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Band-hopping mobility transition in naphthalene and deuterated naphthalene

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Measurements of the mobility, whose temperature dependence suggests a band-hopping transition is occurring near 100 K, are reported for electrons in the c' and b directions of naphthalene and the c' direction of deuterated naphthalene. A review of the status of the theoretical understanding of this transition indicates that while progress is being made toward understanding the hopping mechanism of transport, significant aspects of these data remain unexplained.

I. INTRODUCTION

One of the unsolved charge-transport problems in the crystalline solid state occurs in molecular, insulating crystals, of which anthracene has been the most extensively studied example. Data have accumulated[1] on this class of materials which suggest that, independent of the particular material, the mobility μ is 1 $\text{cm}^2/\text{V sec}$ within an order of magnitude and is weakly temperature T dependent (i.e., $\mu \propto T^n$, $0.1 < n < -2$). These data do not appear to be understandable in terms of band theories[1] (with any known scattering mechanisms) or available hopping models of transport. Band theories fail because (i) given the magnitude of the mobility and estimated bandwidths (0.1 eV), the mean free path is found[2,3] to be approximately equal to the intermolecular spacing, inconsistent with the assumption of weak scattering inherent in a band theory, and (ii) the (narrow) band theory prediction of the temperature dependence of the mobility for any scattering mechanism is inconsistent with at least $\frac{1}{3}$ of the measured mobilities.[1] Available hopping models fail because (i) estimates[4,5] of the polaron binding energy (tenths of eV) predict activated mobilities at room temperature, inconsistent with the data, and (ii) data have been obtained on three molecular cyrstals over a wide enough range to demonstrate[6] that the predicted temperature T dependence of almost all hopping models $[T^{-m}\exp(-E/kT),\ m \approx 1]$ is inconsistent with the data for arbitrary activation energy.

These data ($\mu \approx 1\text{cm}^2/\text{V sec}$, $\mu \propto T^n, 0.1 < n < -2$) are even more puzzling in view of the predictions made by many theorists[7-9] that for narrow-band materials a band-hopping transition should occur which would manifest itself in the temperature dependence of the mobility. At low temperatures, the usual semiconductor-like weak scattering is expected: the mobility, which is determined by phonon scattering, decreases with increasing temperature due to the increasing phonon population. This mechanism continues up to a temperature at which the electron mean free path is decreased to the order of magnitude of an intermolecular spacing. Above this temperature the wave function is expected to be localized and the electron hops from site to site: the mobility is now predicted to increase with increasing temperature since the presence of phonons increases the hopping rate. The lack of observation of this mobility transition and the inadequacy of both band and hopping theories to explain available transport data has made electron transport in molecular crystals a particularly puzzling transport problem in a potentially important class of materials.

Recent observations[10] of a band-hopping transition via low-temperature (down to 54 K) drift mobility measurements for electrons in the c' direction of naphthalene have begun to shed light on the mechanisms of charge transport in molecular crystals. It is the purpose of this paper to discuss this band-hopping transition in more detail. Experimentally, data are presented to much lower temperatures (31 K) in the c' direction of naphthalene and the band-hopping transition is reported in the b direction of naphthalene, and in another crystal, deuterated naphthalene. The experimental procedure for obtaining these measurements is discussed in detail. Finally, the theoretical understanding of the mechanisms of charge transport in this class of materials is summarized, including recent theoretical results obtained since the first observation of the band-hopping transition.

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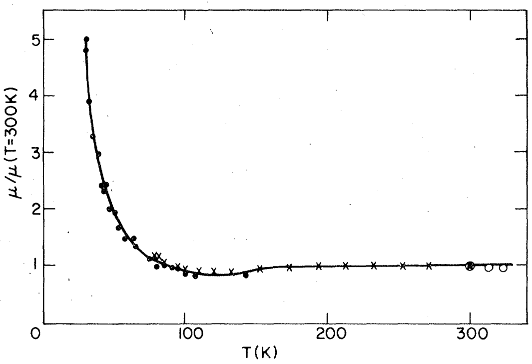

FIG. 1. Normalized mobilty (to the room-temperature value) for electrons in the c' direction of naphthalene from 31 to 324 K. Below 100 K the mobility rises with decreasing temperature; above 100 K the mobility is almost temperature independent. It is argued these data indicate a band-hopping transition occurs at 100 K. The different symbols represent different samples with the mobility normalized at 300 K.

II. EXPERIMENTAL OBSERVATIONS

The normalized mobilities (to the room-temperature value) for electrons in the c' direction of naphthalene from 31 to 324 K are plotted linearly against temperature in Fig. 1, in an expanded linear scale in Fig. 2, and semilogarithmically in Fig. 3. As reported previously,[10] three regions can be distinguished: above 150 K (Fig. 1) the mobility is essentially independent of temperature. Writing the temperature dependence as T^n, we find $n = 0.1 \pm 0.1$. Between 100 and 150 K there is a slight (10%) minimum (Fig. 2). Finally, below 100 K the mobility increases with decreasing temperature. In Fig. 3 it is shown that the temperature dependence in this region (31–100 K) can be described as $\exp(E/kT)$ where $E = 6.6$ meV (53 cm^{-1}), which we consider a more accurate value than the previously reported[10] value (47 cm^{-1}) because of the considerably wider temperature range over which data are reported here. These data have been observed on samples taken from different crystals strongly suggesting that these measurements reflect intrinsic properties of naphthalene.

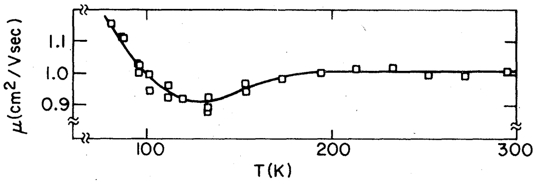

FIG. 2. Region from 78 to 295 K of Fig. 1 is shown in an expanded scale. From 100 to 150 K there is evidence for a minimum of about 10%.

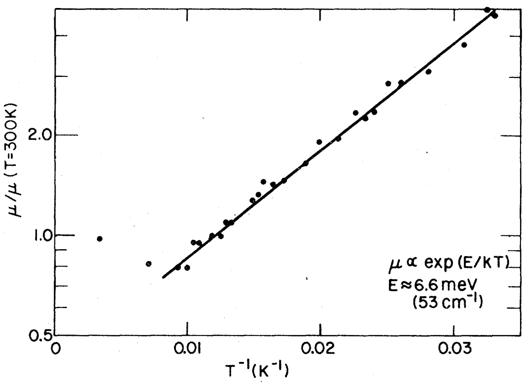

FIG. 3. Low-temperature region of Fig. 1 is plotted semilogarithmically indicating the data can be fit approximately as $\exp(E/kT)$ with $E = 6.6$ meV.

The rapid increase of the mobility below 100 K has recently been confirmed by Karl and co-workers.[11] Our high-temperature measurements are in approximate agreement with previous measurements in naphthalene: we observe a room-temperature electron mobility of 0.44 $\text{cm}^2/\text{V sec}$; Silver[12] reports $\mu = 0.4$, Spielberg, Korn, and Damask[13] report $\mu = 0.6$, and Mey and Hermann[14] report $\mu = 0.68$. Only Mey and Hermann[14] report observations of the temperature dependence of μ (from 220 to 300 K); our data are consistent with their data taking into account their experimental error of ±10%.

The normalized mobilities (relative to room temperature) for electrons in the b direction of naphthalene from 78 to 293 K are plotted linearly in Fig. 4 and semilogarithmically in Fig. 5. The observations have been made on samples taken from our crystals and a crystal supplied by Zschottke–Granacher which is strong evidence that these

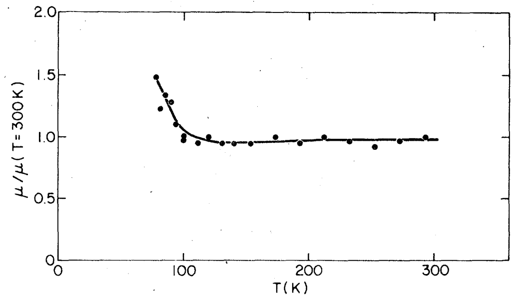

FIG. 4. Normalized mobility for electrons in the b direction of naphthalene from 78 to 293 K. Again there is clear evidence for a change in behavior below 100 K. Note there is no evidence for the minimum seen in Figs. 1 and 2.

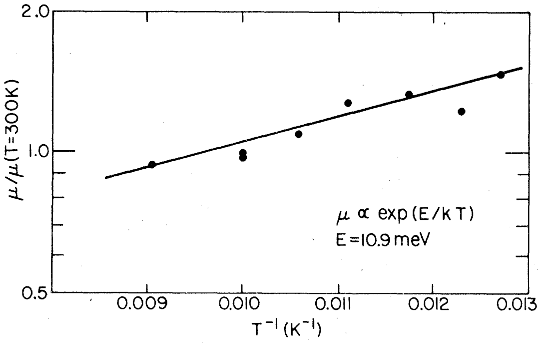

FIG. 5. Low-temperature region of Fig. 4 is plotted semilogarithmically indicating the data can be approximated by $\exp(E/kT)$ with $E=11$ meV, significantly larger than the slope observed in the c' direction (Fig. 3).

measurements reflect intrinsic properties of naphthalene. For these data there appears to be a transition temperature near 100 K at which the temperature dependence of the mobility changes abruptly, similar to the data in the c' direction (Figs. 1–3). However, there is *no* evidence of a minimum between 100 and 150 K. Above 100 K, the temperature dependence can be approximated by T^n, $n \approx 0.1$. Below 100 K the mobility can be described by $\exp(E/kT)$ where $E \approx 11$ meV, a significantly higher value than that observed in the c' direction (Fig. 3).

High-precision measurements of the magnitude of the room-temperature electron mobility in the b direction have not yet been performed. However, our observations of 0.4 ± 0.1 cm^2/V sec and the weak temperature dependence of μ at high temperatures confirm previous work by Mey *et al.*[14]

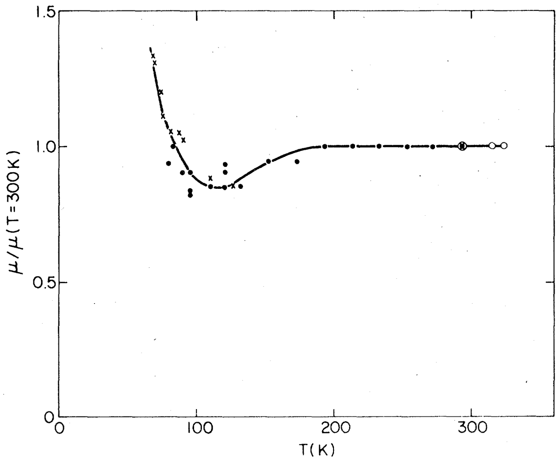

FIG. 6. Normalized mobility for electrons in the c' direction of deuterated naphthalene from 68 to 323 K. These data are within experimental error (±15%) in all respects identical to the data in naphthalene (Fig. 1). Note the presence of the 10% minimum.

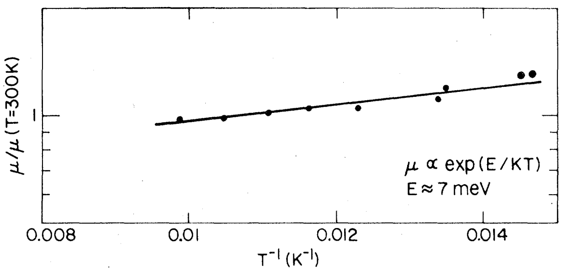

FIG. 7. Low-temperature region of Fig. 6 plotted semilogarithmically indicating the data can be approximated by $\exp(E/kT)$ with $E=7 \pm 1$ meV.

The normalized mobilities for electrons in the c' direction of deuterated naphthalene from 68 to 323 K are plotted linearly against temperature in Fig. 6 and semilogarithmically in Fig. 7. These data are very similar to the observations for electrons in the c' direction of naphthalene: above 150 K the mobility is essentially temperature independent (writing $\mu \propto T^n$, we find $n=0.1 \pm 0.1$), there is evidence of an approximately 10% minimum between 100 and 150 K, and below 100 K the mobility increases with T as $\exp(E/kT)$ where $E \approx 7 \pm 1$ meV (see Fig. 7). Within the accuracy of these measurements, the value of μ (0.4 ± 0.1 cm^2/V sec at room temperature) and E appears to be the same for naphthalene and deuterated naphthalene in the c' direction. To the knowledge of the authors, there have been no previous measurements of mobilities in deuterated naphthalene to compare with these observations. In fact, we have succeeded in obtaining measurements only from samples taken from one crystal. However, the similarity of these measurements to those observed in naphthalene suggests that these measurements reflect intrinsic properties of deuterated naphthalene.

III. EXPERIMENTAL METHODS

These mobility measurements were obtained by the standard transient photoconductivity techniques first applied to molecular crystals by Kepler[15] and discussed extensively by Spear[16] and others: Observations are made of the transit time (see Fig. 8) of a photogenerated sheet of charge carriers which equals the crystal thickness divided by the product of the mobility and the applied electric field. The characteristics of this experimental facility which allowed these low-temperature measurements were a combination of the ability to measure fast transit times and the growth of ultrahigh purity materials.

Fast transit times were obtained by using a twice

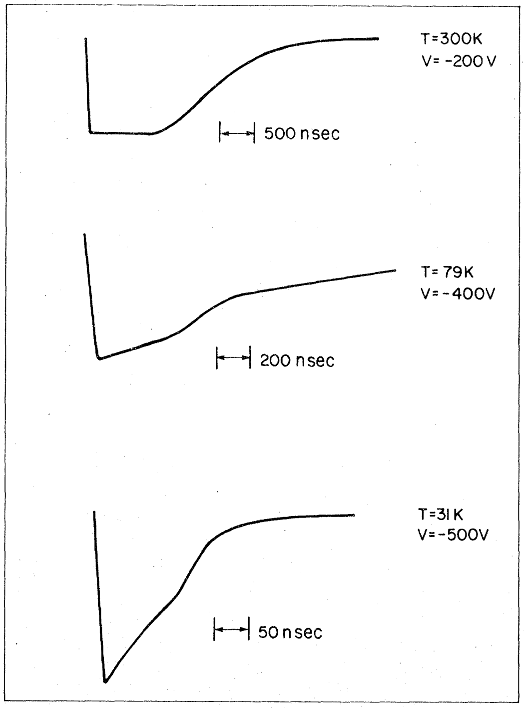

FIG. 8. Transit times from which data in Fig. 1 were taken.

doubled Q switched (20 nsec) and pulse sliced (2.5 nsec) Nd-glass laser Holobeam model 331. This provided light with a wavelength of 2650 Å, which is strongly absorbed in naphthalene, and 1–10 mJ of energy, which allows adequate photogeneration even at low temperatures (however, the mechanism of photogeneration has not been determined for these experiments). Fast rise time electronics were obtained by using a Tektronics 7904 oscilloscope and a FET (P6201) probe. The temperature range of 2–500 K was obtained by using a Janis variable temperature Dewar (2–150 K) and a Statham liquid-nitrogen-fed temperature test chamber (77–500 K).

The other critical requirement to these experiments is crystal purity. Purification and single-crystal growth of naphthalene were carried out as follows: Naphthalene (100 g, Eastman #168, recrystallized from alcohol) was melted under nitrogen into a 500-ml Pyrex flask, the inside of which had been coated with a potassium mirror by evaporation under high vacuum. The vessel was sealed under ~0.75 atm nitrogen and placed in a thermostatted oven at +90 °C overnight. On removal the treated naphthalene was poured into a one-liter round bottom flask and recrystallized twice from ethanol (Pharmco 200 proof). The product was then pot sublimed under vacuum in a large McCarter sublimer to remove occluded solvent and nonvolatile impurities. The sublimate, ~50 g, was melted under nitrogen into a 12-mm diameter Pyrex zone refining tube, degassed with two freeze-thaw cycles, and sealed under 0.75 atm nitrogen. The sample was given 80 zone passes in a high-speed zone refiner with the following operating parameters: tube length of 40 cm, tube diameter of 2 cm, zone speed of 10 cm/h, alternating tube rotation with a 2 sec period and maximum rotation rate ~2000 rpm. On removal the top 10% was rejected (to avoid inverse segregation effects and impurities with $k > 1$), and the remaining top $\frac{1}{3}$ used for single-crystal growth. Crystal growing tubes, 12 mm diameter, were charged with 5 g of zone-refined naphthalene, melted under nitrogen, degassed by three freeze-thaw cycles, and sealed under high vacuum. Crystals were grown in a conventional Bridgman furnace at 1.0 mm/h, oven temperatures 90 °C/55 °C, temperature gradient at the interface ~10 °C/cm. After growth the crystals were allowed to cool naturally to room temperature over several hours and were removed from the Pyrex crystal growing tubes by hydrofluoric acid etching. Crystals were cut only from the center of the boule as recent studies[17] have shown strong radial segregation effects.

The lowest attainable temperature at which a transit time could be observed was clearly determined by crystal purity as evidenced by the variation of this temperature among crystals. At a given temperature the transient current i appears to be determined by a deep trapping lifetime τ, i.e.,

$$i \propto e^{-t/\tau} \tag{1}$$

(until the transit time when most carriers exit the sample). Higher voltages shortened the transit time thereby minimizing the decrease in current due to trapping. However, the τ in Eq. (1) appears to be temperature dependent, being shorter at lower temperatures (see Fig. 8). Whether a temperature-dependent deep trapping lifetime is possible without any evidence for a shallow trap controlled mobility remains unclear.

These measurements required thin (~100 μm thick) platelets. For the c' orientation, the first step involved cleavage. For the b direction, orientation was determined conoscopically using a Leitz polarizing microscope; 1-mm slabs were sectioned by using a solvent string saw with absolute ethanol as solvent. The crystals were then polished by placing them between lens tissue paper wrapped around a glass slide and Buehler #40-7218 polishing cloth stuck to another glass slide, both wetted with cyclohexane. The thickness was determined (for determination of the absolute value of μ) by measuring the mass (using a Cahn RG electrobalance) and the area taking the density of naphthalene to be 1.025 g/cm^3 and of deuterated naphthalene, 1.089 g/cm^3.

It was found critical to these experiments that (i)

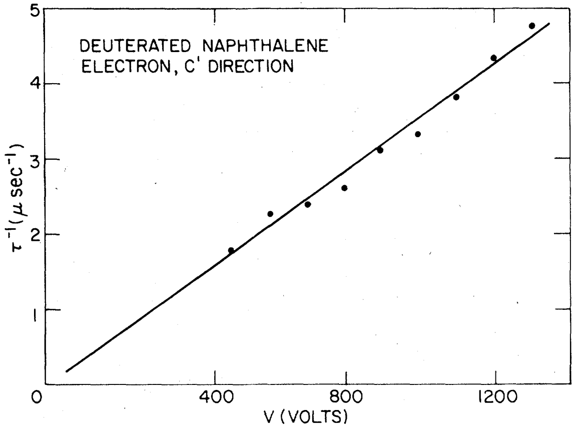

FIG. 9. Inverse transit time plotted against the voltage across the sample for a 79 μm thick samples of deuterated naphthalene at 120 K. The zero intercept indicates negligible space charge in the sample; the straight line suggests the mobility is electric field independent to 17 V/μm.

the samples be room temperature annealed for several days prior to use, and (ii) the sample be cooled from room temperature to 100 K over several hours (by placing them in the Janis Dewar and using the radiation cooling of the central chambers by the liquid nitrogen).

Also critical to these measurements is a knowledge of the electric field in the sample. It was given by the applied potential divided by the crystal thickness only in the absence of space charge. A test for space charge is a plot of the inverse transit time versus the applied voltage: a zero intercept suggests negligible space charge. Such data were shown for naphthalene at 134 K to fields of 8.5 V/μm in Ref. 10 and at 160 K to 17 V/μm in Ref. 18. Figure 9 shows similar data for deuterated naphthalene at 120 K to 17 V/μm. This observation, that negligible space charge exists in the sample, may be due to the fact that between each measurement the front and rear electrodes (Ag print, tin oxide coated quartz) were shorted and several light pulses were flashed on the sample, a technique which should tend to neutralize any trapped space charge.

IV. MECHANISMS OF TRANSPORT

In this section we first eliminate two possible trivial explanations for the data discussed above, a phase transition or a tensor property. Then we discuss separately our interpretation of the low- and high-temperature regions.

We have considered the possibility that the data shown in Figs. 1, 4, and 6 may be due to a phase transition in naphthalene near 100 K. Such an effect should be observable in either specific-heat data, Raman measurements, or a crystal-structure determination as a function of temperature; no evidence of a phase transition near 100 K is present among these types of data.[19–21]

It has been suggested[22] that these observations may be a consequence of the tensor property of the mobility: since c' is not necessarily a principal axis, the mobility along c', $\mu_{c'}$, is related to the mobility along the two principal axes (μ_1, μ_2) by

$$\mu_{c'} = \mu_1 \cos^2\theta + \mu_2 \sin^2\theta \ , \qquad (2)$$

where θ is the angle between the c' and 1 axes. If μ_1 were constant and μ_2 were proportional to T^{-n}, the mobility along c' might rise rapidly as the temperature is lowered below a temperature at which

$$\mu_1 \cos^2\theta = \mu_2 \sin^2\theta \ . \qquad (3)$$

Checking this suggestion requires knowledge of θ as a function of T in naphthalene; at this time θ is only known for anthracene.[11,23] However, a direct test of whether a mobility transition is in fact occurring is to measure μ along the b axis which by symmetry must be a principal axis. Such data is shown in Fig. 4. Clearly a mobility transition is observed which cannot be ascribed to the tensor property of the mobility.

A. Low temperature

Below approximately 100 K both naphthalene (b and c' directions) and deuterated naphthalene (c' direction) exhibit a mobility whose temperature dependence can be described as $\exp(E/kT)$. This is interpreted as strong evidence for band motion. A band mobility determined by phonon scattering should be inversely proportional to the phonon population; the observed temperature dependence is a good approximation for the inverse of the population of optical phonons $[\exp(E/kT)-1]$ with energy E. And the observed energies ($\approx 53\ \mathrm{cm}^{-1}$ in the c' direction of naphthalene and deuterated naphthalene, $88\ \mathrm{cm}^{-1}$ in the b direction of naphthalene) correspond to the low-energy optical phonons of naphthalene and deuterated naphthalene: the energy of the optical phonons for naphthalene at 77 K are given by Suzuki as 141, 121, 88, 83, 67, and 56 cm^{-1} for the rotational modes (i.e., librons), and 106, 75, and 44 cm^{-1} for the translational modes. Hanson's[24] work suggests the same modes in deuterated naphthalene are lower in energy by approximately 10%. Therefore, our suggestion that E should correspond to an optical phonon and the equality of E within experimental error of ±15% observed for naphthalene and deuterated naphthalene in the c' direction is consistent with our suggestion that band motion with optical-phonon scattering is occurring below 100 K. However, the reason significantly different values of

E are observed in the b and c' directions is not obvious from these data.

These data permit an estimate of a lower bound for the electron bandwidth in the c' (6.6 meV) and b (11 meV) directions. This follows because for an electron to be scattered via the emission or absorption of a phonon, both its initial and final states must lie within the band. These estimates are consistent with band-structure calculations.[2,3] The observation of electron scattering by the low-energy optical modes does not preclude scattering by the more strongly coupled higher-energy molecular vibrations although (i) the population of these vibrational phonons is significantly reduced by the Bose–Einstein distribution at 100 K and (ii) if the phonon energy exceeds the bandwidth, higher-order (e.g., two phonons) scattering may be required. At even lower temperatures scattering by acoustical lattice modes and crystalline defects also can become important in determining μ.

An argument that suggests band motion does *not* occur in molecular crystals[1] is that the calculated mean free path λ is too small (on the order of the lattice constant, a). However, this calculation depends explicitly on the value of the electron-transfer integral J (i.e., the bandwidth). For the c' (and b) direction, the estimated mean free paths are much larger than the lattice constant since J is small: Following Frohlich and Sewell,[25] the mobility is given by

$$\mu = \frac{e\lambda}{KT}\frac{Ja}{h} \quad . \tag{4}$$

For $\mu = 1\,\mathrm{cm}^2/\mathrm{V\,sec}$ and the estimated[2,3] J of 10^{-2} eV in the a and b directions of anthracene, or the a direction of naphthalene, this equation gives $\mu = 5$ Å, on the order of the intermolecular spacing. However, in the c' and b directions of naphthalene where J is estimated[2,3] to be much smaller (10^{-3} meV), $\lambda \approx 50$ Å, comfortably larger than a.

These data lend support to the suggestion that cyclotron resonance observed in anthracene[26] is due to electrons orbiting in a band. The observed effective mass in units of the electron mass, 11, and scattering time $\tau = 10^{-13}$ sec, suggest an observed mobility at 2 K of $e\tau/m \approx 10^4\,\mathrm{cm}^2/\mathrm{V\,sec}$. While extrapolation of our data (observed to 30 K) to 2 K can only give an upper bound to μ (since scattering by acoustic phonons or impurities can dominate at low temperatures), we note that a parametrization of the data shown in Figs. 1 and 3,

$$\mu = Ae^{E/kT} \tag{5}$$

extrapolated to 2 K, gives a mobility many orders of magnitude larger than $10^4\,\mathrm{cm}^2/\mathrm{V\,sec}$. This supports the previous interpretation of the cyclotron resonance data and suggests that other phonons or impurities limit the mobility at lower temperatures.

These observations of band motion in a molecular crystal also support recent suggestions[27,28] that band motion can occur in the quasi-one-dimensional salts based on TCNQ (tetracyanoquinodimethane). The assumption that band mobilities can occur in these materials was made in order to explain conductivity and thermopower data. This would seem a reasonable assumption since these direct measurements of mobility in another organic crystal (i.e., naphthalene) which clearly has narrower bandwidths (since charge transfer strengthens bonds and thereby increases the overlap integrals and bandwidths) indicate band motion is occurring.

B. Higher temperatures

Determining the transport mechanism at the higher temperatures (above 100 K) is a much more difficult issue. Study of Figs. 1, 4, and 6 suggests that there is another transport mechanism occurring above 100 K which maintains the mobility to an approximately constant value. Two indirect arguments can be constructed which suggest that the higher-temperature mobility is *not* band motion; i.e., it is hopping of localized electrons:

(a) It has been shown[1] that the temperature dependence of the mobility for a narrow-band semiconductor (i.e., bandwidth less than kT) is

$$\mu \propto T^{-n} \quad , \tag{6}$$

with *n greater than or equal to one.* This result is based on Eq. (4) and the realization that the temperature dependence of J and the mean free path (for any scattering mechanism) are always decreasing functions of temperature. The data shown in Figs. 1, 4, and 6 can be described as T^{-n} with $n = 0.1 \pm 0.1$, clearly inconsistent with the requirements of (narrow) band theory.

(b) Band mobilities for different scattering mechanisms add as their inverses (because the scattering rates are additive). Therefore, with two band mobility mechanisms operative, the smaller mobility should dominate. The curve shape in Figs. 1, 4, and 6 are inconsistent with this requirement. Extrapolating the constant mobility above 100 K to low temperature gives the result that it is experimentally observed that the larger mobility dominates.

The conclusion from both of these arguments is that above 100 K the mobility mechanism is not band motion. However, the difficulty of explaining an approximately temperature-independent and electric-field-independent mobility with available hopping models has been well documented: First,[6] almost all available hopping models predict the mobility to have a temperature dependence of

$$T^{-m}\exp(-E/kT), \quad m \approx 1 \quad , \tag{7}$$

where the exponential dominates at low temperatures (with respect to E/k) and the T^{-m} dominates at high temperatures. For measurements over wide enough temperature ranges, this temperature dependence can be tested for arbitrary E. For at least five materials (electrons in the c' direction of naphthalene, deuterated naphthalene, anthracene, deuterated anthracene, and the molecular direction of As_2S_3) the data are inconsistent with Eq. (7) for arbitrary E. Second,[18] one would expect hopping models to predict the electric field dependence of the mobility to be

$$\exp(eEa/2kT) \ , \tag{8}$$

where a is the intermolecular spacing. Recent measurements[18] at high electric fields (≈ 17 V/μm) and low temperatures ($\approx$100K) have demonstrated μ is electric field independent to values of $eEa/2kT$ of 0.86 in anthracene and 0.46 in naphthalene, inconsistent with Eq. (8).

The above considerations allow one to conclude that while the high-temperature, temperature-independent mobility observed in several molecular crystals is due to the hopping of localized carriers, available hopping models appear unable to account for the data. In order to identify the transport mechanism and the cause of the electron localization, new theoretical input is required.

Mobilities for hopping models are usually predicted by calculating the hopping rate ν between molecules spaced a distance, a, apart. The diffusion constant D is related to ν by

$$D = a^2\nu \ , \tag{9}$$

where a is the intermolecular spacing and the mobility is related to D by the Einstein relation (checked for molecular crystals by Karl[29])

$$\mu = eD/kT \ , \tag{10}$$

giving

$$\mu = \frac{ea^2\nu}{kT} \ . \tag{11}$$

Note that the T^{-1} that appears in the expression for μ comes from the Einstein relation. Hence, to predict μ it is sufficient to calculate the hopping rate within the context of a specific model. For example, the nonadiabatic small polaron model of Holstein[7] gives

$$\nu = \frac{1}{\hbar}\left(\frac{\pi}{2}\right)^{1/2} \frac{J^2}{(kTE_p)^{1/2}} \exp\left(-\frac{E_p}{2kT}\right) \tag{12}$$

and therefore

$$\mu = \frac{ea^2}{\hbar}\left(\frac{\pi}{2}\right)^{1/2} \frac{J^2}{(kT)^{3/2}(E_p)^{1/2}} \exp\left(-\frac{E_p}{2kT}\right) \ , \tag{13}$$

where J is the electron-transfer integral and E_p is the small polaron binding energy. The activated form of μ appears to be a common feature of the hopping models[6] which assume J and E_p are temperature independent. The activation energy equals an energy barrier (that must be overcome) or a phonon energy (that must be absorbed or emitted by the electron). Clearly, at temperatures large compared to the activation energy, the temperature dependence of μ arises from any pre-exponential temperature dependence of ν and the one factor of T arising from the Einstein relation [Eq. (10)].

Gosar and Choi[30] were the first to consider the effect on the mobility of the polarization energy and transfer integral J having temperature dependence. They showed that the temperature dependence of a hopping mobility may be considerably weakened by these considerations. Gosar and Choi coupled the electrons to the acoustic phonons and found that the mobility is determined by two terms. The first was a bandlike mobility (with a $T^{-3/2}$ temperature dependence at high temperature) characteristic of acoustic-phonon scattering and the second was a (acoustic) phonon-assisted hopping mobility whose temperature dependence is determined by $(2n+1)/T\alpha$ where n is the phonon density and α is the decay time of the two-particle correlation function. Since at high temperatures n is proportional to T, the temperature dependence of this hopping mobility is determined by the temperature dependence of α. The temperature dependence of α was determined by the assumption that the two-particle correlation function is Gaussian and that the largest contribution to α came from the fluctuations of the polarization energy due to the electron-phonon interaction, giving α proportional to $T^{1/2}$ and μ proprotional to $T^{1/2}$. The contributions to α due to the spread of the electronic band energies and the fluctuations of the transfer integrals were shown to be an order of magnitude smaller.

Madhukar and Post,[31] following Haken and Reineker's[32] earlier work on exciton transport, were able to predict temperature-independent mobilities by assuming that the electron-transfer integral, J, has a time-dependent part due to disorder introduced by the presence of phonons (i.e., off-diagonal disorder). Without specifying the detailed coupling mechanisms, but taking a high-temperature approximation, this leads to an expression for the mobility of

$$\mu = c_1 + c_2/T^2 \ , \tag{14}$$

(where c_1 and c_2 are independent of temperature) which is temperature independent to first order.

The first theoretical paper to appear after the initial observation[10] of the band-hopping transition was Sumi's.[33] Noting that the experiments suggest that electrons are scattered by librons (rotational optical phonons) in the band region, he suggested a more detailed physical picture of the hopping motion. Sumi noted that the transfer integrals in the c' direction of naphthalene are particularly small because of approximate cancellation of two terms (see the original band-structure calculations[2,3]). It was therefore assumed that small rotations from the symmetry positions (caused by librons) could substantially increase the overlap integrals (which is in essence a more specific way of introducing off-diagonal disorder). Furthermore, Sumi carefully considered the large anisotropy of the bands among the crystal axes and predicted band motion along the a and b directions and band motion along the c' direction at low temperatures (below a band-hopping transition). Above the transition temperature the hopping mobility's temperature dependence is determined by n/T which is temperature independent at high temperatures, in agreement with the data. He predicts that the temperature of the band-hopping transition T_t is related to the slope ($\hbar\omega$) of the mobility in the band region by

$$T_t \simeq \hbar\omega/k \ , \tag{15}$$

where k is Boltzmann's constant. This required him to assume $\hbar\omega = 70 \text{ cm}^{-1}$ (to get the observed $T_t = 100$ K in the c' direction). Experimentally it is found that $T_t = 100$ K in both the b and c' directions, while $\hbar\omega = 53 \text{ cm}^{-1}$ in the c' direction and 88 cm^{-1} in the b direction. Sumi's contention that the earlier work of Madhukar and Post assumes that the electron bandwidth is smaller than the phonon dispersion has been questioned.[34] Sumi[35] has recently calculated the electric field dependence of the mobility within the context of his model. Two predictions of his work do not appear to be borne out by the experiments.[18] First, the hopping mobility is predicted to become electric field dependent when $eaE \approx h\omega$. Experiments[18] indicate no field dependence to μ for $eaE/h\omega = 1.4$ in naphthalene, taking $h\omega = 70 \text{ cm}^{-1}$. Second, the band mobility is predicted to be significantly decreased at high fields; in fact, at the usual electric fields at which mobilities are measured (≈ 5 V/μm) it is predicted that the band mobility should be negligible compared to the hopping mobility at least down to 10 K, inconsistent with the data.

Finally, a different approach has been adapted by Metiu and Efrima.[36] They investigated a Hamiltonian in which were included both linear and quadratic phonon coupling to the site energy plus anharmonic phonon effects and found that the temperature-independent mobility could be obtained if anharmonic effects were included and the minimum in mobility observed in the data near the transition could be produced if site quadratic phonon coupling were considered.

In conclusion, the following data must be explained by a complete theory of charge transport in molecular insulating crystals:

(i) The magnitude[1] of the mobility is almost always 1 cm^2/V sec within an order of magnitude; the temperature dependence of the mobility for almost all molecular crystals[1] goes as T^n with $0.1 \leq n \leq -2$.

(ii) The electron mobility is almost temperature independent over wide temperature ranges for anthracene, deuterated anthracene, naphthalene, deuterated naphthalene, and As_2S_3 (Ref. 6 and Figs. 1, 4, and 6) in the directions in which the bandwidths are expected to be particularly small ($\approx 1-10$ meV).

(iii) Along the directions of naphthalene in which almost temperature-independent mobilities have been observed (b and c' directions of naphthalene, c' direction of deuterated naphthalene), the mobility is observed to go through a transition as the temperature is lowered to a band mobility independent of deuteration and crystal axes. In naphthalene and deuterated naphthalene this transition occurs at 100 K; in anthracene this transition (not yet observed) must be below 77 K.

(iv) The temperature dependence of the band region, $\exp(E/kT)$, and the existence of a minimum near the transition temperature appear to be independent of deuteration but crystal axis dependent. In naphthalene $E = 53 \text{ cm}^{-1}$ and a 10% minimum is observed in the c' direction; $E = 88 \text{ cm}^{-1}$ and no minimum is observed in the b direction.

(v) At high temperatures the approximately temperature-independent mobility has been observed to be electric field independent to very high electric fields[18]: 16.1 V/μm in anthracene at 100 K, 17.3 V/μm in naphthalene at 160 K, and 15 V/μm in deuterated naphthalene at 120 K (Fig. 9). These parameters give for the ratio eaE/kT (a usual measure of the expected field dependence for hopping models), where a is the intermolecular spacing, 0.86, 0.46, and 0.53, respectively.

Comparing the theories to the list of data requiring an explanation, we can see that

(a) No one has yet attempted to explain the surprising regularity in mobilities for almost all molecular crystals ($\mu = 1$ cm^2/V sec independent of material and is weakly temperature dependent). Sumi[33] has begun to try to understand the relationship of the anisotropy of the mobility and the crystal structure.

(b) Temperature-independent mobilities can be obtained by assuming a temperature dependence to the overlap integral[31,33] or by taking into account anharmonic effects on the site energy.[36]

(c) Sumi[33] can qualitatively obtain the transition temperature in napththalene but cannot explain its crystal axes dependence. There are no predictions yet for the transition temperature in anthracene (not yet observed experimentally).

(d) The temperature dependence in the band region appears to correlate with the energies of the optical phonons; however, it is not clear why $E = 53$ cm^{-1} in the c' direction and 88 cm^{-1} in the b direction of naphthalene and it remains unclear why a minimum is observed in the c' direction (which Efrima *et al.*[36] argue can be traced to a site quadratic disorder term) but not the b direction.

(e) The high-field behavior[18] of the mobility has yet to be explained within the context of any proposed hopping models.

V. SUMMARY

Data have been presented for electrons in the b and c' directions of naphthalene and the c' direction of deuterated naphthalene which indicate a change in the temperature dependence of the mobility near 100 K: at lower temperatures the mobility goes as $\exp(E/kT)$; at higher temperatures the mobility is approximately temperature independent.

It has been argued that the low-temperature behavior is due to band motion and the high-temperature behavior is due to hopping motion. Hence, we conclude that the band-hopping transition predicted for narrow-band materials originally by Holstein[7] and subsequently by Munn and Siebrand,[8] Munn and Silbey,[9] and others has been observed.

We argue that while a hopping model is necessary to explain the almost temperature-independent mobility observed at high temperatures, (i) most hopping models cannot explain the observed temperature dependence,[6] and (ii) it remains unclear whether the data in the b direction and the electric field independence[18] of μ can be accounted for with the recent models which can produce temperature-independent mobilities by invoking off-diagonal disorder[31,33,35] or anharmonic effects on the site energy.[36]

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[1] L. B. Schein, Phys. Rev. B 15, 1024 (1977).

[2] J. I. Katz, S. A. Rice, S. Choi, and J. Jortner, J. Chem. Phys. 39, 1683 (1963).

[3] R. Silbey, J. Jortner, S. A. Rice and M. T. Vula, Jr., J. Chem. Phys. 42, 733 (1965); 43, 2929 (1965).

[4] W. Siebrand, J. Chem. Phys. 41, 3574 (1964).

[5] C. B. Duke, N. O. Lipari, and L. Pietronero, Chem. Phys. Lett. 30, 415 (1975).

[6] L. B. Schein, Chem. Phys. Lett. 48, 571 (1977).

[7] T. Holstein, Ann. Phys. (N.Y.) 8, 325 (1959); 8, 343 (1959).

[8] R. W. Munn and W. Siebrand, J. Chem. Phys. 52, 6391 (1970).

[9] R. W. Munn and R. Silbey, J. Chem. Phys. 68, 2439 (1978).

[10] L. B. Schein, C. B. Duke, and A. R. McGhie, Phys. Rev. Lett. 40, 197 (1978).

[11] N. Karl and W. Warta (unpublished); see also W. Warta, diplomarbeit (Stuttgart, 1978) (unpublished).

[12] M. Silver, J. R. Rho, D. Olness, and R. C. Jarnagin, J. Chem. Phys. 38, 3030 (1963).

[13] D. H. Spielberg, A. I. Korn, and A. C. Damask, Phys. Rev. 3, 2012 (1971).

[14] W. Mey and A. M. Hermann, Phys. Rev. 7, 1652 (1973).

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

[16] W. E. Spear, J. Non-Cryst. Solids 1, 197 (1967).

[17] A. R. McGhie and G. J. Sloan, J. Cryst. Growth 32, 60 (1976).

[18] L. B. Schein and A. R. McGhie, Chem. Phys. Lett. 62, 356 (1979).

[19] J. P. McCullough, H. L. Finke, J. F. Messerly, S. S. Todd, T. C. Kincheloe, and G. Waddington, J. Phys. Chem. 61, 1105 (1957). Despite a literature search we have been unable to find a more recent specific-heat measurement near 100 K in naphthalene.

[20] M. Suzuki, T. Yokoyama, and M. Ito, Spectrochim. Acta A 24, 1091 (1968).

[21] I. L. Bakhenkov, E. M. Rodin, E. F. Shekn, and I. Natkaniec, Phys. Status Solidi B 85, 331 (1978).

[22] N. Karl and R. Young (private communication).

[23] E. Irene P. Walker, A. P. Marchetti, and R. Young, J. Chem. Phys. 68, 4134 (1978).

[24] D. Hanson, J. Chem. Phys. 51, 5063 (1969).

[25] H. Frolich and G. L. Sewell, Proc. Phys. Soc. London 74, 643 (1959).

[26] D. M. Burland, Phys. Rev. Lett. 33, 833 (1974); and D. M. Burland and V. Konzelmann, J. Chem. Phys. 67, 319 (1977).

[27] A. J. Epstein, E. M. Conwell, D. J. Sandman, and J. S. Miller, Solid State Commun. 23, 355 (1977); A. J. Epstein, E. M. Conwell, J. S. Miller, Ann. N.Y. Acad. Sci. 313, 183 (1978).

[28] E. M. Conwell, Phys. Rev. Lett. 39, 777 (1977).

[29] N. Karl, E. Schmid, and M. Seeger, Z. Naturforsch. A 25, 382 (1970).

[30] P. Gosar and S. Choi, Phys. Rev. 150, 529 (1966).

[31] A. Madhukar and W. Post, Phys. Rev. Lett. 39, 1424 (1977) and 40, 70(E) (1978).

[32] H. Haken and P. Reineker, Z. Phys. 249, 253 (1972).

[33] H. Sumi, Solid State Commun. 28, 309 (1978).

[34] V. M. Kenkre and C. B. Duke (private communication).

[35] H. Sumi, Solid State Commun. 29, 495 (1979).

[36] S. Efrima and H. Metiu, J. Chem. Phys. 69, 5113 (1978); Chem. Phys. Lett. 60, 226 (1979).