most of the theoretical attempts to understand the behavior of the conductivity near the Peierls transition were based on the idea of Allender, Bray, and Bardeen⁷ who predicted that the fluctuations to the Peierls distorted state should cause an enhancement in the conductivity above the transition. It was argued by Weger *et al.*,⁸ that a meaningful calculation of this kind has to include explicitly the interchain coupling, and when this is done, one finds that: (i) the predicted enhancement may occur only through coupling to high-frequency (intramolecular) phonons; (ii) the contribution of this collective effect to the resistivity is proportional to T just above the transition and changes gradually to T^2 far away from it. However, the treatment is valid only in the neighborhood of the transition and the last result cannot be trusted.

In this work we assume that the observed transition temperature at 54 °K is close to its mean-field value.^{9,10} This approach is different from that of Lee *et al.*¹¹ According to this approach, whatever may be the explanation of the conductivity around 60 °K, the source of the metallic conductivity between, say, 100 and 300 °K, has to be attributed to ordinary scattering mechanisms and the essentially T^2 behavior poses a real problem

as it does not follow from a conventional electron-phonon mechanism. It was suggested by Seiden and Cabib¹² that the observed temperature behavior implies that the dominant scattering mechanism is the electron-electron interaction. This explanation, however, suffers from two difficulties: (i) In a strictly one-dimensional system the inverse electron-electron relaxation time is proportional¹³ to T and not to T^2 . One needs a rather strong interchain transfer integral $t_{\perp} > kT$ to restore the three-dimensional T^2 behavior. A recent measurement¹⁴ of t_{\perp} , based on the frequency behavior of the nuclear magnetic relaxation time T_1 , yields the value of 5.3 meV, which is smaller than kT in the entire range of interest. (ii) Electron-electron collisions contribute to resistivity only through umklapp processes. In one-dimensional systems, umklapp processes involve the simultaneous jump of two electrons from one side of the Fermi surface to the other, and this can happen only in the case of one electron per molecule because only then is $4p_F$ (p_F is the Fermi momentum) equal to an inverse lattice vector. It is now established that TTF-TCNQ is not a one-electron-per-molecule system and therefore there is no simple way to degrade the momentum in electron-electron collisions. This difficulty may be overcome in a two-band model by assuming that the dominant scattering mechanism involves electrons in the two bands, one of TTF and one of TCNQ electrons, and that momentum is transferred to the lattice through the electron-phonon interaction in one of the bands, which is more likely the TTF band because of the sign of the Hall effect¹⁵ and the thermoelectric power.¹⁶ For such a model interchain Coulomb interactions must be very strong and electron-phonon coupling on the TTF chain even stronger, namely $\tau_{\text{el-ph}}^{-1}(\text{TTF}) \gg \tau_{\text{el-el}}^{-1}(\text{interchain}) \gg \tau_{\text{el-ph}}^{-1}(\text{TCNQ})$, where τ is the relaxation time. Thus such a model would raise more problems than it would solve.

In view of the discussion in the last section, we feel that the explanation of the resistivity based on electron-electron interactions has to be abandoned.

We propose an alternative explanation based on two-phonon processes.

The degrees of freedom in an organic crystal like TTF-TCNQ can be classified into translations, intramolecular distortions, and librations (rigid rotations of the molecules). Unlike the first two types of motion, the librational modes in TTF-TCNQ received so far very little attention. It was first pointed out by Morawitz¹⁷ that they may play a role in the Peierls distortion. Weger and Friedel¹⁸ showed in a detailed paper that it is possible to understand the richness of the crystallographic phase transitions in TTF-TCNQ from an explicit consideration of the forces involved in the translational and librational motions of the molecules. Their model is based on the single assumption that the dominant lattice distortions are those which effect the *N-S* bond, and as a result the TCNQ η libration (rotation around the axis perpendicular to the molecular plane) plays a major role in their theory. Likewise, we assume that this mode provides also the dominant scattering mechanism which determines the resistivity. The basic point is that the coupling of the electrons to this mode is a second-order process.¹⁹ The hopping Hamiltonian of an array of molecules, which permits only these η librations, may be written

$$H = \sum_i \epsilon_i a_i^\dagger a_i + \sum_{i,j} J(\theta_{ij}) a_i^\dagger a_j, \quad (1)$$

where a_i destroys an electron on the i th molecule and the overlap integral J depends on the relative rotation of neighboring molecules. Since $(dJ/d\theta_{ij})_0 = 0$, we find that the electron-libron interaction is

$$H' = \frac{1}{2} \sum_{i,j} \left(\frac{\partial^2 J}{\partial \theta_{ij}^2} \right)_0 \theta_{ij}^2 a_i^\dagger a_j, \quad (2)$$

which, after the usual normal mode expansion, becomes

$$H' = \sum_{\vec{k}, \vec{q}, \vec{q}'} g_{\vec{k}, \vec{q}, \vec{q}'} a_{\vec{k} + \vec{q} + \vec{q}'}^\dagger a_{\vec{k}}^\dagger (b_{\vec{q}} + b_{-\vec{q}}^\dagger) (b_{\vec{q}'} + b_{-\vec{q}'}^\dagger), \quad (3)$$

with

$$g_{\vec{k}, \vec{q}, \vec{q}'} = \frac{\hbar \bar{J}}{NI (\omega_q \omega_{q'})^{1/2}} [\cos(\vec{k} + \vec{q} + \vec{q}') \cdot \vec{b} - \cos(\vec{k} + \vec{q}) \cdot \vec{b} - \cos(\vec{k} + \vec{q}') \cdot \vec{b} + \cos \vec{k} \cdot \vec{b}], \quad (4)$$

where $\bar{J} = \frac{1}{2} (\partial^2 J / \partial \theta_{ij}^2)_0$, I is the moment of inertia, and \vec{b} is the lattice vector. To estimate the contribution of the electron-libron interaction to the conductivity, we start from the expression

$$\sigma = ne^2 \tau / m^*, \quad (5)$$

where

$$\frac{1}{\tau} = \int d\Omega (1 - \cos \theta) P_{kk'}, \quad (6)$$

where $P_{kk'}$ is the transition probability from state \vec{k} to \vec{k}' , and θ is the angle of scattering. In a one-dimensional system we get a contribution only from back scattering ($\theta = 180^\circ$). To evaluate $P_{kk'}$, we apply the "golden rule" to the transition which takes an electron from one side of the Fermi surface to the other side, accompanied by the absorption of two phonons of momenta q and q' , respectively. This probability is equal to

$$P = \frac{2\pi}{\hbar} \frac{n(\epsilon_F)}{2} \left(\frac{V}{(2\pi)^3} \right)^2 \left(\frac{4\pi^2}{ac} \right)^2 \times \int_0^{2k_F} dq' \int_0^{2k_F - q'} dq |g_{k_F, q, q'}|^2 n_q n_{q'}, \quad (7)$$

where $(4\pi^2/ac)$ is the area of one Fermi-surface plane, $n(\epsilon_F)$ is the density of states of one spin at the Fermi surface, and n_q is the occupation number of a libron of momentum q . We shall assume that the libron modes are dispersionless. This assumption is consistent with identifying the low-energy flat dispersion curves obtained by Mook and Watson²⁰ in neutron scattering experiments, with these modes. This identification also indicates that the energy of these modes is 20–30 cm^{-1} , which allows us to approximate the libron occupation numbers by $(k_B T / \hbar \omega)$ in the temperature range of interest. From Eqs. (4), (6), and (7), one gets

$$\frac{1}{\tau} = \frac{2\pi}{\hbar} n(\epsilon_F) \frac{\hbar^2 \bar{J}^2}{I^2 \omega^2} \left(\frac{k_B T}{\hbar \omega} \right)^2 f(k_F b), \quad (8)$$

where $f(k_F b)$ is the result of the q, q' integration over the terms in the square brackets on the right-hand-side of Eq. (4). The last expression may be conveniently written in the form

$$1/\tau = (2\pi/\hbar) n(\epsilon_F) (\bar{J} \langle \theta_{ij}^2 \rangle)^2 f(k_F b), \quad (9)$$

where $\langle \theta_{ij}^2 \rangle = k_B T / I \omega^2$ is the amplitude of thermal vibrations. If this amplitude is such that the average overlap decreases by roughly a factor of 2, the lifetime is of the order of the inverse bandwidth. For TCNQ, $I = 1.37 \times 10^{-37} \text{ g cm}^2$, $\omega \approx 5 \times 10^{12} \text{ sec}^{-1}$, thus $\langle \theta_{ij}^2 \rangle^{1/2} \approx 10^{-1} \text{ rad}$ at ambient. The factor $f(k_F b)$ is of order 0.5. [Above, we referred only to the scattering process accompanied by the absorption of two phonons. There are other processes which involve either emission of two phonons or emission of one of them and absorption of the other. The effect of all these processes may be lumped into $f(k_F b)$, giving the quoted result.] Both the inverse bandwidth and relaxation time at ambient are of order $3 \times 10^{-15} - 10^{-14} \text{ sec}$. Thus, we have shown that the proposed mechanism results not only in the observed T^2 behavior of the resistivity, but, under reasonable assumptions on

the variation of the overlap integral with relative rotation of the molecules, it also gives the correct order of magnitude.

The proposed mechanism would predict a threshold in the light absorption at the frequency of 2ω . Since TTF-TCNQ is not metallic below 53 °K, this absorption edge is smeared out and should not be easily discerned from infrared data.²¹ However, hexa-methylene-tetra-selena-fulvalene-TCNQ (HMTSF-TCNQ), which also shows a T^2 law for the resistivity²² (its somewhat higher conductivity may easily be accounted for by a more rigid lattice²³) remains metallic at low temperatures,²⁴ particularly under pressure in excess of 4 kbar. The absorption edge at 2ω should thus be easily observable in this compound. The actual shape of the $\sigma(\omega)$ curve in this region is currently under

investigation.

In conclusion, we would like to point out that this interpretation of the resistivity is within the framework of the "small U " philosophy²⁵ of TTF-TCNQ, which seems to be substantiated by NMR relaxation experiments.²⁶

ACKNOWLEDGMENTS

This work followed in part from extensive discussions of one of us (M.W.) with J. Friedel and D. Jerome concerning the libron mechanism and the various aspects of the properties of TTF-TCNQ. We also benefited from fruitful criticism by Sir N. F. Mott, discussions regarding librions with H. Morawitz, and criticism and suggestions regarding "small U " theory by A. J. Heeger.

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