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Thermal Narrowing of the Electronic Bandwidths in Organic Molecular Semiconductors: Impact of the Crystal Thermal Expansion

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S *Supporting Information*

ABSTRACT: We report on electronic-structure calculations for the pentacene and rubrene crystals, based on experimental crystal geometries measured at different temperatures. The results are in very good agreement with angle-resolved photoelectron spectroscopy data that indicate that the widths of the valence and conduction bands in both materials become narrower at higher temperatures. Our findings strongly suggest that the thermal bandwidth narrowing in the pentacene and rubrene crystals is primarily caused by the thermal expansion of the lattice rather than by a renormalization of the transfer integrals induced by a polaron effect. The effect of thermal expansion on the charge-transport properties is also discussed.
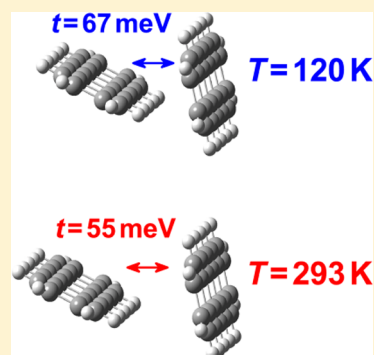
SECTION: Energy Conversion and Storage; Energy and Charge Transport

Understanding the intrinsic nature of charge transport in organic semiconductors is important from both fundamental and practical standpoints. However, in spite of extensive efforts, reaching a complete understanding of the charge-transport mechanism in these systems still remains a challenge.

The electrical conductivity of organic materials usually exhibits a thermally activated behavior. As a result, the rationalization of the intrinsic transport properties is often done in the framework of Marcus electron-transfer theory[1] or Holstein small-polaron model.[2] However, experimental data obtained on high-quality single crystals indicate that the appearance of an activated transport is in many instances more likely due to the presence of structural disorder and chemical defects rather than corresponding to the intrinsic signature of polaron formation. For instance, it was observed that the intrinsic mobilities in pentacene and rubrene exhibit a power-law temperature dependence even around room temperature.[3−5] In addition, the electronic structures of the pentacene[6−8] and rubrene[9,10] crystals were recently probed via angle-resolved photoelectron spectroscopy (ARPES); a clear energy dispersion was measured for the valence band in both systems. Taken together, these results suggest that the electron−phonon (e−ph) coupling in these materials is too weak to lead to polaron formation and that charge transport takes place in a band-like regime. On the other hand, the ARPES data for pentacene also indicate a narrowing of the valence band when going from low to room temperature;[6,8] this observation could, on the contrary, suggest that the polaron effect is significant. Thus, an important question arises: Is the actual e−ph coupling in pentacene and rubrene (and related

systems) consistent with the coexistence of band-like transport and band narrowing?

Band narrowing is a prominent feature of the Holstein small-polaron model.[2] In this model, the e−ph coupling, commonly referred to as local coupling, originates from the modulation of the site energies by vibrations.[11] Its overall strength is given by the polaron binding energy E_{pol} (with $E_{pol} \approx \lambda/2$, where λ is the Marcus reorganization energy). The major manifestation of the polaron effect is to renormalize the transfer integrals.[2,12−14] Since band narrowing is temperature dependent, charge transport can exhibit a conventional band-like behavior at low temperatures with the charge-carrier mobility decreasing in a power-law fashion ($\mu \propto T^{-n}$, $n > 0$) with temperature. At high temperatures, band narrowing becomes more pronounced, and the motion of the carriers switches from band-like to hopping-like, with the mobility displaying an Arrhenius-like (activated) temperature dependence.

However, it must be borne in mind that these results are strictly valid only when the electronic couplings (transfer integrals, t) are much smaller than the polaron binding energy ($t \ll E_{pol}$); this condition is actually hardly fulfilled in a number of organic semiconductors. Indeed, the results of ultraviolet photoelectron spectroscopy measurements and electronic-structure calculations show that E_{pol} in many systems is of the same magnitude as, or even smaller than, the width of the conduction or valence band.[11,15] For instance, in pentacene, along the most favorable transport directions, $E_{pol}/t < 1$ for

both holes and electrons.[11,16] In addition, the largest contributions to the polaron binding energy come from high-frequency intramolecular vibrations (such as carbon–carbon stretching modes) whose excited levels are thermally inaccessible even at room temperature.[11,15,17] This means that the local e–ph coupling in pentacene is not conducive to polaron formation and should not appreciably affect the temperature dependence of the carrier mobility. A similar conclusion can be made for rubrene and other systems.[11,17,18]

A second major e–ph mechanism that is operative in organic semiconductors originates from the dependence of the transfer integrals on the distances between adjacent molecules and on their relative orientations; this is the nonlocal coupling.[11,16,18–24] Calculations also show that this coupling in pentacene and rubrene is moderate.[16,18,23] For instance, in pentacene, the ratio L/t, where the relaxation energy L is the measure of the overall strength of the nonlocal coupling, is in the range of 0.1–0.2.[24] The main contribution to the nonlocal coupling is coming from low-frequency intermolecular (lattice) vibrations, and this mechanism is currently generally considered to represent the origin of the temperature dependence of the transport properties. However, recent results based on semiclassical approximations[19,24] demonstrate that this coupling mechanism does not lead to narrowing of the bands but rather contributes to their thermal broadening.

The conclusion we reach from the discussion at this stage is that the origin of thermal band narrowing is unlikely to be related to e–ph interactions. A common assumption made in the development and application of e–ph models is to use the harmonic approximation for the lattice vibrations. An important consequence of this approximation is the absence of consideration of the lattice thermal expansion. However, thermal expansion was found to be significant in many organic crystals.[25–29] The thermal modification of the structural parameters is accompanied by a rearrangement of the molecular packing, which directly impacts the transfer integrals. While it was suggested earlier that thermal expansion might play a significant role on the electronic properties,[19,24,25] a detailed investigation of this effect for a realistic system has not yet been performed. Thus, our goal here is to obtain a quantitative assessment of the thermal expansion effect. To do so, we have carried out electronic-structure calculations at the density functional theory (DFT) level on the pentacene and rubrene crystals using the experimental crystal structures derived at various temperatures.
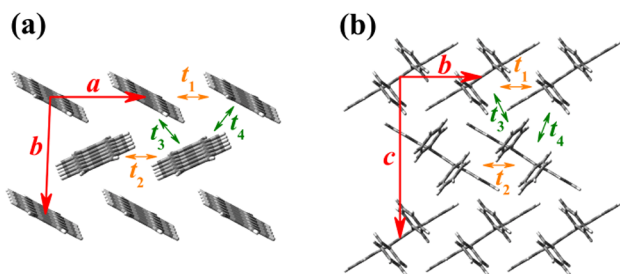
The crystal structures of pentacene and rubrene are illustrated in Figure 1; the crystallographic information[26,28] employed in the calculations is given in the Supporting

Information (SI). The experimental results show that both crystals undergo thermal modification of the lattice constants (along all three directions). Interestingly, in the case of pentacene, the a direction presents a negative thermal expansion (see Figure 1a for the labeling of the cell parameters); the angle parameters are also temperature dependent. Both crystals exhibit an increase in cell volume with temperature. On the basis of the experimental crystal structures, we have computed the energy band structures and the transfer integrals for the molecular pairs shown in Figure 1. The transfer integrals and band structures were derived at the DFT B3LYP/6-31G level. The calculations of the transfer integrals were performed with the Gaussian09 package,[30] and those of the band structures were performed with the CRYSTAL09 package.[31] The inverse effective mass tensor was calculated by Sperling's centered difference method with dk = 0.04/Bohr. The computed band structures are presented in Figure 2, and the results for the transfer integrals are collected in Table 1.

As seen from Figure 2, while the nature of the band dispersions does not change with temperature, a clear narrowing of the valence and conduction bandwidths is observed in both materials. In the pentacene crystal, the total width of the valence band (calculated at the M point) narrows by ~14% when going from 120 K (693 meV) to 293 K (593 meV); this result agrees very well with the value of 15 ± 8% derived from ARPES data taken at 75 and 300 K.[6] Moreover, by comparing the valence-band dispersions in Figure 2a with the experimental results (Figure 3c in ref 6), a reasonable agreement is observed except in some specific regions (X and Y points); the difference could result from the contributions of the intramolecular vibrational transitions as recently proposed by Ciuchi and co-workers.[32] In the rubrene crystals, a narrowing of ~10% for the valence bandwidth (along $\Gamma{\to}Y$) from 100 K (493 meV) to 293 K (445 meV) is obtained; to the best of our knowledge, however, temperature-dependent ARPES measurements have yet to be reported for rubrene. The temperature dependence of the transfer integrals closely follows the temperature dependence of the energy bands. Interestingly, in the case of pentacene, the transfer integrals along the a direction (t_1 and t_2) also decrease with increasing temperature despite the fact that pentacene shows a negative thermal expansion along this direction. This is due to the well-established, important feature that the magnitude of a transfer integral essentially depends on the overlap between the relevant molecular orbitals rather than simply on the spatial overlap between the molecules.[33]

The results for the effective mass calculations are shown in Table 2 (more details can be found in the SI). In line with experimental observations,[6,34,35] the effective mass represents evidence of substantial anisotropy in both materials. For instance, in the case of holes in rubrene, the ratio of the principal mobility components in the plane equivalent to the bc plane in Figure 1b is about 2.7,[35] in good agreement with the ratio of 2.6 based on the components of the effective masses in our calculations.

As expected (see Table 2), thermal expansion leads to an increase in effective masses with temperature. However, the overall effect of thermal expansion on carrier mobility is anticipated to be relatively modest. Indeed, let us consider for the sake of simplicity that the mobility can be described as $\mu = e\tau/m_{eff}$, where τ is the relaxation time. Assuming that thermal expansion only modifies the effective mass, we find that when

Figure 1. Illustration of the crystal structures and of the molecular pairs leading to the largest transfer integrals for the (a) pentacene and (b) rubrene crystals.
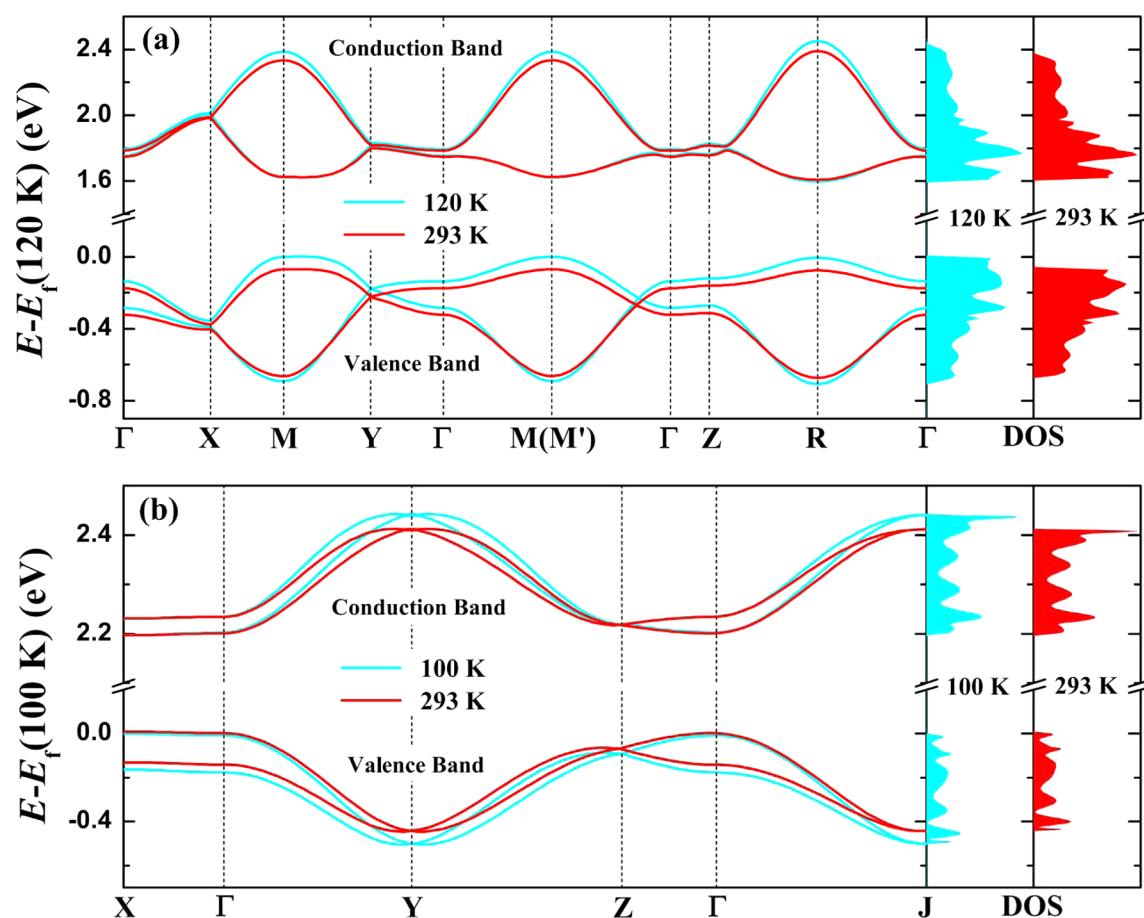
Figure 2. Band structures and density of electronic states (DOS) at different temperatures for the (a) pentacene and (b) rubrene crystals. The points of high symmetry in the first Brillouin zone correspond to $\Gamma = (0, 0, 0)$; $X = (0.5, 0, 0)$ (pentacene); $X = (1, 0, 0)$ (rubrene); $Y = (0, 0.5, 0)$; $Z = (0, 0, 0.5)$; $M = (0.5, 0.5, 0)$; $M' = (0.5, -0.5, 0)$; $R = (0.5, 0.5, 0.5)$; $J = (0, 0.5, 0.5)$, all in crystallographic coordinates.

Table 1. DFT Estimates of the Transfer Integrals (in meV) for the Pairs Illustrated in Figure 1 in the Pentacene and Rubrene Crystals

T (K)	hole				electron			
	t_1	t_2	t_3	t_4	t_1	t_2	t_3	t_4
			Pentacene					
120	45.6	42.1	67.1	−101.5	−55.1	−53.3	−97.0	94.4
293	39.5	36.3	54.6	−88.6	−51.1	−48.8	−89.3	86.6
414	37.3	31.6	45.5	−80.5	−48.2	−46.2	−80.7	79.2
			Rubrene					
100	104.9		−18.9		−55.7		4.7	
200	99.6		−17.7		−51.7		5.2	
293	95.4		−16.1		−48.3		4.6	

Table 2. Principal Components of the Hole and Electron Effective Masses (in Electron Rest Mass) Estimated at the Band Edges of the Pentacene and Rubrene Crystals

T (K)	hole			electron		
	m_1	m_2	m_3	m_1	m_2	m_3
		Pentacene				
120	1.50	6.72	9.15	1.53	3.70	30.76
293	1.65	7.34	10.64	1.64	4.76	11.73
414	1.85	9.49	15.29	1.88	4.94	8.72
		Rubrene				
100	0.78	1.95	11.43	1.25	8.89	16.0
200	0.82	2.05	11.43	1.36	8.0	20.0
293	0.84	2.22	13.33	1.43	8.89	26.67

temperature is increased from 100 to 293 K, the effect would be a decrease in mobility, say for holes in rubrene along the *b* direction, by only about 7%. In contrast, assuming a power-law temperature dependence for the relaxation time $\tau \propto T^{-n}$ and taking as an example $n = 2$, the corresponding decrease in mobility due to e−ph coupling would be about 88%. If we go beyond the effective mass approximation and use the Kubo formalism,[24] we obtain that the decrease in mobility due to thermal expansion is estimated to be about 18%; it would be about 70% in the case of e−ph coupling (see SI for more details). It is clear that, to obtain more reliable estimates, a more advanced transport model should be considered; in

addition, the dependence of the e−ph interactions on thermal expansion should be investigated.

In summary, we have demonstrated that the thermal expansion of the crystal structures, rather than the e−ph couplings, is the main factor responsible for the thermal bandwidth narrowing in organic semiconductors such as pentacene and rubrene. A rough estimation suggests that thermal expansion has a much smaller effect on the charge transport in comparison to the effect of e−ph interactions. Clearly, further developments are warranted in order to obtain more comprehensive transport models.

ASSOCIATED CONTENT

S Supporting Information

Experimental crystallographic parameters used in the calculations; orientations of the principal components of the effective mass; crystallographic coordinates of the band edges; more details of the mobility calculations based on the Kubo formalism; complete ref 30. This information is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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