Solid State Communications, Vol. 15, pp. 849–853, 1974. Pergamon Press. Printed in Great Britain

REFLECTIVITY OF A ONE-DIMENSIONAL ELECTRON–PHONON SYSTEM

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(*Received* 18 *March* 1974; *in revised form* 8 *May* 1974 *by E. Burstein*)

The effect of the giant Kohn anomaly in a one dimensional system on the optical reflectivity is calculated, for parameters believed to be characteristic for TTF–TCNQ. It is found that the Kohn anomaly in the optical phonon branch due to stretching vibrations of the C≡N groups, whose unperturbed frequency is 2100–2200 cm^{-1}, produces a minimum in the reflectivity at 1600 cm^{-1}, approximately. This minimum coincides with the minimum found experimentally by Bright, Garito and Heeger. By this mechanism, phonons with a wavevector of order $2k_F$ affect the reflectivity of photons with $q \approx 0$.

IT WAS suggested in a previous paper that the metal-to-insulator transition observed in TTF–TCNQ at ~60°K[1] may be a Peierls–Fröhlich transition due to the interaction of the one-dimensional electron system with optical phonons at $2k_F$, namely, with the stretching vibrations of C≡N or C=C bonds.[2] Recently, the reflectivity of TTF–TCNQ was shown by Bright *et al.*[3] to possess a very broad minimum around 1500 cm^{-1}. The overall reflectivity curve, except for this minimum, was fitted by the authors of reference 3 using the Drude form of the dielectric constant

$$\epsilon(\omega) = \epsilon_0 - \frac{\omega_p^2}{\omega^2 + i\omega/\tau}, \tag{1}$$

with a frequency independent τ. The reflectivity is given by

$$R(\omega) = \frac{1 + |\epsilon| - [2(|\epsilon| + \mathrm{Re}\,\epsilon)]^{1/2}}{1 + |\epsilon| + [2(|\epsilon| + \mathrm{Re}\,\epsilon)]^{1/2}}. \tag{2}$$

In this note we wish to apply a recently developed formalism[4] to calculate the effect of the coupling of the conduction electrons with the bond vibrations on the reflectivity.

We assume a simple picture of free electrons with a Fermi surface consisting of two parallel planes, coupled to phonons. The system is described by an effective Fröhlich Hamiltonian

$$H = \sum_p \epsilon_p c_p^\dagger c_p + \sum_q \omega_q^0 a_q^\dagger a_q + \sum_{p,q} g_q (a_q + a_{-q}^\dagger) c_{p+q}^\dagger c_p, \tag{3}$$

where a_q, c_p are the phonon and electron destruction operators and g_q is the electron–phonon coupling constant. We characterize the coupling strength by a dimensionless parameter s_q defined by

$$g_q^2 = \frac{\omega_q^0 E_F s_q}{n}, \tag{4}$$

where ω_q^0 is the bare phonon energy, E_F is the Fermi energy and n is the electron density. In such a one-dimensional system there is large phase-space volume available for low-energy electron excitations accompanied by the absorption and emission of phonons at $q \simeq 2k_F$. This leads to a strong coupling with such phonons and thus to a significant renormalization of the phonon spectrum in this region, which results in a Peierls–Fröhlich instability at a critical temperature T_p and a giant Kohn anomaly at $T > T_p$.

The strong coupling to phonons at $2k_F$ results in a frequency dependent life time of an electron state at the Fermi surface, given by

$$\frac{1}{\tau_{\mathrm{ph}}(\omega)} = \frac{1}{\hbar} \operatorname{Im} \Sigma\,(k_{\mathrm{F}}, \omega), \tag{5}$$

where $\Sigma\,(k_{\mathrm{F}}, \omega)$ is the self energy of an electron at the Fermi surface. The latter is obtained simply from the "imaginary time" self energy given by

$$\Sigma\,(k_{\mathrm{F}}, i\omega_n) = -\frac{1}{\beta} \sum_m \int \frac{\mathrm{d}^3 q}{(2\pi)^3} g^2_{2k_{\mathrm{F}}+q} \times$$

$$D(2k_{\mathrm{F}} + q, i\omega_n - i\omega_m) G(-k_{\mathrm{F}} - q, i\omega_m), \tag{6}$$

where $\beta = 1/kT$, $\omega_n = \pi(2n + 1)/\beta$, and D, G are the phonon and electron Green's functions. For G we take the free electron Green's function

$$G(k, i\omega_m) = \frac{1}{i\omega_m - (\epsilon_k - \mu)}, \tag{7}$$

and write D in its spectral representation

$$D(k, i\omega_n - i\omega_m) =$$

$$\int_0^{\infty} \frac{\mathrm{d}\omega'}{2\pi} B(k, \omega') \left[\frac{1}{i(\omega_n - \omega_m) - \omega'} - \frac{1}{i(\omega_n - \omega_m) + \omega'}\right]. \tag{8}$$

We assume that the integrand in equation (6) depends only on the momentum components in the direction of the linear chains and the integration over the transversal components introduces a factor $1/a^2$, where a is the distance between two chains. Inserting equations (7) and (8) into equation (6) and summing over m, we obtain

$$\Sigma\,(k_{\mathrm{F}}, i\omega_n) = \frac{1}{a^2} \int \frac{\mathrm{d}q}{2\pi} \int_0^{\infty} \frac{\mathrm{d}\omega'}{2\pi} g^2_{2k_{\mathrm{F}}+q} B(2k_{\mathrm{F}} + q, \omega')$$

$$\left[\frac{N(\omega') + 1 - n(k_{\mathrm{F}} + q)}{i\omega_n - (\epsilon_{k_{\mathrm{F}}+q} - \mu) - \omega'} + \frac{N(\omega') + n(k_{\mathrm{F}} + q)}{i\omega_n - (\epsilon_{k_{\mathrm{F}}+q} - \mu) + \omega'}\right], \tag{9}$$

where $N(\omega)$ and $n(k)$ are the Bose–Einstein and Fermi–Dirac distribution functions. We expect that the main contribution to the self-energy comes from phonons in a narrow region of momenta Δk around $2k_{\mathrm{F}} (q = 0)$ and evaluate the integrand at that point. To obtain the imaginary part of the "real-time" self energy, we replace $i\omega_n \to \omega - i\delta$. Then

$$\operatorname{Im} \Sigma\,(k_{\mathrm{F}}, \omega) = \frac{g^2 \Delta k}{2\pi a^2} B(2k_{\mathrm{F}}, \omega)[N(\omega) + 1 - n(k_{\mathrm{F}})]. \tag{10}$$

Being interested in frequencies above 1000 cm^{-1} (five times the room temperature), we approximate $N(\omega) \simeq 0$. Finally,

$$\tau^{-1}_{\mathrm{ph}}(\omega) = \frac{g^2 \Delta k}{4\pi a^2 \hbar} B(2k_{\mathrm{F}}, \omega). \tag{11}$$

The spectral density function $B(k, \omega)$ was derived and analyzed in the random phase approximation in reference 4. It reflects the softening and broadening of the phonon spectral density around $2k_{\mathrm{F}}$, as well as the instability when $T \to T_p$. It is shown in reference 4 that

$$B(2k_{\mathrm{F}}, \omega) = \frac{8\omega_0^3 s I_2(\omega)}{[\omega^2 - \omega_0^2 + 2\omega_0^2 s I_1(\omega)]^2 + 4\omega_0^4 s^2 I_2^2(\omega)}, \tag{12}$$

where ω_0 is the bare phonon frequency, s is the value of s_q at $q = 2k_{\mathrm{F}}$ [see equation (4)] and (for $T \ll T_{\mathrm{F}}$)

$$I_1(\omega) = \frac{1}{8}(2 + \ln 4) - \frac{1}{8\tau}[(y + \tau) \ln (y + \tau)$$

$$- (y - \tau) \ln |y - \tau|], \tag{13}$$

$$I_2(\omega) = \frac{\pi}{8}\left[\frac{1}{\exp(-2y/\tau) + 1} - \frac{1}{\exp(2y/\tau) + 1}\right] \tag{14}$$

where

$$\tau = T/T_{\mathrm{F}}, \qquad y = \omega/4\epsilon_{\mathrm{F}}.$$

Let us now turn to the TTF–TCNQ crystal. We assume that the conduction electrons on the TCNQ-chains are most strongly coupled to the C≡N bonds, because they occupy mainly the neighbourhood of these bonds in the TCNQ molecules.[5] The vibration frequency of a C≡N bond is around 2100–2200 cm^{-1}, depending on the material. It is observed experimentally by Bright *et al.* (Fig. 4, reference 3) at 2150 cm^{-1}. This will be our value of ω_0. The Fermi energy is 0.25 eV and $s = 0.36$, as determined by the relation[4]

$$T_p = 2T_{\mathrm{F}} \exp\,[1 - (2/s)], \tag{15}$$

with $T_p = 60$°K. The function $B(2k_{\mathrm{F}}, \omega)$ for these parameters and several values of T is plotted in Fig. 1. It shows a characteristic two-peaked structure which was discussed in reference 4 (a similar structure of the phonon spectral density was also found by Barisic *et al.*)[8] The lower peak grows and moves downwards when $T \to T_p$ until it develops a divergence at $\omega = 0$ for $T = T_p$. At the same time the higher peak is almost independent of T down to T_p.

We shall now make the phenomenological assumption that the life-time defined in equation (5),

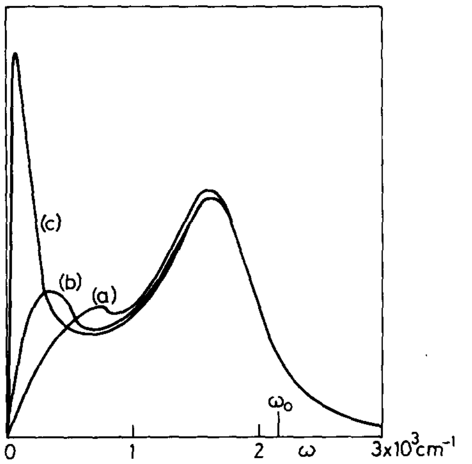

FIG. 1. The function $B(2k_F)$ (in arbitrary units) for various temperatures: (a) –300°K, (b) –200°K, (c) –100°K.

which is determined by the emission and reabsorption of virtual phonons, contributes to the relaxation time in the Drude formula to give an effective τ

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_0} + \frac{1}{\tau_{\text{ph}}(\omega)}, \tag{16}$$

where τ_0 is determined by the emission and absorption of real phonons. In our case ($T = 300°\text{K}, \theta_D = 90°\text{K}, \omega = 2000–3000°\text{K}$) the first term in equation (16) involves only acoustic phonons, whereas only optical phonons (molecular vibrations) contribute to the second term. We have calculated the reflectivity with τ in equation (1) given by equation (16), and the values $\epsilon_0 = 2.43$, $\omega_p = 1.8 \times 10^{15}\,\text{sec}^{-1}$, $\tau_0 = 2.83 \times 10^{-15}\,\text{sec}$, suggested by Bright *et al.*[3]

The resultant reflectivity is plotted in Fig. 2, curve (a). The minimum ($\sim 1600\,\text{cm}^{-1}$) is close to that observed experimentally by Bright *et al.*,[3] and it has the same width and shape. Curve (b) shows the ratio $\tau_0/\tau_{\text{ph}}(\omega)$. There is some uncertainty in the constant coefficient of $B(2k_F, \omega)$ in equation (11), which was chosen so as to give a ~5 per cent reduction in reflectivity at the minimum. Changes in this constant do not effect the position of the minimum, its width and shape. Note that the minimum in the reflectivity is due to the higher peak in the phonon spectral density. Since the position and shape of this peak is almost independent of T, we expect that the minimum in the reflectivity will not change with temperature.

In principle, the minimum in $R(\omega)$ at $1500\,\text{cm}^{-1}$ may be due to C=C bond vibrations which are resonant at this frequency, or to C≡N bond vibrations loaded and shifted down in frequency by the conduction electrons (or a combination of both factors). The present calculation shows that the second possibility is consistent with experiment; however, the other one cannot be definitely excluded. While variation of temperature should not change the reflectivity significantly for wavelength $\lambda < 10\,\mu\text{m}$, the application of hydrostatic pressure is expected to provide a decisive experiment to verify (or refute) the present model. Chu *et al.*[6] measured the electrical

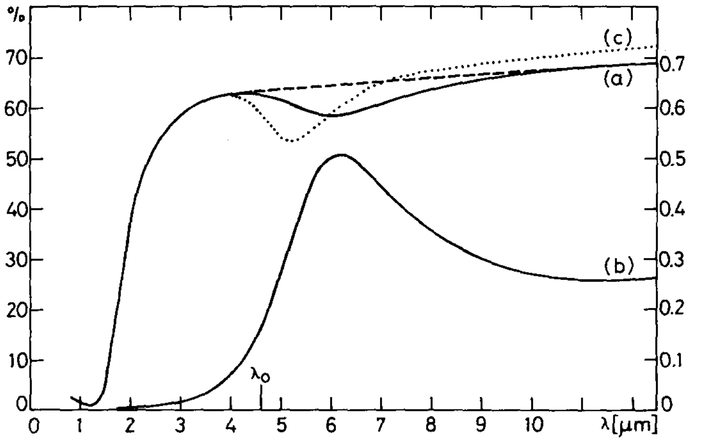

FIG. 2. The reflectivity $R(\lambda)$ [curve (a)] and the ratio τ_0/τ_{ph} [curve (b)]. The dotted curve (c) corresponds to $s = 0.2, E_F = 0.5$.

conductivity of TTF–TCNQ under pressure in the range 7–20 kbar, and found that the conductivity falls rapidly while the metal-to-semiconductor transition temperature rises slowly with pressure. Jerome *et al.*[7] performed a similar measurement in the range 0–6 kbar and obtained in addition to the transition found by Chu *et al.*,[6] an indication of a second transition with a critical temperature decreasing linearly with pressure ($T_c = 32°K$ at 1.5 kbar). An extrapolation of their results indicates that T_c vanishes at 4 kbar. They identified the second transition as the Peierls transition. In any case the variation of the conductivity with pressure (found by both groups) suggests that E_F approximately doubles at 8 kbar and this should roughly reduce s by a factor of 2 [equation (4)]. Such a value of s gives a negligible T_p in accord with the interpretation of Jerome *et al.*[7] With $E_F \sim 0.5$ eV and $s \sim 0.2$ (curve (c) in Fig. 2) the minimum in the reflectivity curve is expected to shift to $\sim 1900\,\text{cm}^{-1}$ if it is due to C≡N bonds. For C=C bonds the shift should be negligible because the observed minimum is already very close to ω_0.

Note that Bright *et al.*[3] observe the minimum in polycrystalline samples, in which they also observe a "normal" line at $2150\,\text{cm}^{-1}$. This unshifted line may be due to defective material at the surfaces of the grains of the crushed sample; alternatively, the phonons with $q = 0$, which are unshifted in frequency by the electron–phonon interaction, may give rise to this line. Also the possibility of molecular normal modes of the C≡N groups of such a symmetry that they are not coupled to the electrons must be considered.

We want to point out that the interpretation of the Peierls transition in TTF–TCNQ assumed in this paper is quite different from that proposed by Bright *et al.*[3] These authors consider acoustic phonons and find a coupling constant $\lambda = s/2 = 1.2$ which in mean field theory gives $T_p \approx 1000°K$. This is in agreement with the model of Lee *et al.*[9] who argue that the mean field value of T_p is much higher than the observed one. We consider optical phonons and assume that the observed T_p is close to the mean field value, which leads to a coupling constant $\lambda = 0.18$.

One point of criticism which can be raised against our procedure may be the use of a free electron approximation, while TTF–TCNQ has a narrow π-band. However, if the gap between the π- and the excited π^*-bands is small compared with the bandwidth the free-electron model should be applicable. Bright *et al.*[3] claim to observe interband transitions at ~ 1 eV indicating that the band gap is smaller than 1 eV and of the same order of magnitude as the band width. The question of the free-electron vs the tight-binding model will be discussed elsewhere.

Acknowledgements – We benefited greatly by criticism and suggestions of S. Alexander and E. Burstein.

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Nous calculons l'effet d'anomalie de Kohn sur les propriétés optiques dans un système unidimensionnel, pour le système TTF–TCNQ. On trouve que l'anomalie de Kohn des phonons optiques dus aux vibrations des groupes C≡N, qui ont (sans perturbation) la fréquence 2100–2200 cm^{-1}, donne un minimum du pouvoir de réflexion à 1600 cm^{-1}. Ce minimum est le même que le minimum trouvé par Bright, Garito et Heeger. Les phonons ayant un vector d'onde $2k_F$ modifient le pouvoir de réflexion des photons ayant un vector d'onde avec $q \approx 0$.