ELECTRONIC SUPPLEMENTARY INFORMATION

Polymorphism in α-sexithiophene crystals: Relative stability and transition path

Bernhard Klett,[1,2] Caterina Cocchi,[1,2] Linus Pithan,[1] Stefan Kowarik,[1] and Claudia Draxl[1,2]

[1] Institut für Physik and IRIS Adlershof, Humboldt-Universität zu Berlin, Berlin, Germany
[2] European Theoretical Spectroscopic Facility (ETSF)

Powder Diffraction Patterns and Phase Coexistence in Sexithiophene Thin Films

Using the crystallographic data available in the Cambridge Structural Database (CSD) for single sexithiophene (6T) crystals in low- and high-temperature (LT and HT) phases, we have simulated the whole powder pattern in the relevant **q**-range for both crystal phase separately. As shown in Fig. S1, there are fully disjoint diffraction patterns with no overlapping peaks. For 6T thin films grown on KCl substrates, we find that the LT polymorph is always present for a substrate temperature range between 0°C and 100°C during thin film growth, whereas the phase content of the HT phase can be tuned by the substrate temperature.
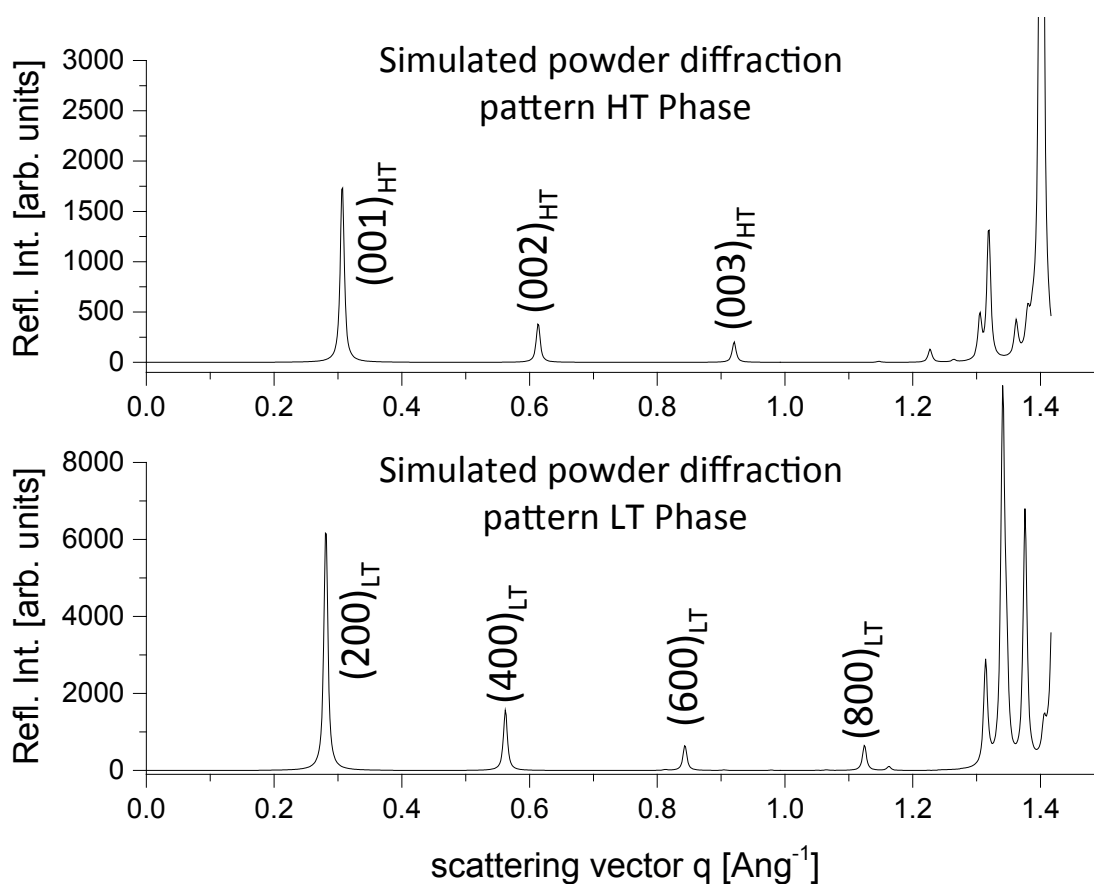

FIG. S1: Simulated powder diffraction patterns for HT and LT phases separately, based on the structural parameters published Refs. [1] and [2].

Phase Coexistence of 6T Crystal Phases at Elevated Temperatures

We can exclude a significant conversion from the HT to the LT phase at temperatures close to the 6T desorption temperature. We experimentally address this issue by performing an additional experiment in order to experimentally probe this conversion. The results are shown in Fig. S2. We slowly increase the sample temperature while monitoring both reflections simultaneously. The LT Bragg reflections intensity stays constant, while the HT Bragg reflection disappears completely. The LT phase only dissolves at even higher temperatures. From this we conclude that there is no significant conversion from HT to LT.
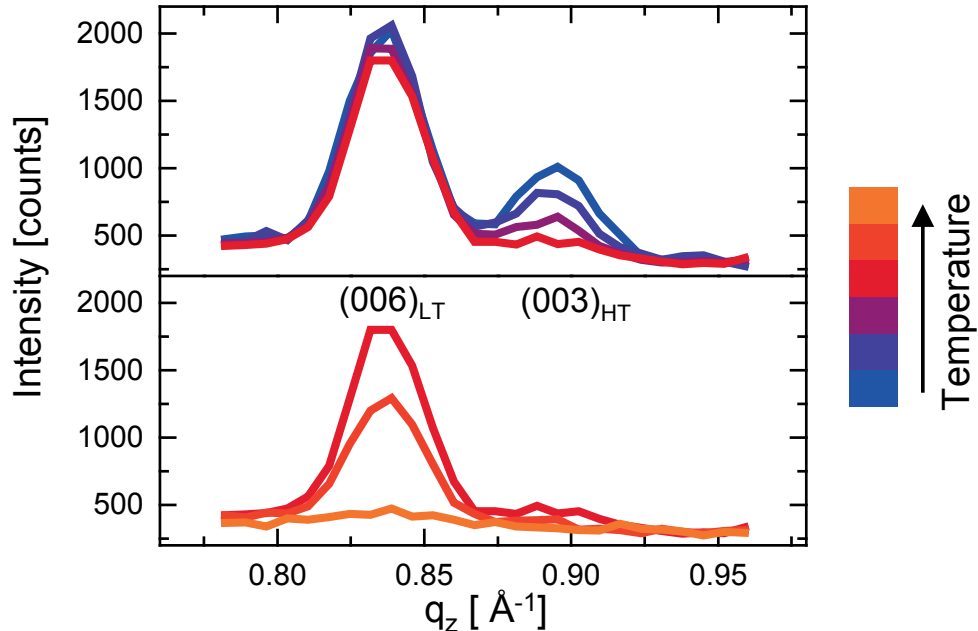

FIG. S2: Desorption of 6T at increasing substrate temperatures. First the HT reflection vanishes while the intensity of the LT reflection stays constant. At higher temperature the LT reflection intensity disappears.

Validation of LT Unit Cell Reduction

In Table S1 we show the total energy difference (ΔE_{TOT}) per molecule of the LT phase of sexithiophene crystals, compared to each half (see Figure 1 of the main text). Calculations are performed using experimental lattice parameters [1, 2] with frozen geometry and adopting the local density approximation for the exchange-correlation functional (Perdew-Wang) [3].

The total energy of the full LT unit cell is less than 5 meV/molecule smaller than the one computed in the reduced unit cells. This value is one order of magnitude smaller than the energy difference per molecule between the HT and LT phase. Therefore, considering the halved LT unit cell gives rise to an underestimation of the relative stability of the LT phase, compared to the HT one, of about 10%. Finally, the energy difference between the two reduced LT unit cells is 0.2 meV/molecule, which is within our computational accuracy (0.4 meV/molecule, see Section 2.2 of the main text). This allows us to consider the two halves of the LT unit cell to be equivalent to each other.

	LT	LT red-1	LT red-2
ΔE_{TOT}/molecule	0.0	4.7	4.5

TABLE S1: Total energy difference per molecule of each half of the unit cell of the LT phase (LT red-1 and LT red-2), compared with the reference value given by the full unit cell of the LT phase (LT). Energies are expressed in meV.

[1] T. Siegrist, R. Fleming, R. Haddon, R. Laudise, A. Lovinger, H. Katz, P. Bridenbaugh and D. Davis, *J. Mater. Res.* , 1995, **10**, 2170–2173.

[2] G. Horowitz, B. Bachet, A. Yassar, P. Lang, F. Demanze, J.-L. Fave and F. Garnier, *Chem. Mater.*, 1995, **7**, 1337–1341.

[3] J. P. Perdew and Y. Wang, *Phys. Rev. B*, 1992, **45**, 13244.