

MS23-01 | CHEMICAL VS CONFORMATIONAL ENTROPIES AT THE INCOMMENSURATE AND LOCK-IN PHASE TRANSITIONS OF MORPHOLINIUM TETRAFLUOROBORATE

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I will give an introduction to ferroelectric molecular crystals [1]. Ferroelectric crystals are pyroelectric crystals that exhibit reversible polarisation. Most applications of ferroelectric materials involve inorganic compounds, such as lead zirconate titanate, barium titanate and layered perovskites. The field of molecular ferroelectrics has started to gain interests only recently. Molecular ferroelectrics can be classified in two groups: pure organic hydrogen bonded supramolecular chains with a polar space group form one class of ferroelectric materials another series of molecular ferroelectrics belong to H-bonded hybrid organic-inorganic assemblies. Inorganic backbones are formed by strong covalent or ionic metal–halogen bonds to form an extended framework. Morpholinium tetrafluoroborate, $[\text{C}_4\text{H}_{10}\text{NO}]^+[\text{BF}_4]^-$, belongs to a class of ferroelectric compounds ABX_4 . However, $[\text{C}_4\text{H}_{10}\text{NO}]^+[\text{BF}_4]^-$ does not develop ferroelectric properties because the incommensurate phase below $T_{c,I} = 153$ K is centrosymmetric with superspace group $\text{Pnam}(\delta_1 00)00s$ and $\delta_1 = 0.42193$ (12) at $T = 130$ K; the threefold superstructure below $T_{c,II} = 117$ – 118 K possesses the acentric but non-ferroelectric space group $\text{P}2_12_12_1$. Switching the modulation wavevector from incommensurate along a^* towards along c^* imposes first-order character onto the transition II–III. Phase transition mechanism is discussed based on crystal structures. The difference in configurational entropy between the disordered and incommensurate phases has been computed from the structure models. These features show that the order–disorder contribution is only a minor contribution to the transition entropy and that other factors, such as conformational changes, play a larger role in the phase transitions.

[1] Noohinejad, L., Aperiodic Molecular Ferroelectric Crystals, PhD Thesis, University of Bayreuth. 2016