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## Report:

### Abstract

The room temperature structure ( $\alpha$ -form) of the organic compound *p*-chlorobenzamide,  $C_7H_6ClNO$ , can be described as a classical three-dimensional periodic superstructure ( $\alpha S$ ) and also as a commensurately modulated structure ( $\alpha M$ ) in (3+1)-dimensional superspace. The diffraction pattern is characterized by a clear difference in intensity between main and satellite reflections. All reflections can be indexed with four indices  $hklm_{[1]}$  in a triclinic unit cell and one modulation vector in the superspace group  $P\bar{1}(\alpha\beta\gamma)$  with the modulation vector  $\vec{q}_{[1]} = \frac{1}{3} \cdot \vec{a}^*$ . The structure undergoes a phase transition at higher temperature. In this phase transition the modulation vanishes as indicated by the disappearance of the satellite reflections. The resulting high temperature phase ( $\gamma$ -form) contains one molecule in the asymmetric unit, the space group is  $P\bar{1}$ . The high temperature structure ( $\gamma$ ) is very close to the *basic structure* of the modulated model at room temperature. The phase transition can therefore be understood as a loss of the modulation at high temperature.

### Experiment

For the X-ray diffraction experiments single crystals of *p*-chlorobenzamide were grown by evaporation from a saturated solution. For evaporation the solution was put in a refrigerator ( $T \approx 277$  K). The crystals were colourless, transparent and platelet-like with a ratio of the edges of about 25 : 10 : 1. A suitable single-crystal with edge sizes in the range 0.1 - 0.2 mm was fixed on the top of a glass fibre with transparent nail enamel.

The X-ray measurements were carried out on a Mar 345 Image Plate at the Swiss-Norwegian Beam Line at the European Synchrotron Radiation Facility in Grenoble. For the temperature control, a nitrogen gas cryostream cooler (Oxford Cryosystems) was used. The relative and the absolute deviations from the nominal temperature were  $\Delta T_{\text{rel}} = 0.5$  K and  $\Delta T_{\text{abs}} = 3$  K. Two data sets ( $\Phi$  scans) were collected, one for the  $\alpha$ -form at  $T = 290$  K, the other for the  $\gamma$ -form at  $T = 323$  K. The wavelength was  $\lambda = 0.700(1)$  Å, the resolution in d-spacing  $0.76$  Å. Owing to rather high internal reliability values for the peaks at high scattering angle and owing to their weakness, the data sets have been limited at a resolution in d-spacing of  $0.8$  Å, *i.e.*  $\frac{\sin \theta}{\lambda} = 0.625$ . For the  $\alpha$ -form the measured oscillation range was  $6^\circ \leq \Phi \leq 334^\circ$ , for the  $\gamma$ -form  $0^\circ \leq \Phi \leq 216^\circ$ . In both cases the increment was  $\Delta\Phi = 2^\circ$ . The measured images were treated (peak search, cell finding, extraction of intensities, ...) with the CrysAlis Software Package. The raw data were corrected for Lorentz and polarization effects, no absorption correction was applied. Lattice parameters for all three structures, *i.e.* for the three-dimensional  $\alpha$ S, the (3+1)-dimensional  $\alpha$ M and the three-dimensional  $\gamma$ , were refined with the program *NADA*.

In the phase transition  $\alpha \rightarrow \gamma$  the satellite reflections vanish and reappear again in the transition  $\gamma \rightarrow \alpha$ . The reversibility of the phase transition was not only confirmed by X-ray diffraction experiments but also by DSC measurements. After several phase transition cycles the single crystal from the X-ray measurement became slightly cloudy, but still gave sharp peaks in the diffraction pattern. The reorientation of the molecules during the phase transition  $\alpha \rightarrow \gamma$  towards a unique orientation for the three molecules results in an increasing of the length of the  $\hat{c}$ -axis of about  $0.3$  Å, while the lengths of the  $\hat{a}$ - and  $\hat{b}$ -axes remain constant within errors. The angles  $\alpha$  and  $\beta$  increase  $0.7^\circ$  respectively  $1.0^\circ$  and  $\gamma$  decreases  $0.8^\circ$ .

## Analysis

With respect to the hydrogen bonding scheme, the structures of the  $\alpha$ - and  $\gamma$ -form are identical. In both structures the molecules form endless chains of dimers along the  $\hat{a}$ -axis, the chains form layers *via* chlorine...chlorine interactions. However, in the  $\gamma$ -form all molecules have the same conformation, whereas in the  $\alpha$ -form three different conformations exist, giving rise to a tripling of the  $\hat{a}$ -axis. The torsion angles in the single molecule of the  $\gamma$ -form are with  $\tau[\text{N09-C01-C02-C03}] = 27.3(3)^\circ$  and  $\tau[\text{O10-C01-C02-C07}] = 27.6(3)^\circ$  equivalent to the average values of the corresponding three independent molecules of  $\alpha$ S (see Table 12). The structure of  $\gamma$  can thus be interpreted as the *average structure* of  $\alpha$ S. The *average structure* of the  $\gamma$ -form undergoes a transition to the  $\alpha$ -form with three, well-defined conformations of the molecule. The modulated structure description consists of a (three-dimensional periodic) *basic structure* with fractional coordinates  $\bar{x}, \bar{y}, \bar{z}$  and displacement parameters  $\bar{U}^{ij}$  plus a periodic modulation thereof, which is described in the additional space. This means *vice versa*, that the *basic structure* is the unmodulated crystal structure. It can therefore be deduced from the modulated structure, removing all modulation parameters and keeping only the fractional coordinates  $x, y, z$  and the displacement parameters  $U^{ij}$ .

It has been shown that applying the superspace approach to the commensurately modulated structure of the  $\alpha$ -form of *p*-chlorobenzamide leads to a better understanding of both the reciprocal and the direct space. The diffraction pattern is characterized by a clear difference in intensities in the  $(\hat{a}^*, \hat{c}^*)$  plane: every third line along the  $\hat{a}^*$ -axis exhibits stronger intensities than the two lines in-between. In addition, the stronger lines survive during the phase transition to the high temperature phase whereas the weaker ones disappear. The stronger peaks can be interpreted as main reflections, the weaker peaks as first order satellite reflections. The description of the structure as a modulated structure in superspace has the advantage that it yields a clear and easy relation between high and low temperature structures: the *basic structure* of the modulated room temperature phase and the structure of the non-modulated high temperature phase are equivalent. The superspace approach makes it possible to describe the structures of the different phases with a unique basic model and provides a unified picture of the relationship between modulated and non-modulated phases.

