High-field mobility in anthracene crystals

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Measurements of the drift mobility of electrons and holes in anthracene have been carried out in high electric fields. It has been shown that the drift mobilities are independent of the electric field up to fields in which the drift velocity of the carrier is comparable to estimates of their thermal velocity as **calculated from the anthracene band structure.**

Anthracene crystals have been the subject of a wide variety of experimental investigations and quite a lot is known about electron and hole transport in this material. In general it is found that the drift mobility for electrons and holes is on the order of 1 cm^2/V sec and that the mobilities are slightly anisotropic and weakly temperature dependent, increasing with decreasing temperature.[1] It has been shown experimentally that the band of states in which transport occurs is narrow, less than kT wide at room temperature,[2] and that the mean free paths of both electrons and holes are small compared to 100 Å.[3]

All these observations are generally consistent with the theory of transport originally worked out by LeBlanc[4] and subsequently expanded upon by a number of workers.[5] This theory consists of a tight-binding-band calculation and the assumption of isotropic and energy-independent mean free paths or mean free times. The uncertainty principle puts very stringent restrictions on the results of these calculations but it seems reasonable that all the criteria could be met. There have, however, been a number of investigations of the electron-phonon interaction[6] and carrier recombination[3] in anthracene and the indications are that the electron-phonon interaction is stronger than is consistent with the simple tight-binding-band calculation and that some form of hopping motion is called for.

In this paper some experimental results on the drift mobilities of electrons and holes in crystalline anthracene at high electric fields are presented. While there appears to be no unequivocal interpretation of these results, they do seem to be more consistent with a localized, rather than a delocalized, picture of carrier motion. Similar observations to those presented in this paper have been reported previously but only in abstract form.[7]

Experimentally, the drift mobility of both electrons and holes was measured by creating a sheet of carriers in the crystal near one electrode and then observing the time it takes the carriers to traverse the crystal.[8] Electron mobility could be measured by exciting the carriers near the negative electrode and hole mobility was observed by reversing the field. All experiments were carried out at room temperature. The light pulse used for these experiments was 3 nsec long, providing excellent time resolution, and was generated by irradiating a fluorescent material ZnS with the electron beam from a high-current short-pulse electron-beam machine. The fluorescent material was excited sufficiently that it emitted a superradiant pulse of light at 3450 Å of approxi-

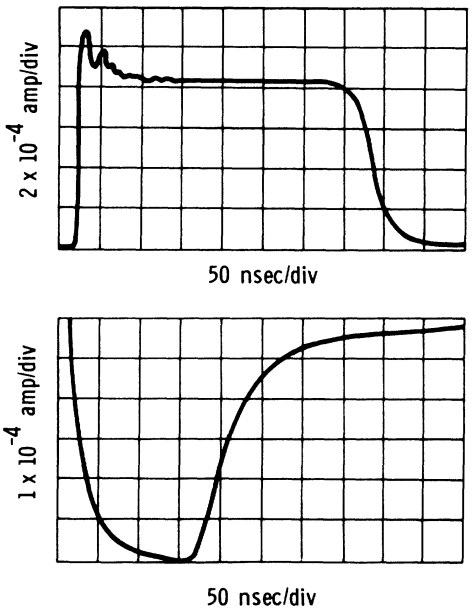

FIG. 1. Current vs time as observed in a 190-μm-thick crystal with 2500 V applied. These figures were traced from oscilloscope pictures. The top picture was obtained by irradiating the negative electrode, so electrons are traversing the crystal and the bottom picture was obtained by irradiating the positive electrode, so holes are traversing the crystal.

mately the same width as the electron-beam pulse.[9] The transit time of the carriers was observed by measuring the current induced in the electrodes. The type of resolution that could be obtained is illustrated in Fig. 1 where current pulses for both electron and hole transport are shown as measured in a crystal 190 μm thick. The difference between the shape of the electron and hole pulses is almost always observed and appears to be associated with some surface phenomenon involved in hole generation. Not all the holes leave the surface immediately upon creation. These measurements were carried out with the electric field in the c' direction, perpendicular to the ab plane, and as has been reported before, the mobility of the electrons and holes was found to be 0.4 and 0.8 cm^2/V sec, respectively. The transit time used to calculate the mobility was the time from the beginning of the current pulse to the beginning of the sharp drop in current.

Figure 2 is a graph of the observed drift velocities as a function of the applied electric field. As can be seen from the figure there is no significant deviation from a linear dependence of the drift velocity on the electric field.

The maximum drift velocities reported here are within a factor of 2 of the thermal velocity deduced from the calculated band structures for anthracene.[4,5] In semiconductors such as germanium,[10] indium antimonide,[11] and argon,[12] field-dependent mobilities appear at drift velocities well below the thermal velocity. The drift velocity at which these nonlinearities appear is not universally related to the ratio of drift to thermal velocity but depends critically upon the dominant scattering processes and the details of the band structure.[10] If carrier transport in anthracene is describable within the band approximation, the departure of the behavior of this material from that of other well-known band systems seems to be significant.

There is experimental and theoretical[6] evidence that carrier transport in crystalline anthracene may be characterizable by a type of hopping motion with a mean free path of the order of a lattice constant. Here, the thermal velocity can be estimated from the Einstein relation $D = kT\mu/e$ and the equation which expresses the diffusion coefficient (isotropic in this example) in terms of the kinetic parameters of the thermally driven carrier motion $D = \frac{1}{6}v\lambda$. In these equations D is the diffusion coefficient, μ is the drift mobility, k is Boltzmann's constant, v is the thermal velocity of a charge carrier, and λ is the mean free path for scattering. Combining these equations and assuming $\mu = 1$ cm^2/V sec and $\lambda = 3$ Å (the smallest reasonable value), we find $v = 5\times10^6$ cm/sec. Within this framework, then, the experimental drift velocities are always small compared to the thermal velocities. The existence of a less-than-unity ratio of the drift to the thermal velocity is certainly no guarantee of a

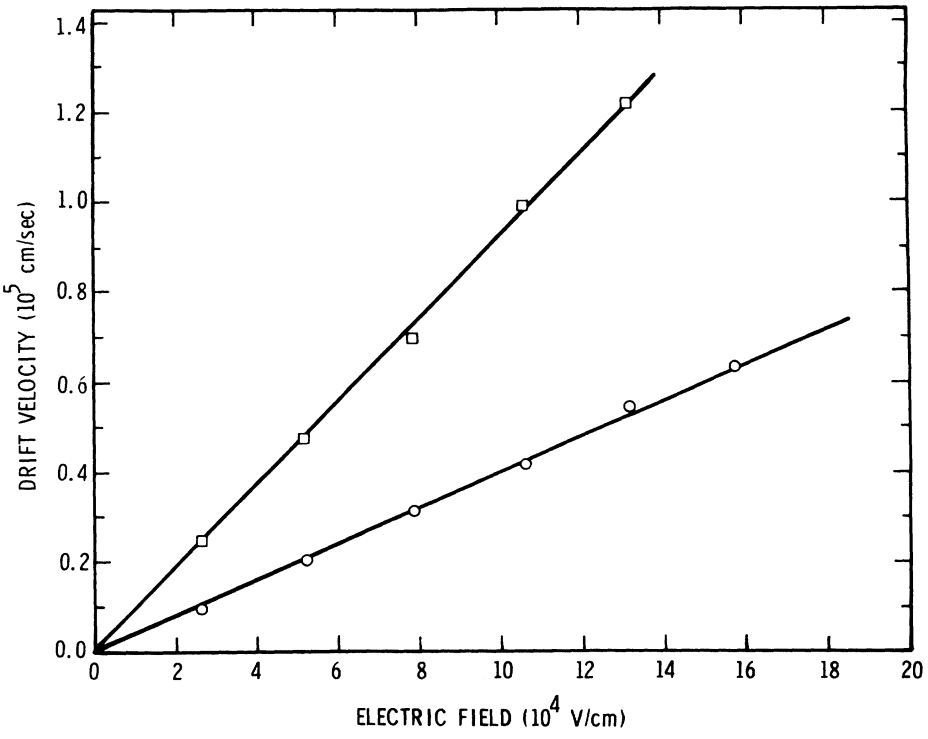

FIG. 2. Reciprocal of the transit time vs applied electric field for a 190-μm-thick crystal. Squares are the data obtained for holes and circles for electrons.

field-independent mobility. General experience seems to indicate, however, that this type of condition favors a drift mobility which is not field dependent.

The experimental results of this paper do not provide a definitive basis for deciding between a localized or delocalized description of carrier transport in crystalline anthracene. However, qualitative arguments and the general behavior of carrier transport at high fields in band-type systems suggest, at this time, that the localized picture for anthracene is more plausible.

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