Solid State Communications, Vol. 53, No. 8, pp. 687–690, 1985.
Printed in Great Britain.

0038–1098/85 $3.00 + .00
Pergamon Press Ltd.

INCOMMENSURATE PINNING MECHANISM IN KCP

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(*Received* 27 *July* 1984 *by A.A. Maradudin*)

An incommensurate pinning mechanism based on the Q-quasimodulated bromine (Br^-) distribution (Q being twice the Fermi wavevector reduced to the first Brillouin zone) is proposed in $K_2Pt(CN)_4Br_{0.3}\ 3.2H_2O$ (KCP) which quantitatively accounts for the neutron scattering and far infrared optical spectroscopy data in this material.

1. INTRODUCTION

THERE HAVE BEEN put forward mainly three mechanisms for explaining the pinning of the phase mode of the charge density wave (CDW) state in the quasi-one-dimensional materials [1]: commensurability of the CDW with the underlying lattice, interchain coupling and the impurity effects. However, neither the commensurability nor the interchain coupling can give a satisfactory quantitative account for the relatively large pinning frequency $\omega_T = 1.9 - 2.5$ meV [2, 3] in $K_2Pt(CN)_4Br_{0.3}\ 3.2H_2O$ (*KCP*): the former due to the large value of the commensurability order $M = 10$ ($Q/G = N/M, N, M$ integers, $2 \leqslant 2N \leqslant M$, Q being twice the Fermi wavevector k_F reduced to the first Brillouin zone, $Q = 0.3\,\pi/c$, c being the Pt–Pt distance along the chain axis and G being the basic vector of the reciprocal lattice) and the latter due to the small extent of the transverse correlations [4, 5]. The randomly distributed bromine anions (Br^-) along the chains, although accounting for the pseudogap at the Fermi points $\pm Q/2$, cause serious disruptive effects even in the presence of the long-range Coulomb interaction [6]. Consequently, the large values of the longitudinal correlation length of the CDW state, the absence of the transverse dispersion of the phasons as well as the critical temperature of the Peierls-Fröhlich transition in KCP can not be understood within the framework of this approach [7]. A simple relationship is predicted by this theory between the longitudinal correlation length and the pinning frequency which fails to be satisfied by the experimentally measured values of these quantities in KCP [6, 7]. In order to circumvent these difficulties it has been claimed [7] that the Br^- distribution is not so random as it seems to be suggested at the first sight by the Br^- concentration $0.3/c$, but instead it is $2Q$-modulated (as an average), which corresponds to a $4k_F$-modulation along the chain axis. Long-range correlated CDW state is obtained thereby as well as a commensurate pinning mechanism (half-filled band). However, the coupling between the higher-order harmonics of the CDW and $2Q$-modulated Br^- distribution requires a fluctuating valence regime between two valence states of the Pt ions, Pt^{2+} and Pt^{4+}, which leads to a somewhat unrealistical conclusion: the Q-anomaly observed in KCP would be only a precursor of a generalized Wigner crystal made by pairs of holes (Pt^{4+}) [6]. Moreover, as the Br^- anions (B, concentration $0.3/c$) and (additional) water molecules (W, concentration $0.2/c$) are placed at well-defined sites in the unit cell [($\frac{1}{2}, \frac{1}{2}, \sim 0.5$) and, respectively, ($\frac{1}{2}, \frac{1}{2}, \sim 0.34$)] [8] it follows that a large amount of disorder is still overimposed on the $2Q$-modulated Br^- distribution. Indeed, the succession $B(\ )B(\ )B(\ )$ of unit cells, where two out of the three blank spaces are filled with (additional) water molecules (W), leads to the correct concentrations $3/10c$ for B and $2/10c$ for W (the length of the unit cell is $2c$) and to the average modulation of wavelength $10c/3$ which corresponds to the wavevector $2Q$. At the same time a rather large amount of disorder is related with this succession: two W to five unit cells.

In order to diminish the amount of disorder on the Br^- chains 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 obtains also the correct concentrations $6/20c$ for B and $4/20c$ for W but the amount of disorder is largely lowered at one W to ten unit cells. In addition, this succession of unit cells predicts an average modulation of the Br^- distribution of wavelength $20c/3$ which corresponds to the wavevector Q. A more simple pinning mechanism, termed incommensurate (with respect to the underlying lattice), is obtained thereby: the Q-modulated electron density of the CDW state couples directly to the Q-modulated Br^- distribution. The remaining small amount of disorder is largely ineffective due to the low rate at which it occurs (one W to ten unit

cells) and to the non-coincidence of the $B + W$ chains and Pt chains, a fact which helps to enhance the three-dimensionality effects.

The incommensurate pinning mechanism is proposed in the present paper in order to account for the experimental data in KCP. A Q-periodic potential of strength $V > 0$, brought about by the Q-modulated Br^- distribution (disorder effects being neglected) is added to the well-known mean-field Hamiltonian (a similar approach has recently been attempted [9]) as well as an extra elastic energy stored by the modulated Br^- distribution in the host Pt lattice. The coupling strength λ_i associated with the latter and the potential strength V are used as fitting parameters for obtaining the neutron scattering and optical spectroscopy data in KCP. Fair agreement is obtained when the bandwidth cut-off parameter k_c [10] and phason life-time Γ^{-1} are included.

2. COLLECTIVE EXCITATIONS AND OPTICAL PROPERTIES OF THE CDW STATE

The Hamiltonian of the pinned CDW state is given by

$$H_{p\mathrm{CDW}} = \frac{\Delta^2}{\pi v_F \bar{\lambda}} + \sum_p (v_F p \psi_p^+ \tau_3 \psi_p + \psi_p^+ A \psi_p), \quad (1)$$

where Δ is the amplitude of the order parameter ($\Delta e^{i\phi}$) v_F is the Fermi velocity, $\psi_p^+ = (c_{1p}^+, c_{2p}^+)$ is the Nambu spinor ($c_{1(2)p}^+$ being the fermion operators for the wave-vectors $Q/2 + p$ (1) and, respectively, $-Q/2 + p$ (2), $|p| < k_c$), τ_3 is the third Pauli matrix, $A_{11} = A_{22} = 0, A_{12} = A_{21}^* = \bar{\Delta}$ with $\bar{\Delta} = V + e^{i(\phi + \pi/2)}$ electron-phonon coupling constant is purely imaginary) and

$$\bar{\lambda} = (\lambda^{-1} + \lambda_i^{-1})^{-1} \quad (2)$$

is the effective coupling strength, λ being the adimensional electron-phonon coupling strength. The spin indices are omitted but the spin contribution are throughout taken into account. The Hamiltonian [equation (1)] is straightforwardly diagonalized by a Bogoliubov-type canonical transformation, its eigen-states being described in terms of two types of fermions with the energy levels $\pm \epsilon_p$,

$$\epsilon_p = \mathrm{sgn}\,(p)(v_F^2 p^2 + |\bar{\Delta}|^2)^{1/2}, \quad (3)$$

the ground state being filled with particles of the first type from $-k_c$ to 0 and with particles of the second type from 0 to k_c. A gap of magnitude $2|\bar{\Delta}|$ is opened up at the Fermi points $\pm Q/2$ ($p = 0$). The mean-field equilibrium condition [11] for the Hamiltonian [equation (1)] leads to

$$\phi + \pi/2 = 0, \quad \frac{1}{\bar{\lambda}} \frac{\Delta}{\Delta_{op}} = v_F \int_0^{k_c} dp \frac{\tanh(\beta \epsilon_{p/2})}{\epsilon_p}, \quad (4)$$

where $\Delta_{op} = V + \Delta$ and $\beta^{-1} = k_B T$ (k_B — Boltzmann constant and T — the temperature). In the limit $\beta \Delta_{op} \gg 1$ the second condition (4) becomes

$$\frac{1}{\bar{\lambda}} \frac{\Delta}{\Delta_{op}} = \ln 2\xi, \quad \xi = v_F k_c / \Delta_{op} \quad (5)$$

for $\xi \gg 1$. The additional Q-periodic potential of strength V enhances the gap in the electronic energy levels (from 2Δ to $2\Delta_{op}$) and smears out the Peierls-Fröhlich transition at the mean-field critical temperature [9]. In addition, one can see from equation (4) that this potential pins the phase mode of the CDW state ($\phi + \pi/2 = 0, A = \Delta_{op}\tau_1$, τ_1 being the first Pauli matrix), thus giving rise to the incommensurate pinning mechanism [12]. The CDW transition is no longer associated with a spontaneous symmetry breaking, but now it is an induced one, driven by the Q-modulated Br^- distribution [13].

Having fulfilled the conditions (4) the collective excitations of the CDW state can be obtained by perturbationally treating the electron-phonon interaction Hamiltonian with respect to $H_{p\mathrm{CDW}}$ and free phonon Hamiltonian. Making use of the phason (ϕ) and amplitudon (R) operators [14] the corresponding degrees of freedom are completely decoupled within the bubble approximation so that one obtains the polarizations

$$\Pi^{\phi}(q, \omega) = -\frac{i}{4}(\pi v_F \lambda \omega_Q) f_{22}(q\omega),$$

$$\Pi^{R}(q, \omega) = -\frac{i}{4}(\pi v_F \lambda \omega_Q) f_{11}(q, \omega), \quad (6)$$

where ω_Q is the bare phonon frequency corresponding to the wavevector Q, $q \sim 0$ ($q \neq 0$) and

$$f_{\alpha\beta}(q, \omega) = 2 \int \frac{dp d\epsilon}{(2\pi)^2} \mathrm{Tr}\,[\tau_2 G(p + q/2, \epsilon + \omega/2)\tau_\beta G(p - q/2, \epsilon - \omega/2)], \quad (7)$$

$\alpha, \beta = 0, 1, 2, 3$, τ_0 being the 2×2 unit matrix and τ_2 the second Pauli matrix, $G(p, \epsilon)$ being the electron Green functions of the Hamiltonian $H_{p\mathrm{CDW}}$ and $|p| < k_c - |q|/2$. In the limit $\beta \Delta_{op} \gg 1$ and ω, $v_F q \ll 2\Delta_{op} \ll 2 v_F k_c$ the integrals in equation (7) can analytically be performed so that the long-wave-length dispersion relations of the phasons and amplitudons can be obtained from the poles of the phonon Green functions:

$$\Omega_\phi^2(q) = \omega_T^2 + \frac{m}{m^*}(v_F q)^2,$$

$$\Omega_R^2(q) = \omega_R^2 + \frac{m}{3m^*}(v_F q)^2, \qquad (8)$$

$$\omega_R^2 = \omega_T^2 + \lambda\omega_Q^2, \quad \frac{m^*}{m} = \frac{1}{\lambda}(2\Delta_{op}/\omega_Q)^2,$$

where the pinning frequency

$$\omega_T^2 = \omega_Q^2\left(1 - \frac{\lambda\Delta}{\bar{\lambda}\Delta_{op}}\right) \qquad (9)$$

comes from the second condition [equation (4)] given by the incommensurate pinning mechanism.

With $\omega_T = 2.5$ meV, $\omega_R = 6$ meV and $\omega_Q = 8.1$ meV [3, 15] the value $\lambda = 0.45$ is obtained from equation (8) in fair agreement with other estimations [10, 16]. The distortion amplitude of the Pt chains

$$u_Q = \frac{2\Delta}{\omega_Q}(c/\pi v_F \lambda M)^{1/2} \qquad (10)$$

(M being the $Pt(CN)_4$ mass) estimated from neutron scattering experiments is about 0.025 Å [4, 17]. Taking for the Pt–Pt distance c the value 2.85 Å [3, 5] and the aforementioned value for λ ($v_F = 11 \times 10^5$ m/s) one obtains from equation (10) $2\Delta = 110$ meV in excellent agreement with the value of the direct current (d.c.) gap [5, 18]. It follows that the d.c. gap is associated with the distortion of the Pt chains while the optical gap $2\Delta_{op} = 200$ meV [2] includes in addition the Br^- chain contribution $V = \Delta_{op} - \Delta = 45$ meV. With these estimations one obtains from equation (9) $\lambda_i = 0.7$ and from equation (5) $\xi = 3.55$ which are consistent with the approximations made in deriving the spectrum given by equation (8). The resulting bandwidth cut-off parameter k_c is of the same order of magnitude as that obtained from the width of the giant Kohn anomaly [10]. The enhanced CDW mass per electron obtained from equation (8) is $m^*/m \cong 1400$ in good agreement with the optical data [2]. The parameters λ, ξ, Δ, V, λ_i and k_c are plotted in Fig. 1 versus temperature. The temperature dependence of all these parameters suddenly changes at about 80 K pointing out a structural transition in KCP around this temperature. It is noteworthy here that 80 K is the temperature reported for the (incomplete) three-dimensional ordering of the CDW state in this material [5]. The uncorrelated, fluctuating CDW state at higher temperatures develops into a stable, more correlated one as the temperature is lowered under 80 K.

Making use of the gauge invariant response theory of the electro-magnetic excitations [14, 19] one obtains,

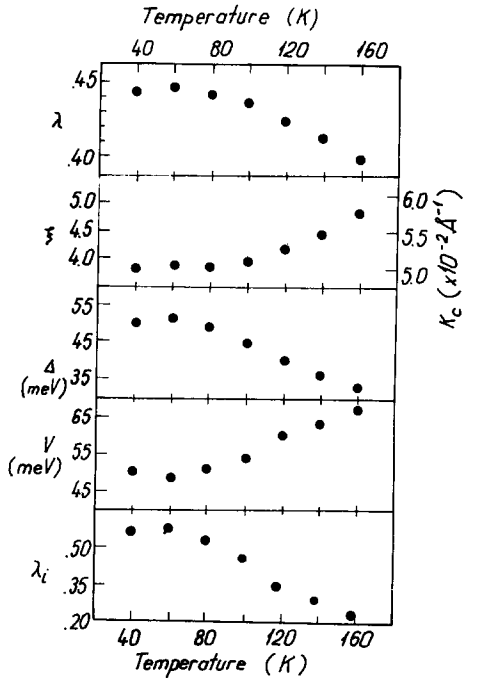

Fig. 1. Parameters of the Br^- induced Peierls-Fröhlich transition in KCP versus temperature: electron-phonon coupling strength λ, bandwidth cut-off parameter $\xi = v_F k_c/\Delta_{op}(\Delta_{op} = V + \Delta)$, distortion parameter Δ of the Pt chains, potential strength V and elastic strength λ_i associated with the Q-modulated Br^- distribution. The input data [2–5, 15, 17] (according to equations (5), (11–13)] are $\omega_Q = 8.1$ meV, $\omega_R = 6$ meV, $2\Delta_{op} = 200$ meV, $v_F = 11 \times 10^5$ m/s as well as the temperature dependent pinning frequency ω_T [3] distortion amplitude of the Pt chains [4, 17] and the Pt–Pt distance c[3].

after a detailed diagrammatical analysis within the bubble approximation, the transverse dielectric function

$$\epsilon(\omega) = \lim_{q \to 0}[1 + iU(q)f_{00}(q, \omega) + \tfrac{1}{4}(\pi v_F \lambda \omega_Q) \times$$

$$U(q)D^\phi(q, \omega)f_{20}(q, \omega)], \qquad (11)$$

where $U(q) = 4\pi e^2/q^2 S$ is the long-range Coulomb interaction (S – the transverse area per chain), f – functions are given by equation (7) and

$$D^\phi(q, \omega) = 2\omega_Q[\omega^2 - \Omega_\phi^2(q) + 2i\omega\Gamma]^{-1} \qquad (12)$$

is the dressed phason Green function with finite phason life-time Γ^{-1}. In the limit $\beta\Delta_{op} \gg 1$, ω, $v_F q \ll 2\Delta_{op} \ll 2v_F k_c$ one obtains the standard form

$$\mathrm{Re}\,\epsilon(\omega) = \epsilon_\infty \frac{\omega_L^2 - \omega^2}{\omega_T^2 - \omega^2},$$

$$\epsilon_\infty = 1 + \tfrac{1}{6}(\omega_p/\Delta_{op})^2, \omega_L^2 = \omega_T^2 + \tfrac{3}{2}\lambda\omega_Q^2 \qquad (13)$$

for the real part of the dielectric function equation (11) with $\Gamma = 0$ (ω_p being the plasma frequency) and the real part of the far infrared conductivity

$$\text{Re}\,\sigma(\omega) = \sigma_{\max} \cdot (2\omega\Gamma)^2\,[(\omega^2 - \omega_T^2)^2 + (2\omega\Gamma)^2]^{-1},$$

$$\sigma_{\max} = \frac{m}{m^*}\frac{\omega_p^2}{8\pi\Gamma}. \qquad (14)$$

With $\omega_p = 2.88$ eV, $\Delta_{op} = 100$ meV, $\omega_T = 1.9$ meV [2, 18], $\omega_Q = 8.1$ meV [3] and $\lambda = 0.45$ obtained before the static dielectric constant from equation (13) is about 1800 in fair agreement with the experimental data [2]. The longitudinal mode ω_L from equation (13), brought about by the Coulomb interaction, acquires in this case the value $\cong 7$ meV in excellent agreement with the plasma edge [2, 5]. For $\Gamma = 0.3$ meV the maximum value $\sigma_{\max} = 950(\Omega\text{cm})^{-1}$ (at $T = 88$K) [2] is obtained from equation (14) whereas for $\Gamma = 1$ meV the shape of the normalized conductivity $\text{Re}\,\sigma(\omega)/\sigma_{\max}$ is identical with that of the experimental curve. An ω -dependent phason life-time Γ^{-1} is expected to give a more satisfactory fit to the far infrared conductivity. The values $\Gamma = 0.3 - 1$ meV are consistent with those derived from the neutron scattering experiments [3].

3. CONCLUSION

The incommensurate pinning mechanism in KCP, based on the Q-modulated Br^- distribution along the chain axis, provides a unified picture of the neutron scattering and far infrared optical data in this material. The present approach explains the different origins of the two gaps, the d.c. gap 2Δ and the optical one $2\Delta_{op}$: the former is related to the distorsion amplitude of the Pt chains while the latter includes in addition the Br^- chain contribution. The Q-modulated Br^- distribution might be observed experimentally at very low temperatures (by neutron scattering experiments, for example) providing thus a direct confirmation of the pinning mechanism proposed here. The present approach can be extended into at least two directions by including (i) the effect of the small amount of disorder in the Br^- chains and (ii) the interchain coupling. The former can be taken into account by allowing a weighted distribution for the parameter $V > 0$ leading thus to a pseudogap centered on $2\Delta_{op}$ and lower-bounded by 2Δ. This extension, together with the interchain coupling, would ensure the precise understanding of the fluctuating CDW state in KCP and the transition this material undergoes around 80 K.

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