Injected Electrons in Naphthalene: Band Motion at Low Temperatures

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A Boltzmann-equation analysis of low-temperature ($T < 100$ K) electron drift mobilities in naphthalene reveals that acoustic-phonon scattering of electrons in extended energy-band states provides a quantitative interpretation of the temperature dependence of these mobilities.

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The nature of the electronic states characterizing electrons injected into naphthalene has been a subject of interest and dispute for the last five years,[1-4] ever since the report[5] in 1978 of a band-to-hopping transition at $T \simeq 100$ K. The determination of the nature of these states is a fundamental problem in the physics of molecular solids as reflected in the failure, thus far, of either band or hopping models to yield a quantitative description of available drift-mobility data.[1,4] An additional complication is generated because the weak interactions between molecules introduce a strong tendency to disorder, both structural[6] and dynamic,[7] which is thought to localize most injected charges in these materials.[1-4,6] Van der Waals monomolecular crystals constitute a particularly interesting special case because dynamic disorder should be frozen out at low temperatures, leading to injected carrier motion in extended energy-band states.[8] This hypothesis has, however, been contested in recent years.[2,3,6] Thus, in spite of extensive theoretical[1-4,6,8-14] and experimental[15,16] efforts during the past five years, the character of the correct description of the low-temperature transport of charge carriers injected into organic van der Waals crystals has remained uncertain.

In this Letter we report a new analysis of measured low-temperature ($T<100$ K) electron drift mobilities in naphthalene.[5,16-18] This analysis establishes two important results. First, a band model embodying the scattering of electrons by acoustical phonons provides a quantitative description of the data for all crystallographic directions for $T<100$ K. Second, the fits to the temperature dependence of the mobilities in the b and c' directions provided by theories which are based on libration-assisted motion, and which use either band models[5,18] or other models,[2,3,10] are considerably poorer. The central conclusion to be drawn from this work is that in the specific case of naphthalene, for which the electron drift-mobility data are far more complete than for other organic van der Waals solids, these mobilities are consistent with a model in which at sufficiently low temperatures they are attributed to the scattering of electrons in energy-band states by acoustical phonons.

A consequence of the monoclinic crystal structure of naphthalene is the off-diagonal nature of the mobility tensor in the crystallographic coordinate system. Since the b axis is a twofold axis of symmetry, it is a principal axis of the mobility tensor corresponding to μ_{bb}. The remaining three independent components, μ_{aa}, $\mu_{c'c'}$, and $\mu_{ac'}$, may be transformed into the principal-axis system via a rotation by $\theta = \frac{1}{2} \times \tan^{-1}[2\mu_{ac'}/(\mu_{aa} - \mu_{c'c'})]$ about the b axis. In general, adequate data to determine θ as a function of temperature are not presently available.[16-18] For $T<100$ K, however $\theta \simeq -5°$ so that transformation to the principal-axis system produces only small (less than 6%) corrections to μ_{aa} and $\mu_{c'c'}$. Consequently, we ignore these corrections herein.

Our model is defined by effective-mass motion of electrons in ellipsoidal energy bands (with masses obtained from band-structure calculations[19]) and harmonic phonon motion with parameters extracted from neutron-scattering meas-

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urements of the phonon spectra,[7] i.e.,

$$H_0 = \sum_{\vec{k},i=1}^{3} (\hbar^2 k_i^2/2m_i^*) a_{\vec{k}}^{\dagger} a_{\vec{k}} + \sum_{\alpha,\vec{q}} \hbar\omega_\alpha(\vec{q})[b^{\dagger}_{\vec{q}\alpha} b_{\vec{q}\alpha} + \tfrac{1}{2}] \tag{1}$$

in which $a_{\vec{k}}$ ($b_{\vec{q}\alpha}$) designate the electron (phonon) operators. The components of the mass tensor are[19] $m_1^* = 100m$, $m_2^* = 90m$, and $m_3^* = 40m$ where m is the free-electron mass. Electrons in the extended band states scatter from the phonons via a linear electron-phonon coupling; i.e.,

$$H_1 = N^{-1/2} \sum_{\vec{k},\vec{q},\alpha} a_{\vec{k}+\vec{q}}^{\dagger} a_{\vec{k}} g_\alpha(\vec{q},\vec{k}) \hbar\omega_\alpha(\vec{q})(b_{\vec{q}\alpha} + b_{-\vec{q}\alpha}^{\dagger}). \tag{2}$$

Using standard Boltzmann equation analysis[20] and

$$g_\alpha(\vec{q},\vec{k}) = g, \quad \omega_\alpha(\vec{q}) = \omega \tag{3}$$

for librational phonon scattering, we find that the electron mobility in the wide-band limit ($\kappa T \lesssim W$ where W is the bandwidth) is given by

$$\mu_i = \left(\frac{e\hbar^2}{g^2\omega^2 m_i^*}\right)(\tfrac{2}{3}v_c)(e^y - 1)\left(\frac{2\pi}{\kappa T m_1^* m_2^* m_3^*}\right)^{1/2}\left[\int_0^y \frac{x^{3/2}e^{-x}\,dx}{(x+y)^{1/2}} + \int_y^\infty \frac{x^{3/2}e^{-x}\,dx}{e^y(x-y)^{1/2} + (x+y)^{1/2}}\right] \tag{4}$$

in which $y = \hbar\omega/\kappa T$ and v_c is V/N, the volume of the unit cell. Evaluation of Eq. (4) reveals that when $\kappa T \gg \hbar\omega$, $\mu \sim T^{-3/2}$. Otherwise, μ decreases more rapidly with increasing temperature. Since the lowest-energy librational modes occur at 5.7 meV (66 K), the full expression given by Eq. (4) must be used to evaluate μ in the low-temperature region considered here.

For longitudinal-acoustical phonons we utilize a Debye model of the phonon dispersion and deformation-potential electron-phonon coupling, i.e.,

$$g(\vec{q},\vec{k}) = [A(\vec{q}/|\vec{q}|)/\hbar\omega(\vec{q})]^{1/2}; \quad \omega(\vec{q}) = qv_s, \tag{5}$$

where A is a known[20] function of the direction of $\vec{q}$, deformation potentials, elastic constants, and effective masses. In the wide-band limit ($\kappa T \lesssim W$) the principal-axis mobilities are given by

$$\mu_i = e\hbar^4[3v_c m_i^* B_i (m_1^* m_2^* m_3^*/2\pi)^{1/2}(\kappa T)^{3/2}], \tag{6}$$

in which the B_i are weighted averages of the $\{A_i\}$.

In the narrow-band limit, $\kappa T \gg W$, both librational and acoustic-phonon scattering yield contributions to the electron mobility proportional to T^{-2}.

In Fig. 1 we replot existing data[16-18,21] to reveal that for $T \lesssim 100$ K the temperature dependence of the mobilities in the a, b, and c' crystallographic directions can be described by a $T^{-3/2}$ dependence on temperature. Hence, all of these data are compatible with electron scattering by acoustical phonons as described by Eq. (6), and also well known earlier in the literature.[8,22] In Fig. 2 we present the data for electron drift mobilities along the c' axis and show that the fits provided by two earlier calculations[2,3,10] based on a combination of band and libration-assisted hopping motion are poorer than that given by

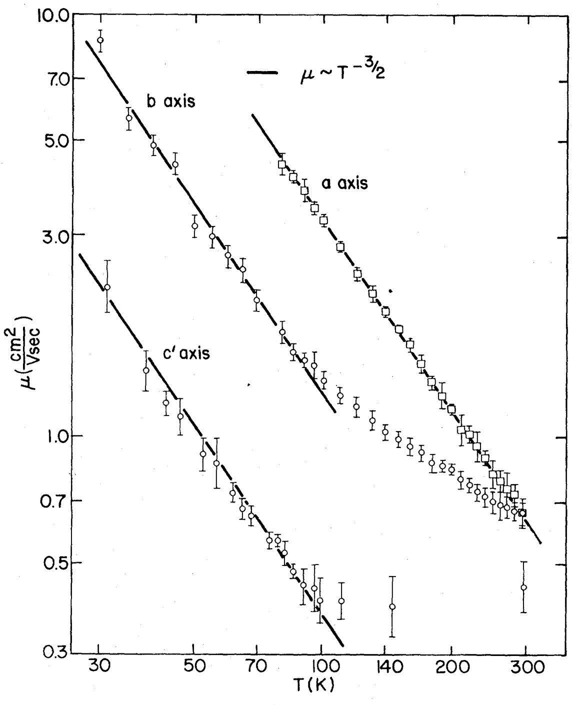

FIG. 1. Measured electron drift mobilities along the a, b, and c' directions in naphthalene as functions of temperature. The error bars are obtained as the averages of repeated runs under nominally identical conditions. The data include those reported in Refs. 5, 16, 17, 18, and 21, but averaged and replotted with use of a log-log scale.

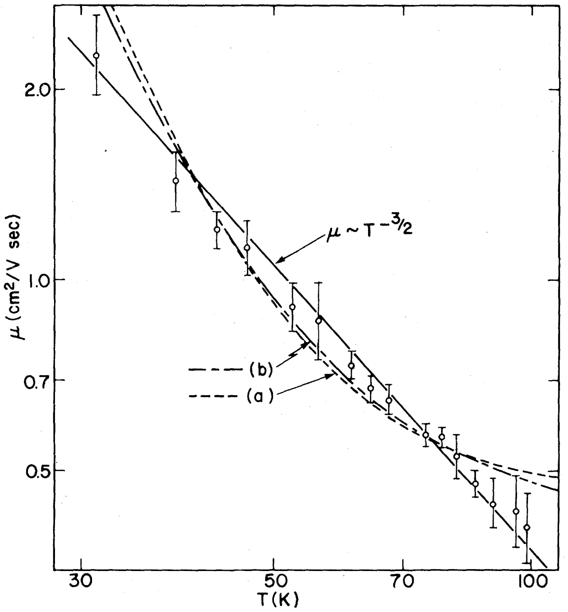

FIG. 2. Comparison of measured electron drift mobilities in the c' direction in naphthalene with the results of the band model with scattering by acoustical phonons as given by Eq. (6) (solid line) and the combination band-hopping models of Ref. 2 (curve a) and Ref. 10 (curve b) which embody electron scattering by librational modes.

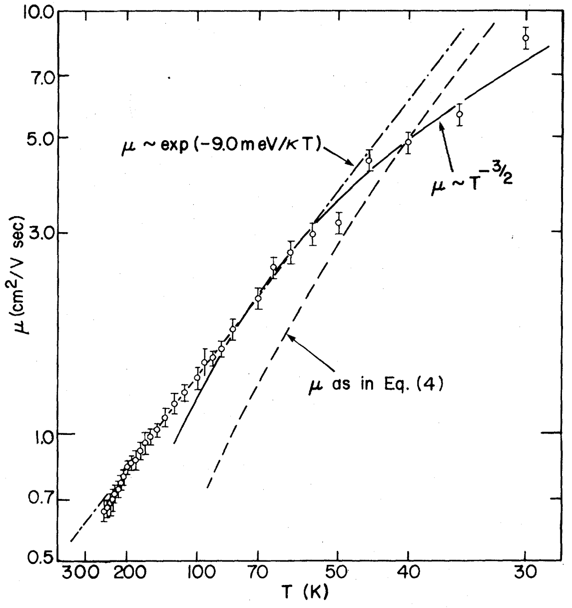

FIG. 3. Comparison of measured electron drift mobilities in the b direction in naphthalene with the results of Eq. (4) obtained from a band model and scattering by librational modes (dashed line), an empirical exponential fit (Refs. 5 and 18) (dot-dashed line), and the band model with scattering by acoustical phonons as given by Eq. (6) (solid line). The measured mobilities were reported in Refs. 16, 18, and 21. The abscissa is linear in T^{-1}.

our present analysis. Although these earlier models[2,3,10] possess the additional feature that they can describe the temperature dependence of the flat portion for $T > 100$ K, they are forced to assume unreasonably low values of the libration frequencies in order to provide satisfactory fits to the data below 100 K. Curves (a) and (b) in Fig. 2 are obtained by use of these combination models (Refs. 2 and 10, respectively) and a libration frequency of 5 meV, i.e., well below the lowest known value[7,23] of 5.7 meV. Moreover, the quality of the fits diminishes as the frequency is increased. In contrast, the solid line in Fig. 2, which is our present calculation, describes the data satisfactorily. The corresponding results for the electron mobilities along the b axis are shown in Fig. 3. Only the solid line, obtained from Eq. (6) for acoustical-phonon scattering of band electrons, describes the temperature dependence of these mobilities for $T < 100$ K. Since, moreover, b is a principal axis of the mobility tensor, the results shown in Fig. 3 are not complicated by its nondiagonal nature.

For $T < 100$ K the mean free paths obtained from Eq. (6) are comfortably larger than the unit-cell dimensions in the a and b directions. In the c' direction, however, they become comparable to the spatial extent of the π-electron wave functions[24] or the intermolecular spacings at temperatures 30 K $\lesssim T \lesssim$ 40 K, in spite of the observed $T^{-3/2}$ behavior of $\mu_{c'c'}$ up to $T \simeq 100$ K. This issue is well known in applying energy-band models to interpret electron mobilities in the c' direction in naphthalene and anthracene.[8,19] We currently are investigating whether a misunderstanding is involved in the traditional interpretation of energy-band calculations in organic solids which contain large molecules as the components of each unit cell.

In summary, we have presented a reanalysis of measured low-temperature electron drift mobilities in naphthalene in which these mobilities are interpreted as reflecting the acoustical-phonon-limited motion of electrons in (three-dimensional) extended energy-band states. This model quantitatively describes both the temperature dependence of the principal-axis mobilities and the temperature independence of the orientation of the mobility tensor for $T < 100$ K. For $T > 100$ K the orientation of the principal axes varies rapidly with temperature in the a-c' plane, and existing data are inadequate to define the mobility tensor uniquely.[15] Hence, additional measurements are required before a quantitative analysis of the electron drift mobilities for $T > 100$ K is possible.

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