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Modulated-impurity mechanism of pinning in KCP

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Abstract. A modulated-impurity (MI) mechanism of pinning is put forward for $K_2Pt(CN)_4Br_{0.3} \times 3.2\,H_2O$ (KCP) based on the Q-quasi-modulated distribution of the bromine anions along the chain axis ($Q/2$ being the Fermi momentum reduced to the first Brillouin zone). The spectrum of the collective excitations (amplitudons and phasons) as well as the dielectric function are calculated for the charge density wave (CDW) state. Fair agreement is obtained with the optical and neutron scattering data in KCP. A possible explanation is suggested of the difference between the DC gap and the optical one.

1. Introduction and description of the model

Perhaps the most appealing issue predicted by the Fröhlich theory (Fröhlich 1954) of the charge density wave (CDW) in the jellium model of a strictly one-dimensional (1D) solid is the sliding phase mode. In a real quasi-1D material additional interactions shift this Goldstone mode towards a non-vanishing frequency and it becomes a pinned one. Three pinning mechanisms of the phase mode have mainly been put forward (Lee *et al* 1974): CDW commensurability with the underlying lattice, interchain coupling and the effect of impurities. None of these can satisfactorily account for the pinning frequency ω_T reported in the quasi-1D compound KCP ($K_2Pt(CN)_4Br_{0.3} \times 3.2H_2O$) (the properties of KCP are reviewed by Schuster 1975a, Keller 1975 and Toombs 1978). The 1D electrical conduction in KCP is ensured by the strong overlapping of the anisotropically oriented $5d_{z^2}$ Pt orbitals along the chain direction whereas the interchain overlapping is very small. The presence of 0.3 Br^- anions per formula unit partially oxidises the platinum from Pt^{2+} to the fractional state $Pt^{2.3+}$ and yields an electronic Fermi momentum $k_F = 1.7\pi/c \simeq 0.92\ \text{Å}^{-1}$ (c is the length of the unit cell along the chain which is twice the Pt–Pt distance $d_\parallel \simeq 2.87$ Å). It is noteworthy how important the Br^- content is for the conduction properties of KCP, a hole-like conduction band of width $Q = 0.3 \times (2\pi/c)$ being formed in the top Pt band (Q being twice the Fermi momentum reduced to the first Brillouin zone). As the CDW in KCP is highly incommensurate with the underlying lattice (the ratio between the CDW wave-vector and the basic reciprocal vector of the lattice is $Q/G = \frac{3}{10}$), the commensurability pinning is altogether ineffective in this material. As regards the interchain coupling mechanism of pinning one can infer from the very short transverse correlation length—$\xi_\perp \leqslant 5a$ ($a \simeq 9.87$ Å is the interchain spacing) even at liquid helium temperature (Lynn *et al* 1975)—that the interchain

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coupling is too weak (Lee *et al* 1974, Dieterich 1974, Horovitz *et al* 1975, Saub *et al* 1976, Nakajima and Okabe 1977, Fukuyama 1978) to produce a relatively large pinning frequency $\omega_T = 1.9$–2.5 meV (Brüesch *et al* 1975, Carneiro *et al* 1976).

The pinning mechanism brought about by the Br^- impurities in KCP deserves a more detailed discussion. The importance of the part played by Br^- in KCP is widely recognised as it is obvious that the electron transfer from Pt to Br renders the latter an essential constituent of this compound. The bromine anions have been supposed to induce the periodic distortion of the Pt chains via the Friedel oscillations (Sham and Patton 1976), thus giving rise to the central elastic peak revealed in neutron scattering experiments. It has been argued (Sham and Patton 1976) that the assumed randomness of the Br^- distribution along the chain prevents the material from undergoing a sharp, three-dimensional, ordered CDW transition. Furthermore, it has been shown that the randomly distributed Br^- anions give rise to a dip in the density of states near the Fermi points so that a pseudo-gap is developed which smears out the Peierls–Fröhlich transition (Bulaevskii and Sadovskii 1974, Bulaevskii 1975). However, the randomly distributed impurities in one dimension have a disruptive effect on the long-range correlated CDW state; although largely diminished, this effect is not suppressed even by the long-range Coulomb interaction (Bergman *et al* 1977, Lee and Fukuyama 1978, Fukuyama 1978). The large values of the intrachain correlation length, $\xi_\parallel > 100 d_\parallel$ (Lynn *et al* 1975), and the absence of the transverse dispersion of the phasons is difficult to understand within the theory of the randomly distributed Br^- (Lee and Fukuyama 1978, Fukuyama 1978). In order to overcome these difficulties Fukuyama (1978) assumed a $4k_F$-quasi-modulated distribution of the Br^- anions along the chain which ensures the long-range correlated CDW state and acts as a commensurability potential (half-filled band) which gives rise to a pinning frequency in fair agreement with experiment. Assuming a uniform distribution of the Br^- anions whose concentration is $0.3/d_\parallel$, an average distance of $d_\parallel/0.3$ is obtained between two neighbouring Br^- anions which corresponds to the wave-vector $2\pi(d_\parallel/0.3)^{-1} = 2Q$, equivalent to a $4k_F$ modulation. To obtain a direct coupling between the $2Q$-modulated Br^- distribution and the CDW Fukuyama (1978) has tentatively claimed that the latter would have higher harmonics with wave-vector $2Q$. However, this suggestion leads to a somewhat unrealistic conclusion: the $2k_F$ anomaly in KCP would only be a precursor of a generalised Wigner crystal composed of pairs of holes ($Pt^{4.5+}$).

Since the sites occupied by Br^- anions (B, concentration $0.3/d_\parallel$) and (additional) water molecules (W, concentration $0.2/d_\parallel$) in the unit cell are well defined at ($\frac{1}{2}$, $\frac{1}{2}$, ~ 0.5) and ($\frac{1}{2}$, $\frac{1}{2}$, ~ 0.34), respectively (Peters and Eagen 1975, Heger *et al* 1976) it follows that the $2Q$ modulation of the Br^- distribution is an average one, over which a certain degree of disorder is superimposed. The succession B( )B( )B( ) of unit cells where two out of the three blank spaces are filled with the (additional) water molecules (W) leads to the correct concentrations $\frac{3}{10}d_\parallel$ for B and $\frac{2}{10}d_\parallel$ for W and to an average modulation of wavelength $10d_\parallel/3$ which corresponds to the wave-vector $2Q$. However, a rather high degree of disorder is associated with such a succession of the unit cells: two W to five unit cells. In order to lower the degree of disorder one can imagine the larger succession (BBW)( )(BBW)( )(BBW)( ) where only one out of the three blank spaces is filled with an extra W. In this case one also obtains the correct concentrations for B and W but the degree of disorder is very much lowered at one W to ten unit cells. In addition, the average modulation of wavelength $20d_\parallel/3$ is obtained which, however, corresponds to the wave-vector Q instead of $2Q$. The proposed periodicity is further supported by the Raman experiments of Steigmeier *et al* (1975) which revealed a water–CDW coupling in KCP. Therefore it seems reasonable to assume a Q-quasi-periodicity of the Br^-

potential along the chain (instead of $2Q$) over which a lower degree of disorder is superimposed. The former induces the Peierls–Fröhlich distortion along the Pt chains (Inkson 1974, Sham and Patton 1976) and ensures the long intrachain correlation length while the latter is largely ineffective due to the low rate at which it occurs (1W to 10 unit cells) and to the non-coincidence of the B+W and Pt chains, a fact which helps to enhance the three-dimensional effects.

The aim of the present paper is to put forward a mechanism of pinning in KCP caused by the Q-quasi-modulation of the Br^- distribution along the chains. It is assumed that the Br^- anions are distributed such as to produce a Q-quasi-periodic potential over which a low degree of disorder is superimposed. The latter is disregarded in the first approximation. The remaining Q-Fourier component acts on the electrons in the Pt chains as an external field giving rise to a pinning mechanism which may be termed the modulated-impurity (MI) mechanism of pinning. The Peierls–Fröhlich state in KCP is assumed to be driven by the modulated Br^- distribution. This mechanism of inducing the Peierls–Fröhlich distortion is essentially one-dimensional, thus accounting for both the large value of the CDW correlation length along the chain and the rather low rate of transverse correlations. The MI mechanism of pinning consists of the Q-periodic potential and, as will be seen in § 2, an extra elastic energy stored by the modulated Br^- distribution. The latter turns out to be important in KCP and it also makes the present approach distinct from those recently developed (Rice *et al* 1979, Hansen and Carneiro 1984) where the effect of a $2k_F$ external field on the Peierls state has been investigated. In addition, one should remark that within the present approach the physical origin is given of this $2k_F$ external field: it is caused by the Q-modulated distribution of Br^- anions in KCP. The pinning frequency and the elementary excitation spectrum (phasons and amplitudons) are obtained in good agreement with the experimental data. In particular, the small width of the giant Kohn anomaly (Carneiro *et al* 1976) is well reproduced by making use of an interaction cut-off parameter previously used (Apostol and Bâldea 1982). The discrepancy between the measured and calculated values of the static distortion amplitude (Brüesch *et al* 1975) is removed within the MI pinning model. The present approach is further extended to the optical properties of KCP within the (gauge-invariant) theory of linear response to electromagnetic perturbations (Schuster 1975b). The dielectric function is calculated within the bubble approximation. The far-infrared (FIR) conductivity and the reflectivity (at normal incidence) are obtained in fair agreement with the experimental data when a finite phason lifetime is allowed for. The different origins of the DC gap and optical gap are also suggested within the present model.

The paper is organised as follows: the MI mechanism of pinning is given in § 2. The excitation spectra are calculated in § 3 and FIR properties (dielectric function, optical conductivity, reflectivity) are derived in § 4 while § 5 is devoted to discussions and conclusions.

2. Modulated-impurity (MI) mechanism of pinning

To account for the extreme narrowness of the giant Kohn dip observed in the $2k_F$ region of the phonon spectrum (Renker *et al* 1973, Comès *et al* 1975, Lynn *et al* 1975, Carneiro *et al* 1976), which must be directly related to the phonon–electron coupling we shall introduce an interaction cut-off k_c over momentum which gives the range of those electron states around $\pm k_F$ that are most affected by the electron–phonon coupling

($k_c \ll k_F$) (Apostol and Bâldea 1982)†. The incommensurate CDW state in KCP can be described within the mean-field approximation with the 1D Fröhlich Hamiltonian by assuming that the Q-phonon modes are macroscopically occupied (Fröhlich 1954, Rice and Strässler 1973). As the electron states with momenta outside the range $(\pm k_F - k_c, \pm k_F + k_c)$ are inert with respect to the electron–phonon coupling (and therefore they are also unaffected by the $2k_F$ lattice static distortion) we can write down the Hamiltonian of the incommensurate CDW state in the form

$$H_{e\text{-}p} = H_{CDW} + H'_{e\text{-}p}$$

$$H_{CDW} = \sum_{|p|<k_c} [\![v_F p(c^+_{1p} c_{1,p} - c^+_{2,p} c_{2,p}) + \Delta\{\exp[i(\phi + \tfrac{1}{2}\pi)] c^+_{1,p} c_{2,p} + HC\}]\!] + \Delta^2/\pi v_F \lambda \tag{1}$$

$$H'_{e\text{-}p} = \sum_{q \neq \pm Q} \omega_q a^+_q a_q + i \sum_{|p|<k_c} \sum_{q \neq 0} (g_{Q+q} c^+_{1,p+q} c_{2,p} \varphi_{Q+q} + g_{-Q+q} c^+_{2,p+q} c_{1,p} \varphi_{-Q+q}).$$

Here $c^+_{1,p}$ ($c^+_{2,p}$) and $c_{1,p}$ ($c_{2,p}$) are the creation and the destruction operators respectively for the electron state having the momentum $k_F + p$ ($-k_F + p$), a_q (a^+_q) is the destruction (creation) operator of the longitudinal acoustic phonon mode with wave-vector q whose frequency is ω_q,

$$g_q, g_q = g^*_q = -g_{-q} = (\tfrac{1}{2}\pi v_F \lambda \omega_q)^{1/2} \operatorname{sgn} q$$

is the electron–phonon coupling constant (v_F being the Fermi velocity and λ the dimensionless electron–phonon coupling strength) and $\varphi_q = a_q + a^+_{-q}$ is the Fourier transform of the phonon field. The electron spin label is omitted but its contribution will be included in all the subsequent calculations. The parameter Δ in (1) is expressed in terms of the quantities $\varphi_{\pm Q}$, in view of the macroscopical occupation of the $\pm Q$-modes they are c-numbers, as

$$\Delta \exp[\pm i(\phi + \pi/2)] = i g_{\pm Q} \varphi_{\pm Q} \qquad (\Delta > 0).$$

It is related to the amplitude of the static ($a_Q = a_{\pm Q}$) Peierls distortion of the lattice

$$u(x) = u_0 \cos(Qx + \phi)$$

$$u_0 = \frac{2\Delta}{\omega_Q} \left(\frac{d_\parallel}{\pi \lambda v_F M} \right)^{1/2} \tag{2a}$$

where M is the mass of the $Pt(CN)_4$ complex, which responds as a unit to the CDW (Eagen *et al* 1975, Lynn *et al* 1975) (the length of the system along the chain is equal to unity). The first term H_{CDW} in the Hamiltonian (1) describes the CDW state whereas the second accounts for the (dynamical) electron–phonon interaction. In the first (adiabatic) approximation the physics of the CDW state is described by H_{CDW}, Δ and ϕ being taken as classical variables. The low-lying excitations associated with these variables (amplitudons and phasons, respectively) are described by $H'_{e\text{-}p}$ which will be treated by perturbation theoretical methods in § 3. The expression (1) gives a fair description of the CDW state as long as the interaction strength Δ associated with the lattice distortion is not so strong as to alter the electron states lying deep in the Fermi sea, i.e. $v_F k_c/\Delta \gg 1$.

As we have seen in § 1, various experimental results for KCP suggest a Q-quasi-

† The parameter k_c has previously been termed the electronic band width (Apostol and Bâldea 1982) in the sense of the width of the range of electron states near $\pm k_F$ which are coupled to phonons.

periodic distribution (BBW)( )(BBW)( )(BBW)( ). This modulated distribution of Br^- anions and extra water molecules stores up an elastic energy which has to be added to that corresponding to the Pt-distorted chains to obtain the total elastic energy stored by the distorted state of KCP. This extra elastic energy may arise from any of the following three effects.

(i) Additional vibrational modes caused, e.g., by the coupling of the water modes to the amplitude mode of CDW as expressed by the considerable isotope effect (the amplitudon frequency is 5.5 meV for undeuterated samples and 4.6 meV for deuterated ones) (Steigmeier *et al* 1976).

(ii) The difference between the interaction energy of the uniform, random B and W distributions (which is probably the case in the absence of any distortion) and that corresponding to the Q-quasi-periodic sequence (BBW)( )(BBW)( )(BBW)( ) (to pass from the former to the latter is like distorting a spring and therefore elastic energy is required).

(iii) The Q-distorted Pt chains interact differently with the Q-modulated B-W distribution as compared with the case where the latter is perfectly random.

The expression for the extra elastic energy can be written by analogy with the elastic energy of the distorted Pt chains as $\Delta^2/\pi v_F\lambda_i$, λ_i^{-1} being a dimensionless elastic strength associated with the modulation of the B + W distribution in the host lattice. Adding this extra elastic energy to the Hamiltonian (1) together with the Q-periodic potential (Rice *et al* 1979, Hansen and Carneiro 1984) of strength V (>0) generated by the Q-modulated distribution of bromine anions we obtain the pinned CDW Hamiltonian, H_{pCDW}:

$$H_{pCDW} = \sum_{|p|<k_c} v_F p(c_{1,p}^+ c_{1,p} - c_{2,p}^+ c_{2,p}) + \sum_{p|<k_c} [\{\Delta \exp[i(\phi + \pi/2)] + V\} c_{1,p}^+ c_{2,p} + HC] + \Delta^2/\pi v_F \tilde{\lambda} \qquad (2b)$$

where $1/\tilde{\lambda} = 1/\lambda + 1/\lambda_i$ is an effective elastic strength. The Hamiltonian (2) can be straightforwardly expressed in diagonal form:

$$H_{pCDW} = \sum_{|p|<k_c} \tilde{\varepsilon}_p(\tilde{c}_{1,p}^+ \tilde{c}_{1,p} - \tilde{c}_{2,p}^+ \tilde{c}_{2,p}) + \Delta^2/\pi v_F \tilde{\lambda} \qquad (3)$$

by means of the canonical transformation

$$\begin{aligned} c_{1,p} &= u_p \tilde{c}_{1,p} - v_p \tilde{c}_{2,p} \\ c_{2,p} &= v_p^* \tilde{c}_{1,p} + u_p \tilde{c}_{2,p} \end{aligned} \qquad (4)$$

where

$$\begin{aligned} u_p &= \cos\theta_p = [(1 + v_F p/\tilde{\varepsilon}_p)/2]^{1/2} \\ v_p &= \exp[i(\phi + \tfrac{1}{2}\pi)] \operatorname{sgn}(p) \sin\theta_p = [(1 - v_F p/\tilde{\varepsilon}_p)/2]^{1/2} \exp[i(\phi + \tfrac{1}{2}\pi)] \operatorname{sgn} p \\ \tilde{\varepsilon}_p &= (v_F^2 p^2 + \tilde{\Delta}^2)^{1/2} \operatorname{sgn} p. \end{aligned} \qquad (5)$$

A gap of magnitude $2\tilde{\Delta}$ ($\tilde{\Delta} = |\Delta \exp[i(\phi + \frac{1}{2}\pi)] + V|$) is opened up at $p = 0$ in the one-particle spectrum, the ground state $|0\rangle$ of the Hamiltonian (3) being filled with particles of type 1 from $-k_c$ to 0 and with particles of type 2 from 0 to k_c. The electron density $n(x)$ of the CDW ground state is modulated with the wave-vector Q,

$$n(x) = n_0 - (2\tilde{\Delta}/\pi v_F) \log(2\alpha) \cos(Qx + \phi + \pi/2)$$

where $\alpha = v_F k_c/\tilde{\Delta}$ and n_0 is the average electron density. The mean-field equilibrium condition with respect to both ϕ and $\tilde{\Delta}$ yields $\phi + \pi/2 = 0$, which corresponds to the maximum lowering of the occupied electron energy levels:

$$\tilde{\Delta} = \Delta + V \tag{6}$$

and the gap equation

$$\frac{1}{\tilde{\lambda}}\frac{\Delta}{\tilde{\Delta}} = v_F \int_0^{k_c} dp \frac{\tanh(\beta\tilde{\varepsilon}_p/2)}{\tilde{\varepsilon}_p}$$

where $\beta = 1/k_B T$ (k_B = Boltzmann constant), which in the low-temperature limit ($\beta\tilde{\Delta} \gg 1$) becomes

$$\tilde{\lambda}^{-1}(\Delta/\tilde{\Delta}) = \log 2\alpha. \tag{7}$$

In the absence of the Q-modulated B + W distribution ($V = 0$, $\lambda_i^{-1} = 0$), the mean-field transition temperature T_0 is obtained from (7) in the form:

$$k_B T_0 = 1.14 v_F k_c \exp(-1/\lambda). \tag{8}$$

It is worth noting that below this very temperature T_0 the undistorted 1D system becomes unstable against the back-scattering electron–phonon interaction (Apostol and Bâldea 1982). As is well known, a real phase transition can never occur at finite temperatures in a strictly 1D system with short-range interaction. The prediction of a sharp Peierls–Fröhlich transition at the temperature given by (8) relies upon the mean-field scheme which singles out the $\pm Q$-components of the interaction and thus converts the real short-range interaction into a long-range one. However, the 1D fluctuation effects brought about by the other Fourier components which preclude the phase transition at finite temperatures may be wiped out by interchain coupling so that a real quasi-one-dimensional material can actually undergo a Peierls–Fröhlich transition (Lee *et al* 1973, Dieterich 1974, Horovitz *et al* 1975) at $T \neq 0$. The mean-field temperature T_0 is a scale temperature at which the 1D fluctuations become large; therefore, the mean-field approach in one dimension is valid in the limit $T/T_0 \ll 1$ (or $k_B T/\Delta \ll 1$). The additional Q-periodic potential of strength V enhances the gap in the electron spectrum (from Δ to $\tilde{\Delta}$), as expressed by (6) and smears out the Peierls–Fröhlich transition at the mean-field critical temperature T_0 (8) (Hansen and Carneiro 1984). There is no longer a real phase transition but an induced one, due to the presence of the Q-modulated B + W distribution.

3. Collective excitations: phasons and amplitudons

The long-wavelength collective excitations of the CDW state can be treated in a convenient way by introducing the phason (ϕ) and amplitudon (R) operators (Lee *et al* 1974, Schuster 1975b)

$$\begin{aligned} a_{\pm Q+q} &= (a_q^{\phi} \mp \mathrm{i}a_q^{R})/\sqrt{2} \\ \phi_q &= a_q^{\phi} + a_{-q}^{\phi+} \\ R_q &= a_q^{R} + a_{-q}^{R+} \qquad |q| < 2k_c \\ [a_q^{R,\phi}, a_{q'}^{R,\phi+}] &= \delta_{qq'}. \end{aligned} \tag{9}$$

It is noteworthy that within the bubble approximation the degrees of freedom of ϕ are completely disentangled from those of R (Lee *et al* 1974, Schuster 1975b). In the

limit of small wave-vectors ($v_F q/2\tilde{\Delta} \ll 1$) and low frequencies ($\omega/2\tilde{\Delta} \ll 1$) the polarisations can be obtained analytically ($\alpha^2 \gg 1$) and the dispersion relations of (pinned) phasons and amplitudons are given by the poles of the corresponding Green functions in the form

$$\Omega_\varphi^2(q) = \omega_T^2 + \frac{m}{m_\varphi^*}(v_F q)^2 \qquad \frac{m_\varphi^*}{m} = 1 + \frac{4\tilde{\Delta}^2}{\lambda\omega_Q^2}$$
$$\Omega_R^2(q) = \omega_R^2 + \frac{m}{m_R^*}(v_F q)^2 \qquad \frac{m_R^*}{m} = 1 + \frac{12\tilde{\Delta}^2}{\lambda\omega_Q^2} \tag{10}$$

$$\omega_R^2 = \omega_T^2 + \lambda\omega_Q^2 \tag{11}$$

and making use of the mean-field equilibrium condition (7) the pinning frequency is

$$\omega_T = \omega_Q \left[\left(1 - \frac{\lambda}{\tilde{\lambda}} \frac{\Delta}{\tilde{\Delta}} \right) \left(1 + \frac{\lambda\omega_Q^2}{4\tilde{\Delta}^2} \right)^{-1} \right]^{1/2}. \tag{12}$$

The form (10) for the effective masses for phasons (CDW), m_φ^*, and amplitudons, m_R^*, has previously been derived (Horovitz and Krumhansl 1978). The pinning frequency (12) we have just obtained differs from that induced by a $2k_F$ external field (Rice *et al* 1979, Hansen and Carneiro 1984) by the presence of the ratio $\lambda/\tilde{\lambda}$, which is a consequence of the extra elastic energy stored by impurities. The phason and amplitudon frequencies at $q = 0$ (Brüesch *et al* 1975, Steigmeier *et al* 1975, 1976, Carneiro *et al* 1976) provide us with a straightforward evaluation of the electron–phonon coupling strength λ by means of (11). Once λ is known we can evaluate the quantity 2Δ by means of (2) employing the experimental values of the static distortion amplitude of the Pt chains and the Pt–Pt intrachain spacing $d_\parallel$ (Eagen *et al* 1975, Lynn *et al* 1975, Carneiro *et al* 1976). With the estimated values of λ and 2Δ one can use (12) and (7) to obtain the quantities λ_i and α (or $k_c = \alpha\tilde{\Delta}/v_F$), the value $2\tilde{\Delta}$ being obtained from the position of the near-infrared peak in optical conductivity (Brüesch *et al* 1975). Table 1 summarises the values of these

Table 1. Values of the parameters λ, 2Δ, λ_i, k_c and ω_L (see text) calculated from (11), (2), (12), (7) and (20) by using the input data at low temperatures $\omega_Q = 8.1$ meV, $d_\parallel = 2.87$ Å, $v_F = 11 \times 10^5\ \mathrm{m\,s^{-1}}$, $u_0 = 0.025$ Å (Eagen *et al* 1975, Lynn *et al* 1975, Carneiro *et al* 1976), $\tilde{\Delta} = 100$ meV (Brüesch *et al* 1975), ω_T and ω_R. The values of ω_T and ω_R used here were obtained by fitting the infrared, Raman and neutron data reported for different samples within very crude models. This may explain the spread of the input data which in turn is reflected in the values of the output parameters. Therefore, a direct comparison of the light and neutron intensity data with theoretical calculations by means of the dynamic structure factor would be desirable. The values of k_c, assigned as the half-width of the giant Kohn dip (see text), of the last two columns are too large (of the order $Q \simeq 0.3\ \mathrm{Å^{-1}}$) so that the corresponding combinations (ω_T, ω_R) appear to be unacceptable within the present model.

ω_T (meV)	1.9[a]	2.5[c]	1.9[a]	2.5[c]	1.9[a]	2.5[c]
ω_R (meV)	5.5[b]	5.5[b]	6.0[c]	6.9[c]	4.6[d]	4.6[d]
λ	0.41	0.37	0.49	0.45	0.27	0.23
2Δ (meV)	104	100	114	110	85	79
λ_i	0.50	0.45	0.77	0.70	0.28	0.18
k_c ($\times 10^{-2}$ Å)	7.0	8.0	4.7	5.0	22.5	35.2
ω_L (meV)	6.6	6.5	7.2	7.1	5.5	5.4

[a] Brüesch *et al* (1975), undeuterated samples.
[b] Steigmeier *et al* (1975), undeuterated samples.
[c] Carneiro *et al* (1976), deuterated samples.
[d] Steigmeier *et al* (1976), deuterated samples.

parameters for various experimental data. The values of the electron–phonon coupling λ (0.23–0.49) are in good agreement with other estimates (Brüesch *et al* 1975, Nielsen and Carneiro 1980, Apostol and Bâldea 1982, Bâldea and Apostol 1983). The interaction cut-off defined in § 2 is related to the ranges of both the electron states around $\pm k_F$ and phonon modes around $\pm 2k_F$ which are most affected by the electron–phonon coupling. Consequently, the parameter k_c is directly connected with the width of the giant Kohn dip. The values of k_c given in table 1 are in fair agreement with the half-width of the giant Kohn dip observed in experiments (Comès *et al* 1975, Lynn *et al* 1975, Carneiro *et al* 1976). This ensures the consistency of the description of the electron–phonon coupling in KCP within the present model which has an explicitly introduced momentum cut-off. By means of (10) the enhanced CDW mass m_ϕ^*/m can also be estimated to be about 1200–1600 in good agreement with the optical data (Brüesch *et al* 1975). It is worth mentioning here that the present model based on the twofold role played by the modulated impurity distribution, to produce a $2k_F$ field and an extra elastic energy, allows us to remove the discrepancy pointed out by Brüesch *et al* (1975) between the measured and theoretically estimated values of the distortion amplitude. This is due to the fact that within the present model the latter is related, as expressed by (2), to the contribution 2Δ of the Pt-distorted chains to the total gap $2\tilde{\Delta} = 2(\Delta + V)$ and not to the full gap. If a finite lifetime γ^{-1} of the electron states (assumed to be frequency independent for the sake of simplicity) is included the phason and amplitudon Green functions become

$$D_{\phi,R}(q, \omega) = 2\omega_Q/(\omega^2 - \Omega_{\phi,R}^2(q) + 2i\Omega_{\phi,R}\Gamma_{\phi,R}) \tag{13}$$

where the phason and amplitudon lifetime $\Gamma_{\phi,R}^{-1}$ are given by (in the limit $(\omega_Q/2\tilde{\Delta})^2 \ll 1$)

$$\Gamma_\phi = 3\Gamma_R = (\lambda\omega_Q^2/2\tilde{\Delta}^2)\gamma \tag{14}$$

and the pinning frequency ω_T and amplitudon frequency ω_R are shifted to

$$\Omega_{\phi,R}^2(0) = \omega_{T,R}^2 + 2\gamma\Gamma_{\phi,R}. \tag{15}$$

Thus, the finite lifetime effects further increase the pinning frequency of the phase mode.

4. Far-infrared properties

It has been shown (Schuster 1975b) that a gauge-invariant response theory is obtained within the bubble approximation. If the long-range Coulomb interaction:

$$H_c = \tfrac{1}{2}\sum_{pp',q}{}' U(q)(\psi_{p+q}^+\psi_p)(\psi_{p'}^+\psi_{p'+q}) \qquad \psi_p = \begin{pmatrix} c_{1,p} \\ c_{2,p} \end{pmatrix} \qquad \psi_p^+ = (c_{1,p}^+, c_{2,p}^+) \tag{16}$$

with $U(q) = 4\pi e^2/q^2 A_\perp$ and $q \neq 0$ is added to the electron–phonon Hamiltonian of the CDW state $H_{pCDW} + H'_{e-p}$, given by (3) and (1), the straightforward diagrammatic analysis within the bubble approximation (Schuster 1975b) then yields the following dielectric function:

$$\varepsilon(\omega) = \lim_{q\to 0}(1 + iU(q)f_{00}(\tilde{q}) + \tfrac{1}{2}g_Q^2 U(q)D_\phi(\tilde{q})f_{20}(\tilde{q})f_{02}(\tilde{q})) \tag{17}$$

where τ_α ($\alpha = 0, 1, 2, 3$) are the Pauli matrices, $\tilde{p} = (p, \varepsilon)$, $\tilde{q} = (q, \omega)$, $f_{\alpha\beta}$ is given by

$$f_{\alpha\beta}(\tilde{q}) = 2\int \frac{d^2\tilde{p}}{(2\pi)^2}\,\mathrm{Tr}[\tau_\alpha G(\tilde{p} + \tilde{q}/2)\tau_\beta G(\tilde{p} - \tilde{q}/2)] \qquad |p| < k_c - |q|/2$$

and G is the matrix propagator of the pinned CDW Hamiltonian

$$G = \tfrac{1}{2}[(\tilde{G}_1 + \tilde{G}_2)\tau_0 + (u_p^2 - v_p^2)(\tilde{G}_1 - \tilde{G}_2)\tau_3 + u_p v_p(\tilde{G}_1 - \tilde{G}_2)\tau_1]$$

$$\tilde{G}_{1,2}(\tilde{p}) = (\varepsilon \mp \tilde{\varepsilon}_p \pm i0\,\mathrm{sgn}(p))^{-1}.$$

One can see that, as expected (Lee *et al* 1974), the amplitudons do not contribute in this lowest order to the optical properties of the system. The dielectric function (17) can be calculated by evaluating the function $f_{00}(\tilde{q})$ and $f_{02}(\tilde{q}) = f_{20}(-\tilde{q})$ in the limit $q \to 0$. Straightforward calculations yield the expressions ($\omega/2\tilde{\Delta} \ll 1$).

$$f_{00}(\tilde{q}) = -iv_F q^2/3\pi\tilde{\Delta}^2$$
$$f_{02}(\tilde{q}) = q/\pi\tilde{\Delta} \tag{18}$$

so that the real part of the dielectric function (17) has the form ($\omega/2\tilde{\Delta} \ll 1$)

$$\varepsilon(\omega) = 1 + \frac{1}{6}\frac{\omega_p^2}{\tilde{\Delta}^2} + \frac{m}{m_\varphi^*}\frac{\omega_p^2}{\omega_T^2 - \omega^2} \tag{19}$$

where $\omega_p^2 = 4\pi n_0 e^2/mA_\perp$ is the plasma frequency, $m/m_\varphi^* = \lambda\omega_Q^2/4\Delta^2$, from (10), and finite phason lifetime ($\Gamma_\varphi = 0$ in (13)) has been assumed in deriving (19). The well known result (19) (Lee *et al* 1974, Schuster 1975b) is in good agreement with the phenomenological oscillator model (Brüesch *et al* 1975). The dielectric function (19) can be cast into another form by introducing $\varepsilon(\infty) = 1 + \omega_p^2/6\tilde{\Delta}^2$:

$$\varepsilon(\omega) = \varepsilon(\infty)(\omega_L^2 - \omega^2)/(\omega_T^2 - \omega^2)$$
$$\omega_L = (\omega_T^2 + \tfrac{3}{2}\lambda\omega_Q^2)^{1/2}. \tag{20}$$

This is the standard form of a dielectric function with a transverse mode ω_T and a longitudinal one ω_L brought about by the Coulomb interaction; with $\omega_p = 2.88$ eV (Kuse and Zeller 1971), $\tilde{\Delta} = 100$ meV, $\omega_Q = 8.1$ meV (Carneiro *et al* 1976), ω_T and λ given in table 1, the microwave ($\omega \ll \omega_T$) dielectric constant $\varepsilon(0)$ estimated from (20) is $\varepsilon(0) \simeq$ 1000–2000. This is in good agreement with the experimental values 1000–3000 (Berenblium *et al* 1971, Jaklevic and Saillant 1974).

When the phason lifetime Γ_φ^{-1} is introduced into the phase Green function (13), the real part of the optical conductivity ($\sigma(\omega) = (\omega/4\pi i)[\varepsilon(\omega) - 1]$) is obtained from (17) and (18) as

$$\sigma(\omega) = \sigma_{max}\frac{4\omega^2\Gamma_\varphi^2}{(\omega^2 - \omega_T^2)^2 + 4\omega^2\Gamma_\varphi^2}$$
$$\sigma_{max} = \frac{m}{m_\varphi^*}\frac{\omega_p^2}{8\pi\Gamma_\varphi} \tag{21}$$

where the lifetime effects have been ignored in the pinning frequency (15).

Equation (21) for $\sigma(\omega)$ has been used to reproduce the experimental FIR peak associated with the pinned Fröhlich mode (Brüesch *et al* 1975) (figure 1). For $\Gamma_\varphi =$ 0.3 meV (all the other parameters being given in table 1) one gets $\sigma_{max} \simeq$ 830–1100 $(\Omega\,\mathrm{cm})^{-1}$, close to the experimental absolute value of the height $\sigma_{max} \simeq 950\,(\Omega\,\mathrm{cm})^{-1}$ (at $T = 88$ K), but the theoretical curve is too narrow as compared with the experimental one. For $\Gamma_\varphi \simeq 1$ meV the shape of the normalised conductivity $\sigma(\omega)/\sigma_{max}$ is almost identical with the experimental curve, σ_{max} being, however, smaller than the experimental value (about one third of the latter). An ω-dependent phonon lifetime would

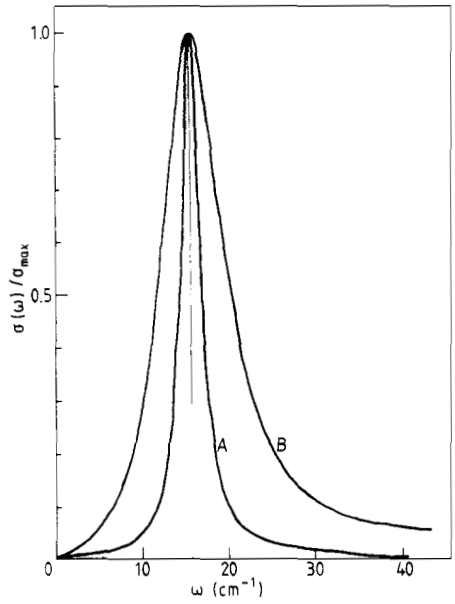

Figure 1. Normalised far-infrared conductivity, $\sigma(\omega)/\sigma_{max}$, given by (21) compared with the experimental one (Brüesch *et al* 1975) for $\omega_T = 15\,cm^{-1}$ (1.9 meV). A, $\Gamma = 0.3$ meV; B, experiment.

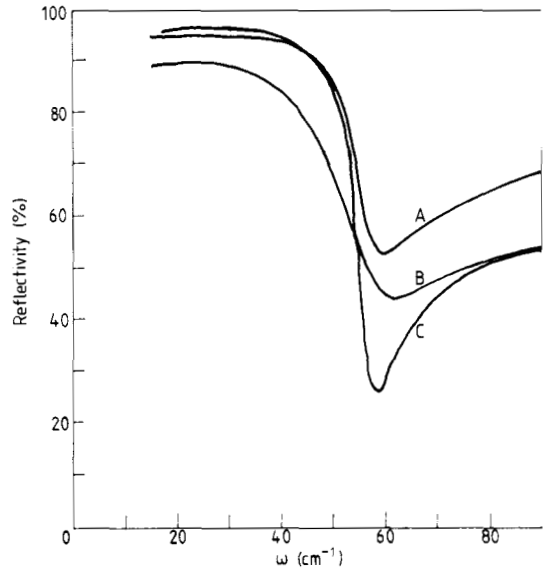

Figure 2. Theoretical reflectivity at normal incidence (22) for two values of the phason lifetime Γ_φ^{-1} compared with the experimental one (Brüesch *et al* 1975). The following values of the parameters are used: $\omega_T = 1.9$ meV, $\tilde{\Delta} = 100$ meV (Brüesch *et al* 1975) and $\omega_p = 2.88$ eV (Kuse and Zeller 1971). The electron–phonon coupling strength is taken to be $\lambda = 0.45$ but the reflectivity is slightly dependent on λ in the range 0.37–0.49 of the most reliable values (see table 1 and discussion therein). The CDW plasma edge ω_L at about 56 cm^{-1} (7 meV) is in excellent agreement with the experimental value. The curves are: A, experiment; B, $\Gamma = 1.0$ meV; C, $\Gamma = 0.3$ meV.

produce an improved fit, as pointed out by the phenomenological model (Brüesch *et al* 1975). Nevertheless, the agreement is satisfactory particularly bearing in mind the difficulties in obtaining the experimental curve (see, for details Brüesch *et al* 1975). The values $\Gamma_\varphi \simeq 0.3$–$1$ meV ($T = 88$ K) are in fact consistent with those derived from the neutron scattering experiments, $\Gamma_\varphi \simeq 0.5$ meV at $T = 80$ K (Carneiro *et al* 1976). The reflectivity at normal incidence R given by the Fresnel formula

$$R(\omega) = \left| \frac{1 - (\varepsilon(\omega))^{1/2}}{1 + (\varepsilon(\omega))^{1/2}} \right|^2 \tag{22}$$

is plotted in figure 2 against ω for the two values of the parameter Γ_φ (0.3 and 1 meV). The values of the CDW plasma edge ω_L derived from (20) for $\Gamma_\varphi = 0$ are given in table 1; excellent agreement with the experimental value of 7 meV (Brüesch *et al* 1975) is obtained.

5. Discussions and conclusions

The MI mechanism of pinning in KCP enables us to obtain a unified picture of the x-ray (elastic and inelastic), neutron scattering and optical (Raman, IR) spectroscopy data in this material. It has been shown that the Peierls–Fröhlich state in KCP can be viewed as being induced by the Q-quasi-modulated Br^- distribution. The MI mechanism of pinning in KCP consists of a $2k_F$ periodic potential, caused by the Q-modulated Br^- distribution, and an elastic energy stored by the quasi-periodic distribution of Br^- anions and extra water molecules (as seen in § 2). The strength V of the assumed Q-periodic potential and the elastic strength associated with the elastic energy stored by impurities are the fitting parameters which, together with the phason lifetime Γ_φ^{-1}, allow the theory to account quantitatively for all the aforementioned experimental data. The electron–phonon coupling strength λ has been derived from the phason and amplitudon spectrum calculated within the bubble approximation in the long-wavelength limit. The present model predicts, as discussed in § 2, that the width of the giant Kohn dip is related to the interaction cut-off k_c; this parameter is evaluated and is in fair agreement with experiment. The CDW plasma edge ω_L, the large values of the microwave dielectric constant and the peak in the far-infrared conductivity are also reproduced within the present approach, the latter by allowing for a finite phason lifetime Γ_φ^{-1}. A finite width γ of the electronic energy levels is suggested as a possible origin for Γ_φ. The large width of the electronic levels yields the broadening of the peak in $\sigma(\omega)$ associated with the transitions across the Peierls gap; a satisfactory agreement is obtained when the ratio γ/Γ_φ given by (14) is compared with the ratio between the width of the broad peak in the near-infrared at 200 meV and that of the far-infrared peak extracted from experiment (Brüesch *et al* 1975). The collective excitation spectrum and the optical properties in the far-infrared of the CDW state in KCP have a slight temperature dependence, in agreement with experiments, whereas all the parameters we have evaluated here, including those of the pinning mechanism by the $2k_F$-modulated B + W distribution (V and λ_i), undergo a sudden change in the temperature range 80–120 K (Apostol and Bâldea 1985). This temperature dependence is similar to that displayed by other parameters straightforwardly extracted from the experimental data: transverse correlation length, $2k_F$ distortion amplitude, pinning frequency, phason lifetime, widths of the near-infrared and far-infrared peaks in $\sigma(\omega)$ etc. This is consistent with the picture which emerges

from experiments (e.g. Lynn *et al* 1975, Steigmeier *et al* 1975, 1976, Carneiro *et al* 1976) that the Peierls-distorted state is present at all the temperatures which are below the room temperature but the CDW state is more fluctuating at higher temperatures and it evolves into a more stable one as the temperature is lowered, 80–120 K being the range of the (incomplete) three-dimensional ordering. A full understanding of the behaviour of KCP around 80–120 K requires the three-dimensional effects to be taken into account.

The estimated values of λ, together with the measured value of the amplitude of the statically distorted $Pt(CN)_4$ chains (Eagen *et al* 1975, Lynn *et al* 1975), allow us to single out the contribution 2Δ of the $Pt(CN)_4$ distorted strands to the full gap $2\tilde{\Delta} = 2\Delta + 2V$ in KCP. A suggestion on the striking difference between the DC gap and the optical one (Brüesch *et al* 1975) could also be given in the framework of the present model of KCP. The full gap $2\tilde{\Delta}$ appearing in the single-electron energy spectrum has a twofold origin. The quantity 2Δ is related to the distorted Pt chains, while $2V$ is brought about by the modulated Br^- distribution. The latter only corresponds to an average periodicity and not, as in the case of the former, to a true one. The disordered effects, much more ineffective as compared with the modulation effect, may be accounted for by assuming a statistical distribution of the parameters V (by contrast with the value Δ whose statistical spread would be ignored). Consequently, the density of single-electron states $N(\varepsilon)$ will vanish in the range 2Δ (true gap) centred on the Fermi level, while outside this range ($|\varepsilon| > \Delta$), the statistically distributed values of $2V$ will cause non-zero values of $N(\varepsilon)$, a pseudo-gap being developed which has the maximum in the density of states around the value $|\varepsilon| = \tilde{\Delta}$, where $\tilde{\Delta}$ is given by the present approach. Experimental data indicate that the DC conductivity is predominantly given by single-particle excitations (Brüesch *et al* 1975). The present model allows us to assign the value 2Δ to the DC gap for the following reason. By lowering the temperature only the single-electron excitations of lowest energy (this is—in view of the aforementioned behaviour of $N(\varepsilon)$—of the order 2Δ) could occur. This yields a single-particle DC conductivity $\sigma(T) \sim \exp(-2\Delta/k_B T)$; thus 2Δ is the activation energy. The values we obtain for 2Δ (table 1) are in fair agreement with the low-temperature value of the DC gap of 110 meV (Zeller and Beck 1974). On the other hand, the optical conductivity $\sigma(\omega)$ is expected to be peaked around $\omega = 2\tilde{\Delta}$ corresponding to the maximum in the density of states. As we move towards lower frequencies this peak is expected to disappear only below the value 2Δ which corresponds to the true gap. This is the actual behaviour of the near-infrared peak in $\sigma(\omega)$ of KCP which develops from the side of lower frequency at about 100 meV, a value which is in excellent agreement with both the evaluated values of 2Δ given in table 1 and the measured DC gap (110 meV) of Zeller and Beck (1974), thus giving the consistency of the present picture of KCP. A weighted distribution of V such as was attempted for the optical gap parameters (Blunck and Reik 1977, Wonneberger 1977) would provide us with a satisfactory fitting of the broad peak in $\sigma(\omega)$ due to the transitions across the Peierls (pseudo-) gap.

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