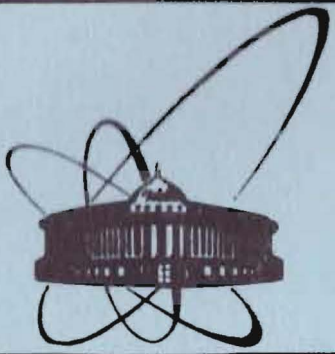

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ON π-PLASMONS IN POLYACETYLENE

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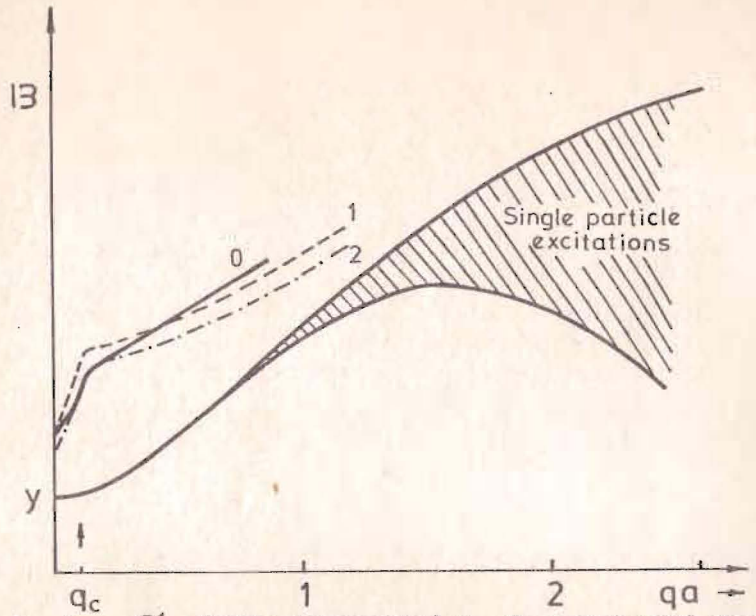
Polyacetylene (PA) is one of the most studied quasi-1D-systems. Nevertheless, there are many unsolved problems even for undoped PA. Such an outstanding problem is the theoretical description of the electron loss spectroscopy (ELS) data. In ELS experiments the intensity of inelastically scattered high energy (~ 50 keV) beam electrons is measured, which loose the energy $\hbar\omega$ and the momentum $\hbar\vec{q}$. Quite general, the loss probability γ is proportional to the imaginary part of the inverse of an effective dielectric function (DF). $\gamma \propto P(q,\omega) = -\mathrm{Im}\, 1/\varepsilon_{eff}(q,\omega)$, where P is the so-called loss function.

In recent experiments on thin trans-PA-films by Ritsko[1] and Zscheile[2] a very unusual behaviour of the π -plasmon peak position of $P(q,\omega)$ was found: (i) a nearly linear dispersion law down to low momenta $q = q_c \approx 1\,nm^{-1}$ instead of the usual nearly quadratic one was detected; (ii) an additional striking feature is the kink at q_c and a stronger decrease of the plasmon energy below this momentum[2] (compare fig.1). The σ -plasmons exhibit similar peculiar behaviour[3].

The corresponding theoretical work was mainly focused on the linear dispersion law. Ritsko[1] has found nearly the same slope of the measured dispersion law and of the lower interband transition edge of a simple tight-binding two-band semiconductor. From an analysis of the Ehrenreich-Cohen formula Mintmire and White[6] have obtained a nearly linear dispersion law very close to the result of[1]. However both approaches should unambiguously give a quadratic behaviour at very low momenta. Besides in[6] the chain density was used as a fitting parameter that seems unphysical.

A universal linear dependence due to the consideration of exchange effects was obtained by March[7], but the slope differs considerably from the experimental one.

In general, a spatial dispersion of $\varepsilon_{eff}(q,\omega)$ is caused by the inhomogeneities of the system under consideration. In the present case the PA-films consist of randomly oriented PA-fibres, and consequently, there are two scales of inhomogeneity: the usual atomic one which is roughly characterized by the chain lattice constant a , and a mesoscopic length like the fibre radius R_f ($\sim 50 \div 250$ Å). The above-mentioned attempts to describe the ELS data are based only on a microscopic level. However, in our



F i g. 1. π -plasmon dispersion law, 0 -experimental curve ($q \gtrsim q_c \approx 1\,nm^{-1}$ /1,2/, $q \leq q_c$ /2/); 1,2 -interpolated theoretical curves assuming cylindrical (1) or spherical (2) fibre orientation distribution.

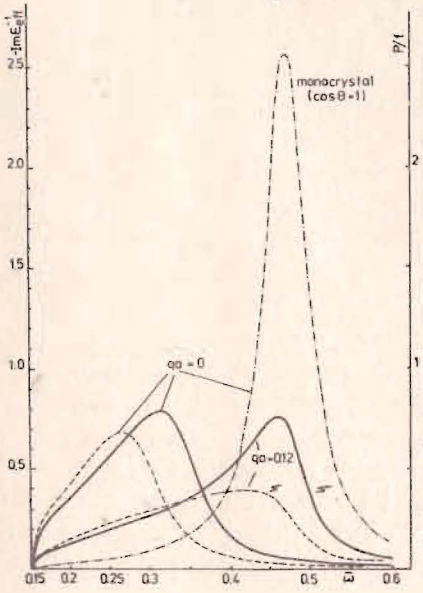


Fig.2. Calculated loss function $P(0,\omega)$ below (to the left) and above (to the right) the kink in the dispersion law versus frequency, full curves-assuming cylindrical fibre orientation distribution, dashed one-for spherical distribution.

opinion, the additional consideration of the mesoscopic structure is very important for the explanation of these data, especially at low momenta. Thereby the crucial point is the calculation of the q -dependent effective DF for the present real fibre structure. A view of the microphotographs of typical PA-films (see, e.g., /4/) suggests a topology of spherical air inclusions (voids) embedded into a nearly dense network of PA-fibres.

Let us now consider two limiting momentum regions. For $qR_f \ll 2\pi$ the beam electron polarizes the fibres not independent of each other owing to the strong polarization stray fields of the dielectric inhomogeneities. Since for our special topology there is no suitable theory available at present, we calculate the effective DF in a crude manner in two steps. At first the effective permittivity $\varepsilon_n(\omega)$ of the random fibre network is estimated as an angle average over the anisotropic DF of the PA-monocrystal which has been obtained within the RPA in a previous paper /5/. This averaging is performed assuming two limiting cases of the fibre orientation distribution: (i) a spherical one, i.e., equal probability of all directions and (ii) a cylindrical one, i.e., equal probability of all directions within the film plane. Because in the ELS experiments thin films are used (the film-thickness $d \lesssim 400$ nm) the real distribution is expected to be ellipsoidal close to the cylindric case. In the second step the effective DF ε_{eff} of the remaining binary mixture of the components $\varepsilon_1 = \varepsilon_n(\omega)$ and $\varepsilon_2 = 1$ is calculated within the well-known effective medium approximation (CPA) /8/:

$$f(\varepsilon_1 - \varepsilon_{eff})/(\varepsilon_1 + 2\varepsilon_{eff}) + (1-f)(1-\varepsilon_{eff})/(1+2\varepsilon_{eff}) = 0\,, \qquad (1)$$

where $f \approx 1/3$ /2,6/ denotes the volume fraction of the PA-fibres. The component ε_1 is given by $\varepsilon_1 = \langle \varepsilon(0,\omega) \rangle_\theta$ with (see /5/)

$$\mathrm{Re}\,\varepsilon(0,\omega) = \varepsilon_\infty + \frac{C\cos^2\theta}{\bar\omega^2}\left[\frac{\gamma^2\,\Pi(k/(1-\bar\omega^2),k)}{1-\bar\omega^2} - E(k)\right],$$

$$\mathrm{Im}\,\varepsilon(0,\omega) = \begin{cases} \frac{\pi}{2} C\gamma^2\cos^2\theta\,\bar\omega^{-3}\left[(\bar\omega^2-\gamma^2)(1-\bar\omega^2)\right]^{-1/2} & \text{for } \gamma \leq \bar\omega \leq 1, \\ 0 & \text{otherwise} \end{cases} \qquad (2)$$

where $k = (1-\gamma^2)^{1/2}$, and θ is the angle between $\vec{q}$ and the chain direction. Π and E denote the complete elliptic integrals of the third and second kind, respectively, and $C = (2e^2/t_0 a)(a^3/\Omega_0) = (\hbar\omega_{pl})^2\varepsilon_\infty/(4t_0)^2$, where ω_{pl} means the plasma frequency of the corresponding quasi-1D-metal. $\Omega_0 = 38.27\,\text{Å}^3$ is the volume of the PA unit cell and $4t_0 \approx 10$ eV

denotes the width of the whole π-band which is used as the scaling energy of our problem $\bar{\omega} = \hbar\omega/4t_c$, and $\gamma = E_g/4t_o \approx 0.15$ where $E_g \approx 1.4$ eV denotes the Peierls gap. From these parameters we obtain $C \approx 0.45$ for trans-PA. The background isotropic permittivity $\varepsilon_\perp$ is taken to be approximately equal to the high frequency dielectric constant $\varepsilon_\infty = 2 \div 3$. (The calculations have been performed with $\varepsilon_\infty = 2.5$). The corresponding loss functions are shown in fig.2 to the left. A comparison with the loss function of a PA-monocrystal for $\vec{q}$ parallel to the chain direction (to the right) shows a remarkable broadening and a down shift of the peak position. The calculated half-width ($\approx$ 1.6 eV) and the peak position ($\approx$ 3.1 eV) are in fairly good agreement with the data of [2] ($\approx$ 1.9 eV and 2.9 - 3 eV).

In the short-wavelength limit $qR_f \gg 2\pi$ the film behaves as a mixture of independent fibres because the polarization stray fields are weak, and the inverse effective DF is given by a volume and angle average of the inverse random DF (compare, e.g., [9])

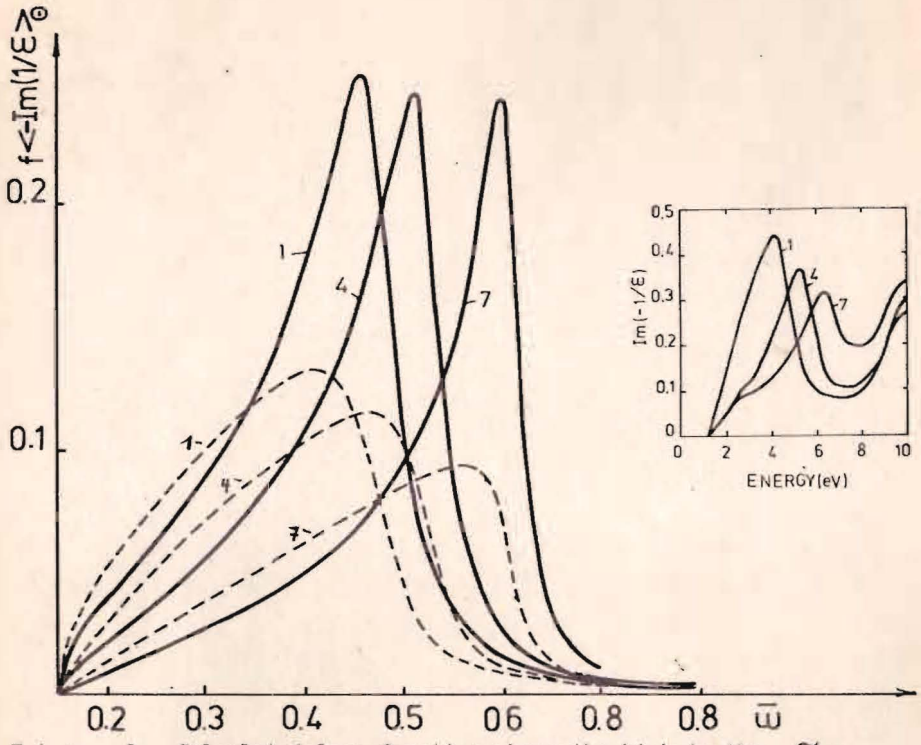
$$\varepsilon_{eff}^{-1}(q,\omega) = f \langle \varepsilon^{-1}(\vec{q},\omega) \rangle_\theta + (1-f)\varepsilon_\perp^{-1} \quad . \qquad (3)$$

Thus we obtain

$$P(q,\omega) \equiv -\mathrm{Im}\, \varepsilon_{eff}^{-1}(q,\omega) \approx f \langle -\mathrm{Im}\, \varepsilon^{-1}(\vec{q},\omega) \rangle_\theta \quad . \qquad (4)$$

This approximation plotted in fig.3 is in good agreement with the measured loss function (insert of fig.3) with respect to the peak position, the magnitude of the maximum as well as to the shape of the spectra. The deviations at high frequencies $\hbar\omega \gtrsim 7$eV are due to transitions neglected in our two-band model. The π-plasmon dispersion law obtained from eq. (4) is plotted in fig.1 for $q \gtrsim q_c = 2\pi/R_f$. In agreement with Ritsko [1] we have found nearly the same slope as the lower interband transition edge.

To get an estimate of the dispersion law for the intermediate momentum region $q \sim q_c$, we extrapolate the short-wavelength result up to $q = q_c$ and interpolate linearly between $q = 0$ and $q = q_c$. In this manner we obtained a kink in the dispersion law like the experimental one (see fig.1). This result suggests that the ELS data are considerably influenced by the mesoscopic structure of the PA-films. The strong quasilinear behaviour approaching q_c from above may be explained presumably due the increasing failure of eq.(4) and a crossover to an approximation like eq.(2) for $q = 0$. The deriva-



F i g. 3. Calculated loss function above the kink in the π-plasmon dispersion law for different wave vectors q (in units of $\hbar m^{-1}$): full curves-assuming cylindrical fibre orientation distribution, dashed one-for spherical distribution. In the insert the data of Ritsko [1] are shown.

tion of an improved expression of the effective DF for the intermediate momentum region $q \lesssim q_c$ requires a more detailed information about the morphology of the PA films. To check our approximations, it would be of great interest to vary the input parameters, the fibre radius and the volume fraction of PA, e.g., by changing the techniques of preparation. Another consequence of our averaging procedure is that in agreement with the ELS data the threshold of the loss function $P(q,\omega)$ (i.e., its low-energy onset at $\bar{\omega} = \gamma$) does not depend on q . Furthermore, the slope $dP/d\omega$ near this point decreases

with increasing q . Thus, in contrast to the statements of[1,2] the mentioned peculiarities of the ELS data can be explained, at least, in a qualitative manner without excitonic effects. However, we cannot exclude that excitons have to be taken into account in describing some details of the loss function.

A c k n o w l e d g e m e n t s:

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Дрекслер Ш.-Л., Бобет М.
E17-85-475

О π-плазмонах в полиацетилене

При учете мезоскопически неоднородной структуры транс-полиацетиленных пленок дано качественное описание спектров потерь быстрых электронов при низких энергиях $\lesssim 7$ эВ.При этом используются результаты вычисления для продольной диэлектрической функции в рамках Су-Шриффера-Хигера. В частности, удалось объяснить измеренную квазилинейность дисперсионного соотношения и излом при малых импульсах.

Работа выполнена в Лаборатории теоретической физики ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна 1985

Drechsler S.-L., Bobeth M.
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On π-Plasmons in Polyacetylene

Taking into account the mesoscopic heterogeneous structure of transpolyacetylene films the electron-loss spectroscopy data at low energies $\lesssim 7$ eV are qualitatively described by using the RPA-result for the longitudinal dielectric function calculated within the Su-Schrieffer-Heeger model. In particular, the observed unusual quasilinearity of the dispersion law and the kink at low momenta may be explained.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

Preprint of the Joint Institute for Nuclear Research. Dubna 1985