$E_m \hbar^{-1} \tau_0 \simeq 10 \exp(-\Delta/300)$; this yields $\tau_0 \simeq 1.2 \times 10^{-16}$ sec. The overall magnitude of T_1 is scaled to agree with experiment near the minimum, and the curve for the above parameters is shown in Fig. 1.

In summary, we have discovered the existence of a T_1 minimum in vitreous B_2O_3 at ~ 300 K, well below its melting point of 730 K. We have developed a theory which explains the experimental properties of the longitudinal relaxation time in the vicinity of the minimum, as well as both the low- and high-temperature behavior. At low temperatures, Raman-like processes involving two-level disorder modes and acoustic phonons are dominant; at high temperatures thermally activated relaxation involving two-level defects dominates. Thus, the anomalous nuclear spin-lattice relaxation in glasses is caused by the same defects which are now believed to be responsible for their anomalous thermal and ultrasonic properties.

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[1]M. Rubinstein and P. C. Taylor, Phys. Rev. B 9, 4258 (1974).

[2]J. Haupt, in Proceedings of the Sixteenth Colloque Ampère, Bucharest, 1970 (unpublished), p. 630.

[3]J. Szeftel and H. Alloul, Phys. Rev. Lett. 34, 657 (1975).

[4]N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. 73, 679 (1948).

[5]F. Kramer, W. Müller-Warmuth, and H. Dutz, Glastech. Ber. 46, 191 (1973).

[6]N. Bloembergen, Physica (Utrecht) 15, 386 (1949).

[7]P. W. Anderson, B. I. Halperin, and C. M. Varma, Phil. Mag. 25, 1 (1972); see also P. W. Anderson (to be published), in which the author interprets some of the disorder modes as the tunneling of electron pairs.

[8]W. A. Phillips, J. Low Temp. Phys. 7, 351 (1972).

[9]Details of the expansion of $\mathcal{H}_Q$ and the resulting T_1 will be presented in a separate publication by T. L. Reinecke and K. L. Ngai.

[10]J. Van Kranendonk, Physica (Utrecht) 20, 781 (1954).

[11]M. Pollack and G. E. Pike, Phys. Rev. Lett. 28, 1449 (1972).

Field-Induced Charge-Carrier Trapping in the Photoconduction of a Quasi One-Dimensional System: Phenanthrene–Pyromellitic Acid Dianhydride

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A field-dependent charge-carrier trapping process has been observed in the photoconduction mechanism of phenanthrene–pyromellitic acid dianhydride. This effect can be observed at electric field strengths exceeding 10^3 V/cm. A calculation on the basis of a hopping model shows that field-induced charge-carrier trapping occurs in a three-dimensional system at critical field strengths well above 10^6 V/cm. In a one-dimensional model, however, the critical field strength can be as low as 1 V/cm.

Organic charge-transfer crystals belong to the class of solids which exhibit quasi one-dimensional properties. This one-dimensionality is due to a characteristic packing of the molecules in the solid state. In phenanthrene–pyromellitic acid dianhydride (-PMDA), which belongs to the class of weak charge-transfer crystals, the molecules form stacks of alternating donors and acceptors. The molecular planes are parallel or close to parallel and have a spacing which is close to 3.5 Å.[1] Consequently, the intermolecular interaction along the stack axis is considerably larger than the interaction perpendicular to the stack axis. This gives rise to an anisotropy of those physical properties which are governed by the overlap of molecular wave functions (short-range interaction) such as triplet-exciton energy transfer[2] and charge-carrier transport.[3,4]

In this Letter we report a specific charge-carrier–trapping phenomenon which has to our knowledge not been reported in the field of photoconduction of organic solids: field-induced charge-

carrier (CC) trapping. We will argue that this effect is an interesting consequence of the quasi one-dimensionality of the system phenanthrene-PMDA. In a simple diffusion model one can show that the observed characteristic trapping process would occur in three-dimensional systems at field strengths well above 10^6 V/cm[5]; in an ideal one-dimensional system, however, the effect should in principle be observable at electric field strengths as low as 1 V/cm. The main difference between the three-dimensional and the one-dimensional cases is the fact that the diffusion process in one dimension reduces the CC trapping by reducing the the number of distinct molecules which the CC encounters during a given time interval without reducing its drift mobility (see below).

Intrinsic properties of photoconduction in weak charge-transfer crystals have been reported recently.[3,4,6] Typical CC mobilities at room temperature have been found to be on the order of 10^{-1} to 10^{-3} cm^2/V sec. The measured anisotropy of the mobility along and perpendicular to the molecular stack axis varied between 1:3 and 1:10. Because of the close molecular packing along the stack axis, however, the measured anisotropy in mobility corresponds to an anisotropy in the CC-jumping rate along and perpendicular to the stack axis of 1:20 to 1:70.

The experimental information which is so far available indicates that the CC mobility has to be interpreted in the framework of a narrow-band conduction process. In the case of phenanthrene-PMDA where the measured mobilities were below 3×10^{-2} cm^2/V sec, a hopping model accounts well for the experimental results at 300°K and above. The application of a hopping model seems to be justified in the light of recent high-field experiments on anthracene which indicate that even in this case a localized model can be applied to explain the experimental findings[7] (anthracene has a CC mobility of about 1 cm^2/V sec).

In the following we will present experimental data which indicate field-induced electron trapping in single crystals of phenanthrene-PMDA at field strengths of 10^3 V/cm and above. These findings are subsequently discussed within the framework of three-, two-, and one-dimensional diffusion models.

As far as the crystal preparation and experimental setup is concerned, we refer to a recent paper.[3] Special care was taken to obtain CC transients which were not distorted by space-charge effects by operating at low light-intensity levels.
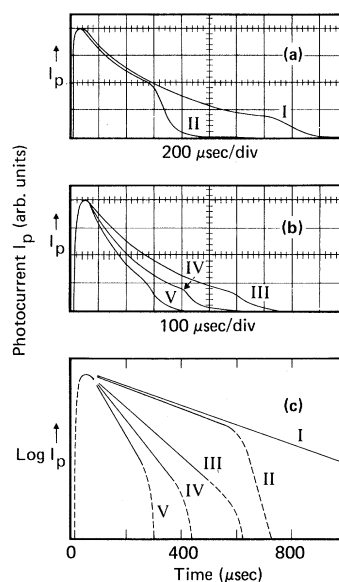
Figures 1(a) and 1(b) show a series of electron

FIG. 1. Electron transients for single crystals of phenanthrene-PMDA (a) perpendicular to and (b) parallel to the molecular stacking axis. Temperature 355°K; crystal thickness 1.2 mm; applied voltage 1000 V (curve I), 2500 V (curve II), 1000 V (curve III), 1500 V (curve IV), 2500 V (curve V); photocurrent between 4 $\times 10^{-7}$ and 10^{-8} A. (c) Summary of (a) and (b) on a logarithmic scale.

transient photocurrents which have been obtained by use of the well-known method of Kepler and LeBlanc.[8,9] For an ideal trap-free system the measured photocurrent should be constant between $t = 0$ and $t = \tau$. The transit time τ is defined as $\tau = d/E\mu = d/v_{\mathrm{drift}}$; here E is the electric field strength, μ is the electron mobility, d is the crystal thickness, and v_{drift} is the electron drift velocity.

For a nonideal system with deep traps the trapping process leads to an exponential decay which is superimposed on the drift current. The characteristic decay time with which the photocurrent decreases is called the CC-trapping time; it is usually a constant for a given crystal depending on crystal purity and perfection. Figure 1(a) shows an electron transient with superimposed trapping for a crystal direction perpendicular to the stack axis; since the trapping time is constant, the fraction of charge carriers which is trapped during the transient experiment is reduced at higher applied electric fields. This is the common situation in photoconduction experiments of organic solids. Figure 1(b) shows the CC trapping in an experiment with the electric field pointing along the stack axis. The oscillo-

scope traces show that the trapping time is not constant, but gets shorter at higher electric fields. One can easily show that, if one assumes a trapping time which decreases linearly with the electric field, the ratio between the initial current and the current at the end of the transient should be constant. This ratio yields directly, within the framework of the presented model, the concentration of deep traps in the crystal which is in our experiment about 10^{-6} mol/mol. Figure 1(c) summarizes the transient experiments from Figs. 1(a) and 1(b) on a logarithmic scale. Within the experimental error the observed trapping processes follow a single exponential decay with a constant decay time perpendicular to the stack axis and with a decay time which gets shorter at higher fields along the stack axis. This field-dependent reduction of the CC-trapping time is referred to as field-induced trapping. Figure 2 shows the measured trapping times as a function of the electric field strength for both crystal directions. Above 5×10^3 V/cm the trapping time decreases in a linear fashion with the applied electric field for E parallel to the stack axis; it is constant for E perpendicular to the stack axis.

In the following calculation we compare two quantities which determine the CC trapping: (a) (a) the number of distinct molecules N_{drift} which the CC encounters as a result of its drift motion, the drift velocity being defined as $v_{\text{drift}} = \mu E$; (b) the number of distinct molecules N_{diff} which the CC encounters as a result of its diffusive motion. Both the drift term and the diffusion term are linked by the Einstein relation $\mu = eD/kT$ (D is the diffusion coefficient).
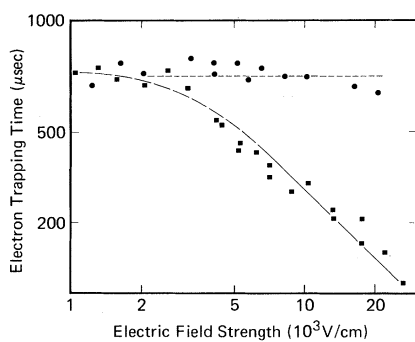
Considering the time interval of the transit

FIG. 2. Electron-trapping time as a function of the applied electric field (double logarithmic plot).

time τ one gets

$$N_{\text{drift}} = v_{\text{drift}} \tau / a = d/a,$$

where a is the lattice constant. This number corresponds to the number of molecules which lie on a CC trajectory across the crystal. The number of distinct molecules which the charge carrier encounters as a result of its diffusive motion has been calculated by Montroll and Weiss[10] for three, two, and one dimension as

$$N_{\text{diff}} \sim n_{\text{diff}} F_3, \quad N_{\text{diff}} \sim [n_{\text{diff}}/\ln(n_{\text{diff}})] F_2,$$

$$N_{\text{diff}} \sim (n_{\text{diff}})^{1/2} F_1,$$

respectively, with $F_1 = (8/\pi)^{1/2}$, $F_2 = \pi$, and $F_3 = 0.66$ for a cubic lattice.[11] The number of jumps performed during the observation period regardless of whether the jump leads to a new molecule or to a molecule which the CC had already encountered before is

$$n_{\text{diff}} = v_{\text{th}} \tau / a,$$

where v_{th} is the thermal velocity of the charge carrier which is in three, two, and one dimension $v_{\text{th}} = 6D/\lambda$, $4D/\lambda$, and $2D/\lambda$, respectively. λ is the mean free path for CC scattering. For simplicity we take this length as being the lattice constant a.

If one defines a critical electric field strength E_c as the electric field strength at which the CC trapping due to the drift term gets as large as the CC trapping due to the diffusion term one can derive the following result for three, two, and one dimension:

$$E_c \sim (6kT/ea) F_3 \quad (4 \times 10^6 \text{ V/cm}),$$

$$E_c \approx (4kT/ea) F_2/\ln(d/a) \quad (8 \times 10^5 \text{ V/cm}),$$

$$E_c \sim (2kT/ea) F_1^2 a/d \quad (1 \text{ V/cm}).$$

It should be noted that the critical field strength is a function of the crystal thickness in two and one dimension. This thickness dependence is a consequence of the fact that the CC-trapping rate is time dependent in both cases for electric fields below the critical field E_c where diffusion is the overwhelming trapping mechanism. The trapping rate has a weak logarithmic dependence in two dimensions and has a $\sqrt{t}$ dependence in the one-dimensional case.[11] This $\sqrt{t}$ dependence makes the trapping process very inefficient in the one-dimensional case since the charge carrier tends to sample previously visited lattice points for large t values.

The critical field does not depend on the CC mobility; this is a consequence of the Einstein

relation which links the drift term and the diffusion term. The field values in parentheses correspond to the experimental situation ($T = 355°K$, $d = 1.2$ mm, and $a = 3.5$ Å). The most interesting aspect of the calculated values for the critical field is the fact that they differ by six orders of magnitude depending on the dimensionality of the problem. The calculated critical fields are very large for the three- and two-dimensional cases; they are extremely low for the one-dimensional case because of the inefficient trapping probability which has been pointed out above. The measured value $E_c = 5 \times 10^3$ V/cm shows that the system phenanthrene-PMDA is not an ideal one-dimensional system. In order to determine the deviation from one-dimensionality more accurate measurements of the mobility tensor have to be performed together with model calculations taking into account the real lattice geometry.[12] The presented experimental data, however, show that it is challenging to search for photoconductive systems with a higher degree of one-dimensionality. Furthermore, the experiments themselves provide a novel method for ascertaining the one-dimensionality of the conduction process.

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[1]F. H. Herbstein, in *Perspectives in Structural Chemistry*, edited by J. D. Dunitz and J. A. Ibers (Wiley, New York, 1971), Vol. 4; W. T. Robinson and D. L. Evans, private communication on structural data of phenanthrene-PMDA prior to publication.

[2]H. Möhwald and E. Sackmann, Chem. Phys. Lett. 21, 41 (1973).

[3]H. Möhwald, D. Haarer, and G. Castro, to be published.

[4]N. Karl and J. Ziegler, to be published.

[5]Experiments on molecular crystals have to our knowledge not been performed at electric fields as high as 10^6 V/cm.

[6]J. H. Sharp, J. Phys. Chem. 71, 2587 (1967).

[7]R. G. Kepler and D. C. Hoesterey, Phys. Rev. B 9, 2743 (1974).

[8]R. G. Kepler, Phys. Rev. 119, 1226 (1960).

[9]O. H. LeBlanc, J. Chem. Phys. 33, 626 (1960).

[10]E. W. Montroll and G. H. Weiss, J. Math. Phys. (N.Y.) 6, 167 (1965).

[11]For times large in comparison with the CC-hopping time one gets a one-dimensional CC-trapping rate of $k_{\text{diff}} = (F_1/2)(v_{\text{th}}/a)^{1/2}/\sqrt{t}$. Experimentally the square-root dependence cannot be verified because it would occur at electric field strengths on the order of 1 V/cm and at photocurrents of less than 10^{-11} A. In the "real experiment" the trapping rate is time independent because of a "residual three-dimensionality" up to fields where the field-induced trapping takes over with a rate which is also time independent and which is $k_{\text{diff}} = \mu E/a$.

[12]As far as the experiments perpendicular to the stack axis are concerned one expects a two-dimensional diffusion process with lower mobility values. For this case a field effect would be expected at much higher electric fields.

Energy Bands of Reconstructed Surface States of Cleaved Si

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Coordinates of atoms in the first and second layers of Si(111) 2×1 have been determined which yield surface energy bands in good agreement with experiment. Two surface resonances in angular photoemission data previously assigned to dangling-bond surface states are identified as arising from the maximum in the lower dangling-bond band and from a saddle point in the upper back-bonding band.

Semiconductor surfaces exhibit superlattice structures which have previously been discussed by many authors. *In principle,* these superlattice configurations can be deduced from sufficiently accurate analysis of low-energy electron-diffraction (LEED) data. *In practice,* however, multiple scattering effects make theoretical calculations extremely sensitive to small errors. Recent difficulties with the structures for chalcogens on Ni(100) surfaces and with the Si(100) superlattice indicate that further theoretical refinements are necessary before this approach can yield structural information.[1] We believe that much more direct and precise determination of atomic coor-