ESRF	**Experiment title:** Crystallization process and structure solution of quinaldine	**Experiment number**: HC-1045
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Report:

Especially organic molecules are commonly known for showing polymorphism, the property of a compound to crystallize in more than one crystal structure. Different crystalline polymorphs of one substance may exhibit different physicochemical properties. The selective crystallization of a specific polymorph requires thorough knowledge of the underlying kinetic and thermodynamic correlation between the polymorphs. Especially metastable phases are challenging to obtain and specific crystallization strategies to capture those phases have become an important issue in material science.

The strongly supercooled liquid of a molecular system can serve as precursor for the crystallization of metastable phases. By increasing the temperature of the highly viscous liquid and thus facilitating diffusion, an occurring phase transition may yield metastable phases. For the elucidation of crystallization pathways and the description of occurring crystalline phases in situ techniques are needed.

The organic compound quinaldine is used as precursor in the synthesis of heterocyclic compounds. The substance, a liquid at room temperature, can be supercooled to the metastable glassy state. Dielectric spectroscopy revealed two subsequent phase transitions of the glassy sample upon heating in the range from 120 K up to the melting point at 266 K.[1] The three observed phases were identified by variable temperature powder diffraction experiments in laboratory as the amorphous supercooled state QN1 and two different crystalline phases QN2 and QN3. Due to the limited diffractometer properties and the polycrystallinity of the sample with preferred orientation, the data quality was not sufficient enough for even indexing of the diffraction patterns. During a preliminary synchrotron experiment, the super-cooled melt

crystallized directly to the phase QN3. In contrast to the laboratory experiments, the first crystalline phase QN2 has not been observed at the synchrotron so far.

An X-ray diffraction experiment of quinaldine was performed on the Spanish CRG Beamline (BM25A) at ESRF. The crystallization process of quinaldine was monitored using high-resolution powder diffraction applying variable temperatures in the range from 120 K to 295 K. The liquid quinaldine was prepared in capillaries which then were cooled down fast from room temperature to 120 K using a cryojet. Subsequently, the temperature of the sample was increased gradually. A X-ray diffraction pattern of the super-cooled liquid recorded at 120 K shows broad amorphous scattering. The X-ray diffraction patterns in the range from 8.2°2θ to 10.2°2θ recorded during a temperature run starting with the supercooled liquid at 120 K are shown in Figure 1 (left). The diffraction patterns at the beginning of the experiment display no reflexes of a crystalline phase. The first reflexes appear at 220 K indicating the crystallization of the sample. The diffraction pattern can be assigned to the pure crystalline phase QN2 (Figure 1 right). So far, this phase has only been observed during the laboratory experiments, crystallizing prior to the transformation to polymorph QN3. QN2 seems to be a metastable phase of quinaldine that crystallizes only under certain conditions. Therefore, the temperature run was stopped and a high-quality diffractogramm of the hitherto uncaptured phase was recorded. The data quality of the recorded diffraction pattern should be high enough to index the unit cell of the crystal structure of phase QN2.

Due to technical problems with the alignment and the remote control of the setup, further measurements of different quinaldine samples and records of a whole temperature run were not possible. Further experiments have to be performed to elucidate the complete crystallization process starting with the super-cooled liquid (QN1) via the presumably metastable form (QN2) to the second crystalline phase (QN3). The polycrystallinity of the sample, presumably different sized crystal grains and also possibly preferred orientation of the crystallites in the capillary might reduce the statistical distribution. To exclude an insufficient statistic distribution of the crystallites in the capillary, the whole crystallization experiment should be performed multiple times.

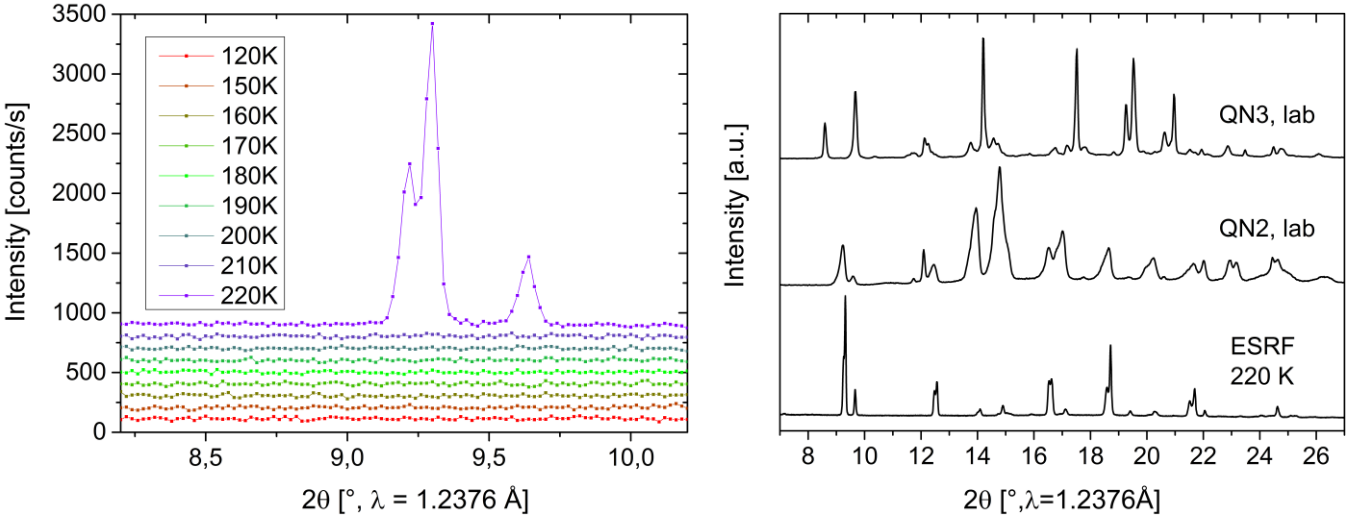

Figure 1: In situ XRD pattern recorded during a variable temperature program starting with the supercooled liquid at 120 K to 220 K (left). XRD pattern of the crystalline phase at ESRF in comparison to two crystalline phases observed in the laboratory experiments (right).

[1] Kahlau, R.; Gnutzmann, T.; Emmerling, F.; Rademann, K.; Rossler, E. A., Quinaldine: Accessing two crystalline polymorphs via the supercooled liquid. *J. Chem. Phys.* **2012**, 137 (5), 054505