A crystalline organic semiconductor grown from a mesophase: A test of polaron band theory

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Abstract

We find that the hole mobility of the crystal smectic phases of the liquid crystal 1,4-di-(5-n-tridecylthien-2-yl)-benzene increases exponentially with decreasing temperature. While qualitatively consistent with transport via polaron bands, we find that it is quantitatively difficult to explain the data with physically realistic parameters. In particular, the data demand either quite large typical optical phonon frequencies and/or phonon bandwidths. We also find evidence that an unusually highly ordered high temperature smectic-F phase templates the formation of crystalline smectic phases, which may have implications for device development.

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The behavior of the charge mobility of organic semiconductors as a function of temperature and electric field, $\mu(T, E)$, may change qualitatively based on, e.g., the polarizability of the host lattice, the phonon spectrum, and the electronic bandwidth of the valence (for hole transport) or conduction (electron) band. Many refinements of the basic ideas of Holstein[1] have been developed, dealing with both non-adiabatic[2] (hopping conduction with activated-like temperature dependence) and adiabatic[3] (tunneling-dominated or band-like) transport. We report here studies of a material that exhibits polaron band behavior. However, while qualitatively consistent with the model, the data exhibit a major inconsistency (exponential growth of mobility with decreasing temperature), the resolution of which appears to require parameter values bordering on the unphysical. The rapid increase of mobility at lower T also makes related systems of real interest for, e.g., thin-film transistor fabrication. Of practical interest are the facts that the high-order smectic mesophase exhibits very long correlation lengths (i.e., is highly ordered) and that the crystal smectic phases appear to inherit this order and therefore easily form domains large enough to transport holes without a great deal of trapping at boundaries.

Our material is built around a thiophene-benzene-thiophene core with alkyl tails. A detailed description of the synthesis and purification of the mesogen, 1,4-di-(5-n-tridecylthien-2-yl)-benzene, may be found in the auxiliary information at EPAPS. Powder x-ray studies were performed at the Advanced Photon Source at Argonne National Laboratory using 0.765335 Å photons with the sample contained in a Lindeman capillary. Hole time-of-flight (TOF) mobility data were collected using 10 ns Nd:YAG frequency-doubled stimulated Raman shifted laser pulses to photoexcite a sample contained in an ITO/glass capacitor[4] of thickness $\approx 20\ \mu$m. Laser pulse intensities were kept low to avoid space-charge effects (manifesting as TOF traces that rise during the charge transit period). The temperature range over which we could collect data was limited on the low end by trapping and on the high end by melting. Electron TOF traces were too dispersive to allow for mobility measurement. Differential scanning calorimetry (Fig. 1), powder x-ray diffraction (see below), and polarized light microscopy indicate the phase sequence Cr_1 76.6 S_H 91.7 S_G 122.4 S_F 134.0 I (on cooling)[5]. Polarized light microscopy images are available as part of the EPAPS entry for this article.

The temperature dependence of the mobility, taken on cooling, is shown in Fig.2. The mobility in the S_F phase is of order 6×10^{-3} cm^2/Vs and appears to decrease with T over

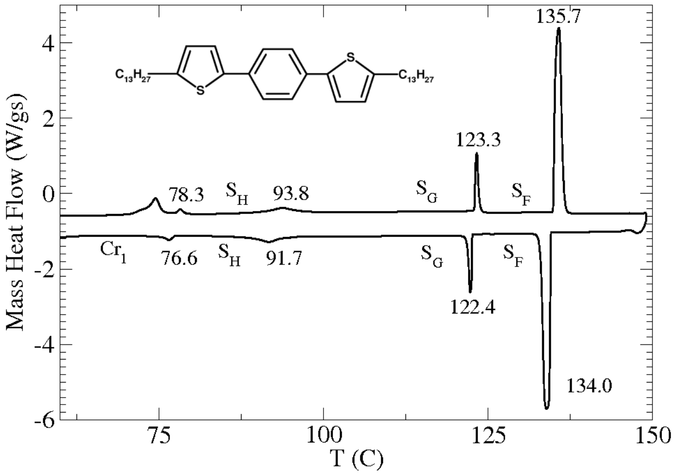

FIG. 1: Differential Scanning Calorimetry data. The smectic mesophase and some of the crystal phases are labeled.

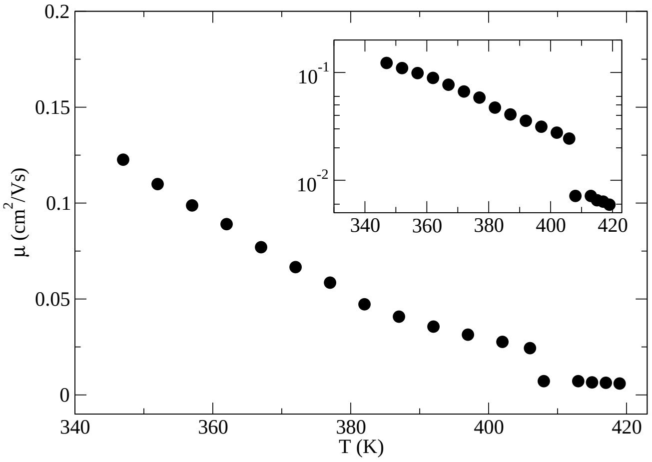

FIG. 2: Temperature dependence of the hole mobility measured at 5400 V/cm. The change at the S_F to S_G transition is clearly visible, as is the rapid increase in $\mu(T)$ as T decreases. The inset shows the same data on a semilog scale.

the narrow temperature range of the phase. Compared to most calimitics (e.g., phenyl-napthalenes or biphenyl-based materials[6, 7]), the mobility is quite large. This is likely explained by the large correlation lengths in the "medium order" smectic S_F phase. In

Fig. 4, we show powder diffraction data in the S_F phase, which shows very large correlation lengths, both orthogonal (112.2 nm) and parallel (10.85 nm) to the smectic planes. However, there is dynamic disorder, as shown by the sizable jump in mobility (a factor of 3.4) at the transition from the S_F to the much more ordered S_G phase, presumably due to the loss of the fluctuations in the mesophase on cooling (the S_G phase is a three dimensional crystal in which, however, the molecules are, roughly speaking, free to rotate about their long axes). As T falls, the mobility sharply increases, to a maximum $>$ 0.1 cm^2/Vs at the lowest temperature measured. There is a crystalline structural transition at $T_{SG} \rightarrow T_{S_H} \approx$ 365 K, with only a small signature in the mobility. Since the main difference between the G and H phases is a much reduced degree of molecular rotation in the lower temperature state, it appears that the exact alignment of adjacent molecular cores is not critical for transport.

Our data in the crystal smectic phases may be well described by either a power-law form ($\mu \sim T^{-n}$, not shown) or by an exponential, $\mu \sim exp(-\alpha T)$, shown in the inset to Fig 2. While power-law forms for $\mu(T)$ are predicted by various theories, we find a best-fit power $n \approx 10$, far greater then the 1.5 predicted theoretically[3, 8] or the $n \sim 2-4$ found in other organics[8, 9]. A general result of polaron band theories, such as that described by Silbey and Munn[3], and present in the early theory of Holstein[1], is that there is a narrow crossover temperature regime (characteristic temperature T_a) between non-adiabatic and adiabatic conduction, with the latter taking over at low T. The crossover temperature is critical in describing our results: above T_a, $\mu(T)$ has positive slope while below T_a, the mobility typically has negative slope and can exhibit qualitatively exponential behavior. Four parameters control both T_a and the shape of $\mu(T)$: the electron bandwidth, B, the characteristic optical phonon frequency, ω, the phonon bandwidth, Δ, and the dimensionless electron-phonon coupling, g. The predicted mobility, both above and below T_a, is given by[3]

$$\mu(T) = \mu_H + \mu_T \tag{1}$$

$$\mu_H = \frac{\beta e a^2}{\pi^{1/2} h [I_0(y)-1]} \frac{\tilde{B}^2+\Gamma^2}{\sqrt{\tilde{B}^2+2\Gamma^2}} \tag{2}$$

$$\mu_T = \frac{\beta e a^2}{4h} \pi^{1/2} [I_0(y) - 1] \frac{\tilde{B}^2}{(\sqrt{2\tilde{B}^2+\Gamma^2}} \exp\{-\tfrac{1}{4}\beta^2 \tilde{B}^2/(2\tilde{B}^2 + \Gamma^2)\} \tag{3}$$

where

$$\tilde{B} = B \exp\{-g^2/\tanh(\beta\hbar\omega/2)\} \tag{4}$$

$$y = 4g^2\sqrt{n(n+1)} \tag{5}$$

with μ_H and μ_T the hopping and tunneling contributions to mobility, $\beta = 1/k_BT$, and a the intermolecular distance. $\tilde{B}$ is the renormalized (Huang-Rhys) polaron bandwidth[1] which decreases sharply with increasing temperature, Γ is a modified phonon bandwidth[3], and n is the phonon distribution function, $n = 1/[\exp(\beta\hbar\omega) - 1]$. The hyperbolic Bessel function $I_0(y)$ is a sharply increasing function of its argument and therefore of T ($y \sim n$ and n increases with T). We use the x-ray derived value of a=4.2 nm (i.e., we assume transport is orthogonal to the smectic layering). Note that these expressions provide a prediction for the mobility in absolute units. Given the small region of temperature (even though we consider both the S_G and S_H phases collectively in our analysis), it is impossible to constrain all of the four parameters. However, we find that, in order to move the low-T quasi-exponential region of μ to the high experimental temperature range and to account for the measured values of mobility, the model requires large coupling $g \geq 1$ and small raw electronic bandwidth $B \ll \omega$. (The data do not constrain B except that they require $B/\omega \ll 1$.) In this regime, we must then have either *large phonon bandwidth* $\Delta > \hbar\omega$ and/or *high center frequency* ω. This is logical - the value of the crossover temperature T_a is set partly by the phonon energies the system supports, i.e., either by ω itself or by the high energy tail of the Gaussian distribution whose width is set by Δ. The model, however, is limited to $\Delta/\omega < 1$ (so that the phonon distribution can be modeled as a Gaussian[3]). Letting the phonon bandwidth take on a maximal value, say $\Delta/\hbar\omega = 0.5$, we find that the data may be fit albeit with $\omega/k_B \approx 440$ K. Typical acenes and simple aromatics like perylene have experimentally measured phonon bands centered around 200 K or less (an oft-used approximate value is 100 $\mathrm{cm}^-1 \approx 150$ K). It is hard to understand why a relatively "floppy" molecule like ours would have a much stiffer lattice than these materials. Indeed, the small electronic bandwidth would suggest that the molecular cores are relatively weakly interacting, which at least naively would lead to a softer lattice. We therefore conclude that the present model is quantitatively incorrect. Given the simplifications inherent in the theory (greatly simplified phonon band structure, including the limitations on Δ, isotropy, etc.), this is not too surprising. We note that more complete theories including non-local electron-phonon interactions[10, 11] are unlikely to resolve our difficulties since they seem to *reduce* the slope at low T, while our data demand moving the regime of quasi-exponential growth to higher temperature. Perhaps a more promising direction is supplied by theories of intermediate bandwidth organic semiconductors, such as those explored by Kenkre and

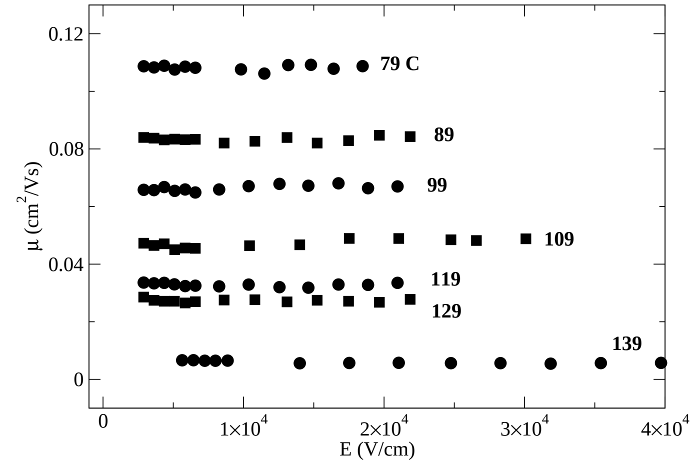

FIG. 3: Mobility as a function of electric field at various temperatures. At each temperature, the mobility appears to be ohmic, i.e., independent of field.

coworkers[12].

The electric field dependence of the mobility is a powerful probe of the microscopics. In the case of hopping conduction[2], $\mu(E)$ can be super-exponential. On the contrary, we find the E is irrelevant. In Fig. 3, we show the hole mobility over a wide range of field and temperatures in each phase. In every case, μ is essentially independent of field, i.e., ohmic. This is consistent with a band model. We note that we do not observe any sign of a drop in mobility at large fields that would indicate hot-carrier effects.

There are a number of other high order crystals smectics that have been studied as semiconductors[13–17], some (though by no means all) with mobilities in the 0.1 cm^2/Vs range. To our knowledge, however, this is the first smectic H material so studied, and the first very high mobility smectic with polaron band-like transport. It is interesting and potentially of practical utility that the highly crystalline H phase supports high-quality hole transport in 1,4-di-(5-n-tridecylthien-2-yl)-benzene in our 20 μm cells, since, in our experience, "true" crystal phases grown from smectics usually have too much structural disorder (and therefore trapping) to even show measurable TOF transients. One possible explanation is that the highest temperature crystal smectic, S_G, inherits the impressive long-range order of the mesophase, both orthogonal and parallel to the smectic planes, which in turn templates the H phase. The powder diffraction results shown in Fig. 4 suggest that the S_F state

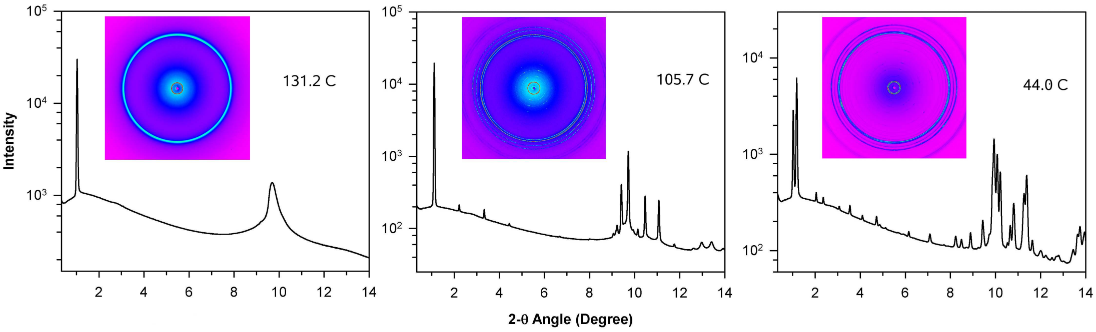

FIG. 4: Powder diffraction results on the S_F, Cr_1, and Cr_2 phases. Note both the high degree of order in the mesophase and the similarity of the structures of the smectic and crystalline phases.

templates the structure of the S_G crystal, which presumably crystallizes in larger, better ordered grains due to the order of the adjacent smectic. This presents a very interesting technological advantage of these crystal smectics: thin samples of a high-mobility essentially crystalline organic may be grown with large-grained structure by using a less-ordered smectic phase as a template. Indeed, by using standard methods to align the liquid crystal phase (appropriately rubbed polyimide alignment layers, magnetic and electric fields, etc.), it may be possible to stabilize a fully crystalline thin film *via* the mesophase. The implications for device (for example, thin film transistor) development, where a high-mobility film must be produced, preferably at low temperatures, are obvious. Another interesting possibility is to use the mesophase to anneal away damage in the semiconductor and then to re-crystallize the ordered film *in-situ*.

This is not the first liquid crystal with a thiophene-benzene-thiophene core found to have a high mobility. In 2005 Oikawa *et al.*[18] measured $\mu(T)$ in the C_8 analog of our material and found similar mobilities, though the increase with decreasing T was less pronounced. Whether this is due to an intrinsic difference in the materials or to cell thickness (they used 15.9 μm), alignment, or cooling rate is unknown. The authors found the phase assignment I 145 S_1 87 S_2 71 S_3 Cr, i.e., three unidentified smectic phases followed by a crystal phase on cooling. This is similar to our results. Interestingly, Oikawa *et al.* found large ($\sim 0.1 cm^2/Vs$) mobilities in the lower mesophases, and much higher values of μ in the highest temperature smectic S_1 phase than we find in our S_F regime. Obviously, further mobility and structural studies (including phase assignment) of this series are warranted. Duzhko *et al.*[9] found evidence for polaron band transport in a very different mesogen, the hexapentyloxydiphenylene (HAT5), a discotic material with a mobility at least three orders of magnitude smaller than the (S_H phase) of the present material. Apparently, charge transport via renormalized polaronic bands is a fairly generic occurrence in organics of widely differing morphology.

Our material, 1,4-di-(5-n-tridecylthien-2-yl)-benzene, appears to be a prototype narrow polaron band semiconductor, which presents opportunities for refining the relevant theories. The principal theoretical question is, why is "the low temperature regime" accessed for T greater than the likely phonon frequencies? We also find that the high mobility *essentially crystalline* phases may be reliably formed in thin films by using the high temperature liquid crystalline state as a template, opening interesting technological vistas.

Acknowledgments

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