

Temperature independent drift mobility along the molecular direction of As_2S_3

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Electron drift mobilities have been observed in As_2S_3 crystals along the molecular direction by transient photoconductivity techniques. The mobility is $1.0 \text{ cm}^2/\text{V sec}$, independent of temperature from 207 to 465 K. This result is consistent with a trend among inorganic and organic molecular crystals, all of which have drift mobilities on the order of $1.0 \text{ cm}^2/\text{V sec}$ (within an order of magnitude) and weak temperature dependence. It is argued that the observed temperature dependence of the mobility appears to be inconsistent with the temperature dependence predicted by narrow-band theory. This result is in agreement with, and more general than, standard arguments used against band theory in molecular crystals which depend on a comparison between the intermolecular spacing and the mean free path based on calculated bandwidths, and reinforces the view that the charge carriers should be regarded as localized.

I. INTRODUCTION

The direct determination of microscopic drift mobilities in high-resistivity materials became experimentally accessible with the introduction of transient photoconductivity techniques by LeBlanc,¹ Kepler,² and Spear.³ Since then data have accumulated¹⁻⁴⁵ which suggest that for relatively pure organic and inorganic molecular crystals a remarkable trend exists (see Table I): Independent of the particular material the drift mobility μ is

$$\mu \approx 1 \text{ cm}^2/\text{V sec} \quad (1)$$

within an order of magnitude, and μ is weakly temperature T dependent

$$\mu \propto T^{-n} \quad \text{with } n \approx 1. \quad (2)$$

Such data remain to be understood in terms of a microscopic theory of charge transport.

Attempts to explain these data have been formulated in terms of band theories, in which the electrons interact weakly with the lattice resulting in mean free paths much larger than the lattice constant, and hopping theories in which the hop distance is comparable to the intermolecular spacing. The difficulties that arise in attempts to make these theories consistent with the data appear to be related to the fact that the observed mobilities are extremely close to the theoretically estimated⁴⁹⁻⁵¹ borderline value of μ between band and hopping theories, $1 \text{ cm}^2/\text{V sec}$. For example, in anthracene the application of band theory⁵²⁻⁵⁵ led to an inconsistency: Given the magnitude of μ and calculated values of the bandwidths (0.1 eV), the resulting mean free path λ [using the expression for μ from tight-binding theory, Eq. (14)] is approximately equal to the intermolecular spacing a , inconsistent with the assumed weak-scattering formulation inherent in a band theory.

This inconsistency led to serious consideration of hopping theories.⁵⁵⁻⁶² However, hopping theories generally predict activated temperature dependence at room temperature,⁵⁷⁻⁶² and estimates of the activation energy suggest it should be large with respect to kT at $T = 300 \text{ K}$. (The activation energy for small polaron hopping⁵⁸ under appropriate conditions is half the polaron binding energy E_p , which occurs only for $E_p \gg W$, where W is the bandwidth, estimated in anthracene to be 0.1 eV.) More recent attempts at explaining the data with hopping theories which assume quadratic electron-phonon coupling⁶² have been unsuccessful in explaining the observed T^{-n} temperature dependence and have predicted hopping mobilities at least an order of magnitude too small. And no attempt has been made using any of the available hopping theories to explain the trend apparent in Table I.

Perhaps the weakest link in the above logic is the elimination of band theories based on the magnitude of calculated bandwidths. An error of a factor of 5 would satisfy the necessary inequality $\lambda \gg a$; indeed, early calculations⁵² of the bandwidth were an order of magnitude lower than the presently accepted ones (0.01 eV versus 0.1 eV) leading to the conclusion that band theory was acceptable. With due respect for the care with which these calculations were done, it is worth recalling⁶³ that first-principles calculations of band-structure features such as bandgaps and bandwidths even in germanium and silicon were in error by factors of at least 2; it was only with the introduction of semiempirical techniques, where some of the parameters were determined from experimental data, that agreement for other parameters (effective masses) within 20% was achieved. An additional difficulty is that while bandwidths and bandgaps can usually be determined experimentally (by optical measurements) in semiconductors, the

TABLE I. Mobilities of molecular crystals.^a

Crystal	Carrier	Orientation	μ (cm ² /V sec) ($T=300$ K)	$\mu \propto T^n$ n	Range (°K)	Reference
Benzene	-	A	1.5 ($T=5$ °C)	-2.0	173-278	4
Naphthalene	-	A	0.51	-0.1	220-300	5-7
	-	B	0.63	0	220-300	
	-	C'	0.68	-0.9	220-300	
	+	A	0.88	-1.0	220-300	
	+	B	1.41	-0.8	220-300	
	+	C'	0.5, 0.99	-2.1	220-300	
Anthracene ^{1,2,8-21}	-	A	1.6	-1.0	77-300	8, 11
	-	B	1.0	-0.2, -0.6	170-380	11, 12
	-	C'	0.4	+0.8, 0	80-450	8, 11, 16, 21
	+	A	1.2	-1.0	300-400	2, 29
	+	B	2.0	-1.0	300-400	12, 16
	+	C'	0.8	-1.0	170-450	9, 12, 16, 21
Perdeuterated anthracene	-	A	1.7	-1.8	280-400	22
	-	B	0.99	-1.4	280-400	
	-	C'	0.35	0	280-400	
	+	A	1.1	-1.7	280-400	
	+	B	2.0	-1.4	280-400	
	+	C'	0.78	-1.0	280-400	
Pyrene	-	A-B	0.7	-1.5	260-350	23, 24
	-	C'	0.5	-2.0	260-350	
	+	A-B	0.7	-1.6	260-350	
	+	C'	0.5	-1.3	260-350	
Tetracyanoquinodimethane (TCNQ)	-	$\perp(001)$	0.4	0	204-306	25
	+	$\perp(001)$	0.4	0	204-306	
N-isopropyl carbazole	-	C	1.0	0	244-370	26
<i>p</i> -diiodobenzene	+	A	12	-0.5	240-310	27
	+	B	4	0	240-310	
	+	C	2	-0.8	240-310	
β -Phthalocyanine	+	C	1.1	-1.3	290-600	28
	-	C	1.4	-1.5	290-600	
Phenazine	-	A	0.29	0	180-360	29
	-	B	1.1	-0.65	230-360	
	-	C'	0.5	-0.1	230-360	
1,4 dibromonaphthalene	-	A	0.017	≈ -2	270-300	29, 30
	-	B	0.013	≈ -2	270-300	
	-	C'	0.034	≈ -2	270-300	
	+	A	0.66	≈ -2	270-300	
	+	B	0.25	≈ -2	270-300	
	+	C'	0.87	≈ -2	270-300	
Azulene	-		0.15	0	220-360	31
Phenothiazine	-	in cleav. plane	1.7	-3	300-350	29
	+	\perp to plane	5.0	-3	300-400	
Se ₈ (Monoclinic)	-	$\perp(101)$	2	-1.5	300-400	32
S ₈	-	all	10 ⁻⁴	exp (-0.17/ kT)	220-413	33, 34
	+	$\perp(111)$	10	-1.5	300-400	

TABLE I. (Continued)

Crystal	Carrier	Orientation	μ (cm ² /V sec) ($T=300$ K)	$\mu \propto T^n$ n	Range (°K)	Reference
As ₄ S ₄	+	$\perp(010)$	12	-2.5	280-400	35
I	+	B	0.7	-1.2	230-340	36
As ₂ S ₃	-	\perp to layers	1.0	0	207-465	
β -N ₂	-		1.7×10^{-3} (36 K)	exp (-0.007/ kT)	36-67	37
γ -O ₂	+		2.3×10^{-3} (43 K)	exp (-0.014/ kT)	43-55	37

^aMeasured microscopic mobilities (by time of flight measurement) for organic and inorganic molecular crystals, including the carrier sign (electrons or holes), orientation in the crystal, room-temperature mobility, temperature dependence of μ , the temperature range over which the temperature dependence was determined, and references. Inspection of this table reveals the following trend: independent of the particular material, $\mu \approx 1$ cm²/V sec (within an order of magnitude) and μ is weakly temperature dependent. The only exception is electrons in S₈ for which the observed experimental temperature dependence was demonstrated to be an intrinsic property, independent of impurities. Spear³³ has suggested this may be an example of small polaron motion. Electrons in N₂ and holes in O₂ may also be exceptions if the exponential temperature dependence is confirmed to be an intrinsic property of the crystals. Recently, measurements on solid H₂ have been reported.³⁷ Excluded from this table are those measurements of the drift mobility which were demonstrated to be determined by impurities (holes in Se₈,³² *n*-terphenyl,³⁵ phenanthrene,³⁹ rubrene,⁴⁰ and holes in As₂S₃), or measurements in which the temperature dependence or the impurity dependence was not determined, making it impossible to determine whether the microscopic mobility has been observed (stilbene,⁴¹ *m*-terphenyl,⁴¹ ferrocene,⁴² triphenylamine,⁴² trans-stilbene,⁴² tetracene,^{43,44} violanthrene,⁴⁵ electrons in³⁵ As₄S₄). Rare-gas solids,⁴⁶⁻⁴⁸ which are not molecular, are also excluded.

situation is different in molecular crystals.⁶⁴ Here exciton effects are strong (exciton binding energies are approximately half the one-electron "bandgap") resulting in optical absorption curves dominated by the effects of electron-electron interactions and phonon emission and absorption. In fact, the "conduction band" has not been identified definitively in any molecular crystal by optical measurements. Only internal-photoemission measurements have been used⁶⁵ to determine bandwidths in molecular crystals; however, doubts have been expressed concerning the interpretation of these measurements.⁶⁶ Recent reviews of the subject of charge transport in molecular solids and more detailed discussions of these points are available.^{29,67}

The purpose of this paper is twofold. First, data on the temperature dependence of the drift mobility in a layered crystal As₂S₃ in its molecular direction (perpendicular to the layers) are presented. Second, it is argued that the observed weak temperature dependence appears to be inconsistent with the predictions of narrow band theory using a single (or a combination of) scattering mechanism. These arguments are more general than and complement the standard arguments against the band-theory approach for molec-

ular crystals. Therefore, we strengthen the case against the band-theory approach to charge transport in molecular crystals and bring together for the first time the predictions of the temperature dependence of various scattering mechanisms in the narrow-band approximation (bandwidth less than kT where k is the Boltzmann constant).

Previous work^{68,69} on As₂S₃ has revealed that it has a relatively large, electric-field-dependent quantum efficiency for photogeneration, between 0.1 and 1.0. ac conductivity,⁷⁰ photoemission,⁷¹ photoluminescence,⁷¹ x-ray photoemission,⁷² and infrared⁷³ measurements have been made on single-crystal As₂S₃. As₂S₃ is a layered compound, molecular in one dimension and covalent in two dimensions.⁶⁹ It has been suggested that the anisotropic mechanical properties of layered crystals should be reflected in their electrical properties.⁷⁴ Studies⁷⁵ of transport properties of layered crystals within the layers have produced evidence for normal semiconductor behavior. Only recently have mobility measurements been made on this class of materials perpendicular to the layers.^{75,76} The results ($\mu \gg 1$ cm²/V sec) surprisingly again suggest semiconductor behavior. Therefore, the transport measurements reported here on As₂S₃ crystals ($\mu \approx 1$ cm²/V sec) represent the first lay-

ered crystal to exhibit transport behavior perpendicular to the layers like a molecular crystal, e.g., $\mu \approx 1 \text{ cm}^2/\text{V sec}$.

II. EXPERIMENTAL PROCEDURE

The technique used for determining the drift mobility is the standard^{77,78} transient photoconductivity experiment, see Fig. 1. The sample is provided with electrodes and is the capacitor in an RC circuit. A short (with respect to the transit time) flash of highly absorbed light photogenerates a sheet of charge carriers which drift across the sample in the applied voltage V in a time τ

$$\tau = L/\mu E = L^2/\mu V, \quad (3)$$

where L is the sample thickness and E is the electric field (V/L).

This experiment requires a pulsed source of highly absorbed light and appropriately fast electronics. The light source used in these experiments was a 20-nsec, 2650-Å light from a quadrupled Nd:glass laser, Holobeam model 331. The electronic equipment consisted of a Tektronic oscilloscope model 547 and a Polaroid camera for recording the transient signals. Since the absorption coefficient⁶⁹ of As_2S_3 at 2650 Å is approximately 10^5 cm^{-1} , most of the light is absorbed within 10^3 Å of the surface.

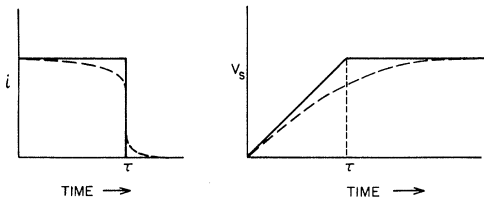
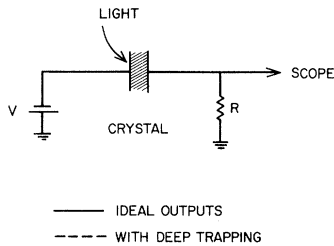


FIG. 1. Schematic of the experiment and "current" and "voltage" mode outputs with and without deep-trapping effects. A short light flash photogenerates a sheet of carriers which drifts across the sample in time τ . The current mode measures the current flowing in the capacitor, constant until time τ , zero afterwards. The voltage mode measures the change in voltage across the capacitor, a ramp function.

Deviations from the ideal behavior shown in Fig. 1 can be due to several sources (e.g., the light pulse not short compared to the transit time, space charge limited behavior⁷⁹) but the most serious problem (for these crystals) was carrier lifetime effects. A carrier is deep trapped if it can no longer contribute to the measured current, i.e., if the release time from the trap is large compared to τ . As electron release times (in a band model) are exponential in the energy depth of the trap below the conduction band and more than one trap level can exist, one would expect the deep-trapping lifetime to monotonically decrease as the temperature is lowered. In the absence of deep trapping the current flowing in the sample is

$$i = N/\tau, \quad t < \tau, \quad (4)$$

where N is the number of carriers photogenerated per cm^2 . Deep trapping reduces N exponentially with time constant τ_d

$$i = (N/\tau)e^{-t/\tau_d}, \quad t < \tau \quad (5)$$

and the voltage across the sample V_s is

$$V_s = \frac{1}{C} \int i dt = \frac{N}{C} \frac{\tau_d}{\tau} (1 - e^{-t/\tau_d}), \quad t < \tau; \quad (6)$$

both the current and voltage mode curves merge into exponentials (Fig. 1) and the asymptote of a plot of (estimated transit time)⁻¹ versus the applied voltage V is the deep-trapping lifetime at $V=0$ (Fig. 2). To reduce field distortion due to these trapped carriers the front and rear electrodes were shorted between each measurement and several light pulses were flashed on the sample causing generated charge to neutralize trapped space charge.

Blocking electrodes are necessary for these measurements. In this work several kinds of electrodes were used and tested by the following criteria: In the absence of field distortion and deep trapping, the "current" mode should approach

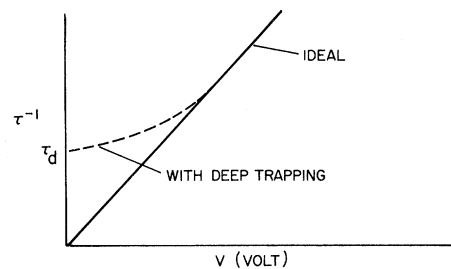


FIG. 2. With no deep trapping in inverse transit time τ^{-1} is linear in the applied potential V . With deep trapping the asymptote of the curve is the deep-trapping lifetime at $V=0$.

the ideal curve shape, rectangular in shape, and the same results should be obtainable for different electrodes. Such curves were approximately observed, as shown in Fig. 3, along with the corresponding voltage mode ramp. Identical values for μ were obtained for a variety of ionic electrodes, 0.1 and 1 M NaCl aqueous⁸¹ electrodes, methanol saturated with NaCl, as well as evaporated (≈ 300 - \AA thick) Au-Au electrodes. Au-A electrodes gave unreproducible results.

The crystals were cleaved by touching an edge of the crystal with Scotch tape and gently removing a layer, usually 5–15- μm thick. The thickness was determined interferometrically as follows⁷²: The optic axis was aligned along a linear polarizer by observing extinction with the crystal between two linear polarizers. Then the wavelength λ_i spacing between the N_i th and N_{i+1} th peak in absorption (using a model 14 Cary spectrometer) caused by constructive interference between light waves reflected from the front and back face which is given by

$$N_i \lambda_i = 2L\alpha, \tag{7}$$

where α is the (wavelength-dependent) index of refraction (available from Ref. 80), was used to calculate L . This technique allowed determination of L within 0.1 μm , the limitation being the value of L determined along the two different crystal axes.

No attempt was made to study the electric field or temperature dependence of the quantum efficiency, although it was qualitatively consistent with the Onsager model.^{68, 82–85}

The temperature was varied by placing the sample in a Satham SD14 temperature chamber with an added quartz window for optical access and the

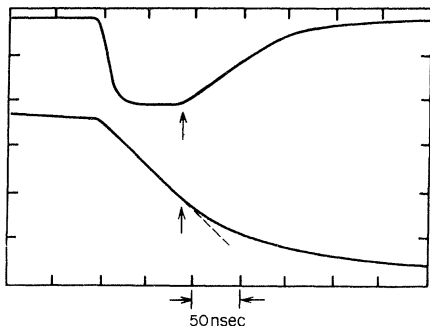


FIG. 3. "Current" and "voltage" mode data on As_2S_3 for electron motion with Au contacts. The applied voltage was 10 V across the 11- μm -thick sample. The time constant for the initial rise of the current mode is due to the duration of the light pulse; the fall of the current suggests some dispersion of the sheet of photogenerated charges is occurring. The transit time, marked by the arrow, can be determined with $\pm 10\%$.

temperature was monitored with a chromel-constantan thermocouple. The samples were checked for any evidence of amorphousness (there was none) and for impurity content by optical emission spectroscopy via a dc arc. The impurities present in the samples were Si, Sb, and Bi. Only in those samples in which the Sb (Si) impurity concentration was less than 10 ppm could electron (hole) transit times be observed, suggesting the Sb impurity may be associated with the electron deep traps and the Si impurity may be associated with the hole deep traps.

III. EXPERIMENTAL RESULTS

Shown in Fig. 4 are data of the inverse transit time τ^{-1} versus the applied potential V . According to Eq. (1), the curve should be linear under ideal conditions with a slope equal to μ/L^2 . Linearity is observed at high V indicating a field-independent mobility. At low V , the curves asymptotically approach a finite time, the deep trapping lifetime, as expected (see Fig. 2), which is temperature dependent. It is also clear that within experimental error there is no dependence of μ on temperature (for clarity data taken at only a few temperatures

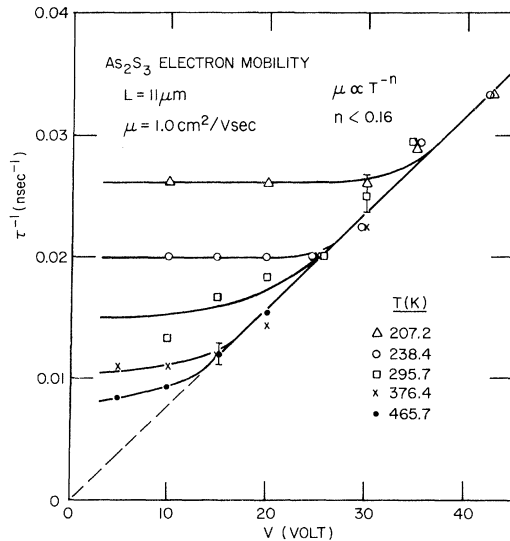


FIG. 4. Inverse transit time for electrons vs the applied voltage for an 11- μm -thick sample, with temperature as a parameter (same sample used for Fig. 3). At high V the inverse transit time is linear in V giving a temperature-independent drift mobility within experimental error. At low V the curves asymptotically approach the deep-trapping lifetime which is temperature dependent, decreasing as T decreases. The applied voltage was purposely kept as small as possible (consistent with obtaining μ) to avoid catastrophic dielectric breakdown.

are shown). Fitting μ to a functional form of

$$\mu \propto T^{-n} \quad (8)$$

the data of Fig. 4 give $n < 0.16$, given the experimental error in determining τ . The value of μ of approximately $1 \text{ cm}^2/\text{Vsec}$ is in excellent agreement with previous⁸⁶ room-temperature measurements. This result was reproduced on a dozen samples cleaved from four separate crystals.

Hole drift mobilities were also measured, as shown in Fig. 5, where the inverse transit time is plotted against the applied potential. Linearity is again observed. For the holes, the mobility is clearly sensitive to the temperature. Figure 6 is a semilog plot of μ vs T^{-1} for two samples, indicating that the hole mobility is activated (activation energy: 0.14 eV) and that the magnitude of the mobility varies among samples.

The fact that the hole drift mobility varies among samples strongly suggests that the measured mobilities are not determined by an intrinsic property of As_2S_3 . Using the language of band theory, these data may be described as shallow-trap-controlled drift mobility, i.e., the drift mobility is determined by the time a carrier spends in a shallow

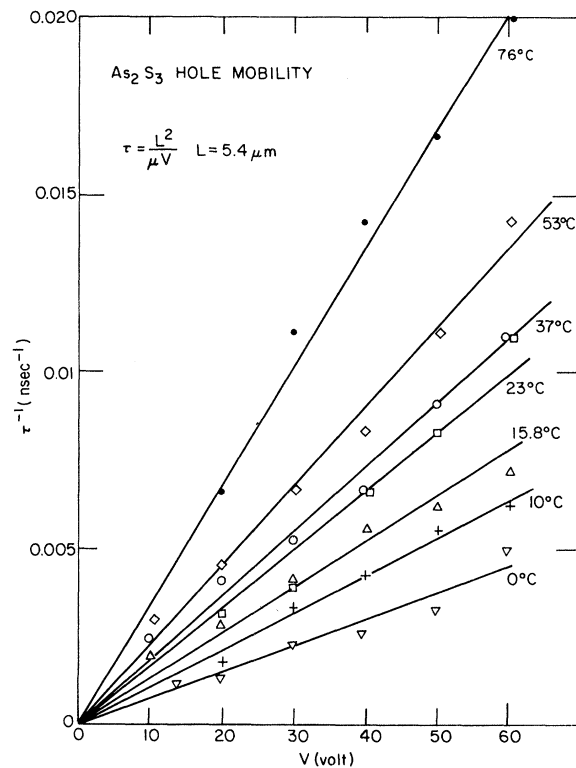


FIG. 5. Inverse transit time for holes vs the applied voltage, for a $5.4\text{-}\mu\text{m}$ -thick sample using 1 M NaCl aqueous electrodes. The mobility is independent of the electric field and is sensitive to the temperature.

trap produced by, for example, an impurity. Such effects have been observed in anthracene doped with naphthalene by Hoesterey and Letson.⁴² Whatever microscopic theory is eventually used to explain transport in molecular crystals, it will have to allow for "shallow-trapping" effects.

IV. NARROW-BAND THEORY

These measurements on As_2S_3 are part of an effort to understand on a microscopic basis the data shown in Table I. As a first step, we have attempted to establish hopping theories as the most likely candidates. To that end, a more general argument than is presently being used in the literature has been constructed to demonstrate the inadequacy of the band-theory approach. We proceed by assuming a band-theory approach is applicable and then investigating the predicted temperature dependence. This predicted temperature dependence is then shown to be inconsistent with the data.

If we assume a band-theory approach, transport properties can be calculated using a relaxation time τ_R approximation to the Boltzmann equation.⁸⁷ In particular the mobility for a nondegenerate semiconductor is given by

$$\mu = (e/kT) \langle \tau_R v_i^2 \rangle, \quad (9)$$

where v_i is the electron velocity in the i th direction and $\langle \dots \rangle$ indicates appropriate thermal averaging. Usually one takes the kinetic energy in the

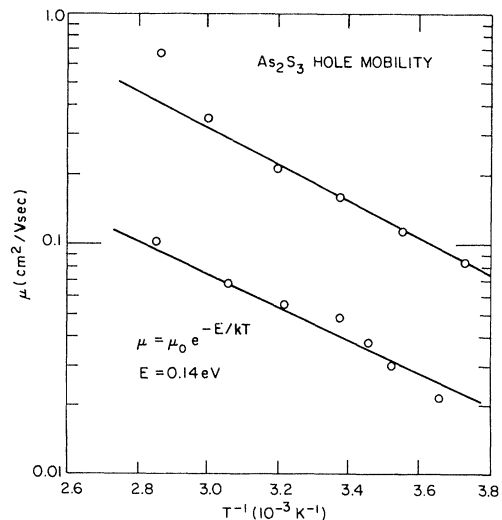


FIG. 6. Semilog plot of mobility vs T^{-1} showing the hole mobility is activated and the magnitude of the mobility varies among samples.

i th direction equal to

$$\frac{1}{2}mv_i^2 = \frac{1}{2}kT \quad (10)$$

and obtains

$$\mu = e\tau_R/m \quad (11)$$

(taking τ_R out of the average), where m is the effective mass.

However, in the narrow-band approximation, when the bandwidth is less than kT , the effective-mass approximation becomes invalid simply because all k states in the band are thermally occupied instead of just the states at the minimum of the band. In this case Frohlich and Sewell⁸⁸ suggested that the magnitude of v_i be estimated as some fraction of the maximum velocity in the band, which from the tight-binding approximation, is⁸⁷

$$|v_i| \approx Ja/\hbar, \quad (12)$$

where J is the electron overlap integral (the bandwidth is $6J$ in a three-dimensional cubic crystal), a is the lattice constant, and \hbar is Planck's constant. This gives

$$\mu = \frac{e\tau_R}{kT} \frac{J^2 a^2}{\hbar^2} \quad (13)$$

using Eqs. (9) and (12), or

$$\mu = \frac{e\lambda}{kT} \frac{Ja}{\hbar}, \quad (14)$$

where $\lambda (=v_i\tau_R)$ is the mean free path.

The essential difference between the usual semiconductor and narrow-band theory is the loss of temperature dependence of v_i , as expressed by Eqs. (10) and (12). This changes the predicted temperature dependence of μ both directly [since $\mu \propto v_i^2$, Eq. (9)] and indirectly (the relaxation time for some scattering mechanisms is velocity dependent, see below). [Temperature-independent electron velocities are also characteristic of metals, where the electron velocity is the Fermi velocity. However, in this case Eq. (9) is not valid since the T^{-1} dependence of Eq. (9) arises from the derivative of the Boltzmann distribution function. The temperature dependence of μ for a metal arises solely from the temperature dependence of τ_R .]

As the temperature independence of v_i is important to these arguments, careful consideration has been given to the assumption inherent in deriving Eq. (12). In fact v_i does have some temperature dependence, $v_i \propto 1$ plus terms of the order W/kT , which is second order in temperature dependence in the narrow-band limit $W \ll kT$ and is ignored here. The temperature dependence arises from the necessity for the electron energy

distribution to obey Fermi-Dirac statistics; the weakness of the temperature dependence arises because the Fermi-Dirac distribution function for any energy relative to the quasi-Fermi level changes very little over a range W if $W \ll kT$ (the narrow-band limit), e.g., the energy states in the narrow band are almost uniformly occupied at all temperatures.

Using Eq. (14) one can understand the standard arguments that have been advanced against band theory. Katz *et al.*,⁵³ Silbey *et al.*,⁵³ and Glaeser and Berry⁵⁵ have estimated $W \approx 0.1$ eV and $J \approx 0.01$ eV for anthracene. With the measured value of μ , λ can be calculated from Eq. (14). The result is $\lambda \approx 4$ Å which is approximately equal to the lattice constant, inconsistent with the band approach. Note that this argument depends critically on the calculated value of J . (Katz *et al.*, Silbey *et al.*, and Glaeser and Berry actually calculate a band structure from which correct averages were numerically calculated for the velocity components.)

The approach being used here is different than the standard arguments. We construct a qualitative argument based on the temperature dependence of μ as given by Eq. (13). Temperature dependence of μ can be attributed to the temperature dependence of a , J , and τ_R .

The temperature dependence of the lattice constant is

$$a = a_0(1 + \beta T), \quad (15)$$

where

$$\beta \approx 10^{-4} \text{ K}^{-1} \quad (16)$$

which is small⁸⁹ and can be ignored for our purposes.

One source of the temperature dependence of J is the temperature dependence of a : As the lattice expands, the electron overlap integral decrease. Delacote⁹⁰ has shown this is small for anthracene, 5% in 200 K. Another source is the modification to the bandwidth due to the formation of polarons. The effective (polaron) bandwidth⁵⁸ is We^{-S} , where S is a vibrational overlap integral which is exponential in the phonon occupation number and therefore in T . In either case as T increases J (or the effective bandwidth) decreases; the temperature dependence of J is at least

$$J \propto T^{-p}, \quad p > 0. \quad (17)$$

It remains to establish the temperature dependence of the relaxation time τ_R for various scattering mechanisms. Consider, for example, acoustic phonon scattering. The cross section σ is linear^{91,92} in T and therefore the inverse of the mean free path (the product of σ and the number of scattering events per unit volume N) goes

as T

$$N\sigma \propto T. \quad (18)$$

The relaxation time therefore goes as

$$\tau = (Nv\sigma)^{-1} \propto v^{-1}T^{-1}. \quad (19)$$

For normal (wide band) semiconductors, Eqs. (10), (11), and (19) give

$$\mu = \frac{e\tau}{m} \propto v^{-1}T^{-1} \propto T^{-3/2} \quad (20)$$

which is the temperature dependence found in the familiar Bardeen-Shockley⁹¹ formula. In the narrow-band case, neglecting the temperature dependence of J for the moment, Eqs. (12), (13), and (19) give

$$\mu \propto T^{-2}, \quad (21)$$

a result obtained by Glarum⁵⁰ and Friedman⁹³ independently. The different temperature dependence of Eqs. (20) and (21) is directly determined by the temperature dependence of v_i as given by Eqs. (10) and (12) for wide- and narrow-band semiconductors.

This result is shown in Table II along with results obtained similarly for two-phonon acoustic, Coulomb, neutral impurity, one- and two-phonon optical, and dislocation scattering. The column labeled "usual semiconductor" are the standard results arrived at by Shockley and Bardeen⁹¹ (acoustic scattering), Conwell and Weisskopf⁹⁴ (Coulomb scattering), Erginsoy⁹⁵ (neutral impurity), Petritz and Scanlon⁹⁶ (optical phonon), and Read⁹⁷ (dislocation). Some of the narrow-band results have been obtained before. The one-phonon acoustic scattering results have been obtained by Glarum⁵⁰ and Friedman,⁹³ and Frohlich and Sewell⁸⁸ derived the two-phonon acoustic scattering temperature dependence. Frohlich and Se-

well⁸⁸ also derived the neutral impurity scattering using a cross section of $\pi a^2(v^0)$ instead of the usual v^{-1} [which, however, does not change the predicted temperature dependence because of Eq. (12)].

The structure of the results is clear: from Eq. (13), at least T^{-1} is obtained. If phonons are involved extra temperature dependence is obtained in the dominator to account for the thermal occupation of the phonon states. Including the temperature dependence of J (ignored in Table II) only increases the temperature dependence in the dominator, i.e.,

$$\mu \propto T^{-(1+m)}, \quad m > 0 \quad (22)$$

for narrow-band theory.

Equation (22) is clearly inconsistent with the data obtained on electron mobilities in As_2S_3 ($\mu \propto T^0$) and some of the other crystals shown in Table I, a result which suggests that band theories cannot explain these data. Hopping theories, in which the charge carrier is pictured as localized, would seem a more profitable path to explore further. We note for completeness that a temperature-independent mobility within $\pm 10\%$ from 207 to 465 K is not necessarily inconsistent with the predicted temperature dependence of hopping mobilities if one is willing to admit a sufficiently small activation energy, i.e., the temperature dependence of Ref. 58 is $T^{-3/2} \exp(-E_p/2kT)$ which is constant within 7% between 207 and 465 for $E_p = 75$ meV.

The above argument is based on the narrow-band expression for the mobility which appears to be universally accepted as applicable to molecular solids. Similar conclusions are reached, however, by considering the usual semiconductor results: only neutral impurity scattering predicts a temperature-independent mobility but the number of impurities required⁹⁵ to give $\mu = 1$ $\text{cm}^2/\text{V sec}$ is

TABLE II. Temperature dependence of μ (excluding temperature dependence of J).

Scattering	σ	$\tau_R = (N\sigma v)^{-1}$	μ	
			Usual	Narrow band ($W \lesssim kT$)
Acoustic				
one phonon	T	$(vT)^{-1}$	$T^{-3/2}$	T^{-2}
two phonon	T^2	$(vT^2)^{-1}$		T^{-3}
Coulomb	v^{-4}	v^3	$T^{3/2}$	T^{-1}
Neutral impurity	v^{-1} v^0	v^0 v^{-1}	T^0	T^{-1} T^{-1}
Optical				
one phonon	$T^{-1}[\exp(h\nu/kT) - 1]$	$(T/v)[\exp(h\nu/kT) - 1]$	$T^{1/2}[\exp(h\nu/kT) - 1]$	$[\exp(h\nu/kT) - 1]$
two phonon	$T^{-1}[\exp(h\nu/kT) - 1]^2$	$(T/v)[\exp(h\nu/kT) - 1]^2$		$[\exp(h\nu/kT) - 1]^2$
Dislocation	v	v^{-1}	$T^{-1/2}$	T^{-1}

$7 \times 10^{21} \text{ cm}^{-3}$ (for an effective mass of one) or $7 \times 10^{22} \text{ cm}^{-3}$ (for an effective mass of 10) which is approximately equal to the density of atoms in these crystals and is 10^5 higher than the measured impurity concentration. Combining two scattering mechanisms might give a temperature-independent μ over a narrow temperature range, but not over the observed temperature range of 207–465 K.

V. CONCLUSIONS

A complete (to the author's knowledge) bibliography of mobilities measured by time of flight techniques on organic and inorganic molecular crystals has been assembled and a remarkable trend is noted: that, independent of the particular crystal, all molecular crystals have room-temperature mobilities of $1 \text{ cm}^2/\text{Vsec}$ (within an order of magnitude) and weak temperature dependence (T^{-n} with $0 < n < 2$) with the exception of electrons in S_8 .

An additional material has been added to the list of measured microscopic mobilities, electrons in As_2S_3 , and it has been found that its mobility is in conformity with the above-mentioned trend

$$\mu = 1.0 \pm 0.1 \text{ cm}^2/\text{Vsec}$$

$$\mu \propto T^{-n}, \quad 207 < T < 465 \text{ K}$$

$$n < 0.16.$$

As_2S_3 appears to be the first layered compound to exhibit molecular transport behavior perpendicular to the layers. The determination of the temperature dependence is made over one of the larg-

est temperature range yet reported for a molecular crystal.

Hole drift mobility data is also presented but the magnitude of the mobility varies among samples suggesting that the observed mobility is not an intrinsic property of the As_2S_3 crystals.

It has been argued that the observed temperature dependence of μ appears to be inconsistent with the predictions of band theory, suggesting that the charge carriers should be regarded as localized. This argument is more general than, and in agreement with, standard arguments against band theory which depend critically on calculated electron overlap integrals. The essence of the argument is that for narrow-band theory the temperature independence of the electron velocity leads to the prediction that the mobility $\mu \propto T^{-(1+m)}$ with m positive, whereas the data gives $\mu \propto T^0$. These arguments equally well apply to those organic crystals which have temperature-independent mobilities suggesting the term "organic semiconductor," sometimes used to describe transport properties of organic molecular crystals, may be a misnomer.

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