We wish to thank G. Devlin for his continual advice and assistance on many experimental details. We also thank R. Romestain for supplying us with the sample of CdS and many helpful discussions, along with S. McCall, L. R. Walker, and P. A. Wolff.

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[1] E. L. Hahn, Phys. Rev. 80, 580 (1950). For detailed discussion see, for example, W. B. Mims, in *Electron Paramagnetic Resonance*, edited by S. Geschwind (Plenum, New York, 1972).

[2] N. A. Kurnit, I. D. Abella, and S. R. Hartmann, Phys. Rev. Lett. 13, 567 (1964). See also, for example, J. P. Gordon, C. H. Wang, C. K. N. Patel, R. E. Slusher, and W. J. Tomlinson, Phys. Rev. 179, 294 (1976).

[3] J. A. Giordmaine and W. Kaiser, Phys. Rev. 144, 676 (1966); for later references see A. Laubereau, G. Wochner, and W. Kaiser, Phys. Rev. A 13, 2212 (1976).

[4] S. R. Hartmann, IEEE J. Quantum Electron. 4, 802 (1968); R. Weingarten, Ph.D. thesis, Columbia University, 1972 (unpublished).

[5] See, for examples, Richard G. Brewer and E. L. Hahn, Phys. Rev. A 8, 464 (1973); M. M. T. Loy, Phys. Rev. Lett. 36, 1454 (1976); V. T. Nguyen, E. G. Burkhardt, and P. A. Wolff, Opt. Commun. 16, 145 (1976), and references therein.

[6] R. E. Slusher, C. K. N. Patel, and P. A. Fleury, Phys. Rev. Lett. 18, 77 (1967).

[7] C. K. N. Patel and E. D. Shaw, Phys. Rev. Lett. 24, 451 (1970); C. K. N. Patel, in *Laser Spectroscopy*, edited by R. G. Brewer and A. Mooradian (Plenum, New York, 1974).

[8] D. G. Thomas and J. J. Hopfield, Phys. Rev. 175, 1021 (1968).

[9] J. F. Scott, T. C. Damen, and P. A. Fleury, Phys. Rev. B 6, 3856 (1972).

[10] For a discussion of noncubic symmetry, see R. Romestain, S. Geschwind, and G. E. Devlin, Phys. Rev. Lett. 35, 803 (1975).

[11] Y. Yafet, Phys. Rev. 152, 858 (1966).

[12] R. Romestain, S. Geschwind, G. E. Devlin, and P. A. Wolff, Phys. Rev. Lett. 33, 10 (1974).

[13] Terrence L. Brown and P. A. Wolff, Phys. Rev. Lett. 29, 362 (1972); V. T. Nguyen and T. J. Bridges, Phys. Rev. Lett. 29, 359 (1972).

[14] Romestain, Geschwind, and Devlin, Ref. 10.

Trap-Controlled Dispersive Hopping Transport

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(Received 16 August 1976)

The transition from transient trap-controlled hopping among traps has been observed in a polymer matrix doped with two transport molecules of different ionization potential. The nonequilibrium properties of the transport, characteristic of the disordered molecular state, are manifested by an apparent concentration-dependent trap depth.

The modulation of the microscopic charge transport through extended states by interaction with energetically shallow traps results in a trap-controlled drift mobility measured by the time-of-flight technique. A good example for an inorganic solid is the case of electron transport in CdS crystals.[1] This transport mechanism is characterized by the existence of thermal equilibrium in occupancy between extended states and shallow traps which is established in a time much shorter than the transit time t_T. Under these conditions the injected sheet of excess charge is said to move "coherently," since on the average the carriers experience the same large number of trapping events such that the relative dispersion of the propagating carrier sheet can be described with Gaussian statistics. Trap-controlled drift mobilities have also been measured in doped molecular crystals.[2] In this case, however, questions remain about the precise nature of the microscopic mobility in the ordered molecular state since the validity of a band picture is seriously in question.

Recent time-of-flight studies in molecularly doped polymers have provided firm evidence of an alternative microscopic mobility process. The ability to study charge transport as a function of the dopant molecule concentration allowed a clear identification of the mechanism as one involving the hopping of charge carriers within a random array of molecules.[3,4] This is consistent with the complete breakdown of a band picture in the disordered molecular state leaving hopping as the only possible process for the microscopic mobility in such systems. The dynamics of transient transport in disordered materials such as these are determined by stochastic processes and general agreement exists between experimental observation and recent theoretical work by Scher and Montroll.[5] The central point of this theory is the totally "incoherent" drift of an injected sheet of charge because of a wide distribution of hopping times which leads to a completely nonthermal equilibrium character of the transport process in which carriers may experience quite different histories during their transit.

These features coupled with the relative ease with which the concentration and nature of several dopant molecules may be varied make molecularly doped polymers interesting model systems to search for the analogous trap-controlled mode of transport where the microscopic transport process involves hopping.

Substantial evidence exists that the distribution of nonequilibrium excess charge in the molecular state is determined by the relative values of the ionization potential (for excess holes) and electron affinities (for excess electrons) of the molecules present.[2,6] Such reasoning suggests that by molecularly doping an electrically inert polymer matrix with, as an example, two donor molecules of different ionization potentials, it should be possible to measure a trap-controlled hopping drift mobility. The expectation is that hopping transport of holes through an appropriate concentration of one molecule will be modulated by trapping on a molecule of lower concentration if the latter has a smaller ionization potential. The converse would not be true; i.e., if the molecule of lower concentration has the higher ionization potential it will not act as a hole trap.

In this Letter, we report the first unambiguous experimental observation of a trap-controlled hopping mode of transport by measuring the hole drift mobility as a function of the relative concentration of two different donor molecules molecularly dispersed in an inert polymer. Being inert, in this context, means that the undoped polymer exhibits no photoinduced charge displacement on the time scale typical of the drift experiments (10 μsec–10 sec).

The polymer matrix used in the experiments described was Lexan[7] polycarbonate and the molecules dispersed were *N*-isopropylcarbazole (NIPC) and triphenylamine (TPA) which have gas-phase ionization potentials of 7.27 and 6.8 eV, respectively.[8] Weighed amounts of Lexan, NIPC, and TPA were dissolved in spectral-quality 1, 2-dichloroethane. Lexan was used as received. TPA and NIPC were purified by sublimation and recrystallization from methanol and isopropylalcohol, respectively. The mixture was cast onto ball-grained Al using a doctor blade technique; dry film thicknesses were typically 9–11 μm. The films were allowed to dry at room temperature for 15 h before they were heated at 40°C in vacuum for 1 h. Transparent Au electrodes of 0.32 cm^2 were then deposited by slow vacuum evaporation. The transport parameters were determined by the time-of-flight technique which was modified as described elsewhere for analysis of the typically featureless current signals in logarithmic units of current versus time.[4,9,10] Free carriers were photogenerated close to the surface provided with the Au electrode by a 5-nsec 3371-Å light pulse derived from a N_2 laser. At 3371-Å Lexan is transparent and all the light is absorbed by the NIPC and TPA molecules. Only hole transport could be observed, which is expected, since both molecules are donorlike.[4]

Figure 1 summarizes the results of the time-of-flight experiments conducted at room temperature and with an applied field of 50 V/μm. Plotted along the ordinate is the drift velocity L/t_T, where L is the sample thickness and t_T is the transit time determined from the logarithmic current-versus-time plots. It should be pointed out that at t_T about 10–15% of the injected carriers transited the sample.[5] Plotted along the abscissa is the TPA concentration, $n_{\rm TPA}$, in units of mol-

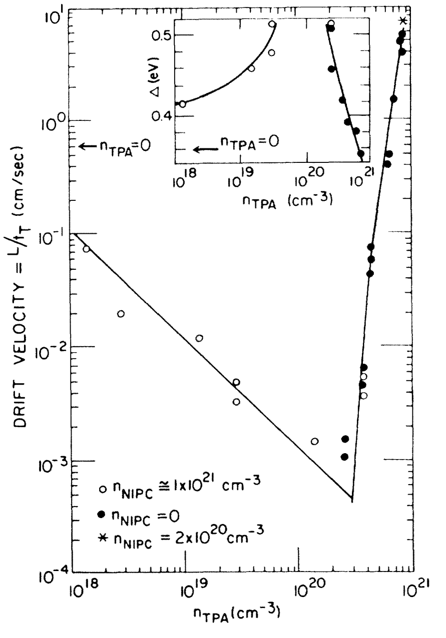

FIG. 1. Plot of hole velocity L/t_T at 50 V/μm and 296 K as a function of the concentration of triphenylamine molecules. The open circles are for samples which also contain 1×10^{21} NIPC molecules per cubic centimeter. The inset shows the dependence of the activation energy of transport at 75 V/μm on triphenylamine concentration.

ecules per cubic centimeter. Concentrations were calculated from the weight ratio of dopant molecule to Lexan with 1.16 g/cm^3 as an average density.

Two sets of samples were measured. In one set the NIPC concentration was zero and the TPA concentration was varied. The hole velocities measured for these samples are shown as solid circles in Fig. 1. With use of the same argument applied to establish hopping transport in NIPC-doped Lexan,[4] the strong concentration dependence of L/t_T shown in Fig. 1 also confirms this transport mechanism for the TPA/Lexan system. Thus at fixed temperature and field, the drift velocity is controlled by the overlap of the wave functions localized at neighboring TPA molecules with average intersite distance $\rho_{\mathrm{TPA}} \sim n_{\mathrm{TPA}}^{-1/3}$.

In the other series of samples Lexan was doped with NIPC molecules (with $n_{\mathrm{NIPC}} = 1 \times 10^{21}$ cm^{-3}) and the TPA concentration was varied. n_{TPA} was kept below $\sim 3 \times 10^{20}$ cm^{-3} to ensure that the average intersite distance $\rho_{\mathrm{NIPC}} \sim (n_{\mathrm{NIPC}})^{-1/3}$ among the NIPC molecules was not changed by the TPA molecules. The drift-velocity results at 50 V/μm are shown in Fig. 1 as the open circles. For $n_{\mathrm{TPA}} = 0$ (arrow), transport occurs via hopping among NIPC molecules.[4] Note that for the same concentration of $\sim 1 \times 10^{21}$ cm^{-3} transport via TPA molecules exceeds that via NIPC molecules by more than one order of magnitude.

The addition of TPA reduces the drift velocity from the value at $n_{\mathrm{TPA}} = 0$ in a manner which, for $n_{\mathrm{TPA}} \sim 10^{18} - 10^{20}$ cm^{-3}, is approximately proportional to n_{TPA}^{-1}. With further increasing TPA concentration, the velocity goes through a minimum at $\sim 2 \times 10^{20}$ cm^{-3} and begins to rise again, approaching, at $\sim 3 \times 10^{20}$ cm^{-3}, the value obtained with films of the first sample series, which contained no NIPC. Samples with $n_{\mathrm{TPA}} > 4 \times 10^{20}$ cm^{-3} cannot be prepared without changing the average intersite distance among NIPC molecules. Also for total concentrations in excess of 2×10^{21} cm^{-3} crystallization effects became apparent.

From these concentration studies alone, it is possible to explain the general features of the observations in a relatively simple way. For $n_{\mathrm{TPA}} = 0$, the hole transport occurs via hopping among the NIPC molecules present in a fixed concentration. As TPA molecules are introduced at low concentrations, carriers occasionally become localized on a TPA molecule which, because its ionization potential is lower than NIPC, acts as a trap for holes. Since the overlap between TPA molecules is so small at these concentrations, further drift of the charge localized on TPA must await thermal excitation back to an NIPC molecule. The data points for $n_{\mathrm{TPA}} \lesssim 2 \times 10^{20}$ cm^{-3} pertain to this mechanism. At sufficiently high TPA concentrations the overlap among the TPA molecules becomes sufficiently large that TPA-TPA hopping begins to compete with the hopping among NIPC-NIPC and TPA-NIPC pairs observed at low TPA loading. This process causes the drift velocity to rise for $n_{\mathrm{TPA}} \gtrsim 2 \times 10^{20}$ cm^{-3}; and it appears from the data shown in Fig. 1 that at $n_{\mathrm{TPA}} \sim 4 \times 10^{20}$ hopping among TPA completely dominates the charge transport.

TPA in low concentrations inhibits hole transport through NIPC because its ionization potential is lower. It follows then that, in the converse case, charge transport through TPA should not be influenced by NIPC as long as the intersite distance $(n_{\mathrm{TPA}})^{-1/3}$ remains constant. This is experimentally confirmed in Fig. 1 by the coincidence of the velocities measured for $n_{\mathrm{TPA}} \sim 4 \times 10^{20}$ cm^{-3} for both sample series and by the point identified by an asterisk which pertains to a sample with the loadings $n_{\mathrm{NIPC}} \sim 2 \times 10^{20}$ cm^{-3} and $n_{\mathrm{TPA}} \sim 8.5 \times 10^{20}$ cm^{-3}.

In the absence of TPA the activation energy for transport, Δ_{NN}, characterizes the transfer of holes among NIPC molecules. In the trap-controlled region ($n_{\mathrm{TPA}} < 2 \times 10^{20}$ cm^{-3}), "coherent" charge transport would predict that the activation energy is to be associated with the transfer of holes from TPA to NIPC sites; viz., $\Delta_{\mathrm{TN}} \sim \Delta_{\mathrm{TT}} + I_{\mathrm{N}} - I_{\mathrm{T}}$, where Δ_{TT} is the energy for hopping among TPA and $I_{\mathrm{N}} - I_{\mathrm{T}}$ is the energy difference between the highest occupied molecular orbitals of TPA and NIPC, respectively. Since $\Delta_{\mathrm{NN}} \approx \Delta_{\mathrm{TT}} + 0.1$ eV and $I_{\mathrm{N}} - I_{\mathrm{T}} \sim 0.4$ eV (difference of gas-phase ionization potentials), one expects that in the trap-controlled region $\Delta_{\mathrm{TN}} \sim \Delta_{\mathrm{NN}} + 0.3$ eV, independent of TPA concentration. The inset in Fig. 1 shows that this is not the case. The ordinate of this plot is the activation energy for transport determined from the temperature dependence of t_T (measured at 75 V/μm) and is plotted versus the concentration of TPA molecules. Focusing attention on the open circles which again show the data for mixed doped samples, one can see that the activation energy is dependent on the concentration of the TPA molecules. The full circles again refer to samples containing no NIPC. With increasing TPA concentration, the activation energy increases from $\Delta_{\mathrm{NN}} \sim 0.36$ eV to $\Delta_{\mathrm{TN}} \sim 0.52$ eV at $\sim 2 \times 10^{19}$ cm^{-3} and then approaches the value Δ_{TT} characteristic of hopping among

TPA molecules at that concentration. It is suggested that this concentration dependence arises purely from statistical considerations and, specifically, from the detailed nature of the dispersive-charge drift characteristic of an increasing number of disordered solids.[4,5,9]

The nonequilibrium transport in the presently discussed system is characterized by a broad distribution of hopping times. In fact, the distribution extends beyond the time range of the experiment since at t_T only 10-15% of the carriers have left the sample. Hence, carriers reaching the substrate electrode at a time of the order of t_T will have experienced different combinations of hopping sequences. For a system with only one transport molecule, NIPC for instance, the hopping-time distribution function $\psi(t)$ is concentration-dependent but temperature-independent if we assume, as did Scher and Montroll,[5] that the hopping distance rather than the activation energy is the dominant stochastic variable. The addition of varying amounts of a second transport molecule, TPA for instance, makes the distribution function explicitly temperature-dependent, in addition to its dependence on NIPC and TPA concentration, since $\Delta_{\text{NN}} \neq \Delta_{\text{TN}}$; and, consequently, the temperature dependence is no longer a simple scaling factor. It is suggested that the concentration dependence of the activation energy observed in TPA/NIPC-doped Lexan is a manifestation of the concentration- and temperature-dependent hopping-time distribution function. The observed activation energy is interpreted as an average of Δ_{NN} and Δ_{TN}, reflecting the various hopping sequences of the carrier for the particular TPA concentration. If it were possible to increase the TPA loading to a point where all carriers in transit experience similar trapping histories with respect to TPA, the increase of the activation energy over Δ_{TT} would be expected to approach a concentration-independent value ~ 0.3 eV. However at these concentrations, activation from TPA to TPA dominates the activation from TPA to NIPC and the activation energy approaches the value characteristic of hopping among TPA molecules. The concentration dependence of the latter activation energy is the subject of our current investigation.

Trap-controlled hopping has recently been proposed as a viable mechanism for transient hole transport in a-As_2Se_3.[10] In this case, however, the model cannot be tested by concentration studies and the interpretation in terms of trap-controlled hopping has to rely on numerical arguments. This further illustrates the usefulness of molecularly doped polymers as model systems for the study of various aspects of charge transport pertinent to the disordered solid state in general.

We would like to acknowledge enlightening discussions with Dr. H. Scher.

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[1] W. E. Spear and J. Mort, Proc. Phys. Soc., London 81, 130 (1963).

[2] K. M. Probst and N. Karl, Phys. Status Solidi (a) 27, 499 (1975).

[3] W. D. Gill, in *Proceedings of the Fifth International Conference on Amorphous Liquid Semiconductors, Garmisch-Partenkirchen, West Germany, 1974*, edited by J. Stuke and W. Brenig (Taylor and Francis, London, 1974), p. 901.

[4] J. Mort, G. Pfister, and S. Grammatica, Solid State Commun. 18, 693 (1976).

[5] H. Scher and E. W. Montroll, Phys. Rev. B 12, 2455 (1975).

[6] T. Shida and W. H. Hamill, J. Chem. Phys. 44, 2369 (1966).

[7] Lexan is a registered trademark of the General Electric Co.

[8] G. P. Ceasar, private communication.

[9] G. Pfister, Phys. Rev. Lett. 33, 1474 (1974), and 36, 271 (1976).

[10] G. Pfister and H. Scher, to be published.