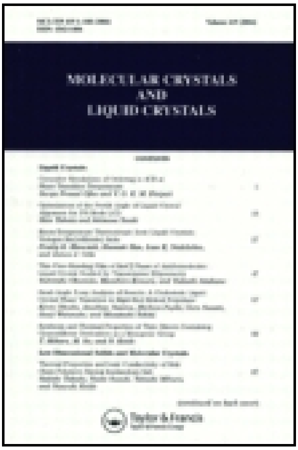

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Carrier Transport in van der Waals Solid: 1,3-Diphenyl-5-(p-chlorophenyl)-2-pyrazoline in Single Crystalline State, Glassy State and in Supercooled Liquid State

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Version of record first published: 20 Apr 2011.

To cite this article: Hiroyuki Kitayama , Masaaki Yokoyama & Hiroshi Mikawa (1981): Carrier Transport in van der Waals Solid: 1,3-Diphenyl-5-(p-chlorophenyl)-2-pyrazoline in Single Crystalline State, Glassy State and in Supercooled Liquid State, Molecular Crystals and Liquid Crystals, 69:3-4, 257-271

To link to this article: http://dx.doi.org/10.1080/00268948108072706

Mol. Cryst. Liq. Cryst., 1981, Vol. 69, pp. 257-271
0026-8941/81/6903-0257/$06.50/0

Printed in the United States of America

Carrier Transport in van der Waals Solid: 1,3-Diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline in Single Crystalline State, Glassy State and in Supercooled Liquid State

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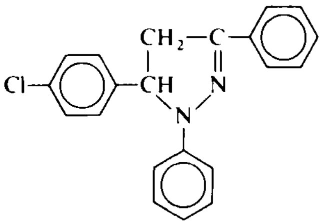
(*Received July 30, 1980*)

The hole drift mobilities in the title compound were measured in the single crystalline state (mp. 130°C), the glassy state (Tg, 16.5°C) and the supercooled liquid state up to 50°C by a time-of-flight method. The mobility (μ_h) in a single crystal was about 10^{-2} cm^2/V·sec and its activation energies were 0.103 eV below 12°C and 0.037 eV above this temperature. A weakly endothermic solid phase transition was observed in a single crystal corresponding to this temperature. In the glassy state, μ_h was about 10^{-5} cm^2/V·sec. In the supercooled liquid state, μ_h was also of the order of 10^{-5} cm^2/V·sec and showed a maximum value at around 35°C, which appeared reproducibly and depended on the heating and cooling rate showing hysteresis phenomena. The Scher-Montroll transport theory for non-crystalline solids could be applied to our material but in a rather limited temperature range.

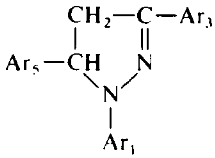
INTRODUCTION

There has currently been an increasing interest in the investigation of the effect of structure, i.e., crystalline, supercooled liquid or glassy states, on the migration of excited state[1] and/or the charge carriers in van der Waals solids.[2,3] Migration of the singlet excited state in the compound I in different aggregation states was recently reported from our laboratory.[1] In the present paper we wish to report charge carrier transport in this compound in different states of aggregation.



1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline

(I)



1,3,5-triaryl-2-pyrazoline

(II)

1,3,5-Triaryl-2-pyrazolines, cf. structural formula II, are a class of compounds, which are very interesting in that they give stable glassy state near room temperature, and even up to well above the glass transition temperature they keep a hard supercooled liquid state without crystallizing. In addition, most of these compounds are intensely fluorescent and also photoconductive. Among these compound, 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline, mp. 130°C, formula I, is a typical one, having a Tg of 16.5°C and the glass remaining uncrystallized up to *ca.* 80°C. Large single crystals can also be obtained by an usual Bridgman furnace. This compound, therefore, provides a material to investigate and compare transport phenomena in single crystalline, glassy and supercooled liquid states with the same compound over a considerably wide temperature range.

In the present work, transport phenomena of the hole carriers were measured by the so-called time-of-flight method with the use of the nitrogen laser pulse in such various aggregates. In the single crystalline state, the hole carrier drift mobility was of the order of 10^{-2} cm^2/V·sec and in the glassy state of the order of 10^{-5} cm^2/V·sec in the room temperature range. In the supercooled liquid state, the drift mobility was about the same order as in the glassy state. Some complex but interesting phenomena were observed.

EXPERIMENTAL

1. Materials and sample preparation

1,3-Diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline (I) was prepared from *p*-chlorobenzaldehyde, acetophenone and phenylhydrazine according to the method described in the literature.[5] The crude material was purified first by recrystallization from ethanol, next by chromatography on an alumina column with benzene, and finally was zone-refined with more than 600 passes of the melt-zone using a Shimazu Cryogenic Zone Refiner CZ-1.

The purity of the material was monitored by confirming the absence of any spectral dependence of the fluorescence lifetime as has been suggested by Kobayashi *et al.*[6] The melt zone in the zone-refining tube solidified in a transparent glassy state when the zone tube was taken out from the refiner and allowed to cool down to room temperature. This enabled the measurement of the fluorescent lifetime of each transparent portion in the tube. A sample of *ca.* 250 zone passes showed no spectral dependence of the fluorescence lifetime in each portion along the tube except for the lowest one.

A single crystal was obtained from the zone-refined material by the Bridgman method. As has been reported,[1(b)] compound I has two monoclinic crystal forms α and β as shown in Figure 1, of which only α-form was grown by melt growing method. The transport data reported here, therefore, are concerned with the α-form and especially along the c-axis, which is the crystal growing direction. Details of the zone refining and crystal growing procedures were reported previously.[7,12]

Properly sized single crystal specimens were cut by a diamond cutter, after an initial x-ray alignment had been performed. The cut section was then polished by benzene-soaked filter paper to give thin samples. The polished planes are perpendicular to the c-axis.

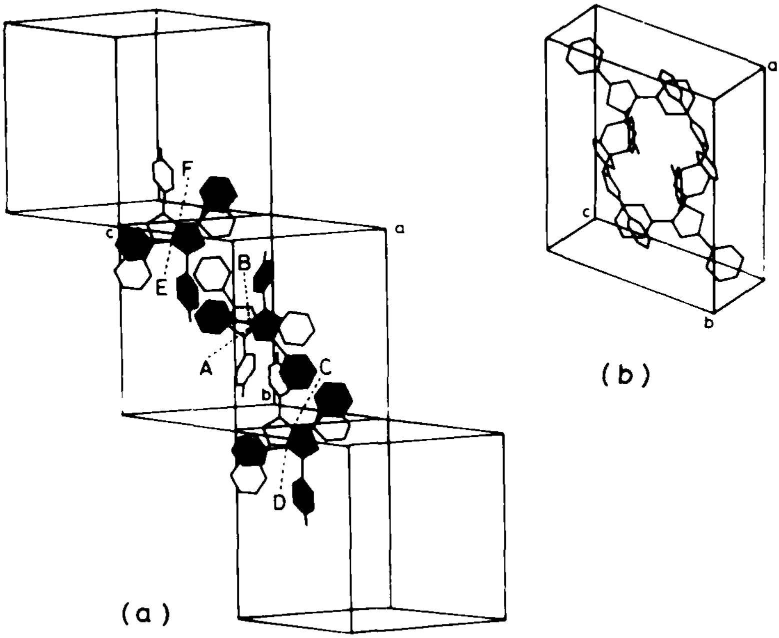


FIGURE 1 Crystal structure of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline. (a) α form. The distance between number 1 nitrogen atoms A and B is 4.2 Å. C-D and EF are also the same. A-C and B-E are 8.6 Å. (b) β form.

2. Measurements

The circuit for the drift mobility measurement and the cell assembly are shown in Figure 2. The sandwich cell assembly consists of a transparent conducting (Nesa-coated) quartz electrode, the material, and a copper electrode. The glass or the supercooled liquid was prepared into the cell by rapid quenching of the melt, which is sandwiched between quartz and copper with a teflon spacer of $6 \sim 30$ μm thick. This was used immediately for measurement. On the other hand, the crystal was polished to reduce the thickness to 0.1cm and was directly sandwiched between quartz and copper for measurements. In this case, a plot of the reciprocal of the transit time against applied voltages gave a straight line passing through the origin, and hence a uniform electric field is supposed to have been applied to the crystal. The cell assembly was mounted in a cryostat.

Drift mobility was measured by a conventional time-of-flight method as shown in Figure 2. The photocarriers were produced by a nitrogen laser pulse (half width 5 *n*sec) of wavelength 3371 Å with an intensity of $\sim 10^{15}$ photons/cm^2 pulse. The applied voltage of $0 \sim 1$ kV induced a transient current across a sample and load resistor (R_L) upon excitation with the laser. This pulse was fed to a current amplifier (×500) and was traced on a memory synchroscope (Tektronix 5103N). Time sequence of the measurement is shown in the inset of Figure 2.

Some devised experimental techniques in the present measurement are as follows. Starting pulse was generated by a manual switch. With this pulse, electric field is applied to the material with the duration of 5.8 sec. This

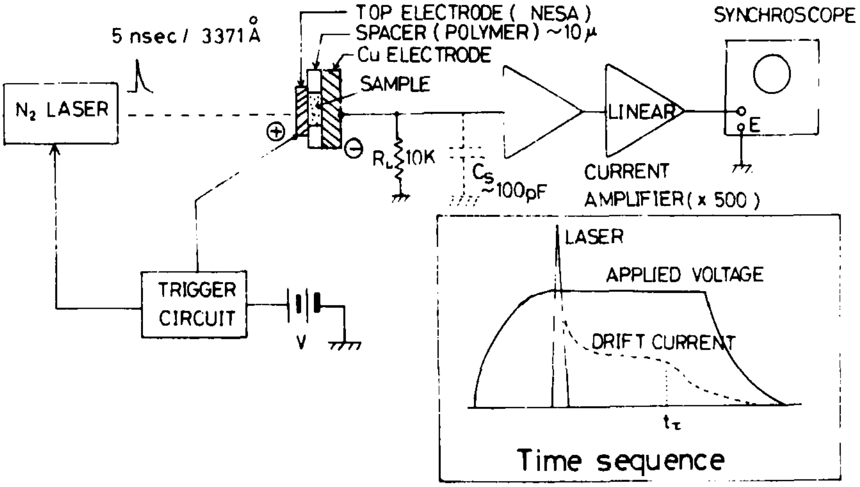


FIGURE 2 Schematic diagram of the experimental apparatus and the time sequences of the drift mobility measurements.

starting pulse, after being delayed about 1.2 sec until the charging current was completely diminished, triggered an N_2 laser shot of 5 *n*sec half width. To avoid large polarization current to feed into a pre-amplifier, the load resistor was kept very low (~ 100Ω) during the rising and falling time of the applied voltage by inserting a photocoupler (P873-G35-552) parallel to the load resistor R_L (10 KΩ). The photoconductive element in the coupler was operated by a suitable IC. The stray capacitance C_s (~ 100 pF) was cancelled with the first amplifier. In the case of glassy or supercooled liquid states, the drift mobility μ was obtained by measuring the transit time t_T by the plots based on the theory of Scher and Montroll.[4] In the crystal, t_T was obtained directly by a clear shoulder of the drift current trace.

When the illuminated Nesa electrode was negatively biased, no drift current was observed. Thus, only the hole drift mobility was observable in this material.

RESULTS AND DISCUSSION

1. Mobility in the single crystal

A typical current transient in the single crystal is shown in Figure 3. The transient current measured was of the holes and along the *c*-axis. The crystal

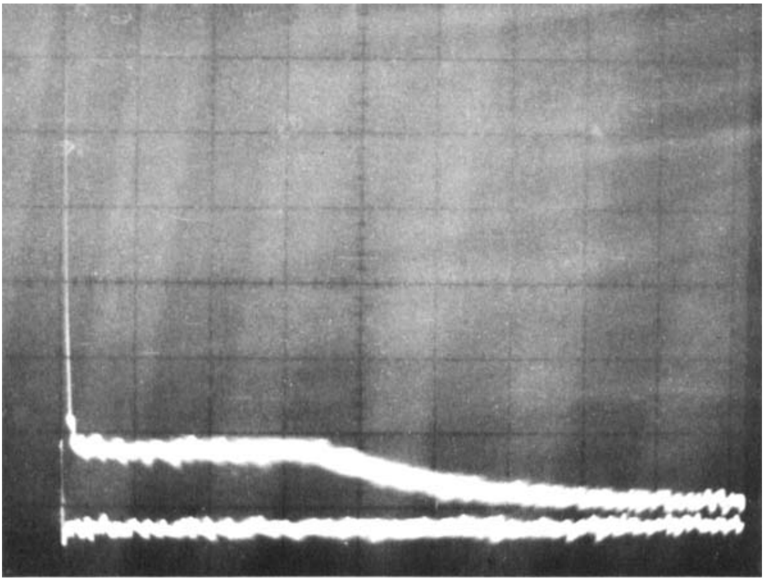


FIGURE 3 A typical current signal in an α-form single crystal. (*c*-direction, at 23°C, R_L = 10 KΩ) Vertical: 100 mV/division, Horizontal: 0.2 msec/division, Thickness: 0.1 cm, Applied voltage: 935 V.

thickness was 0.1cm. The mobility was almost independent on the applied electric field, and the typical value of the drift mobility was found about 10^{-2} $cm^2/V \cdot sec$. The observed temperature dependence of the *c*-axis hole drift mobility is shown in Figure 4. Measurements below −20° C were difficult due to small signals and poorly defined transit times. This figure indicates that in spite of the single crystal, small but significant change of activation energies exist, which differ on both sides of *ca.* 12° C. This temperature happens to be almost the same as the glass transition temperature of the compound. As can be seen in the DSC of the crystal shown in Figure 5, a change of baseline was clearly observed almost at the same temperature.

In general, it is understood that the glass transition is the liquid-glass transition due to loss of equilibrium. Recently, it has been reported that glass transition phenomena occur even in the stable crystalline phases of $SnCl_2 \cdot 2H_2O$, H_2O and CO crystals by Suga and Seki[8] and in that of 2-methylthiophene crystal[9] by Pennington *et al.* That is, glass transition is essentially a freezing-in phenomenon which is not limited to the supercooling of liquid. For instance, Bernal and Fowler[10] stated that ice would be crystalline only in the position of its molecules but glass-like in their orientation.

Some intramolecular degree of freedom, probably due to the rotational freedom of a *p*-chlorophenyl group, might be released at this temperature. It seems that this appreciable solid state phase transition in pyrazoline crystal is reflected in the change of the activation energy for the hole drift mobility

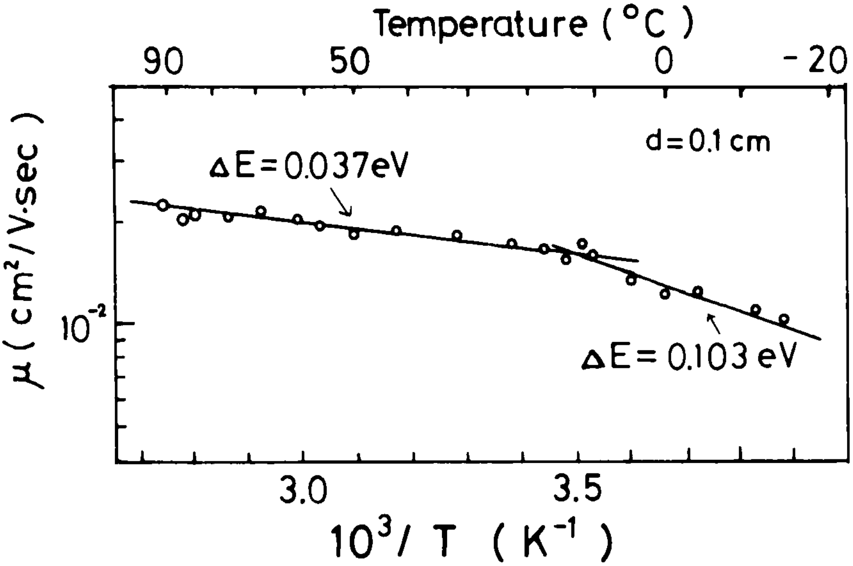


FIGURE 4 Hole mobility in the single crystal in the *c*-axis direction.

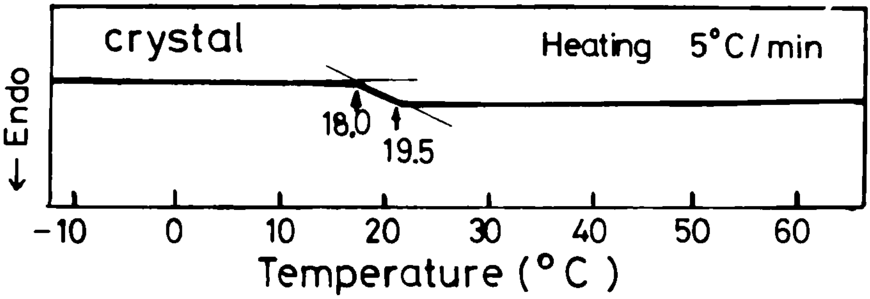


FIGURE 5 DSC curve of the pyrazoline in a crystalline state.

above and below this temperature. The value of the order of 10^{-2} cm^2/V·sec for the drift mobility indicates that the transport of charge carrier in this material is hopping conduction in nature. The release of the local freedom seems to lower the activation energy for hole migration.

2. Mobility in the glassy state ($T < T_g$)

As shown in Figure 6, the hole drift mobility in the glassy state changed not only with temperature but also with applied voltage, in contrast to the case of single crystal which was voltage independent. The thickness of the sample, the spacer thickness, was 21 μm. Thus, the value of the hole mobility below T_g was about $10^{-6} \sim 10^{-5}$ cm^2/V·sec. Measurements below $-50°$C could not be made because of the same reason as described previously in the case of the single crystal. The results are well explained by Gill's empirical relation[11] which implies the carrier transport of Poole-Frenkel type,

$$\mu = \mu_0 \exp\{-(E_0 - \beta_{ex}F^{1/2})/kT_{eff}\} \qquad (1)$$

where,

$$1/T_{eff} = 1/T - 1/T_0 \qquad (2)$$

and F is the electric field. The values of the parameters are estimated as follows.

$\mu_0 = 3.6 \times 10^{-5}$ cm^2/V·sec
$T_0 = 315$ K (42°C)
$E_0 = 0.63$ eV
$\beta_{ex} = 1.78 \times 10^{-3}$ eV(V/cm)$^{-1/2}$

Usually, the Poole-Frenkel constant β_{PF} is related to the relative dielectric constant κ in the following manner,

$$\beta_{PF} = (q^3/\pi\kappa\epsilon_0)^{1/2} \qquad (3)$$

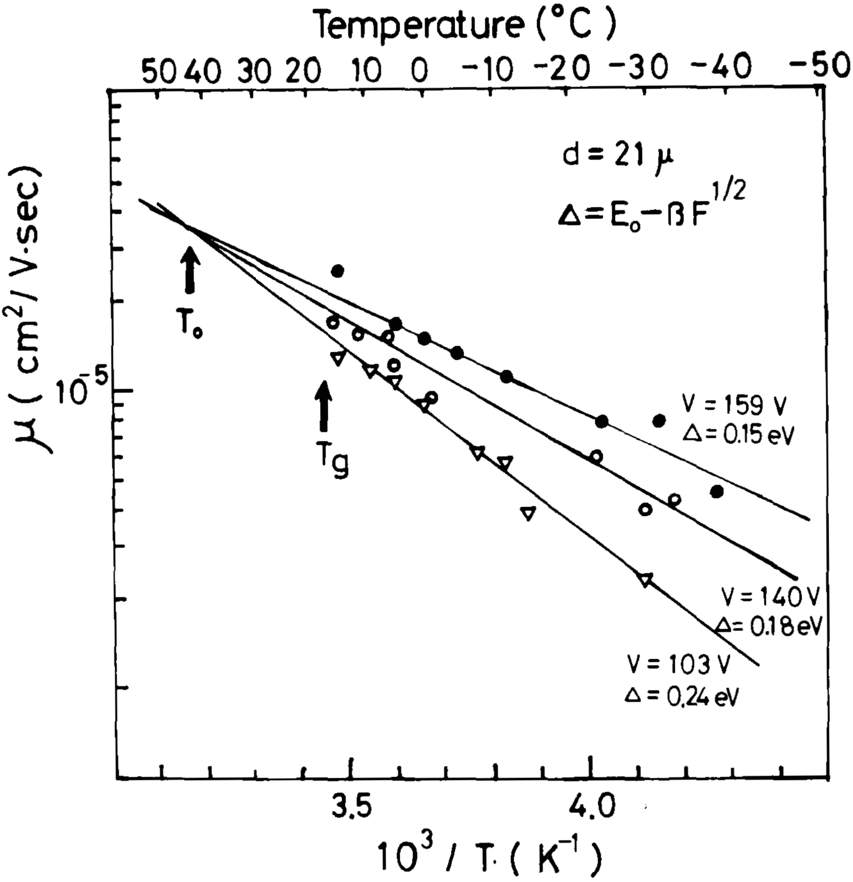


FIGURE 6 Hole mobility in the glassy state.

where q is electronic charge and ϵ_0 is the vacuum dielectric constant. The values of relative dielectric constant κ of this material is about 2.2 (−40°C ~ 0°C), the calculated value of β_{PF} is 5.12×10^{-4} eV(V/cm)$^{-1/2}$, which is slightly small comparing with the value of β_{ex}. This deviation seem to be caused by some hysteresis effect which will be discussed in the next section.

3. Mobility in the supercooled liquid state ($T > T_g$)

A typical hole current is shown in Figure 7. Usually, due to crystallization, measurements of the drift mobility in the supercooled liquid state are difficult and have hardly been tried so far.[12] In the case of the pyrazoline, this state remains stable nearly up to 50° C and well reproducible results can be obtained and moreover the values of the mobility in this state smoothly connect with those of glassy state as indicated in Figure 8, which shows the mobility in the glassy and supercooled liquid state below and above T_g in the same sample. As shown in this figure, however, the results are somewhat complicated above 30° C due to the presence of some hysteresis phenomena. Figure 9 clearly shows the hysteresis behavior. Run-1 in the figure shows the mobility change in a virgin sample with increasing temperature from below T_g to 50° C. Below 30° C, the drift mobility gradually increases with almost the same apparent activation energy, ΔE, as shown in Figure 8, but beyond 30° C the mobility increases with a different slope against inverse temperature, and on further heating exhibits a complicated behavior.

Usually, many physical quantities such as molar volume, specific heat, viscosity, etc. change at the glass-transition temperature T_g. In the case of pyrazoline, the supercooled liquid state just above the glass-transition temperature is very hard and the material remains solid even up to 30° C. The hardness decreases rather rapidly above 30° C.[13] Thus the break point in the slope is closely related to the temperature at which the physical properties characteristic of the supercooled liquid state become predominant. The sample (Run-2) after cooling down to room temperature did not trace the

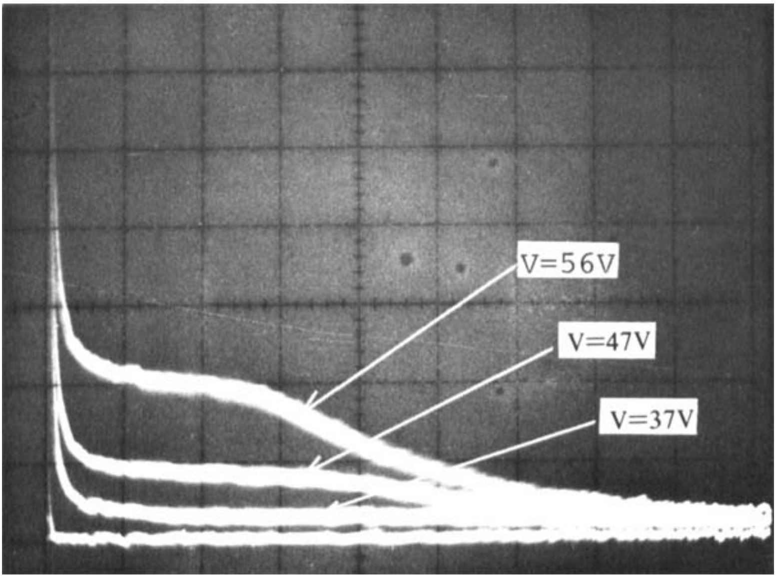


FIGURE 7 A typical hole current transient signals in the supercooled liquid state. (at 44° C, R_L = 10 KΩ), Vertical: 50 mV/division, Horizontal: 1 msec/division, Thickness: 14 μm, Applied voltage: as indicated.

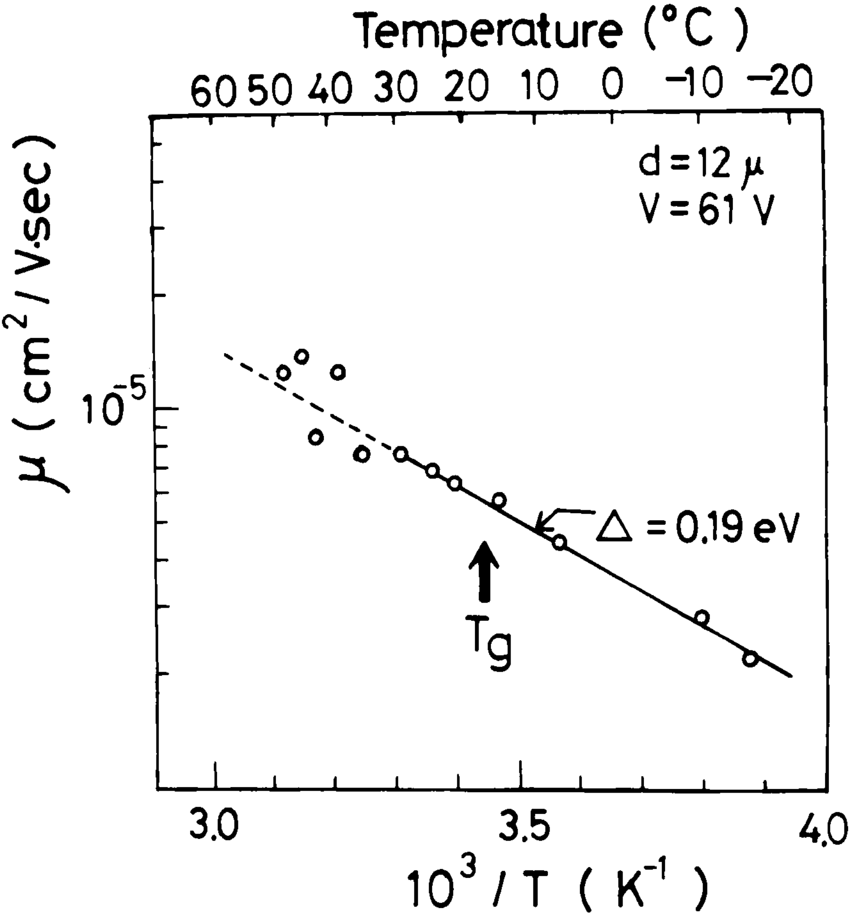


FIGURE 8 Hole mobility in the glassy and supercooled liquid states.

plots of Run-1, and two peaks of the mobility appear reproducibly at about 35°C and 45°C. Once the temperature becomes higher beyond 35°C, the activation energy falls into almost the same value in the case of Run-1, and the drift mobility follows Run-1. This fact seems to suggest that the molecular alignments in the sample which was once in a higher temperature than 40°C could not be attained reproducibly on cooling because of high viscosity below 30°C; that is, there is a memory effect of molecular alignments. Contribution due to ionic conduction is ruled out in this temperature range since the dark current remains less than 10^{-12} *A* up to 70°C. The major carrier in the supercooled liquid state must still be the hole.

Figure 10 shows the annealing effect in the drift mobility. The value of the mobility becomes smaller by annealing at 35° C for 27 hr and finally decreases along the extension have the higher temperature region (35°C ~ 45°C), as indicated by a downward arrow in Figure 9.

Thus, the carrier transport mechanism in the supercooled liquid state seems to be greatly dependent on the experimental time scale. For the explanation of the mobility peak which appeared at about 45°C further investigation is required.

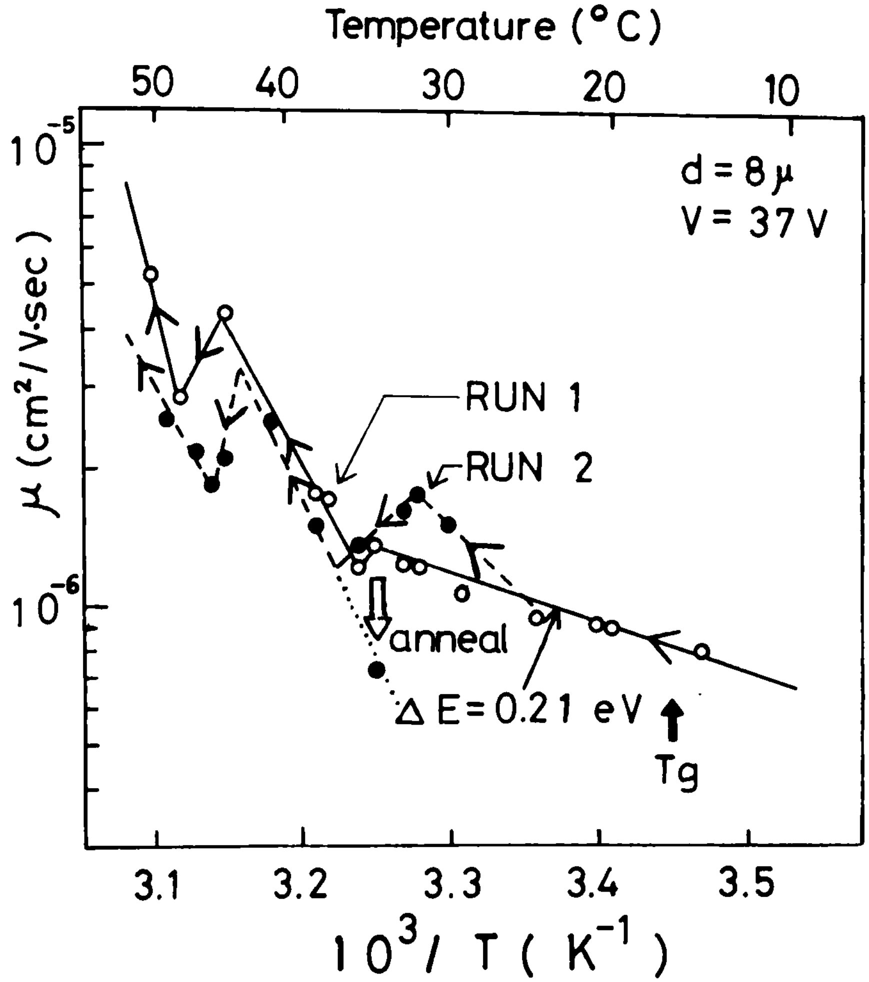


FIGURE 9 Hole mobility in the supercooled liquid state.

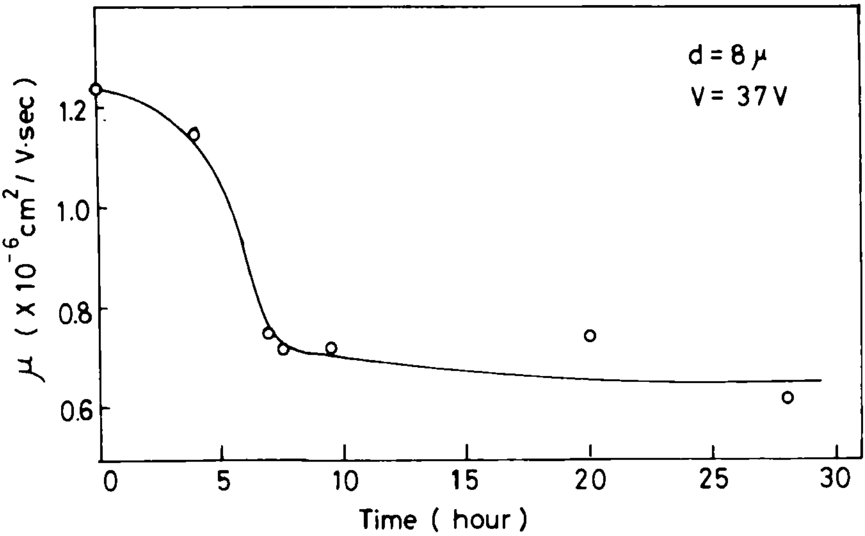


FIGURE 10 Annealing effect in the mobility at 35°C.

4. Comparison of the mobility value of the glassy state with that of the single crystal

From the above-mentioned values of the single crystal and the glassy states, it has become apparent that the value of the mobility in the single crystal is about 10^3 times larger than that of the glassy state. Similar results are reported with both 2,4,7-trinitro-9-fluorenone[2] and *o*-terphenyl.[3] The fact that similar differences in the mobility values are reported for other glass-forming materials, may suggest that a similar change in the transport mechanism occurs between the crystalline and glassy states. Interestingly, this difference of the carrier migration between the glassy and single crystalline states happens to be close to the difference of the singlet energy migration of the same material between the glassy and single crystalline states reported by Sano *et al.*[1(b)]

5. The applicability of the Scher-Montroll theory

An important progress has been made recently on the theoretical background of the transport problem for non-crystalline solids by Scher and Montroll.[4] Sowe tried to examine whether or not the Scher-Montroll theory could be applied to the glassy and supercooled liquid states of the present material.

Dispersive transient currents $I(t)$ in non-crystalline solids are analyzed in the plots of log I versus log t by the theory of Scher and Montroll.[4] For an approximate hopping time distribution function $\psi(t) \propto t^{-(1+\alpha)}$, $I(t)$ should exhibit the power dependences of $t^{-(1-\alpha)}$ and $t^{-(1+\alpha)}$ for $t < t_r$ and $t > t_r$, respectively, where, t_τ is a measure of the transit time. This functional form of the distribution function is an asymptotic form for $t \ll t_\tau$ and $t \gg t_\tau$ of the complicated theoretical function, which is obtained in the configurational average of the hopping probability of inverse proportionality to the exponent of intersite distance. One conveniently defines α_i and α_f as the α values determined from the initial ($t < t_\tau$) and final ($t > t_\tau$) slopes of the hole transient, respectively, according to the notation introduced by Pfister and Griffiths.[14] Evidently $\alpha_i = \alpha_f$ must hold without depending on temperature, and in addition, the relation $t_\tau \propto (E/d)^{-1/\alpha}$ is derived from the S-M theory, where E is electric field.

Figure 11 shows the E/d dependence of t_τ for various temperatures. The

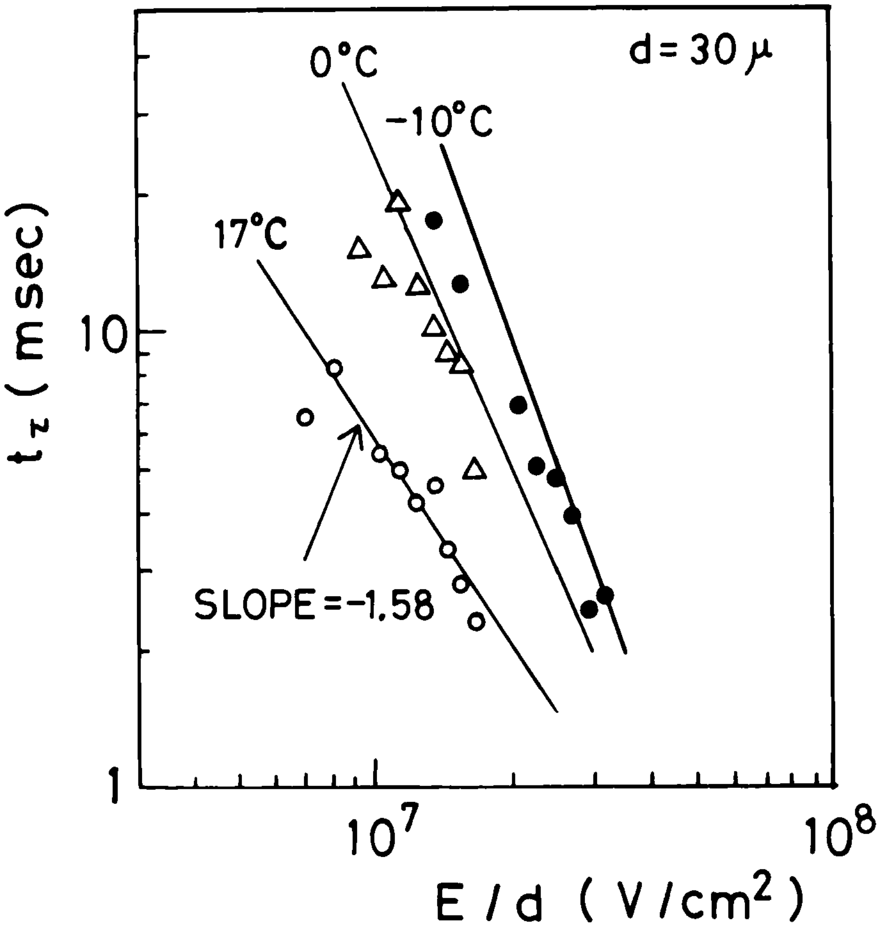


FIGURE 11 E/d dependence of the transit time (t_τ) in the glassy and supercooled liquid states.

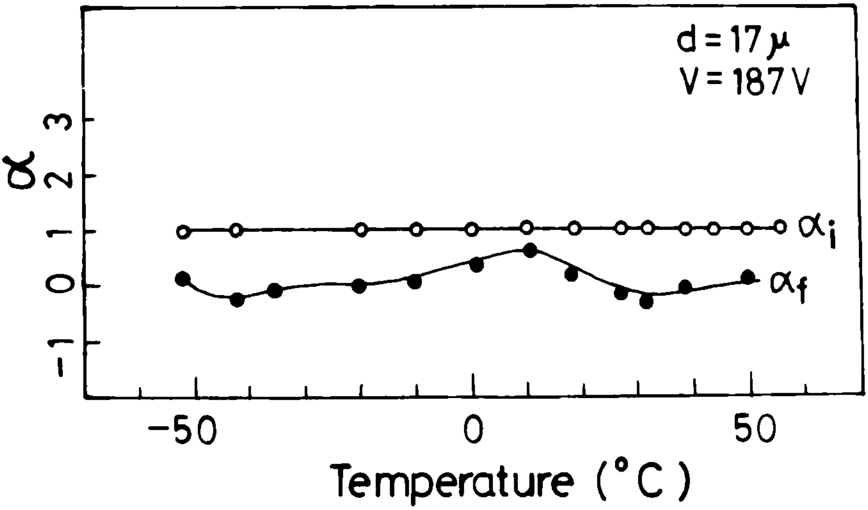


FIGURE 12 α_i *(T)* and α_f *(T)* in the glassy and supercooled liquid states.

linear relationship was obtained with a well-defined α, i.e., $\alpha = 1/1.58 = 0.63$ at $T = 17°C$. As shown in Figure 12, however, the experimental values of α_i and α_f determined directly from the slopes in current transients show that the Scher-Montroll relation $\alpha_i = \alpha_f$ is not satisfied over a wide temperature range covering the glassy and supercooled liquid state, except near 10°C. Similar results are reported by Pfister and Griffiths for PVK and 3Br-PVK.[14]

Thus, the S-M theory could be applied to our material but in rather limited temperature range.

Acknowledgment

We wish to thank Dr. K. Nobugai and Mr. K. Horioka of the Institute of the Scientific and Industrial Research of Osaka University for their help in determining the crystal axis and cutting of the crystal.

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