Vibrational Excitations of Solitons in Polyacetylene

Mele and Rice[1] have recently shown that charged solitons in the Peierls model of polyacetylene lead to infrared-active modes within the semiconductor gap. They suggest that the experimentally observed[2] modes at 900 and 1370 cm^{-1} result from two vibrational normal modes while the oscillation of the soliton pinned to an ionized impurity yields a mode at a much lower frequency. Fincher *et al.*,[2] however, claimed that the 900-cm^{-1} mode is the pinned mode since its width is unusually large (~400 cm^{-1}).

I have carried out the same calculation within the continuum model.[3] Consider the charge with a dimerization amplitude $\Delta(x-\varphi(t))$, i.e., its position is a time-dependent field. At frequencies low compared with the gap $2\Delta_0$ this leads to a current $j(t)=e\rho\partial\varphi/\partial t$ where ρ is the charge density.

Each phonon has an order parameter $\Delta_n(x-\varphi_n(t))$ $(n=1, 2, \ldots, N)$ with $\varphi_n(t)$ its oscillation degree of freedom. In the ground state[3] $\Delta_n(x)=\Delta(x)\lambda_n/\lambda$ where λ_n is the dimensionless electron-phonon coupling and $\lambda=\sum_n\lambda_n$. After expansion $\Delta(x-\varphi)=\sum_n\Delta_n(x-\varphi_n)$ the translation mode φ is identified as $\varphi=\sum_n\varphi_n\lambda_n/\lambda$. The effective Lagrangian to second order in φ_n is

$$L_{\text{eff}}=\tfrac{1}{2}M_s\Omega_0^2\Big\{\sum_n\Big[-\varphi_n^2+\Big(\frac{\dot{\varphi}_n}{\omega_n^0}\Big)^2\Big]\frac{\lambda_n}{\lambda}+(1-\alpha)\varphi^2\Big\}, \qquad (1)$$

where $M_s=4\Delta_0^3/(3\pi\lambda\Omega_0^2v_F^2)$ is the soliton kinetic mass, $\Omega_0^{-2}=\sum_n\lambda_n/\lambda(\omega_n^0)^2$, ω_n^0 are the bare phonon frequencies, and α represents pinning to an ionized impurity. The φ^2 term in (1) comes from the electron-phonon interaction and if $\alpha=0$ it reduces the translation mode frequency to zero.

Adding to (1) the coupling of $j(t)$ to an electric field leads to a set of equations of motion for $\varphi_n(t)$ which determine $\varphi(t)$ and the conductivity

$$\sigma(\omega)=e^2i\omega\rho M_s^{-1}\Omega_0^{-2}D_0(\omega)/[1+(1-\alpha)D_0(\omega)], \qquad (2)$$

where $D_0(\omega)=\sum_n[(\omega/\omega_n^0)^2-1]^{-1}\lambda_n/\lambda$.

For $\alpha=0$ Eq. (2) yields the Fröhlich type superconductivity with an oscillator strength $\pi\rho/M_s$. For $\alpha\neq0$ this sliding mode appears at a finite frequency. For two or more phonons additional peaks in $\mathrm{Re}\,\sigma(\omega)$ appear at ω_n^φ, one in each interval $(\omega_n^0, \omega_{n+1}^0)$, just as in the incommensurate limit of the Peierls model.[4,5]

Note that the number of ω_n^φ modes, *including* the sliding mode, equals the number N of bare modes. Reference 1 suggests that there are three ω_n^φ modes which means that there must be another coupled vibration in addition to the two modes in their Fig. 3.

However, if the mode at 900 cm^{-1} is not the pinned mode, then 900 $cm^{-1}>\omega_1^0$ which is inconsistent with both Fig. 1(a) of Ref. 1 and with experimental data, as I show next.

Since ω_n^0 is not available experimentally I use the Raman frequencies ω_n^R which correspond to amplitude oscillations. The calculation is the same as in the incommensurate case[5] except $\lambda\to2\lambda$.[3] For $\omega\ll2\Delta_0$ ω_n^R satisfy $1=(2\lambda-1)D_0(\omega)$; thus $\omega_1^R<\omega_1^0$ and the other modes are in the intervals $(\omega_n^0,\omega_{n+1}^0)$. Experimentally[6] the lowest frequency Raman mode is at ~1075 cm^{-1} (or the very weak mode at 1015 cm^{-1}); thus ω_1^0 is at a higher frequency and the 900-cm^{-1} mode cannot be but the pinned mode.

The data thus support a two-phonon system: $\omega_1^\varphi=900$ cm^{-1} as the pinned mode and $\omega_2^\varphi=1370$ cm^{-1}. With use of $2\lambda=0.38$,[3] $\omega_1^R=1075$ cm^{-1} and $\omega_2^R=1470$ cm^{-1},[6] the equations for ω_n^φ and ω_n^R yield $\omega_1^0=1210$ cm^{-1}, $\omega_2^0=2110$ cm^{-1}, $\lambda_1/\lambda=0.08$, $\lambda_2/\lambda=0.92$, and $\alpha=0.23$. The intensity ratio of ω_1^φ to ω_2^φ modes is 2.3 in good agreement with experimental data. The dielectric constant $\epsilon(0)=1+4\pi\rho e^2/\alpha M_s\Omega_0^2$ can now be used to determine M_s, the *single* parameter in the theory which contains the identity of the charge carrier.

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