

# The (3 + 1)-dimensional superspace description of the commensurately modulated structure of *p*-chlorobenzamide ( $\alpha$ -form) and its relation to the $\gamma$ -form

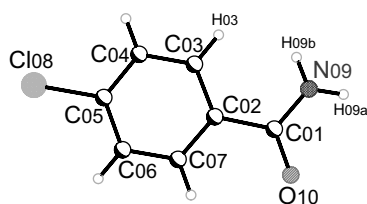
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**Abstract.** The room temperature structure ( $\alpha$ -form) of the organic compound *p*-chlorobenzamide,  $C_7H_6ClNO$ , can be described as a classical three-dimensional periodic superstructure ( $\alpha_S$ ) and also as a commensurately modulated 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  $hklm$  in a triclinic unit cell and one modulation vector in the superspace group  $P\bar{1}(\alpha\beta\gamma)$  with the modulation vector  $\vec{q} = \frac{1}{3} \cdot \vec{a}^*$ . 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 reference structure of the modulated model at room temperature. The phase transition can therefore be understood as a loss of the modulation at high temperature.



**Fig. 1.** Structure and atom labelling in the molecule of *p*-chlorobenzamide.

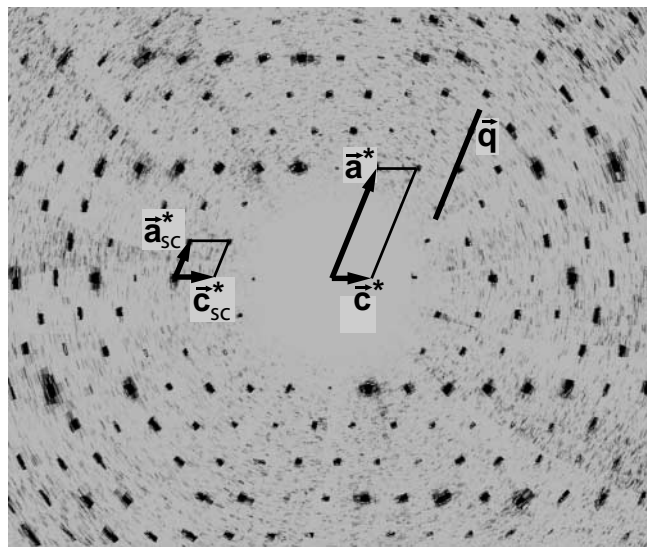
## 1 Introduction

The superspace approach [1–5] was introduced to describe aperiodic crystals, *i.e.* incommensurately modulated structures, composites and quasicrystals. It was however realized that the superspace formalism can not only be applied to describe incommensurately modulated but also commensurately modulated structures as well as complete sequences of phase transitions [6–8].

The superspace approach applied to a commensurately modulated structure is illustrated in the present article with the example of *p*-chlorobenzamide,  $C_7H_6ClNO$ . This molecule consists of two planar groups, a phenyl ring (C02 to C07) and an amide group (N09–C01–O10). The molecular structure and the atom labelling are presented in Fig. 1. The chlorine atom Cl08 lies in the plane of the phenyl ring. Although the phenyl ring and the carboamide group (the amide group together with the carbon atom C02) are planar, the entire molecule is not. The two planar units are twisted around the connecting C01–C02 bond. This non-planarity is explained by steric hindrance because of a strong interaction between the hydrogen atoms H03 and H09b [9, 10].

The commensurately modulated room temperature structure ( $\alpha$ -form) of *p*-chlorobenzamide can be described by two different models:

- A classical three-dimensional superstructure with three independent molecules in the asymmetric unit. The diffracted intensities indexed by three integers  $hkl$  are all treated in the same way.



**Fig. 2.** The centre part of the reconstructed layer  $h0l$  of the  $\alpha$ -form with the two possible cells: the supercell ( $\vec{a}_{sc}^*$ ,  $\vec{c}_{sc}^*$ ) on the left and the unit cell ( $\vec{a}^*$ ,  $\vec{c}^*$ ) with modulation vector  $\vec{q}$  on the right.

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- A commensurately modulated structure in (3+1)-dimensional superspace with one molecule per asymmetric unit. The diffracted intensities are interpreted as main and satellite reflections and indexed by four integers  $hklm$ .

The first model was proposed by Taniguchi *et al.* [11]. They described the structure of the  $\alpha$ -form as a 3-fold superstructure (in the following called “ $\alpha_S$ ”). The three independent molecules A, B and C differ in their molecular conformation: the dihedral angles between the phenyl- and the amide-planes are  $\delta_A = 20.3^\circ$ ,  $\delta_B = 33.8^\circ$  and  $\delta_C = 30.3^\circ$ . The analysis of the diffraction pattern showed that one can distinguish two sets of reflections: the reflexions  $hkl$ :  $h \neq 3n$  ( $n =$  small integer) are considerably less intense than those with  $hkl$ :  $h = 3n$  [11]. After refinement these weaker reflexions gave a final  $R$  value of 13.2% whereas the strong reflexions gave a final  $R$  of 9.6%. In addition, the intensities of reflexions  $hkl$ :  $h \neq 3n$  are globally more intense at  $T = 153$  K than at room temperature [11]. A solid-solid transition ( $\alpha$ -form  $\leftrightarrow$   $\gamma$ -form) is observed at  $T = 317$  K. In this transition the reflections of the  $\alpha$ -form with  $hkl$ :  $h = 3n + 1$  and  $hkl$ :  $h = 3n + 2$  disappear [12]. The major change of the structure is a reorientation of the molecules. The structure of the  $\gamma$ -form is a classical three-dimensional periodic structure with one molecule in the asymmetric unit. Its dihedral angle between the phenyl- and the amide-planes is the average of the three dihedral angles in the  $\alpha$ -form,  $\delta = 28.1^\circ$ .

The  $\beta$ -form is the room temperature polymorph to the  $\alpha$ -form [11]. It is monoclinic and crystallizes in the space group  $P2_1/a$ .

The aim of this article is to present the second model and to interpret and describe the structure of the  $\alpha$ -form as a modulated structure (in the following called “ $\alpha_M$ ”) in (3+1)-dimensional superspace and to deduce the relation

between the two structures  $\alpha_M$  and  $\gamma$ . Please note, that  $\alpha_M$  and  $\alpha_S$  refer only to two different ways of describing the same structure  $\alpha$ .

## 2 Experimental

### 2.1 Sample preparation

For the X-ray diffraction experiments single crystals of *p*-chlorobenzamide were grown by evaporation from a saturated solution. A commercial polycrystalline powder of *p*-chlorobenzamide was dissolved in acetone (using ethanol as solvent as described by [11] gave crystals of optically bad quality, the crystals had a needle-like shape and were grown together in agglomerates). 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.

For the DSC experiment the commercial powder was used directly.

### 2.2 DSC measurement

A Mettler Toledo STAR<sup>c</sup> System (a DSC 30 module in operation with the TC15 TA Controller for thermal analysis) was used for measurements in the temperature range 173–373 K. The heating and cooling speed was 1 K/min. The relative and absolute deviations from the nominal temperature were  $\Delta T_{\text{rel}} = 1.0$  K and  $\Delta T_{\text{abs}} = 3$  K.

The observed anomaly at  $T = 313$  K is in good agreement with the literature [12] and the result observed by X-ray

**Table 1.** Crystal data for  $\alpha_S$ ,  $\alpha_M$  and  $\gamma$ .

Structure	$\alpha_S$	$\alpha_M$	$\gamma$
Formula	C <sub>7</sub> H <sub>6</sub> ClNO	C <sub>7</sub> H <sub>6</sub> ClNO	C <sub>7</sub> H <sub>6</sub> ClNO
No of independent molecules $Z'$	3	1	1
Formula weight (g mol <sup>-1</sup> )	466.8	155.6	155.6
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}(\alpha\beta\gamma)$	$P\bar{1}$
Temperature (K)	290	290	323
Lattice parameters (Å, °)	$a = 14.990(11)$ $b = 5.467(6)$ $c = 14.436(14)$ $\alpha = 97.76(7)$ $\beta = 111.91(6)$ $\gamma = 95.16(5)$	$a = 4.997(4)$ $b = 5.467(4)$ $c = 14.433(12)$ $\alpha = 97.76(5)$ $\beta = 111.90(5)$ $\gamma = 95.15(5)$	$a = 4.992(8)$ $b = 5.468(10)$ $c = 14.71(3)$ $\alpha = 98.43(11)$ $\beta = 112.91(12)$ $\gamma = 94.35(10)$
Modulation vector parameters	–	$\alpha = 0.333(1)$ $\beta = 0.000(1)$ $\gamma = 0.000(1)$	–
Refinement program	NADA [14]	NADA [14]	NADA [14]
Cell volume (Å <sup>3</sup> )	1074.8(19)	358.3(5)	361.9(12)
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	1.442(2)	1.442(2)	1.427(5)
$\mu$ (mm <sup>-1</sup> )	0.45	0.45	0.45

diffraction. The difference of about  $\Delta T = 5$  K can be explained by the absolute errors of the temperature controls and lack of calibrated thermal devices.

### 2.3 X-ray diffraction analysis

The X-ray measurements were carried out on a Mar 345 Image Plate at the Swiss-Norwegian Beam Lines 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 [13]. 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 [14]. For consistency, the cell setting of [11, 12] was adopted. The refined lattice parameters and other crystallographic data are given in Table 1.

The structures  $\alpha_S$  and  $\gamma$  were solved by direct methods with SHELXS [15] as well as the (three-dimensional) average structure of  $\alpha_M$ . The "average structure" was solved from the main reflections only, neglecting the contribution of satellite reflections. The structure refinements of the  $\alpha_S$  and  $\gamma$  in three-dimensional space and of  $\alpha_M$  in (3+1)-dimensional superspace were performed with JANA2000 [16].

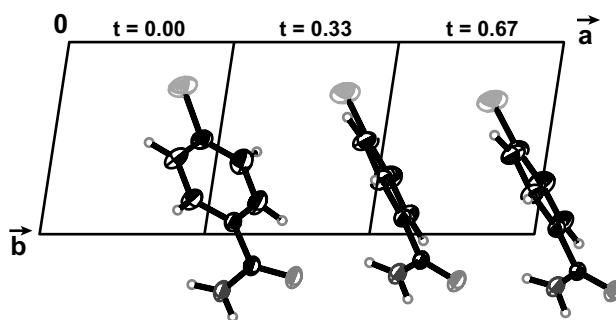
The positions of the hydrogen atoms were refined with restrained bond lengths to their respective bonded atoms:  $[N-H] = 0.86$  Å and  $[C-H] = 0.93$  Å. The isotropic displacement parameter  $U_{\text{iso}}^{\text{calc}}$  was calculated from the  $U^{ij}$  of the bonded atoms. Relation (1) was applied for all hydrogen atoms. It is illustrated for the hydrogen atom H03 bonded to the carbon atom C03.

$$U_{\text{iso}}^{\text{calc}}[H03] = 0.396 \cdot U^{11}[C03] + 0.396 \cdot U^{22}[C03] + 0.396 \cdot U^{33}[C03] \quad (1)$$

## 3 The $\alpha$ -form at room temperature

### 3.1 The diffraction pattern

The diffraction pattern is characterized by a clear difference in intensities between main and satellite reflections. In Fig. 2 the reconstructed layer  $h0l$  is shown and in Ta-



**Fig. 3.** The three molecules of  $\alpha_M$  in the  $(\vec{a}, \vec{b})$  plane as function of the modulation parameter  $t$ . The displacement ellipsoids are drawn at the 30% probability level.

ble 2 the average intensities are given as a function of the Miller index  $h$  (with respect to the indexation in the supercell model).

The diffraction peaks can be indexed by three indices  $hkl$  in a triclinic supercell with space group  $P\bar{1}$  as well as by four indices  $hk\ell m$  in a triclinic unit cell and one modulation vector in superspace group  $P\bar{1}(\alpha\beta\gamma)$  with the modulation vector  $\vec{q} = \frac{1}{3} \cdot \vec{a}^*$ . The supercell (which is based on main and satellite reflections) is along the  $\vec{a}^*$ -axis three times shorter than the unit cell (which is based on main reflections only).

### 3.2 The superstructure $\alpha_S$

The results of [11] are well reproduced. There are three independent molecules A, B and C in the asymmetric unit: their dihedral angles between the phenyl- and the amide-planes are  $\delta_A = 19.96(15)^\circ$ ,  $\delta_B = 33.73(15)^\circ$  and  $\delta_C = 29.69(14)^\circ$ . Two different hydrogen bonds can be identified in the structure, the one  $N09-H09a \cdots O10'$  linking dimers, the other  $N09-H09b \cdots O10''$  forming endless chains. Consequently the centrosymmetric dimer A–A and the non-centrosymmetric dimers B–C and C–B are formed. Details on the crystal structure refinement are given in Table 3.

### 3.3 The commensurately modulated structure $\alpha_M$

In a general one-dimensional commensurately modulated structure relation (2) is fulfilled [4]:

$$N \cdot \vec{q} = \vec{l}_0^* \quad (2)$$

$N$  is the smallest possible integer,  $\vec{q}$  the modulation vector and  $\vec{l}_0^*$  a reciprocal lattice vector of the basic structure. This general one-dimensional commensurately modulated structure has then a three-dimensional translational symmetry with respect to a  $N$ -fold supercell. The correspond-

**Table 2.** Average intensities ( $\alpha$ -form) as a function of the Miller index  $h$  (with respect to indexation in the supercell model).

Miller index	$\langle I \rangle$	$\langle I/\sigma(I) \rangle$
$h = 3n$ ( $\cong$ main reflection)	375.11	47.56
$h = 3n + 1$ ( $\cong$ satellite reflection)	110.87	21.58
$h = 3n + 2$ ( $\cong$ satellite reflection)	110.96	21.47

**Table 3.** Experimental and refinement data for  $\alpha_S$ ,  $\alpha_M$  and  $\gamma^a$ .

Structure	$\alpha_S$	$\alpha_M$	$\gamma$
2 $\theta$ -range	3.30–25.94	3.30–25.94	3.75–25.95
$hkl$ -range	$-18 \leq h \leq 18$ $-6 \leq k \leq 6$ $-18 \leq l \leq 18$	$-6 \leq h \leq 6$ $-6 \leq k \leq 6$ $-18 \leq l \leq 18$ $-1 \leq m \leq 1$	$-6 \leq h \leq 6$ $-6 \leq k \leq 6$ $-18 \leq l \leq 18$
No. of reflections	14506	14506	3202
$R_{\text{int}}$ all, main, satellite	0.0489, –, –	0.0489, 0.0433, 0.0582	0.0256, –, –
No. of independent reflections all, main, satellite	4057, –, –	4057, 1339, 2718	1352, –, –
No. of parameters	325	325	109
No. of restraints	18	6	6
Refinement program	JANA2000 [16]	JANA2000 [16]	JANA2000 [16]
$R(I > 3\sigma_I)/R$ (all reflections) all, main, satellite	0.0497 / 0.0698, – / –, – / –	0.0510 / 0.0710, 0.0474 / 0.0584, 0.0552 / 0.0571	0.0494 / 0.0650, – / –, – / –
$wR(I > 3\sigma_I) / wR$ (all reflections) all, main, satellite	0.0531 / 0.0545, – / –, – / –	0.0549 / 0.0563, 0.0544 / 0.0552, 0.0552 / 0.0571	0.0553 / 0.0563, – / –, – / –
GooF	2.28	2.35	2.65
Weighting parameter $a^b$	0.0001	0.0001	0.0001
Largest difference peaks $\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ ( $\text{e}\text{\AA}^{-3}$ )	0.20, –0.21	0.23, –0.22	0.15, –0.14

a: Supplementary crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre for  $\alpha_S$  (supplementary publication no. CCDC 193979) and for  $\gamma$  (supplementary publication no. CCDC 193980), and at the Bilbao Incommensurate Structures Database for  $\alpha_M$ . These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK, [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)) respectively via <http://www.cryst.ehu.es/icsdb/search.html> (or Laboratorio de Materiales de UPV, Departamento de Física de la Materia Condensada and Departamento Física Aplicada II, Facultad de Ciencias, Universidad del País Vasco, Apartado 644, 48080 Bilbao, SPAIN, [cryst@wm.lc.ehu.es](mailto:cryst@wm.lc.ehu.es)). The lists of  $F_o/F_c$ -data are available from the authors up to one year after the publication has appeared.

b:  $w = 1/(\sigma_F^2 + aF^2)$

ing Fourier expansion contains  $(N-1)/2$  harmonics for  $N$  being odd and  $N/2$  harmonics for  $N$  being even [4].

In the present case with relation (2) being  $3 \cdot \vec{q} = \vec{a}^*$  the modulated structure has to be described with  $(3-1)/2 = \text{one}$  harmonic wave. This corresponds with the satellite order of  $|m| = (3-1)/2 = 1$ .

Consequently to the description of the commensurate modulation by a finite Fourier expansion, not every point (as for incommensurate structures) but only  $N$  discrete points of the atomic modulation functions have a physical meaning in the interval  $0 \leq t < 1$ . This corresponds to the  $N$  displacements of each atom in the  $N$ -fold superstructure. These  $N$  values are equally spaced along the fourth dimension. This means, that only phase shifts of multiples of  $1/N$  give identical structures. Other phase shifts produce different structures. In this way, infinitely many different structures can be described with infinitely many sets of  $N$  equal sections [17]. Therefore the starting point of the set of the  $N$  discrete points along the fourth dimension, *i.e.* the global phase of the modulation function  $t_{\text{zero}}$ , has also to be specified. In the present case, the global phase has been selected as  $t_{\text{zero}} = 0$ . With this starting point and the phase shifts being  $1/N$ , the  $N = 3$  points with physical meaning have the coordinates  $t = 0, 1/3$  and  $2/3$ .

Because the number of independent parameters has to be in principle the same for the modulated structure and the superstructure [18], the modulation of  $\alpha_M$  is described by one harmonic wave for displacive modulation (which affects the fractional coordinates  $x, y, z$  of the single

atoms) for all atoms and one harmonic wave for thermal modulation (which affects the anisotropic displacement parameters  $U^{ij}$ ) for the non-hydrogen atoms. With this model the observations of the X-ray diffraction measurements can be equally well reproduced as with the superstructure model (see Table 3). The results are essentially the same for both descriptions, *e.g.* the difference for the  $R$  and  $wR$ -values is 0.0013 and 0.0018, respectively. The slight deviations can be explained by the different functional expressions, which have been minimized during refinement.

To summarize the results of the crystal structure refinement, the fractional coordinates  $x, y, z$  and displacement parameters  $U_{\text{eq}}$  respectively  $U_{\text{iso}}^{\text{calc}}$  of the atoms are given in Tables 4 and 5, the harmonic displacive modulation parameters  $\cos_1^p$  and  $\sin_1^p$  in Table 6.

The three different orientations of the molecules can be recovered from the structure refinement by selecting the three specific values of the modulation parameter  $t$ . To obtain the corresponding  $x_4$  values for the atoms, equation (3) must be applied. These  $x_4$  depend on the fractional coordinates  $x, y, z$  of the single atoms in real space [19]:

$$x_4 = t + \vec{r} \cdot \vec{q} \quad (3)$$

$\vec{r}$  is the position vector of the respective atom in physical space. Using the three atomic positions in superspace, one deduces, that the molecule at  $t = 0$  corresponds to molecule A in the superstructure,  $t = 1/3$  to B and  $t = 2/3$  to C (for the choice of  $t_{\text{zero}} = 0$ ). The three molecules are

**Table 4.** Atomic parameters (e.s.d.s) and  $U_{\text{eq}}^a$  (in  $\text{\AA}^2$ ) for the non-hydrogen atoms in  $\alpha\text{M}$ .

Atom	$x$	$y$	$z$	$U_{\text{eq}}$
O10	1.56258(16)	1.25934(15)	0.90713(6)	0.0561(3)
N09	1.1820(2)	1.26244(17)	0.94807(8)	0.0504(4)
Cl08	0.69116(11)	0.26721(6)	0.57318(3)	0.0941(2)
C01	1.3175(2)	1.16773(18)	0.89328(8)	0.0411(4)
C02	1.1591(2)	0.94185(19)	0.81406(8)	0.0419(4)
C03	0.9541(3)	0.7777(2)	0.82043(10)	0.0549(5)
C04	0.8125(3)	0.5690(2)	0.74669(11)	0.0639(5)
C05	0.8747(3)	0.5281(2)	0.66573(9)	0.0586(5)
C06	1.0740(4)	0.6884(3)	0.65689(11)	0.0722(6)
C07	1.2197(3)	0.8941(2)	0.73150(10)	0.0619(5)

a:  $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

shown as function of the modulation parameter  $t$  in Fig. 3 in the  $(\vec{a}, \vec{b})$  plane.

Intramolecular atomic bond lengths and angles are given in Tables 7 and 8. It is seen, that the three conformations, *i.e.* the modulation of the molecule are not reflected in the interatomic bond lengths and angles. In all three conformations the phenyl ring shows some distortion from

**Table 5.** Atomic parameters (e.s.d.s) and  $U_{\text{iso}}^{\text{calc}}$  (in  $\text{\AA}^2$ ) for the hydrogen atoms in  $\alpha\text{M}$ .

Atom	$x$	$y$	$z$	$U_{\text{iso}}^{\text{calc}}$
H09a	1.268(3)	1.3968(12)	0.9918(7)	0.0567(6)
H09b	0.9988(7)	1.217(2)	0.9299(9)	0.0567(6)
H03	0.910(3)	0.805(2)	0.8766(6)	0.0632(8)
H04	0.668(2)	0.466(2)	0.7529(10)	0.0703(9)
H06	1.118(3)	0.661(3)	0.6010(7)	0.0813(10)
H07	1.357(2)	1.0065(19)	0.7248(10)	0.0713(9)

**Table 6.** First harmonic displacive modulation parameters  $\cos_1^{\text{p}}$  and  $\sin_1^{\text{p}}$  for the atoms in  $\alpha\text{M}$ .

Atom	$x \cos_1^{\text{p}}$	$x \sin_1^{\text{p}}$	$y \cos_1^{\text{p}}$	$y \sin_1^{\text{p}}$	$z \cos_1^{\text{p}}$	$z \sin_1^{\text{p}}$
O10	-0.0162(2)	-0.0228(2)	0.02565(19)	0.03425(19)	-0.01164(9)	-0.01670(9)
N09	0.0111(3)	-0.0262(3)	-0.0054(2)	0.0547(2)	0.00713(11)	-0.02037(11)
Cl08	-0.04939(14)	0.04511(14)	0.02023(9)	-0.03889(9)	-0.00214(4)	0.01442(4)
C01	-0.0060(3)	-0.0191(3)	0.0124(2)	0.0325(2)	-0.00372(11)	-0.01226(11)
C02	-0.0192(3)	-0.0207(3)	0.0239(2)	0.0223(2)	-0.00794(11)	-0.00771(11)
C03	-0.0076(4)	-0.0735(4)	0.0215(3)	0.0579(3)	-0.00091(13)	-0.01942(13)
C04	-0.0382(4)	-0.0618(4)	0.0364(3)	0.0415(3)	-0.00501(14)	-0.01461(14)
C05	-0.0489(4)	0.0080(4)	0.0323(3)	-0.0123(3)	-0.00847(13)	0.00591(12)
C06	-0.0819(5)	0.0393(4)	0.0555(4)	-0.0394(3)	-0.02263(14)	0.01346(14)
C07	-0.0754(4)	0.0136(4)	0.0582(3)	-0.0142(3)	-0.02382(14)	0.00238(13)
H09a	0.012(3)	-0.023(3)	-0.0146(16)	0.0555(16)	0.0108(8)	-0.0207(9)
H09b	0.0022(9)	-0.0323(9)	0.018(3)	0.067(3)	0.0039(11)	-0.0252(11)
H03	0.004(3)	-0.101(3)	0.031(3)	0.086(3)	0.0011(7)	-0.0262(7)
H04	-0.064(2)	-0.080(2)	0.064(2)	0.047(2)	-0.0065(12)	-0.0230(12)
H06	-0.121(4)	0.051(3)	0.068(3)	-0.059(3)	-0.0316(8)	0.0161(8)
H07	-0.104(2)	0.003(2)	0.075(2)	-0.013(2)	-0.0308(13)	-0.0062(12)

ideal shape: all bond lengths are within the error about 1.38 $\text{\AA}$  except C04–C05 with 1.37 $\text{\AA}$  and C05–C06 with 1.36 $\text{\AA}$ . C05 is the carbon atom linked to the chlorine. It is displaced by the chlorine atom towards the centre of the phenyl ring shortening the bond lengths and widening the angle C04–C05–C06, which is the largest one inside the phenyl ring.

Selected torsion angles are listed in Table 9. To a good approximation the chlorine atom is positioned in the plane defined by the phenyl ring. The torsion angles along the C01–C02 bond reflect the twist of the complete molecule.

## 4 Phase transition and the high temperature $\gamma$ -form

### 4.1 The phase transition

In the phase transition  $\alpha \rightarrow \gamma$  the satellite reflections vanish and reappear again in the transition  $\gamma \rightarrow \alpha$ . After several phase transition cycles the initially transparent single crystal became slightly cloudy, but still gave sharp peaks in the diffraction pattern. The reversibility of the phase transition was not only confirmed by X-ray diffraction experiments but also by DSC measurements.

The reorientation of the molecules during the  $\alpha \rightarrow \gamma$  phase transition towards one unique orientation results in an increase of the length of  $\vec{c}$  of about 0.3  $\text{\AA}$ , while the lengths of  $\vec{a}$  and  $\vec{b}$  remain constant within errors. The angles  $\alpha$  and  $\beta$  increase by 0.7° respectively 1.0° and  $\gamma$  decreases by 0.8°.

### 4.2 The $\gamma$ structure

A rather complex model was proposed by [12] for  $\gamma$ . It contains four different “structural units”, one unit for each conformation of the three independent molecules A, B and C (with equal proportions) and the fourth one with positional parameters very close to the mean values derived

**Table 7.** Intramolecular atomic bond lengths (Å) in  $\alpha_M$  and  $\gamma$ .

	$\alpha_M$			$\gamma$
	$t = 0$	$t = 1/3$	$t = 2/3$	
O10–C01	1.232(2)	1.228(2)	1.229(2)	1.224(2)
N09–C01	1.329(3)	1.328(3)	1.323(3)	1.316(3)
Cl08–C05	1.739(2)	1.732(2)	1.734(2)	1.732(2)
C01–C02	1.492(2)	1.491(2)	1.497(2)	1.488(2)
C02–C03	1.379(3)	1.387(3)	1.380(3)	1.362(3)
C02–C07	1.377(3)	1.378(3)	1.379(3)	1.359(4)
C03–C04	1.379(3)	1.381(3)	1.381(3)	1.379(3)
C04–C05	1.371(4)	1.375(4)	1.363(4)	1.345(4)
C05–C06	1.353(4)	1.358(4)	1.359(4)	1.355(4)
C06–C07	1.379(3)	1.379(3)	1.379(3)	1.373(3)

**Table 8.** Intramolecular atomic angles (°) in  $\alpha_M$  and  $\gamma$ .

	$\alpha_M$			$\gamma$
	$t = 0$	$t = 1/3$	$t = 2/3$	
O10–C01–N09	121.7(1)	122.0(2)	122.3(2)	121.5(1)
O10–C01–C02	121.1(2)	120.7(2)	121.5(2)	121.0(2)
C04–C05–Cl08	118.8(2)	118.9(2)	118.8(2)	119.1(2)
C01–C02–C03	122.8(2)	122.2(2)	121.7(2)	122.0(2)
C02–C03–C04	120.9(2)	120.8(2)	121.2(2)	120.9(3)
C03–C04–C05	118.9(2)	119.1(2)	119.2(2)	119.5(3)
C04–C05–C06	121.2(2)	121.1(2)	121.2(2)	120.7(2)
C05–C06–C07	119.6(3)	119.5(2)	119.8(3)	119.2(3)
C06–C07–C02	120.6(2)	120.5(2)	120.8(2)	121.3(3)
C07–C02–C03	118.3(2)	118.7(2)	118.6(2)	118.2(2)

**Table 9.** Selected torsion angles (°) in  $\alpha_M$  and  $\gamma$ . For  $\alpha_M$  also the respective average values are indicated.

	$\alpha_M$			$\gamma$	
	$t = 0$	$t = 1/3$	$t = 2/3$	$\langle av \rangle$	
O10–C01–C02–C07	20.4(2)	32.3(2)	29.5(2)	27.4	27.6(3)
N09–C01–C02–C03	19.0(2)	33.9(2)	28.6(2)	27.2	27.3(3)
C03–C04–C05–Cl08	178.4(1)	177.7(1)	178.2(1)	178.1	179.5(2)
Cl08–C05–C06–C07	177.8(1)	179.5(1)	180.0(1)	179.1	179.0(2)

from the above three units [12]. These difficulties in describing the structure might have its origin in crystal quality and/or the poor quality of the data.

In contrast, we can better interpret our data by applying only one structural model which corresponds to the fourth unit mentioned above. Details on the crystal structure refinement are given in Table 3, the fractional coordinates  $x$ ,  $y$ ,  $z$  and displacement parameters  $U_{eq}$  respectively  $U_{iso}^{calc}$  of the atoms in Tables 10 and 11.

Intramolecular atomic bond lengths and angles are listed in Tables 7 and 8, torsion angles in Table 9. In the  $\gamma$ -form, the intramolecular torsion angles are almost, within the errors, equivalent to the mean values of the corresponding three independent molecules of the  $\alpha$ -form.

As in the  $\alpha$ -form two different hydrogen bonds can be identified in the structure, the one N09–H09a  $\cdots$  O10' linking centrosymmetric dimers, the other N09–H09b  $\cdots$  O10''

**Table 10.** Atomic parameters (e.s.d.s) and  $U_{eq}^a$  (in Å<sup>2</sup>) for the non-hydrogen atoms in  $\gamma$ .

Atom	$x$	$y$	$z$	$U_{eq}$
O10	1.5624(2)	1.2599(2)	0.90710(11)	0.0788(6)
N09	1.1814(3)	1.2605(3)	0.94914(13)	0.0722(7)
Cl08	0.69283(18)	0.26605(12)	0.57409(6)	0.1336(4)
C01	1.3157(3)	1.1674(3)	0.89356(13)	0.0570(7)
C02	1.1581(3)	0.9416(3)	0.81450(13)	0.0562(6)
C03	0.9556(5)	0.7751(4)	0.82288(19)	0.0863(10)
C04	0.8137(5)	0.5665(4)	0.7489(2)	0.0976(12)
C05	0.8747(5)	0.5275(4)	0.66699(17)	0.0821(9)
C06	1.0729(7)	0.6915(5)	0.6563(2)	0.1087(13)
C07	1.2181(5)	0.8956(4)	0.73155(18)	0.0922(11)

a:  $U_{eq}$  is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

**Table 11.** Atomic parameters (e.s.d.s) and  $U_{iso}^{calc}$  (in Å<sup>2</sup>) for the hydrogen atoms in  $\gamma$ .

Atom	$x$	$y$	$z$	$U_{iso}^{calc}$
H09a	1.271(5)	1.391(3)	0.9964(15)	0.0883(11)
H09b	0.996(4)	1.212(4)	0.9324(18)	0.0883(11)
H03	0.900(5)	0.803(5)	0.8773(15)	0.0988(17)
H04	0.682(5)	0.450(4)	0.760(2)	0.1068(19)
H06	1.133(6)	0.677(6)	0.6035(18)	0.1229(21)
H07	1.353(5)	1.001(5)	0.721(2)	0.1062(17)

linking endless chains. This is the same hydrogen bonding scheme as found in the  $\alpha$ -form. In both structures the molecules form endless chains of dimers along the  $\vec{a}$ -axis and the chains form layers *via* chlorine  $\cdots$  chlorine interactions. However, in the  $\gamma$ -form all molecules have the same conformation, whereas in the  $\alpha$ -form three different conformations A, B and C exist, giving rise to a tripling of  $\vec{a}$ .

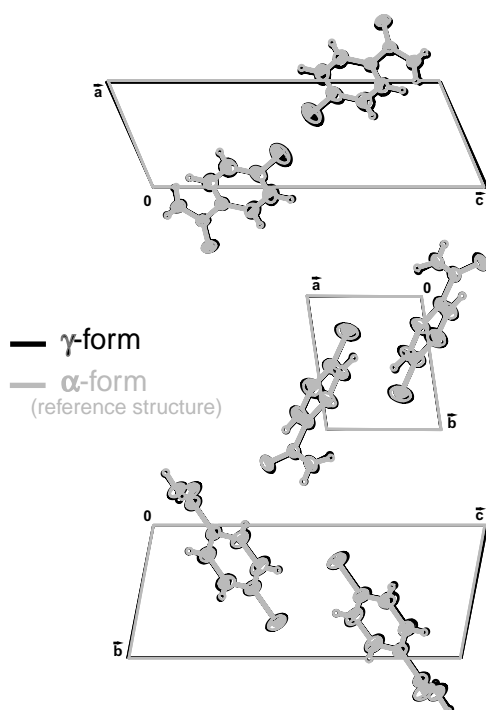
## 5 The relation between $\alpha$ - and $\gamma$ -form

The modulated structure description consists of a (conventional three-dimensional periodic) *reference 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 this *reference structure* is the crystal structure, onto which the modulation is applied. 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  $U^{ij}$ .

In the present case the reference structure is the so-called “average structure”, *i.e.* the structure description of  $\alpha_M$  consists of the average structure plus a sinusoidal modulation.

The relation between this *reference structure* of  $\alpha_M$  and the structure of  $\gamma$  is presented qualitatively in Fig. 4 by superposing the unit cells. Both cells differ slightly from each other.

It is striking that both structures are very close. The atomic positions switch within the limits of the displace-



**Fig. 4.** Superposition of the structure of  $\gamma$  (black) and the *reference structure* of  $\alpha_M$  (grey) with the displacement ellipsoids drawn at the 30% probability level.

ment ellipsoids. Only the hydrogen atoms of the amide group (H09a and H09b) show small deviations. The displacement ellipsoids of the  $\gamma$ -form (high temperature) are, as expected, larger than those of the  $\alpha$ -form (room temperature), but they present the same shape.

Therefore one might interpret the relation between the structures of the  $\gamma$ - and  $\alpha$ -form as the periodic, high-symmetry phase at high temperature and the commensurate modulated phase at lower temperature [8].

## 6 Conclusion

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  $(\vec{a}^*, \vec{c}^*)$  plane: every third line along the  $\vec{a}^*$ -axis exhibits stronger intensities than the two lines in-between (see Fig. 2). In addition, the stronger lines remain 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 same structural model can be applied for the *reference structure* of the modulated room temperature

phase and for the structure of the high temperature phase. Therefore the superspace approach provides a unified picture of the relationship between modulated and non-modulated phases.

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