

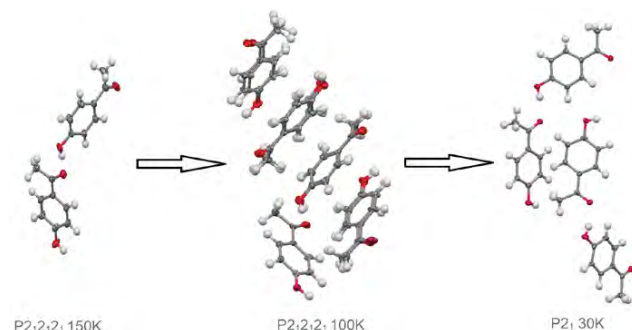
MS26-P04**Exploring modulation in molecular crystals at low temperatures**Marcin Sztylko¹, Anna Hoser¹

1. Faculty of Chemistry, University of Warsaw, Warsaw, Poland

email: marcin.sztylko@gmail.com

Technical progress in crystallographic instruments allows contemporary crystallographers to more routinely conduct low-temperature diffraction measurements. Additionally, modern diffractometers have stronger sources and more sensitive detectors than they had a few years ago. As a consequence, even crystal structures that have been extensively studied at ambient conditions start to reveal their more complex nature. The importance of low-temperature measurements is discussed for polymorphs of 4'-hydroxyacetophenone (HAP)¹.

For this enantiotropic polymorphic system, we collected single crystal X-ray diffraction data in the temperature range from 30 K to 330 K. At 123 K orthorhombic form II of HAP appears to be a new, commensurately modulated structure with a modulation vector $q = [0.4, 0.0, 0.0]$. The structure can be solved in a supercell with 10 molecules in the asymmetric unit. Interestingly, further lowering of temperature down to 30K resulted in a discovery of a new, incommensurately modulated phase with 4 independent molecules and crystal lattice of the P2₁ space group and modulation vector $q = [0.37, 0.17, 0.0]$. Consequences of modulation for the relative stability of polymorphs will be discussed.



References:

[1] Bernardes, C. E. S.; Piedade, M. F. M.; Minas, M. E. 2008, *Cryst. Growth Des.* 8 (7), 2419–2430.

Keywords: polymorphism, commensurate modulation, incommensurate structure

MS26-P05**Unraveling the structure of Vaterite using precession electron diffraction tomography**Gwladys Steciuk¹, Daniel Chateigner², Lukáš Palatinus¹

1. Department of Structure Analysis, Institute of Physics CAS (FZU) Na Slovance 2, 182 21, Prague, Czech Republic

2. CRISMAT-ENSICAEN Laboratory (CNRS UMR6508), IUT Caen, Caen Normandie University., Caen, France

email: gwladys.steciuk@gmail.com

Among the three crystallized anhydrous polymorphs of CaCO₃, vaterite is the least stable form under natural conditions and has been identified as a constituent of various biominerals such as sea crustaceans, mollusk pearls, fish otoliths, ascidians and even human organic tissues (heart valve) or plants. As a metastable phase, vaterite is involved in the first step of crystallization of the two stable calcite and aragonite polymorphs and in several carbonate-forming systems. Its complete structural determination would consequently shed important light to understand scaling formation and biomineralization processes. While vaterite hexagonal substructure ($a \approx 4.1 \text{ \AA}$ and $c \approx 8.5 \text{ \AA}$) and the organization of the (CO₃)²⁻ and Ca²⁺ within a single layer is known, conflicting interpretations regarding the stacking sequence remain and preclude the complete understanding of the structure. Indeed, earlier workers reported the presence of additional Bragg peaks and diffuse features in diffraction patterns of vaterite together with twinned domains, and the likely coexistence of several polymorphs [1-2].

In order to resolve the ambiguities in the structural description of vaterite, we performed precession assisted electron diffraction tomography (PEDT) to collect single crystal data on beam sensitive nanocrystalline vaterite. Several data sets were collected with low-dose technique at low-temperature with a nano-size beam and processed using programs PETS, Jana2006 and Dyngo [3]. Our results unambiguously demonstrate that vaterite grows up mostly as a coherent intergrowth of two ordered and twinned polymorphs having the same composition. Their structures were solved ab initio and described as commensurate modulated structures. The models were refined against electron diffraction data using the dynamical refinement procedure including both modulation and twins. Our results are also consistent with Rietveld refinement from x-ray powder data [3] at low and ambient temperature. This study brings a new perspective by giving a better understanding of the existing stacking sequences and the possible rotations of the (CO₃)²⁻ groups in vaterite.

References:

[1] Christy, A.G. (2017). *Crystal Growth Des.* 17, 3567-3578.
 [2] Kabalah-Amitai, L. et al. (2013). *Science.* 340, 454-456.
 [3] Palatinus, L. et al. (2015). *Acta Crystallogr. A* 71, 235-244.

Keywords: vaterite, precession electron diffraction tomography, intergrowth