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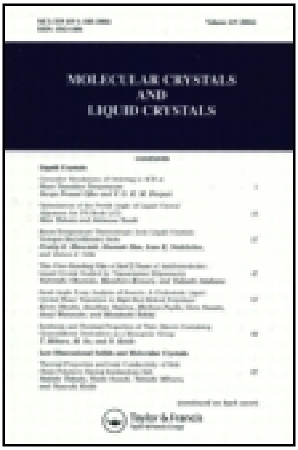

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Charge-Carrier Mobilities in Organic Molecular Solids

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Version of record first published: 06 Dec 2006.

To cite this article: Y. Maruyama (1989): Charge-Carrier Mobilities in Organic Molecular Solids, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 171:1, 287-303

To link to this article: http://dx.doi.org/10.1080/00268948908065802

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Mol. Cryst. Liq. Cryst., 1989, Vol. 171, pp. 287–303
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Charge-Carrier Mobilities in Organic Molecular Solids

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This review article is divided into following four parts. The first part is just to state rather general and essential points on the charge-carrier mobility in organic molecular solids along with a very brief historical survey of the study. The second part is to remind us the starting point or early period of the research on the charge-carrier mobilities in organic molecular crystals. The third part is to introduce later developments in this field especially for more elaborated treatments of materials, measurements, and discussions. Final part is to look over the present stage and future prospects on the subject according to many new developments in the field of molecular materials.

1. INTRODUCTION

The conductivity of a material is, in principle, determined by the amounts of charge-carriers and their mobility. In conventional organic molecular materials, both of them are usually very small, and many efforts to increase both of them have been pursued so far. Introduction of charge transfer interactions between donor and acceptor molecules are one of the most important points to improve both of them, and organic conductors or even superconductors have been developed in this line. As for single component materials, however, extensions of π-electron conjugated systems and/or introduction of external or internal pressure have been investigated to increase the mobility and conductivity. The infinitely extended π-conjugated two-dimensional system is graphite of which mobility parallel to the π-electron plane is extremely high, $\sim 10^4$ cm^2/Vsec, as expected. Conductive polymers are usually one-dimensional systems, of which mobilities have been scarcely reported, to my knowledge. They should be very high in one continuous polymer chain, but the bulk mobility is rather dominated by from chain to chain tunneling or resonance interaction, or hopping probability of charge carriers. For macromolecules the situation is similar, and the overlap integrals between molecules are in almost the same order of magnitude as the smaller molecules. Substitution of molecular edge carbon atoms by large atoms, such as sulfur or selenium, is known to be very effective for increasing intermolecular overlap or resonance integrals.

Such a relatively small intermolecular resonance interaction leads the difficulty in the coherent itinerant motion of charge carriers throughout the solid, and the electron–phonon interaction becomes crucially important for the electronic state of the solid even in zeroth order. In this sense the small polaron theory developed by Holstein[1] should be a starting point of the theoretical approach to the mobility in molecular materials. A slowly moving excess charge-carrier in a lattice would polarize the molecule or the neighboring region about the carrier in such a way that a potential well is produced about the carrier which tends to trap it at its position in the lattice. If the potential well associated with the carrier-induced distortion is sufficiently deep that a bound state is formed, the carrier will be unable to move unless accompanied by its induced lattice deformation. The unit comprising the carrier and its associated lattice distortion is called a polaron. Furthermore, if the spatial extent in which the carrier is localized is the order of the lattice spacing, the polaron is referred to as a small polaron.

The motion of a small polaron is strongly dependent on the temperature at which it is observed. At sufficiently low temperatures it can be described in terms of motion in a small-polaron band, the width of which is a decreasing function of increasing temperature since it associates with not only electronic but also vibrational overlaps.[2] Consequently, the drift mobility of carriers will increase with decreasing temperature in this temperature range, just like in band picture. At higher temperatures the band width becomes narrower and finally above a temperature which is characterized by the energy uncertainty associated with the finite life time of a carrier in a band state being of the order of the width of the small-polaron band, it is no longer appropriate to view the motion of the small polaron in terms of the band picture. In this range, the small polaron is essentially localized and it will be able to move only via thermally activated hopping through the lattice points. Thus, the drift mobility of carriers will increase exponentially (not always, however) with increasing temperature in this temperature range.

There have been known, however, no actual systems in the organic molecular materials which manifest exactly the above mentioned typical temperature dependence of carrier mobilities. The well-established results for organic molecular crystals are, as for the magnitude of the mobility μ, independent of the particular materials,

$$\mu = 1 \text{ cm}^2/\text{Vsec}$$

within an order of magnitude at room temperature, and μ is almost always weakly temperature dependent

$$\mu \propto T^{-n} \quad \text{with} \quad n = 0 - 3.$$

A complete list of mobilities in molecular organic crystals up to 1982 was presented by Schein and Brown.[3] The interesting point is, as they pointed out there, that the magnitude and temperature dependence of μ exhibit a remarkable trend independent of the particular material and such data challenges both band and hopping theories of charge transport.

The compromise of the band and hopping pictures has been an essential point to be studied since the first pioneering works for mobilities in anthracene single crystals by Le Blanc[4] in 1959, and Kepler[5] in 1960 until now. The early stage of the experimental and theoretical approach to the mobility in organic molecular crystals is described in Section 2. In nearly the end of 1970s and early in 1980s, many important developments occurred including the first measurements below 77 K by Schein *et al.*[6] which revealed a sharp change in the temperature dependence of μ at 100 K for electrons in the c' direction of naphthalene, and the observations of high mobilities at low temperature (order of magnitude 100 $cm^2/Vsec$) in durene by Burshtein and Williams[7] and perylene by Stehe and Karl,[8] which led to a new theoretical approach to the problem by Sumi,[9] and the experimental test of the proposed theory by the measurements of the electric field dependence of μ by Nakano and Maruyama,[10] and by Schein *et al.*[11] More details are presented in Section 3.

Finally in Section 4, the present stage and future prospects on the mobility and related phenomena are stated especially in relation with new materials and new concepts, such as molecular electronics.

2. EARLY STAGE OF MOBILITY MEASUREMENTS FOR ORGANIC MOLECULAR SOLIDS

a. Drift mobility measurements

An electric current density J is formulated as

$$J = ne\mu_D F$$

where n, e, μ_D, and F denote change-carrier density, elementary charge, drift mobility, and electric field, respectively. Here, $\mu_D F$ is called as drift velocity, v_D. The first direct measurement of μ_D in organic molecular crystals was carried out by LeBlanc[4] for anthracene single crystals, and at almost the same time by Kepler,[5] followed by many others.[3] The experimental method was a "time-of-flight" measurements, and it is still a standard method to measure μ_D at present. An anthracene single crystal was sandwiched between two electrodes, one of which was a 50% transparent silver film, and light pulses generated with a spark gap were impinged on the crystal through the film.[4] The resulting photoconduction transients induced by the movement of carriers which were created at the irradiated surface were displayed on a oscilloscope screen, as shown in Figure 1 (Kepler's original figure). The light source has been replaced by many kinds of short-pulse lasers and for a transparent electrode a tin-oxide coated glass or quartz (Nesa) is usually used recently. A geometrical arrangement of the electrodes in a parallel direction to the crystal surface is also now available in some cases.[12]

The almost flat part of the photocurrent in Figure 1 corresponds to constant velocity motion of carriers, and the abrupt decay point at time t_t indicates the arrival of majority of carriers to the opposite surface, so that t_t means a transit

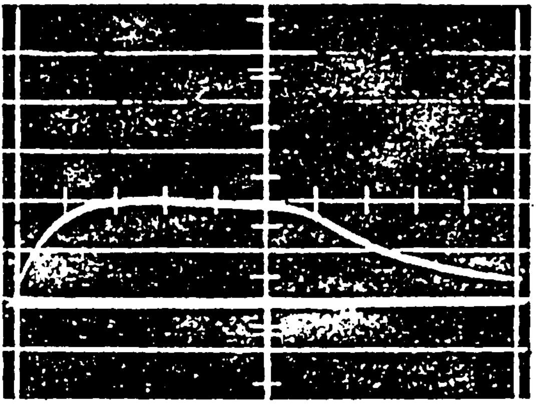

FIGURE 1 An example of the photocurrent pulses obtained by R. G. Kepler.[5] Each division on the horizontal axis represents 50 μsec.

time. t_t should vary with the applied voltage V proportionally in usual cases. With the definition of ν_D, μ_D can be evaluated by the following simple relation,

$$\mu_D = d^2/V \cdot t_t,$$

where d is the thickness of the crystal. The reported values for μ_D are summarized in Table I. A more complete list up to 1982 is in Reference 3, and the data after 1982 and some parts of the table in Reference 3 are listed in Table I.

Remarkable anisotropies in μ_D have been observed depending on the crystal and molecular structures; μ_D is usually higher in *ab* plane than in *c′* direction in a monoclinic system. Evaluation based on the overlap or resonance integral calculation was developed at first by Murrell for overlap integrals in anthracene crystals,[13] and by LeBlane for resonance or transfer integrals.[14] More elaborate calculations were carried out by Katz *et al.*,[15] and Friedman,[16] and afterwards by Silbey *et al.*,[17] taking into consideration the vibrational wavefunction overlaps between molecules. They evaluated the electron and hole band widths in each crystal direction using a tight-binding calculation, and also the anisotropy ratios of the drift mobilities for anthracene and naphthalene. Pure electronic band width was estimated to at most 0.2 eV for anthracene,[15] whereas it should be reduced to about 0.02 eV by vibronic coupling.[17] The anisotropy ratios are qualitatively corresponding with the observed values.

Pressure dependence of μ_D observed by Kepler[18] and Kajiwara *et al.*[19] is very important information to elucidate the transport mechanism. The behavior is almost correspondent with the compressibility ratio measured by Danno and Inokuchi.[20]

Other methods for μ_D measurement (e.g., space-charge-limited current method) and the corresponding results may be found in the text book.[21]

Theoretical approaches besides the band calculations mentioned above were carried out more or less based on electron–phonon coupling regime. The small

TABLE I

Charge-carrier mobilities in organic molecular solids.

	Sign of carrier	Orien- tation	Room temp. mobility (cm^2/Vsec)	$\mu \propto T^{-n}$ (n)	Temp. range (K)	References
Anthrancene	+	*a*	1.13(2)	−1.5(2)	78–300	1[a]
	+	*b*	2.07(4)	−1.5(2)	78–300	
	+	*c′*	0.73(2)	−1.5(2)	78–300	
	−	*a*	1.73(3)	−1.57	78–300	
	−	*b*	1.05(2)	−0.84	78–300	
	−	*c′*	0.39(1)	−0.16(2)	78–300	
Benzene	−	*a*	1.5 (@ 278 K)	−2.0	173–278	2[b]
Biphenyl	−	*a*	0.42	−1.0	135–300	3[c]
	−	*b*	1.25	−1.25	76–300	
	−	*c′*	0.51	−1.0	100–250	
p-Diiodbenzene	+	*a*	12.0	−0.5	250–300	4[d]
	+	*b*	4.0	0	250–350	
	+	*c*	1.7	−0.8	250–320	
Durene	+	*ab*	5.0(50 @ 120 K)	−2.5	130–300	7
	+	*c′*	0.1	−2.8	130–300	
	−	*ab*	8.0(30 @ 120 K)	−2.5	130–300	
Iodoform	+	‖6-fold axis	0.18(5)	$0.2 < n < 1$	270–340	5[e]
	+	6-fold axis	0.7(15)		270–340	
Naphthacene (Tetracene)	+	*c′*	0.85(5)	$-3 < n < -2$	300–350	6[f]
Naphthalene	+	*a*	0.90(1)(400 @ 10 K)	−2.9(1)	78–300	7[g]
	+	*b*	1.5(1)	−2.5(3)	78–300	
	+	*c′*	0.30(3)	−2.82(2)	78–300	
	−	*a*	0.65(10)	−1.52(5)	78–300	
	−	*b*	0.63(5)	exp(9 ± 1 meV/kT)	75–100	38
	−	*c′*	0.44(1)	exp(6.6 ± 0.1 meV/kT)	31–100	
				0.1(1)	100–325	
Perylene	−		2(100 @ 30 K)	−1.7	30–300	43
Phthalocyanine (β-form)	+		1.1(@ 373 K)	$-1.6 < n < -1.1$	300–630	8[h]
	−		1.2(@ 373 K)	$-1.6 < n < -1.3$	300–630	
Pyrene	+	*ab*	0.7	−1.6	260–350	9[i]
	+	*c′*	0.5	−1.3	260–350	
	−	*ab*	0.7	−1.5	260–350	
	−	*c′*	0.5	−2.0	260–350	
p-Terphenyl	−	*a*	0.34	−2.5	70–180	10[j]

				−0.5	180–300	
	−	*b*	1.2	−2.5	90–180	
				−0.7	180–300	
	−	*c*′	0.25		160–300	
	+	*c*′	0.8		160–300	
o-Terphenyl	−	*b*	3	exp(−140 meV/kT)	210–270	11[k]
TCNQ	−	(001)	0.65(10)	−1.0	210–350	12[l]
TSeC$_2$-TTF	+		1.4(2)			54
	−		1.7(3)			
TTC$_9$-TTF	+		8.7(15)			53
	−		19(4)			
TTeC$_1$-TTF	+		28.5(5)			55
	−		18.6(4)			
TTF-TCNQ			3(1)(450 @ 54 K)			46
HMTSF-TCNQ	−		4 × 10^4 @ 4 K			48
	+		1.2 × 10^4 @ 4 K	Hall Effect		
(TMTSF)$_2$PF$_6$			10^5–10^6 @ 4 K			49
Anthracene	+		−35 200			13[m]
	−		−2 50			
Polyvinyl carbazole	+		10^{-6}			14[n]
PVK:TNF	+		10^{-8}–10^{-5}			15[o]
	−		10^{-8}–10^{-6}	Polymers (Insulating)		
Polyethylene	+		10^{-10}			16[p]

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polaron theory (Yamashita and Kurosawa,[22] and Holstein[1]) was applied to anthracene crystal taking into account the acoustic lattice phonons (Glarum[23] and Glaeser and Berry[24]). Gosar and Choi[25] reported the effect of the fluctuations of the polarization energy and the transfer integrals on the excess electrons and holes motion in anthracene crystals using the Kubo linear-response theory. This theory was applied to the evaluation of the drift mobility in perylene crystals by Maruyama *et al.*[26] taking into account the fluctuation of transfer integrals and a stabilization of electron energy due to the excimer-like excess electron state. Munn and Siebrand[27] studied more explicitly the fundamental processes in carrier transport in organic molecular crystals in terms of small polaron theory. They noted that in the localized hopping mode in interaction with the intramolecular vibrational modes could be significant, and the quadratic interaction with respect to the vibrational displacement is particularly dominant.

The drift mobility in disordered solids has been an important topic in this field. In some cases it becomes difficult to define μ_D in rigorous sense, since μ_D depends on the electric field and/or the sample thickness in some disordered materials. A typical example is PVK (poly-*N*-vinyl carbazole) polymer[28] in which carrier hopping times have a wide dispersion, and it should be treated by a stochastic theory.[29] The drift mobilities of PVK systems are very low ($\leq 10^{-6}$ cm^2/v.s.) and electric field dependent ($\mu_D \propto \exp[\gamma F W^{1/2}]$).[28] In some simpler cases, e.g., evaporated amorphous organic films, observed μ_D are not so low, 10^{-1}–10^{-2} cm^2/Vsec.[30,31] Anyhow, the magnitude of μ_D in disordered materials has very wide dispersion depending on the systems, and more comprehensive studies should be carried out in this field.

b. Hall mobility measurements

Hall mobility measurements for organic semiconductors in the early stage of the research were investigated in comparison with the corresponding drift mobilities since the Hall mobility, μ_H, is more microscopic and, hence, more reflective of the electronic band structures. The transit time in μ_D measurement may involve a mean trap-residence time and a mean trapping time in the presence of shallow traps, and hence the observed μ_D might not always correspond with the microscopic mobility. On the other hand, the Hall mobility could ignore any trapping effect the carries might undergo, and give only the intrinsic mobility. Moreover, the sign, temperature dependence and magnitude of Hall mobilities could provide more direct clues for the mechanism of carrier transport. The Hall effect in the regime of hopping conduction is still in challenging situation, and Freedman and Holstein,[32] and Munn and Siebrand[33] explored the problem from the theoretical point of view.

Dark conductivities of conventional organic semiconductors are usually so low to measure a reliable Hall signal that almost measurements were tried by photo-Hall effect technique. The large inconsistency, however, exists in the reported μ_H of anthracene, ranging from 0.8 to 200 cm^2/Vsec.[34] μ_H reported so far are listed in Table I including more recent results for charge transfer complexes.

As another example for the measurement of microscopic mobility of anthracene, Burland reported a mobility larger than 10^4 cm^2/Vsec at 2 K as the results of a cyctron resonance observation.[35] Although the difficulty in reproducibility of the experiment was claimed,[36] this result will become important in relation to the band-type transport at low temperatures as was discussed afterwards.

3. SECOND STAGE OF MOBILITY MEASUREMENTS FOR ORGANIC SEMICONDUCTORS

In the later half of 1970s many new developments on the μ_D measurements occurred especially for the temperature dependence around and below 77 K. Such wide temperature range behaviors induced more explicit theoretical discussions on the charge-carrier transport mechanism in organic semiconductors.

a. 'New' experimental results

Burshtein and Williams[37] reported very high mobilities in durene single crystals; i.e., they found that in the *ab* plane hole and electron mobilities are 5 cm^2/Vsec and 8 cm^2/Vsec, respectively, at room temperature, and both increase to around 60 cm^2/Vsec at 120 K. The temperature dependences were a $T^{-2.5}$ in *ab* plane and a $T^{-2.8}$ in c' direction, respectively, and thus, they claimed that charge-carrier transport in durene can be treated within the frame of the band model.

Schein[37] pointed out a common feature in the drift mobilities of "layer" type molecular solids irrespective of organic or inorganic. The drift mobilities in the perpendicular direction to the layer are about 1 cm^2/Vsec in the magnitude and very weakly dependent on temperature in fairly wide range, and he claimed that the observed temperature dependence is inconsistent with the temperature dependence predicted by narrow-band theory and the charge-carriers should be regarded as localized, whereas conventional hopping theory cannot explain it satisfactorily. Such almost-temperature-independent *electron* mobility over wide temperature ranges was observed for anthracene (c'-direction), deuterated anthracene (c'), naphthalene (b and c'-direction), deuterated naphthalene (c'), and As_2S_3 (perpendicular direction to layers).[37,38] In these directions the bandwidths are expected to be particularly small ($\approx$1–10 meV) compared with those in other directions.

Furthermore, Schein *et al.*[6] discovered that the mobility of electrons in the c' direction of naphthalene rises abruptly as the temperature decreases below 100 K as shown in Figure 2. Subsequently, the same behavior was found in the b direction of naphthalene and in c' direction of deuterated naphthalene.[38] They attributed the rising mobility with decreasing temperature to scattering by optical phonons of electrons in Bloch-type extended states. Such a band-type mechanism leads to an exponential mobility with an exponent equal to a phonon energy divided by k_BT, and this was the observed behavior. Above 100 K, however, another mechanism, i.e., a hopping-type transport, should limit the mobility, even though, as Schein *et al.* remarked,[6,37] existing analyses based on a hopping regime appear to be inadequate to explain the observed failure of the mobility to depend on the temperature and the electric field. So, they claimed the observed behavior as the band-hopping transition.[39]

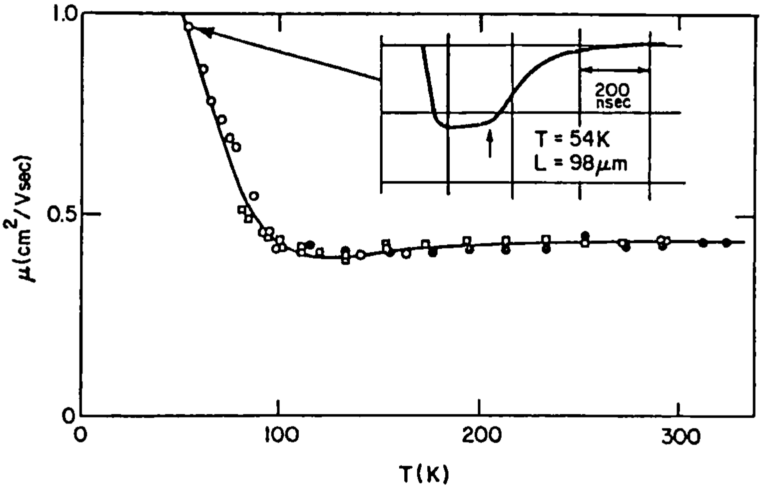

FIGURE 2 The mobility of electrons in the c' direction of naphthalene from 54–324 K observed by L. B. Schein *et al.*[6] At low temperatures the mobility is exponentially increasing with temperature. The different symbols represent measurement on different samples. A "current" mode pulse at 54 K with the transit time marked by an arrow is shown in the insert.

Sumi[9] developed a more comprehensive theory for the almost-temperature-independent (at higher temperature) and steeply-rising (below 100 K) mobility. He pointed out that the intermolecular overlap in c' direction is not necessarily small but the resonance integral terms with different signs are almost cancelled out. So the resultant small resonance integral value is very sensitively changed to the orientation of molecules, and consequently the rotational vibrations of molecules are very effective for the carrier transport. According to his model the transfer integral of electron in the c' direction is expressed by the sum of the term J of the rigid lattice and the term induced by the rotational vibrations[9];

$$J_{m,n} = J + (1/2\gamma\hbar\omega_2)^{1/2}(c_m + c_m^+ - c_n - c_n^+) \qquad (1)$$

where c_m and c_m^+ represent the annihilation and creation operators for the rotational vibration at the lattice site m, respectively, and its energy is denoted by $\hbar\omega_2$. The sites m and n are a pair of nearest neighbors in the c' direction. There are two hopping processes; one is due to J of the Equation (1) which conserves the momentum component along the *ab* plane, and the other is due to the second term of (1), *i.e.*, the phonon induced term in which electron can hop to every momentum state uniformly. Thus, the electron mobility in the c' direction is composed of two terms which are derived from each transition probability corresponding to two terms of Equation (1). Sumi showed, through the explicit calculation, that the almost-temperature-independent mobility is ascribed to diffusive electron hopping induced by lattice distortions in the course of lattice vibrations (the second term in (1)), and the steep rise of the mobility below 100 K is ascribed to the increasing contribution of the mobility component (the first term in (1)) determined by the electron transfer of the rigid lattice at low temperatures.[9]

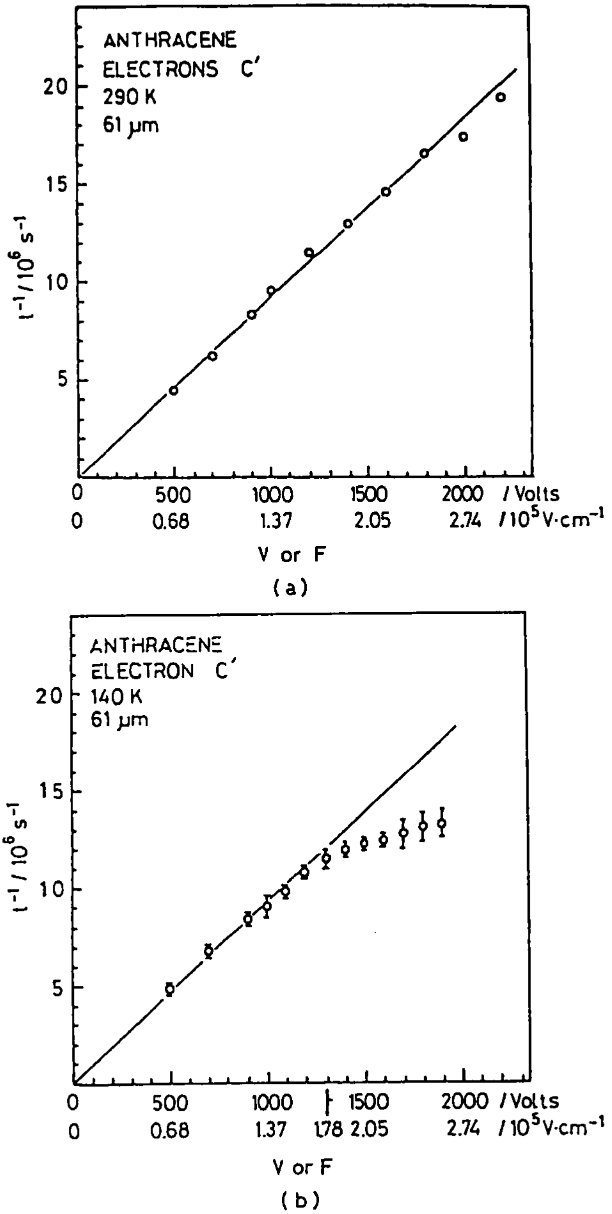

FIGURE 3 Electric-field dependence of the inverse transit-time observed by S. Nakano and Y. Maruyama.[10] (a) at 290 K and (b) at 140 K.

Furthermore, Sumi predicted as the consequence of his model that for $k_BT < \hbar\omega_2$ the drift velocity in the c' direction should become saturated with electric field, F, when the consequent energy difference, eFa, between neighboring ab planes exceeds $\hbar\omega_2$.[39] Thus, the electric field dependence of the c' mobility becomes a critical test for the proposed model by Sumi. Schein and McGhie[40] demonstrated

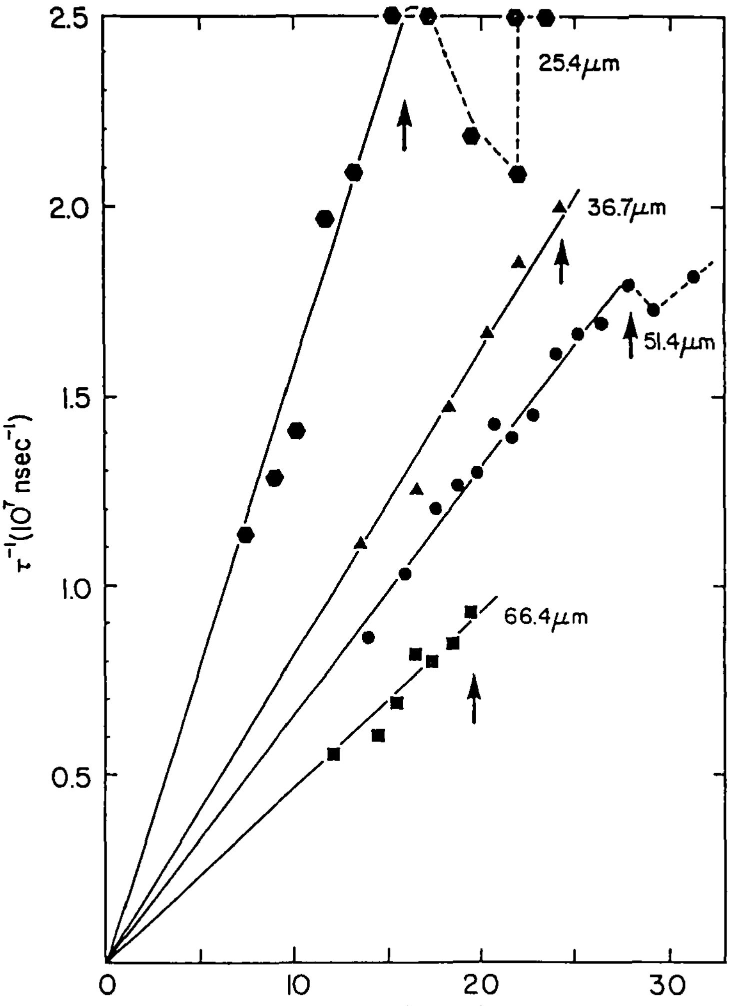

FIGURE 4 The inverse transit time versus applied electric field at a temperature of 140 K (by L. B. Schein *et al.*[41]). The crystal thickness is indicated on each curve. An arrow on each curve indicates the field at which departure from linearity is observed.

that the electron drift velocities in the c' direction of anthracene and naphthalene are directly proportional to electric field up to 1.6×10^5 V/cm at 100 K. Nakano and Maruyama[10] extended the electric field up to 3.0×10^5 V/cm, and found out a distinct saturation behavior of the c' velocity in anthracene above the electric field of 1.8×10^5 V/cm at 140 K (Figure 3). Schein *et al.*[41] carried out a similar experiment using very thin sublimation flakes instead of polished melt-grown crystals, and claimed that the electron drift mobility in the c' direction of anthracene is independent of the electric field up to 2.8×10^5 V/cm at 140 K (Figure 4), and consequently these data can never be explained within the frame of Sumi's theory.

The controversial point has not become clear yet (*mizukake-ron* in Japanese), and still now it has been left as an unresolved problem to be challenged.

Other charge transport high field measurements along crystal directions in which band transport is believed to be the dominant mode of charge carrier motion have recently been carried out by Karl's group for naphthalene[42] and perylene.[43] Karl succeeded in preparation of ultra pure materials by a very elaborated technique,[43] which led to the observation of very high mobilities at low temperatures. In the low temperature range the charge carrier transport becomes nonlinear (sub-Ohmic) with the carrier velocity tending to saturate with increasing electric field. The highest μ_{aa} (hole) for naphthalene was 400 cm²/Vsec at 10 K and 3 KV/cm (Figure 5) and

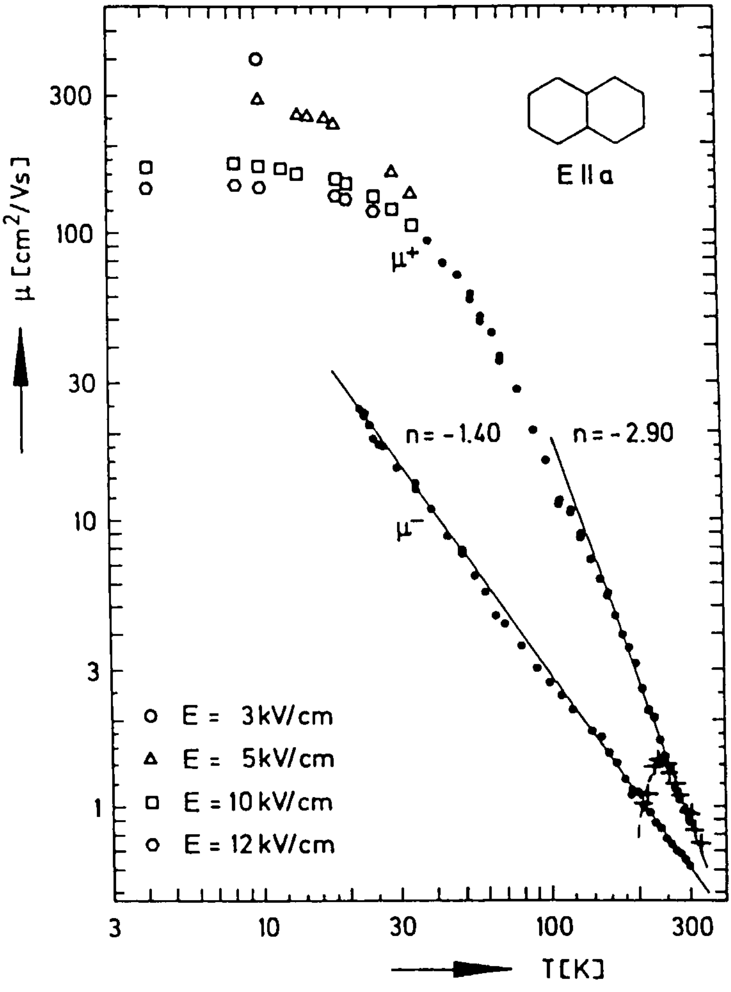

FIGURE 5 Electron and hole mobilities in naphthalene for the electric field *F* parallel to the *a* axis, for different field strengths (marked by different symbols) between 3 and 12 KV/cm (after N. Karl *et al.*[42]).

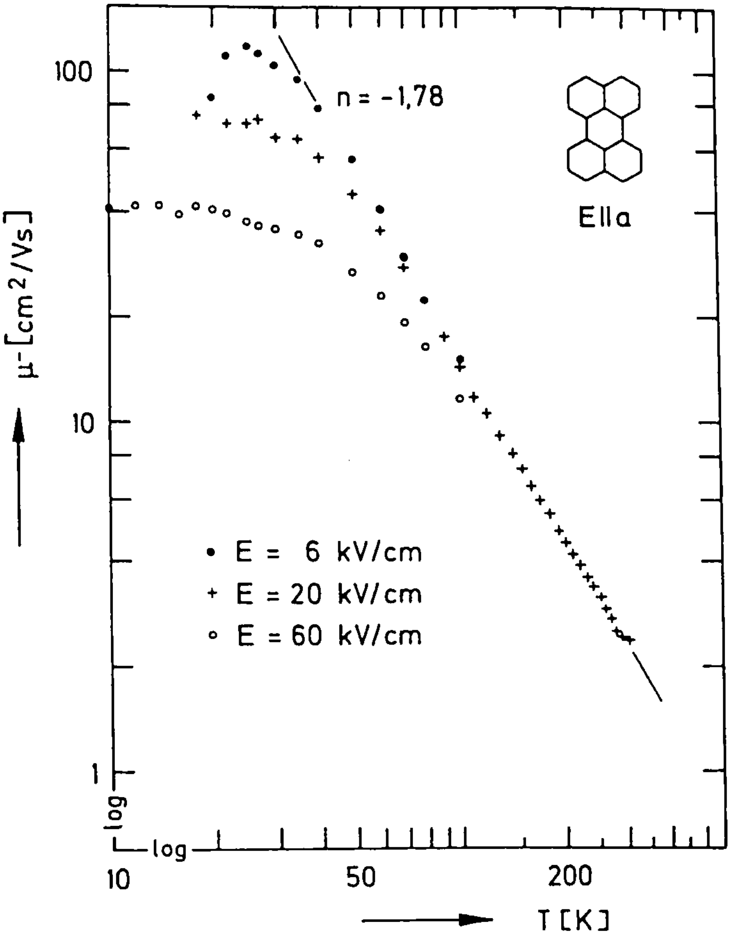

FIGURE 6 Electron mobilities in perylene for the electric field F parallel to the a axis for different field strengths (marked by different symbols) between 6 and 60 KV/cm (after N. Karl *et al.*[43]).

μ_{aa} (electron) and $\mu_{c'c'}$ (electron) for perylene were 100 cm²/Vsec at 30 K and 6 KV/cm (Figure 6). It was shown[42] that the low-temperature results can be understood in terms of a standard band-model description, and the strong non-Ohmic behavior of drift velocities in these substances closely resembles the observations which were reported before for conventional inorganic semiconductors and explained as hot carrier effects.[44] Karl *et al.*[43] also demonstrated how sensitive mobilities are to deep traps by comparing their best results with those of less purified crystals, and claimed that the extensive purification procedures are crucially important to discuss on microscopic mobilities of organic molecular substances especially at low-temperatures.

It should be noted here that a very comprehensive compilation of relevant numerical data and functional relationships for typical organic materials including the charge carrier mobilities was issued by Karl in 1985 in a New Series of Landolt-Börnstein.[45]

4. PRESENT STATUS AND FUTURE PROSPECTS OF CHARGE CARRIER MOBILITIES IN ORGANIC MOLECULAR SOLIDS

It is a quite difficult work to survey the problems included in this title in general way, so in this section the description is rather focused only on the topics of the author's personal concerns.

a. Charge-carrier mobilities in organic conductors

The recent most remarkable development in the field of organic semiconductor was the discovery of organic conductors and superconductors. The interesting point is that the inherent molecular nature is still remaining even in organic metals, and the low-dimensional instability of the electronic structure is caused by the narrow and anisotropic electronic band for itinerancy and the strong electron–phonon coupling together with the large electron correlation energy. Consequently, the mobilities in organic metals usually have large anisotropy, and can be estimated by dark conductivity measurements and, more rigorously, by magnetoresistance or Hall effect measurements.

The sum of the electron and hole mobilities of the first organic metal TTF-TCNQ was estimated to be 3 ± 1 cm^2/Vsec at room temperature and 300–450 cm^2/Vsec at 58 K simply from the charge transfer rate, $\rho = 0.59$, and the conductivity.[46] The temperature dependence of the mobilities was also calculated by assuming proper phonon scattering characteristic to metallic transport.[46] Magnetoresistance of TTF-TCNQ was also tried for the metallic and semiconducting region.[47] The Hall effect in HMTSF-TCNQ was carried out in metallic and semi-metallic region, and with combining the magnetoresistance measurement the mobilities of electrons and holes were obtained to 4×10^4 and 1.2×10^4 cm^2/Vsec at 4 K, respectively.[48] The similar measurements were carried out for the first organic superconductor $(\mathrm{TMTSF})_2\mathrm{PF}_6$ under high pressure.[49] Observed Hall mobility was in the order of 10^5–10^6 cm^2/V sec at 4 K, and the angular dependence of the Shubnikov-de Haas oscillations under high magnetic field indicated the two-dimensional character of the Fermi surface. Such Shubnikov-de Haas oscillations were also observed in the novel organic superconductor $(\mathrm{BEDT\text{-}TTF})_2\mathrm{Cu(NCS)}_2$.[50] Anyway, rather conventional theories for metals (not always simple) could be applied for the understanding of the electronic behaviors, or mobilities, in these organic conductors with very high conductivities. Anisotropic mobilities or low dimensionality would be the most important character in higher T_c ($T_c > 11$ K) organic superconductors in future.

b. Molecular fastener effect

Charge-carrier mobilities in organic solids are usually increased by applying external pressure.[18,19] The effect is caused by the broadening of the electronic band width due to the increase of the intermolecular interactions. Not only the external pressure but also internal pressure should be effective for this effect. Inokuchi *et al.* discovered this internal pressure effect for conductivity and/or mobility, and named it as a "Molecular Fastener Effect."[51] In the study on the electrical conductivities of TTC$_n$-TTF (tetrathiotetra-alkyl (n)-TTF: $n = 1-18$) compounds, they found out the clear n dependence of the resistivities in which the resistivities monotonously decrease as the n increases until $n \simeq 10$ and become almost constant beyond $\sim$10.[51,52] The TTF moiety planes of the molecules are aligned in one-dimensional columns in the crystals and the interplane distances (or the shortest distance between sulfur atoms of nearest neighbor moieties) become shorter corresponding to the increase of n (at least $n \leq 10$). They ascribed the cause of these phenomena to the increasing van der Waals interaction between long alkyl chains in each side between molecules.

Mobility measurements for the system are still inadequate to confirm the molecular fastener effect. Only for TTC$_9$–TTF needle-like crystals, the drift mobilities were observed at room temperature by using surface-type time-of-flight method,[12] and they are found to be quite high compared with ordinary values of organic molecular crystals, i.e., $\mu_{\text{hole}} = 8.7 \pm 1.5$ and $\mu_{\text{electron}} = 19 \pm 4$ cm^2/Vsec, respectively.[53] For a little different systems, i.e., TSeC$_n$-TTF and TTeC$_n$-TTF where sulfur atoms in TTC$_n$-TTF are replaced by selenium or tellurium atoms respectively, the drift mobilities of TSeC$_2$-TTF and TTeC$_1$-TTF were measured. In these two systems, the chalcogen atom contribution to the intermolecular interactions becomes more important compared with that of TTC$_n$-TTF especially for small n compounds and for tellurium compounds. $\mu_{\text{hole}} = 1.4 \pm 0.2$ and $\mu_{\text{electron}} = 1.7 \pm 0.3$ cm^2/Vsec for TSeC$_2$-TTF,[53] and $\mu_{\text{hole}} = 28.5 \pm 0.5$ and $\mu_{\text{electron}} = 18.6 \pm 0.4$ cm^2/Vsec for TTeC$_1$-TTF[54] were reported respectively. In the former compound, the resistivity is rather high and the crystal structure is unfavorable to strong intermolecular interaction,[54] and on the contrary in the latter the resistivity is very low (8.1×10^4 Ωcm) and there exists the strong intermolecular interaction through the one-dimensionally aligned tellurium atoms chains.[55] The high mobility observed in TTeC$_1$–TTF is not due to the molecular fastener effect but to intermediate —Te—Te— interaction between van der Waals' and covalent bonding. It is very important to introduce a new type of intermolecular interaction to improve the small mobility in organic molecular solids.

c. Molecular devices or electronics

Recently "Molecular Devices" or "Molecular Electronics" is expected to play an important role in the high technology of a next generation. In molecular devices, anyhow, each molecule should have some useful functions which could be available as the macroscopic functions as well. Thus, such functions or informations should be transferred through molecules or stored in some regions, and the mobility (not always of charge-carrier) should be very high or very low. So, the control of the mobility is essentially important for realizing any molecular devices.

In the field of inorganic semiconductor devices, modulation doping for a superlattice, such as GaAs–GaAlAs heterojunctions, was applied to fabricate a high electron mobility transistor (HEMT).[56] The essential point is to separate the hole conduction layer and the electron conduction layer by superlattice fabrication technique. A similar application could be attempted for organic systems. Alternate deposition of donor and acceptor thin layers may be a novel system not only in the sense of the high mobility but also the new material development. For the first step to such systems, Maruyama *et al.* have been trying to prepare ultra thin well-oriented organic films.[57]

Hydrogen-bonded charge transfer systems should also be explored in the field of molecular devices. Proton motion in such systems could be regarded as a switch or a memory element, and consequently the systems may act as a regulator or gate, or a information storage. More fundamental approach to such systems may lead to exotic electron–phonon coupling systems, and the correlated tunneling motion of protons should be noted as a most important key in such systems. More details about this problem is discussed in this Proceedings by Mitani.[58]

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