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ACOUSTIC SOLITARY WAVE POLARON MOTION IN POLYDIACETYLENE CRYSTALS

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Abstract This paper describes experiments on the motion of an extra electron (or hole) on perfect straight polymer chains. The mobility is found to be ultra high, greater than for any conventional semi-conductor, and yet the drift velocity is found to saturate at a low value, close to the velocity of sound. This new form of motion is that expected theoretically for an acoustic polaron in one dimension.

INTRODUCTION

Pulse photoconduction experiments on the motion of an extra electron (or hole) on perfect straight polymer chains are described. The low field mobility is found to be ultra high, $\mu > 20\ m^2 s^{-1} V^{-1}$, greater than for any conventional semi-conductor. The drift velocity is found to saturate at a low value of $2.2 \times 10^3\ m\ s^{-1}$, close to the velocity of sound of $3.6 \times 10^3\ m\ s^{-1}$. Thus over many decades of field the drift velocity is essentially independent of the field.

This new form of motion is that expected theoretically for an acoustic polaron in one dimension. Such a polaron creates a local density variation which cannot travel faster than the sound velocity. The only energy dissipation is weak and due to ambient acoustic phonons bouncing off the polaron with a Doppler shift. The polymer chains are the backbone of the polydiacetylenes (PDA) of repeat unit (=CR-C≡C-CR=) obtained by solid state polymerisation as single crystals in which the chains are straight and parallel for macroscopic distances.

EXPERIMENTS

Experiments have been performed on TS and DCH in which

$$R = -(CH_2)-O-(SO_2)-(C_6H_5)-CH_3 \quad \text{(TS)}$$

$$R = -(CH_2)-N-(C_{12}H_8) \quad \text{(DCH)}$$

which both yield good crystals.

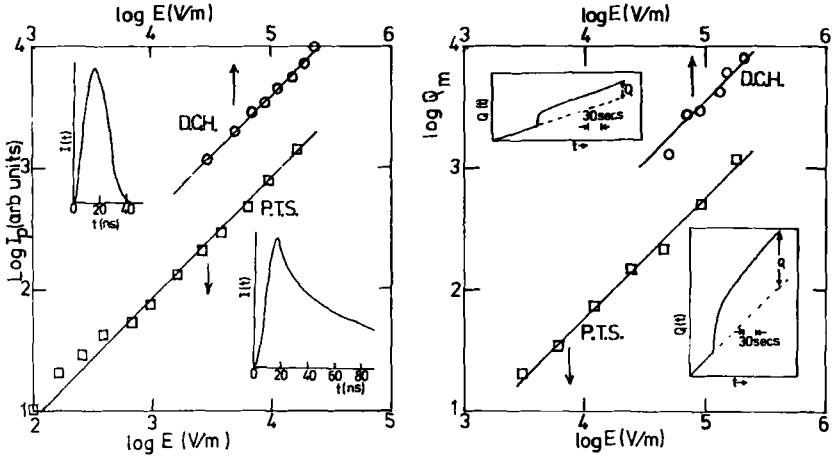

FIGURE 1 Photocurrent I_p in arbitrary units as a function of applied electric field E in PDATS and PDADCH. The inserts show the time dependence of the photocurrent in response to a 10 n s duration N_2 laser pulse.

FIGURE 2 Q_m in arbitrary units as a function of applied field E in PDATS and PDADCH. The inserts show the time evolution of Q_m in response to one laser pulse; the steady growth of Q_m is due to the sample dark current.

The carriers are created with quantum efficiency η, by absorption of N photons from a laser pulse of duration T . The probability $\phi(E)$ of the electron hole pair avoiding geminate recombination in an applied field E, and thus contributing to transport, is dependent on the dimensionality. At low E in one dimension, there is an abundance of theories[1,2,3] and experiments[4,5], supported by elegant computer simulations[6], that $\phi(E)$ is linear in E. Thus the mobile charge Q created is

$$Q = e(\eta\phi)\, N \qquad (1)$$

and Q is linear in E. The peak photocurrent I_p recorded at electrodes at the end of the laser pulse is then

$$I_p = Q\, v\, /d \qquad (2)$$

where v is the carrier velocity and d is the electrode seperation, always provided that most of the carriers have not trapped in the duration T .

Fig. 1 shows that I_p is linear in E in both DCH and TS. Moreover Fig. 1 also shows that after the duration T most of the carriers are still not trapped. Thus the carrier velocity v is independent of field, ie. saturated. For the field dependence of I_p is entirely accounted for by the expected field dependence of Q.

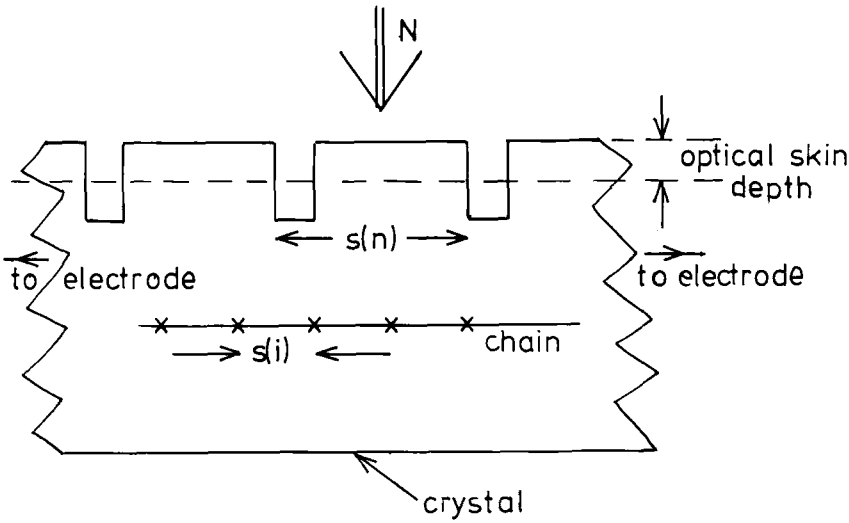

FIGURE 3 Cuts, of depth greater than the optical skin depth, which stop the flow of carriers along the polymer chains. The experiments show that carriers of opposite sign accumulating at opposite sides of a cut eventually recombine.

Fig 1 displays the trapping of the carriers. This typically occurs in times of 10 to 100 ns, is sample dependent, and is typically faster in DCH than TS.

Following a succesion of trapping and release events the carriers are expected to reach recombination centres, having travelled a distance $\langle s \rangle$. Thus the charge eventually recorded at the electrodes, after the carriers have recombined, is Q_m, and

$$Q_m = Q \langle s \rangle / d \tag{3}$$

Fig. 2 shows that $\langle s \rangle$ is independent of field E; for the linear field variation of Q_m is entirely due to the field dependence of Q.

We have found it is possible to effectively introduce recombination centres into the sample and so reduce $\langle s \rangle$. This can be done by cutting the sample into n parts as in Fig. 3. In this way (n-1) cuts create new recombination centres of a controlled and known seperation s(n)=d/n. The mean distance between recombination centres, both intrinsic and introduced is then

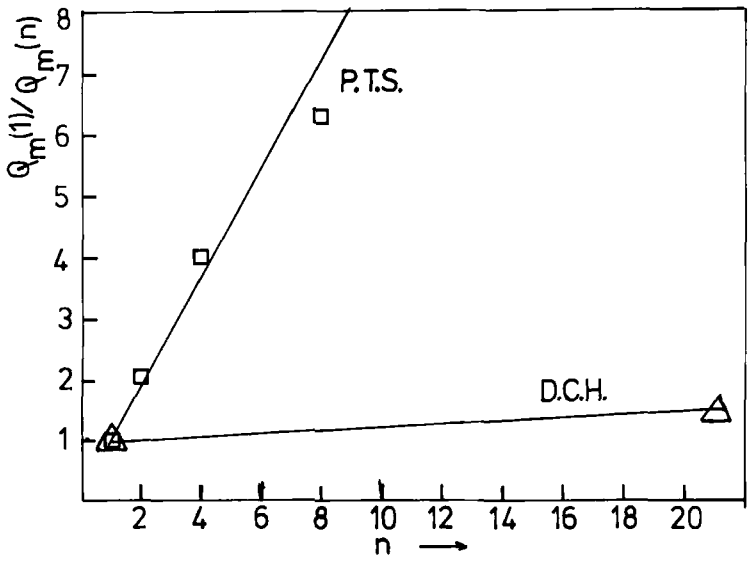

FIGURE 4 Dependence of Q (1)/Q (n) on n in PDATS and PDADCH.

$$1/\langle s \rangle = 1/s(i) + 1/s(n) = 1/s(i) + n/d \tag{4}$$

where s(i) is the distance apart of the intrinsic centres. Thus observation of the dependence of Q_m on n

as cuts are made allows determination of s(i).

The data of Fig. 4 shows:-

a) that in PDATS, s(i) >> d,

b) and in PDADCH, s(i) << d,

for then Equs. 3 and 4 account for the observed dependence of Q_m on the number of cuts. Moreover, I_p does not depend on the number of cuts in either case. This is expected, following Equ. 2, provided the carriers do not travel a distance s(n) in the duration T, and provided the cuts do not damage the sample. Thus recombination centres exist in PDADCH but not in PDATS.

Given <s>, the absolute magnitude of the saturated drift velocity then follows from the ratio of two observables in an uncut virgin sample:-

$$v = I_p / Q_m \langle s \rangle \qquad (5)$$

$$= I_p / Q_m d \qquad \text{in PDATS}$$

$$= I_p / Q_m s(i) \qquad \text{in PDADCH}$$

In PDATS $v = 2.2 \times 10^3$ m s^{-1}. Preliminary results on PDADCH indicate that s(i) $\approx$ 0.1 mm and $v = (3 \pm 2) \times 10^3$ m s^{-1}.

No regime has been seen in which the drift velocity is linear in the field. Presuming such a regime exists at low field then a lower limit to the mobility is the saturated drift velocity divided by the smallest field of observation. This gives $\mu > 20$ $m^2 s^{-1} V^{-1}$ in PDATS, and $\mu > 0.07$ $m^2 s^{-1} V^{-1}$ in PDADCH.

A comprehensive account of the cuts experiment in PDATS has been given already[7]. The cuts experiment is a new experiment which can only be contemplated in a highly anisotropic material. Our original account was recieved with legitimate scepticism. The data here on PDADCH are new; a full account will be given elsewhere. However the new data support the original interpretation. Cuts, for the first time, are seen to be a minor contributor to recombination; previously they had been the only contributor.

THEORY

The existence of such a high mobility, and yet the saturation of the drift velocity at such a low value, is not explainable by any conventional semiconductor theories.

We suggest the motion is that of the acoustic solitary wave polaron formed in a one dimensional

system.[8] The dispersion curve of this polaron, and of a band electron, are shown in Fig. 5. It is characteristic of this polaron that with increasing K value the velocity saturates at the velocity of sound S. As the energy increases the polaron shrinks in size but undergoes a greater lattice distortion.

Fig. 5 displays the characteristic Cerenkov emission and absorption of acoustic phonons by a band electron. This process, which gives rise to dissipation by acoustic phonons in conventional semiconductors, is absent in the acoustic polaron. This is because the polaron is always travelling slower than the sound velocity. The dissipation is due to ambient phonons bouncing, with a Doppler shift, off the moving polaron[9]

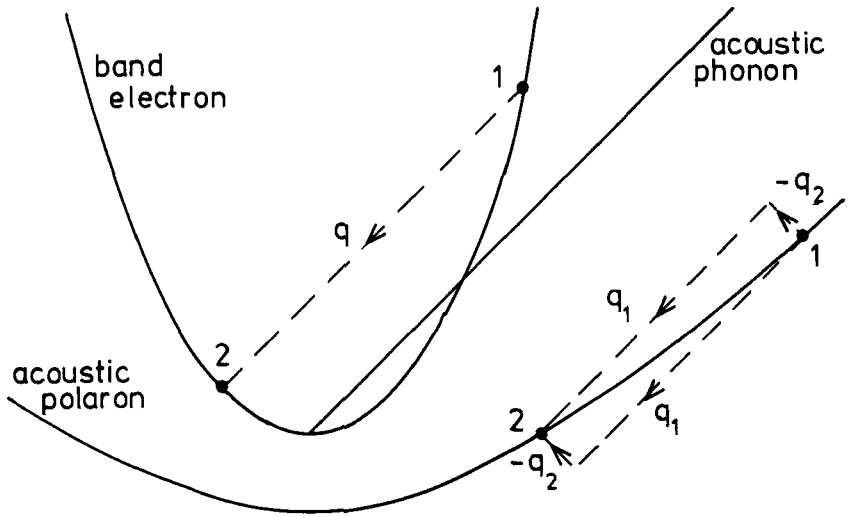

FIGURE 5 Dispersion curves of an acoustic phonon, a band electron and an acoustic polaron. The band electron is undergoing Cerenkov scattering by emission of a phonon q. The acoustic polaron is undergoing Doppler shifted phonon bouncing, the incident phonon $-q_2$ scattering as $+q_1$.

Numerical estimates give the polaron being many lattice spacings large. Thus only small K phonons participate in the scattering. Thus back scattering, which is dominant in the Cerenkov case, is rare in polaron scattering. Thus, when considering such Doppler

scattering alone, the weak dissipation and the absence of back scattering means that in a very small field the polaron will both increase its energy without limit and remain on the (say) positive branch of the dispersion curve. The velocity however saturates at the sound velocity S. A study of the Boltzmann Transport Equation suggests the low field mobility is ultra high, and is not the relevant concept; rather the important idea is the time taken, as limited by scattering, to aquire the saturated drift velocity[9].

It is necessary to investigate how a moving polaron decays into a free electron and free phonons. This is a multi phonon process and thus rare. Nevertheless it may be the dominant polaron energy dissipation mechanism.

CONCLUSION.

Experimental and theoretical reasons are given for the acoustic solitary wave polaron being the dominant excitation of one carrier in one dimension. The polaron essentially moves at just below the sound velocity at all fields.

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