

⁴H.-J. Güntherodt, E. Hauser, and H. U. Künzi, *J. Phys. F* **5**, 889 (1975).

⁵H.-J. Güntherodt, E. Hauser, H. U. Künzi, R. Evans, J. Evers, and E. Kaldis, *J. Phys. E* **6**, 1513 (1976).

⁶O. Dreirach, R. Evans, H.-J. Güntherodt, and H. U. Künzi, *J. Phys. F* **2**, 709 (1972).

⁷See, for example, J. O. Dimmock, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1971), Vol. 26, p. 103; A. J. Freeman, in *Magnetic Properties of Rare*

Earth Metals, edited by R. J. Elliott (Plenum, New York, 1972).

⁸J. C. Duthie and D. G. Pettifor, *Phys. Rev. Lett.* **38**, 564 (1977).

⁹H. Rudin, A. H. Millhouse, P. Fischer, and G. Meier, in *Proceedings of the Third International Conference on Liquid Metals in Bristol*, edited by R. Evans and D. A. Greenwood (The Institute of Physics, Bristol and London, 1976), p. 241.

¹⁰Y. Waseda, private communication.

Observation of the Band-Hopping Transition for Electrons in Naphthalene

L. B. Schein and C. B. Duke

Xerox Corporation W114, Rochester, New York 14644

and

A. R. McGhie

Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

(Received 26 October 1977)

Transient photoconductivity has been used to measure the electron drift mobility in the c' direction of single-crystal naphthalene from 54 to 324 K. Below 100 K the mobility rises exponentially with decreasing temperature, an effect which we attribute to the onset of band-type motion limited by optical-phonon scattering. This observation allows the identification of the approximately constant mobility at higher temperatures ($T > 100$ K) with the hopping of localized charge carriers.

In this Letter we report the first extension of drift mobility measurements for crystalline molecular insulators to temperatures below 77 K. Our measurements reveal the important result that for naphthalene the electron drift mobility rises dramatically from its (approximately constant) high-temperature value as T is decreased below 100 K. We interpret this observation as the long-anticipated¹⁻³ but previously unobserved transition from hopping to band-type motion. This observation of a transition from a roughly constant hopping mobility to one which increases with decreasing temperature is a direct confirmation of the existence at low temperatures of semiconductor (i.e., band)-like mobilities in molecular solids, an effect essential to earlier interpretations of cyclotron resonance⁴ in anthracene and the dc conductivities^{5,6} of quasi one-dimensional salts based on TCNQ (tetracyanoquinodimethane).

The mobilities for electrons in the c' direction of naphthalene from 54 to 324 K are shown in Figs. 1 and 2. Three regions can be distinguished. From 150 to 324 K the mobility is essentially independent of temperature, similar to the behavior of the electrons in the c' direction of anthracene.^{7,8} Writing the temperature dependence as

T^n , we find $n = 0.1 \pm 0.1$. Below 150 K the mobility initially decreases by about 10% as shown in

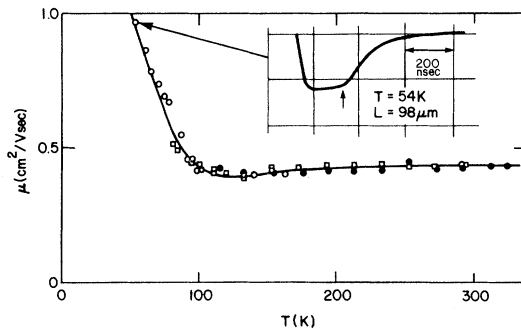


FIG. 1. The mobility, as measured by transient photoconductivity techniques, of electrons in the c' direction of naphthalene from 54 to 324 K. At low temperatures the mobility is exponentially increasing with temperature (see Fig. 2). The different symbols represent measurement of different samples (which have been normalized to $0.44 \text{ cm}^2/\text{V} \cdot \text{sec}$ at room temperature). A Janis 8DT He Dewar was used to make measurements below 140 K and a Stratham SD14 was used to make measurements above 77 K (both having control to ± 0.1 K). A "current" mode pulse at 54 K with the transit time marked by an arrow is shown in the inset. The smooth curves drawn through the data (in Figs. 1 and 2) indicate the features of the data which were reproducible among all our samples.

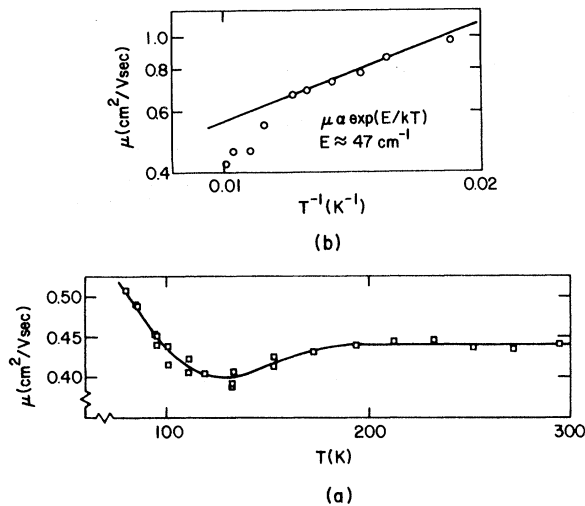


FIG. 2. (a) The same data marked as open squares in Fig. 1 plotted on an expanded vertical scale, which shows the 10% decrease in mobility from 100 to 150 K. (b) The lowest-temperature data plotted semilogarithmically. The slope, outside the transition region (below 80 K), is approximately equal to 5.8 meV (47 cm^{-1}).

a blown-up scale in Fig. 2(a). While such a small decrease is only slightly larger than the error bars, this region of decreased mobility is observed in all samples. Finally, below 100 K, the mobility increases rapidly with decreasing temperature. In Fig. 2(b) it is shown that within experimental error the temperature dependence in this region can be described by $\exp(E/kT)$ where $E \approx 5.8 \text{ meV}$ (47 cm^{-1}).

These data were obtained by standard transient-photoconductivity^{9,10} techniques. The transit time, which equals the crystal thickness divided by the product of the mobility and the applied electric field, of a photogenerated sheet of carriers is measured. The experiments were performed with a quadrupled (2650-Å light) Nd:glass laser (Holobeam Model 331) which provides a highly absorbed laser flash of sufficient energy (1 mJ) and of short enough duration (2.5 nsec) to avoid carrier trapping. A transit pulse observed at 54 K is shown in the inset of Fig. 1.

The naphthalene was purified by a potassium treatment followed by extensive zone refining under an argon atmosphere. Single crystals were grown in a Bridgman oven at 1 mm/h. As described earlier,⁸ these crystals were polished with cyclohexane to thicknesses on the order of 50–100 μm . Then they were painted with a thin layer of silver print and were allowed to anneal at room temperature for several days. Data

identical to those shown in Figs. 1 and 2 to 77 K were obtained on samples taken from two of our boules and from one boule obtained from a separate source. Data below 77 K were obtained on two separate crystals taken from the same boule. The lowest attainable temperature for this measurement was determined by a range limitation on the carriers or dielectric breakdown at high electric fields ($\approx 10 \text{ V}/\mu\text{m}$). That these data could be obtained on samples taken from different boules strongly suggests that the mobilities shown in Figs. 1 and 2 are *intrinsic* properties of crystalline naphthalene.

Only one measurement of the temperature dependence of both the electron (μ_e) and hole (μ_h) mobilities in naphthalene has been reported previously,¹¹ over a temperature range of 220–300 K. It is particularly difficult to measure the magnitude of the mobility in naphthalene because it rapidly sublimates at room temperatures: If the crystal thickness is overestimated, the mobility will be overestimated. Our room-temperature values of μ_e and μ_h in the c' direction, $\mu_e = 0.44 \pm 0.02 \text{ cm}^2/\text{V sec}$ and $\mu_h = 0.39 \pm 0.04 \text{ cm}^2/\text{V sec}$, are in agreement with those of Silver *et al.*¹² ($\mu_e = 0.4$, $\mu_h = 0.4$), but are somewhat smaller than the measurements of Spielberg, Korn, and Damask¹³ ($\mu_e = 0.6$, $\mu_h = 0.5$) and Mey and Hermann¹¹ ($\mu_e = 0.68$, $\mu_h = 0.99$). We confirm the temperature dependence of the hole mobility quoted by Mey and Hermann¹¹ (approximately T^{-2} over the temperature range 170–325 K). The temperature dependence of μ_e is consistent with their data¹¹ (from 220 to 300 K) if we take into account the experimental error of $\pm 10\%$.

To obtain the mobilities plotted in Fig. 1 the electric field must be known. It is given by the applied potential divided by the crystal thickness in the absence of space charge. In Fig. 3 we show the inverse transit time versus applied potential at 134 K. These data were taken on a sample after the transit measurements were made down to 77 K. That the intercept is zero within experimental error suggests that negligible space charge exists in this sample. This may be due to the fact that between each measurement the front and rear electrodes (Ag print, NESA glass) were shorted and several light pulses were flashed on the sample, a technique which should tend to neutralize any trapped space charge. This test for space charge was carried out at lower temperatures over smaller voltage ranges. In addition, the linearity evident in Fig. 3 demonstrates that the mobility remains electric-field

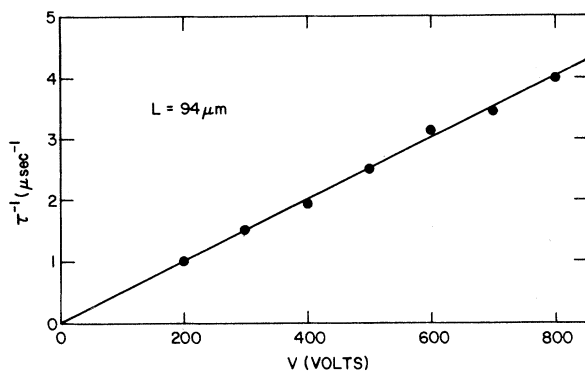


FIG. 3. The inverse transit time versus voltage at 134 K. The zero intercept suggests that there exists negligible space charge in the sample. The linearity demonstrates that the mobility is independent of the electric field up to $10 \text{ V}/\mu\text{m}$ at this temperature.

independent up to a field strength of $10 \text{ V}/\mu\text{m}$ at 134 K.

The change in behavior of μ_e near 100 K cannot be associated with a phase transition since there is no evidence for a phase transition in naphthalene near 100 K in either specific-heat data¹⁴ or Raman spectra.¹⁵ We interpret the sharp rise in μ_e below $T = 100 \text{ K}$, evident in Figs. 1 and 2, as due to the onset of band motion. The observed temperature dependence in this low-temperature region, which can be fitted by $\exp(E/kT)$, is consistent with electron scattering by lattice modes. Specifically, the value of $E \approx 47 \text{ cm}^{-1}$ is the energy of one of the lowest out-of-phase lattice vibrations in naphthalene.¹⁵ (The low-energy lattice modes, which we shall refer to as "optical" modes, are classified by Suzuki, Yokoyama, and Ito¹⁵ as "rotational modes," i.e., librions, at 125, 109, 74, 71, 51, and 46 cm^{-1} , and "translational" modes at 98, 73, and 39 cm^{-1}). There is no self-evident reason why the lowest-energy modes should interact with electrons more strongly than the other lattice modes or symmetric molecular vibrations. Hence, we suggest that many of the lattice modes and molecular vibrations will scatter electrons. Only after they are frozen out at low enough temperatures is the electron scattering sufficiently weak that band motion occurs. The observed value of E is simply characteristic of that vibration which limits the electron mobility at $T \leq 100 \text{ K}$. Obviously, at still lower temperatures scattering by acoustical lattice modes¹⁶ and crystalline defects can become important and limit μ_e .

These data permit an estimate of a lower bound for the electron bandwidth in the c' direction

(5.8 meV). 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. Our estimate of 5.8 meV is consistent with calculations of Katz *et al.*¹⁷ (1–4 meV).

It can be inferred directly from Figs. 1 and 2 that the transport processes for $T \lesssim 100 \text{ K}$ and $T \gtrsim 150 \text{ K}$ must be different in character; i.e., the high-temperature, temperature-independent mobility (characteristic of almost all molecular crystals at room temperature¹⁸) is a hopping motion. If the band model described motion over the entire temperature range, then we should have $\mu_e^{-1} \cong \sum_i (\mu_{ei})^{-1}$, where the μ_{ei} designate the contributions of the various electron-scattering mechanisms in limiting the conductivity. This implies that the small mobility always dominates. Given the previous conclusion that the low-temperature ($T < 100 \text{ K}$) regions of Figs. 1 and 2 are manifestations of band motion, if the constant mobility for $T \gtrsim 150 \text{ K}$ also were a consequence of band motion, then it should dominate at $T < 100 \text{ K}$ and be dominated at $T > 150 \text{ K}$ by the monotonically decreasing phonon-scattering mobility, a conclusion in obvious disagreement with the data. The intermediate temperature region between 100 and 150 K, which exhibits a shallow minimum, is, therefore, interpreted as a region in which both band and hopping motion occur (e.g., such a minimum can be seen in the predictions of Munn and Silbey¹⁹).

A band to hopping transitions has been anticipated for nearly twenty years in the polaron literature,^{1,3} although never before observed so unambiguously. Early model predictions of this transition from small-polaron "band" to "hopping" motion were based on the molecular crystal model^{1,3} in which the electron's energy at a given site is modulated linearly by a single branch of vibrations (i.e., a model embodying diagonal disorder and linear electron-vibration coupling). Although in the original papers^{1,3} these vibrations were envisioned to be intramolecular in character, Gosar and Choi¹⁶ extended the model to encompass acoustical lattice modes.

While other pertinent extensions^{19–21} of the early papers have been reported, the temperature dependence of μ_e observed for $T \gtrsim 150 \text{ K}$ still has not been accounted for in detail by these models.^{8,16} One possible reason for this fact is the neglect within the framework of the molecular crystal model of lattice-vibration-induced off-diagonal disorder. Specifically, the lattice vibra-

tions modulate the one-electron hopping integrals as well as the site energies of the electron. Describing these fluctuations as a Gaussian distribution of random variations in the hopping integrals yields an exact solution of the equations of motion for the one-electron density matrix in one dimension, a solution which leads to a temperature-independent mobility.²² Therefore we anticipate that off-diagonal as well as diagonal vibration-induced disorder must be considered to interpret in detail the temperature dependence of μ_e in the hopping regime $T \geq 150$ K.

In summary, data have been presented for electron mobilities in the c' direction of naphthalene from 54 to 324 K. These data constitute the first measurements of mobility in a molecular crystal below 77 K. From 150 to 324 K, μ_e is essentially temperature independent. Below 150 K, μ_e at first decreases by 10% and then rises exponentially with decreasing temperature. We have argued that the low-temperature mobility is associated with band motion limited by optical-phonon scattering. The approximately temperature-independent mobility above 150 K is interpreted as a manifestation of a hopping mobility which may require consideration of off-diagonal disorder for its detailed interpretation. These data constitute the first observations of a band-hopping transition in the electron transport properties of molecular crystals. Moreover, they suggest that very large low-temperature mobilities may be obtained for suitably pure and perfect molecular crystals.

The authors would like to acknowledge the supply of additional crystals of naphthalene by I. Zschokke-Granacher and discussions with W. Mey and R. Anderson, and to thank A. Madhukar and W. Post for a preprint of their work prior to publication. This work was supported in part by a National Science Foundation Materials Research Laboratory program under Grant No. DMR 76-80994.

¹T. Holstein, *Ann. Phys. (N.Y.)* **8**, 343 (1959).

²J. Yamashita and T. Kurosawa, *Phys. Chem. Solids* **5**, 34 (1958), and *J. Phys. Soc. Jpn.* **15**, 802 (1960).

³J. Appel, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1968), Vol. 21, p. 193.

⁴D. M. Burland, *Phys. Rev. Lett.* **33**, 833 (1974); D. M. Burland and V. Konzelmann, *J. Chem. Phys.* **67**, 319 (1977).

⁵A. J. Epstein, E. M. Conwell, D. J. Sandman, and J. S. Miller, *Solid State Commun.* **23**, 355 (1977).

⁶E. M. Conwell, *Phys. Rev. Lett.* **39**, 777 (1977).

⁷K. H. Probst and N. Karl, *Phys. Status Solidi (a)* **27**, 499 (1975); N. Karl, *Adv. Solid State Phys.* **14**, 261 (1974).

⁸L. B. Schein, *Chem. Phys. Lett.* **48**, 571 (1977).

⁹R. G. Kepler, *Phys. Rev.* **119**, 1226 (1960).

¹⁰W. E. Spear, *J. Non-Cryst. Solids* **1**, 197 (1967).

¹¹W. Mey and A. M. Hermann, *Phys. Rev.* **7**, 1652 (1973).

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

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

¹⁴J. P. McCullough, H. L. Finke, J. F. Messerly, S. S. Todd, T. C. Kincheloe, and G. Waddington, *J. Phys. Chem.* **61**, 1105 (1957).

¹⁵Masako Suzuki, Toru Yokoyama, and Mitsuo Ito, *Spectrochim. Acta* **24A**, 1091 (1968).

¹⁶P. Gosar and Sang-il Choi, *Phys. Rev.* **150**, 1529 (1966).

¹⁷J. I. Katz, S. A. Rice, Sang-il Choi, and J. Jortner, *J. Chem. Phys.* **39**, 1683 (1963).

¹⁸L. B. Schein, *Phys. Rev. B* **15**, 1024 (1977).

¹⁹R. W. Munn and R. Silbey, in *Proceedings of the Eighth Molecular Crystal Symposium*, edited by M. A. El Sayed (Univ. of California, Los Angeles, 1977), pp. 259-264, and to be published.

²⁰R. W. Munn and W. Siebrand, *J. Chem. Phys.* **52**, 6319 (1970), and **53**, 3343 (1970).

²¹H. Sumi, *J. Phys. Soc. Jpn.* **33**, 327 (1972).

²²A. Madhukar and W. Post, *Phys. Rev. Lett.* **39**, 1424 (1977), and **40**, 70(E) (1978). The results reported by these authors are extensions of those obtained earlier for excitons by H. Haken and P. Reineker, *Z. Phys.* **249**, 253 (1972).