Checklist for the Description of Incommensurate Modulated Crystal Structures
Report of the International Union of Crystallography Commission on Aperiodic Crystals†

G. CHAPUIS (Chairman), a M. FARKAS-JAHNKE, b J. M. PÉREZ-MATO, c M. SENECHAL, d W. STEURER, e C. JANOT, f D. PANDER G AND A. YAMAMOTO h

a Institut de Cristallographie, Université de Lausanne, BSP Dorigny, 1015 Lausanne, Switzerland, b Research Institute for Technical Physics, Hungarian Academy of Sciences, PO Box 76, 1325 Budapest, Hungary, c Departamento de Fisica de la Materia Condensada, Facultad de Ciencias, Universidad del Pais Vasco, Apartado 644, 48080 Bilbao, Spain, d Department of Mathematics, Smith College, Northampton, MA 01043, USA, e Institut für Kristallographie und Petrographie, ETH-Zentrum, 8092 Zurich, Switzerland, f Institut Laue-Langevin, 156 Centre de Tri, Avenue des Martyrs, 38042 Grenoble CEDEX, France, g School of Material Science and Technology, Banaras Hindu University, Varanasi 221 005, India, and h National Institute for Research in Inorganic Materials, Sakura-mura, Niihari-gun, Ibaraki 305, Japan. E-mail: gervais.chapuis@ic.unil.ch

(Received 4 June 1993; accepted 8 August 1996)

Abstract

One of the terms of reference published in 1992 (Acta Cryst. A48, 922-946) in the report of the (at that time) Ad Interim Commission on Aperiodic Crystals was 'to co-operate with other Commissions of the IUCr in establishing adequate guidelines and standards for articles to be published in IUCr journals reporting structural investigations of aperiodic crystals and theoretical investigations of aperiodic patterns'. It was soon recognized by the Commission that the establishment of a checklist for the publication of incommensurately modulated structures was perhaps the most urgent task. One of the first attempts to address the problem of publishing incommensurate structures was presented during a discussion organized in 1991 in Lekeitio, Spain, in a workshop dedicated to methods of structural analysis of modulated structures and quasicrystals. Since this meeting, the work of the Commission progressed interactively by numerous exchanges on the occasions of international meetings and mostly by electronic correspondence. The Checklist was accepted in 1994 by the Executive Committee of the IUCr. The opinion of the Commission on Journals was also requested and, following the comments of its members, the Checklist has been completed with an example of an incommensurate crystal structure illustrating each specific item that is required in the Checklist.

† Final checklist accepted on 15 January 1996 by the Commission on Aperiodic Crystals, on 1 September 1994 by the Executive Committee and on 25 November 1994 by the Commission on Journals.


In this column, an example of an incommensurate structure is presented in order to illustrate the corresponding items required by the checklist. The structural data are taken from Acta Cryst. (1994), BSO, 333–343.

<table>
<thead>
<tr>
<th>Crystal data</th>
<th>Crystal data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula.</td>
<td>(C3H7NH3)2MnCl4</td>
</tr>
<tr>
<td>Formula weight.</td>
<td>316.98</td>
</tr>
<tr>
<td>Source of material.</td>
<td>Slow evaporation at room temperature of a stoichiometric aqueous solution of n-C3H7NH3Cl (Sigma) and MnCl2 (Merck, &gt;98%)</td>
</tr>
<tr>
<td>Crystal shape and size.</td>
<td>Platelet, {001} pinacoid [0.064(4) mm thick], {111} orthorhombic dipyramid [base: 0.618(4) mm x 0.612(4) mm]</td>
</tr>
<tr>
<td>If observed, mention the existence of crystal faces associated to incommensurate modulation vectors.</td>
<td>The crystals were grown at room temperature at which the structure is commensurate</td>
</tr>
</tbody>
</table>

© 1997 International Union of Crystallography
Printed in Great Britain – all rights reserved
**Crystal system of the incommensurate structure.**

**Orthorhombic**


**Set of generators of the superspace group in explicit form (choice of origin and setting).** In the case of an alternative symmetry description, minimal mathematical information sufficient for deriving the implied symmetry restrictions on the atomic modulations.

The superspace group as generated from the above symbol contains no inversion center that coincides with the origin. A transformation with \( t = t' - 1/4 \) was therefore performed. The representative elements for the space group Abma can be obtained by disregarding the fourth coordinate. The superscripts enumerate the symmetry operations to identify the distances and angles that can be used in the structure description. The origin of the superspace group is on the inversion center.

The two operators \((0000)^+\); \((0\frac{1}{2} \frac{1}{2})^+\) generate the full set of operations:

1. \([1, 3, E]: \{xyz\}[/]
2. \([2, 10, \sigma]: \{x + \frac{1}{2}yz + \frac{1}{2} t\}[/
3. \([3, 11, \sigma]: \{xyzt\}[/
4. \([4, 12, \sigma]: \{x - \frac{1}{2}yz - \frac{1}{2} t\}[/
5. \([5, 13, F]: \{xyz\}[/
6. \([6, 14, C_{x+y}]: \{x + \frac{1}{2}yz + \frac{1}{2} t\}[/
7. \([7, 15, C_{x-y}]: \{xyz\}[/
8. \([8, 16, C_{y-z}]: \{xyz\}[/
9. \([9, 17, C_{z-x}]: \{xyz\}[/

Generators of the superlattice:

\([1, 0, 0, 0], (E[0, \frac{1}{2}, \frac{1}{2}, 0], (E[0, -\frac{1}{2}, \frac{1}{2}, 0], (E[0, 0, 0, 1])[/

**Diffraction symmetry (Laue symmetry, systematic absences) and possible superspace group(s) compatible with it.**

**Unit-cell dimensions (cell parameters and volume) of the average lattice deduced from main reflections; number and \( \theta \) range of main reflections used for this measurement.**

Lattice parameters (Å): \( a = 7.414 (2), b = 7.289 (2), c = 26.803 (7) \)

Unit-cell volume (Å³): \( V = 1448 (1) \)

Number of independent reflections measured: 1846; \( > 3\sigma(I) \): 1331

Line instrument, absorption correction.

\((\sin \theta/\lambda)_{\text{max}}(\AA^{-1})\):

- 0.53 for \(|m| = 0, 1\)
- 0.37 for \(|m| = 2\)

**Independent modulation wave vector(s) \( q_i \) (with standard deviations) with which diffraction vectors are indexed in the form \( h a^* + k b^* + l c^* + \sum m_i q_i \) \( (a^*, b^*, c^*): \) unit-cell parameters of the average lattice; \( h, k, l, m_i: \) integers. For commensurately modulated structures described in the superspace formalism, the rational components of the modulation vector(s) should be given.

\( q_i = 0.176 (1) a^* \)

**Z**

4

**Measured and calculated densities \( D_m \) and \( D_x \)**

\( D_x = 1.462 \text{ Mg m}^{-3} \)

**Radiation and wavelength.**

\( \lambda_{\text{Cu}} = 1.54184 (\text{Å}) \)

**Linear absorption coefficient.**

\( \mu(\text{Cu K}\alpha) = 140.1 \text{ cm}^{-1} \)

**F(000)**

652

**Data collection**

**Diffractometer used.**

Syntex P2₁

**Temperature of measurement.**

351 (5), 365 (5) K for the first, second crystal, respectively. Temperature stability better than ±0.3 K

**Method to measure diffraction data.**

2θ–ω scans, graphite monochromator
Method of determining the independent modulation wave vector(s) \( \mathbf{q}_m \).

Obtained by averaging the fractional parts of index \( h \) of ten accurately centered first-order satellites at \( 2\theta \approx 50^\circ \)

Temperature variation of the modulation wave vector(s), if measured.

Reported in *Solid State Commun.* 45, 1089–1092

Method of measuring satellite reflections \( (m_i \neq 0) \). Comparison between intensity profiles of satellite reflections and main reflections \( (m_i = 0) \).

Same as for main reflections

Absorption correction applied (maximum and minimum transmission values).

FWHM \( \sigma, hklm \): 0.60 (4000), 0.52 (0400), 0.48 (0080), 0.59 (04,13,1), 0.52 (1181)

Absorption correction (analytical correction method applied)

For each reflection class \( m (= \sum n_i) \): number of measured reflections; range of \( h, k, l \); \( \sin \theta/\lambda \) range; internal \( R \) value from merging equivalent reflections.

\( |m| = 0 \) \( |m| = 1 \) \( |m| = 2 \) Total

\( R_{int} (20; 3-70^\circ, \text{full sphere}) \)

\begin{array}{cccc}
| & 0.063 & 0.067 & 0.083 & 0.064 \\
\text{with absorption correction} & 0.137 & 0.186 & 0.134 & 0.144 \\
\text{without absorption correction} & & & & \\
\text{Number of reflections} & 1846 & 3820 & 897 & 6563 \\
\text{[> 3\sigma(\|)]} & 1331 & 2126 & 127 & 3584 \\
\text{Independent reflections} & 524 & 1072 & 292 & 1888 \\
\text{[> 3\sigma(\|)]} & 369 & 627 & 60 & 1056 \\
\end{array}

Number of independent reflections, total and for each reflection class.

Standard reflections chosen (at least one reflection for each measured reflection class should be included) and their intensity variation during the measurement.

1190; 0080; 4400; 0011; 2211; 0411
Loss of intensity: \( \approx 30\% \) within 216 h
Equal decay for \( |m| = 0, 1 \)

Number of observations, total and for each reflection class.

Freshly grown crystals at room temperature were heated once to the temperature of measurement. The temperature was estimated from the \( T \) dependence of the modulation vector \( \mathbf{q}(T) \)

Thermal history of the sample(s). Temperature stability during the measurement.

Characteristics of diffuse scattering phenomena if any.

- 

**Refinement**

Brief outline of the refinement method used. Computer programs employed.


Structure-factor calculation: analytical expression for the structure factor and all the modulation functions used. This information should be sufficient to reproduce the modulations of all the symmetry-equivalent atoms. Method and accuracy of numerical integration, if any.

Structure-factor expressions taken from Paciorek & Chapuis [*Acta Cryst.* (1994), A50, 194–203]. Additional modulated functions are derived in the original paper

Gaussian integrations with 32 divisions

Type(s) of modulation. Parameters used to describe the individual atomic modulation functions (including the modulation of thermal parameters, if any). Mention all tested models.

\[ u_\mu^i(t) = \sum_{n=0}^\infty \left[ c_{n\mu}^i \cos(2\pi nt + \frac{x_{\mu}^1}{X_\mu}) \right] + x_{\mu}^2 \sin(2\pi nt) \]
\[ \beta_\mu^i(t) = \beta_{0\mu}^i 2 \cos(4\pi t + \frac{x_{\mu}^1}{X_\mu}) \]
\( t \) is the internal coordinate ranging between 0 and 1; \( i \) refers to the direction and \( \mathbf{r}^\mu \) is the average position of atom \( \mu \) within the unit cell \( n \) of the average structure

Symmetry restrictions and/or constraints on the structure parameters, if any.

Symmetry restrictions on coordinates, thermal displacement parameters and modulation parameters for the atoms on special sites. The parentheses indicate those Debye-Waller-factor (DWF) modulation parameters that are set to zero according to the phason/amplitudon parametrization proposed by Pérez-Mato *et al.* [*Solid State Commun.* (1991), 78, 33–37]
The restrictions are calculated according to expressions
\( u'(t) - R u(t - r_i) \) and \( T'(t) - R T(t - r_i) R' \), where \( u \) is a vector of the displacive modulation functions, \( T \) the DWF tensor, \( R \) and \( R' \) the rotational part and its transpose of the standard space group and \( r_i \) the internal coordinate translation.

Wyckoff notation: 4(a); site symmetry: (\( i \))\textsubscript{y}, (\( 1 \))\textsubscript{y}; atom: Mn;
\[
\begin{array}{cccccc}
0 & 0 & x_{1s1} & 0 & x_{1s2} \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & x_{3s1} & 0 & x_{3s2} \\
\end{array}
\]

Source of scattering factors.

Starting structural model. Parameters refined.
As starting parameters, the coordinates of the \( \delta \) phase at room temperature [Peterson & Willet (1972). *J. Chem. Phys.* 56, 1879–1882] were used. An improved model with C1 and C2 on general positions 16(a) in *Abma* yielded a significantly better agreement. N and C3 were refined on the mirror plane 8(f)

Use of \( F \), \( F^2 \) or \( I \) in the refinement.
Refinement based on \( F \)

Constraints in the refinement process if any; restraints on stereochemical quantities or other parameters and their weights, if any.
Bond distances and angles constraints for \( H \) atoms in the average structure
Constraints on first-order harmonics of the temperature-factor modulation

Number of reflections used in the refinement; number of refined parameters.
Model 5a 1058 reflections 80 parameters
Model 5b 1888 reflections 80 parameters

Method of locating and refining \( H \) atoms.
From stereochemical considerations. The modulation parameters were approximately constrained to the values of the bonded atom

Weighting scheme in the refinement: definition of \( w \) for reflections and, in the case of the refinement restraints, for the pseudo-observations introduced.
1/\( \sigma^2(F) \)

Overall, and for each reflection class, final values of \( R = \sum |F_o| - |F_c|/\sum |F_o|, wR = \sum w(Y_o - Y_c)^2/\sum wY_o^2]^{1/2} \), where \( Y_o \) and \( Y_c \) are the observed and calculated coefficients specified above (\( F \), \( F^2 \) or \( I \)). Final value of \( \Sigma = \sum w(Y_o - Y_c)^2/(m - n)^{1/2} \) for all reflections. Ratio of maximum least-squares shift to error in final refinement cycle.

R factors for various models of modulated structures: No. 5a harmonic displacive, Axe correction (global phason), \( I > 3\sigma(I) \);
No. 5b harmonic displacive, Axe correction (global phason), all observed reflections
For all models: \( \Delta_{\text{max}}/\sigma < 0.001 \), goodness of fit \( \sigma \approx 2 \), OSR\textsubscript{all} = 0.999, \( R \) values are multiplied by \( 100 R_{\text{all}} R_{\text{MSR}} = \sum |F_o| / \sum |F_c| ; R_w = R_{w,\text{MSR}} = (\sum w(F_o^2 - F_c^2) / \sum wF_o^2)^{1/2} ; \) OSR:

\[
\begin{array}{cccccc}
5a & 5.22 & 3.93 & 3.1 & 6.8 & 6.5 & 11.9 & 0.91 & 80 & 0.17 (1) \\
5b & 9.81 & 6.82 & 6.2 & 9.1 & 6.6 & 18.9 & 0.72 & 80 & 0.17 (1) \\
\end{array}
\]

Maximum and minimum of \( \Delta \rho \) in final superspace difference Fourier synthesis.
Not available

Extinction correction method (if applied). Primary- and secondary-extinction values.
Isotropic extinction \( F^\text{corr} = F/(1 + 10^{-4}C_{\text{ext}}F^2 / \sin \theta)^{1/4}, C_{\text{ext}} = 2.6 (2) \)
$F_o$ versus $F_o$ plots for the different reflection classes, or other plots for data and refinement quality assessment.

Final structural model, expressed in terms of the average structure plus atomic modulation functions with zero mean values. Values of all refined parameters with standard deviations. If Fourier series are used for the description of the modulation functions, presentation of Fourier complex coefficients in terms of amplitudes and phases is preferred.

The DWFs are refined as $\beta^2 \mu$. $U^{ij}$ of the modulated and the average (obtained from a refinement using main reflections only) structure are given for comparison. The coordinates $(x, y, z)$ and modulation amplitudes $(a_x, a_y, a_z)$ are multiplied by 10^4; the DWFs by 10^3 and the modulation phases $(\varphi_x, \varphi_y, \varphi_z)$ are given as multiples of 2$\pi$. The modulations are expressed by

$$u^m_i(t) = \sum_{n=0}^{\infty} a^m_{m,n} \cos[2\pi(n t + \varphi^m_{m,n})]$$

In the following selection, the refined parameters of Mn in model 5 are listed:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x$</td>
<td>0</td>
<td>8 (2)</td>
</tr>
<tr>
<td>$y$</td>
<td>0</td>
<td>$a_y$</td>
</tr>
<tr>
<td>$z$</td>
<td>0</td>
<td>139.5 (8)</td>
</tr>
<tr>
<td>$\beta^{11}$</td>
<td>12.2 (4)</td>
<td>$U^{11}$</td>
</tr>
<tr>
<td>$\beta^{12}$</td>
<td>12.5 (4)</td>
<td>$U^{12}$</td>
</tr>
<tr>
<td>$\beta^{13}$</td>
<td>2.46 (4)</td>
<td>$U^{13}$</td>
</tr>
<tr>
<td>$\beta^{12}$</td>
<td>12.2 (4)</td>
<td>$U^{22}$</td>
</tr>
<tr>
<td>$\beta^{13}$</td>
<td>12.5 (4)</td>
<td>$U^{23}$</td>
</tr>
<tr>
<td>$\beta^{23}$</td>
<td>2.46 (4)</td>
<td>$U^{33}$</td>
</tr>
<tr>
<td>$U_{eq}$</td>
<td>5.3</td>
<td>$U_{eq,av}$</td>
</tr>
</tbody>
</table>

Graphic representation of a selection of the modulation functions.

Atomic modulation functions in $x$ direction. The numbers given on the right-hand side of the graphs refer to the following atoms:
1 Mn; 2 Cl1; 3 Cl2; 4 N; 5 Cl1; 6 C2 and 7 C3

Discussion of experimental procedure (including method to measure density, discussion of absolute structure and justification of any unusually high $R$ values or shift-to-e.s.d. ratios >1.0).
100 Checklist for Incommensurate Modulated Crystal Structures

Selected geometrical data

<table>
<thead>
<tr>
<th></th>
<th>Short selection of bond distances of model 5; $d_{av}$: average distance (Å), standard deviations are given in parentheses; $d_{min}$: minimum distance; $d_{max}$: maximum distance; $\Delta$: difference between max. and min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>N—C1</td>
<td>$d_{av}$</td>
</tr>
<tr>
<td></td>
<td>1.48 (2)</td>
</tr>
<tr>
<td>C1—C2</td>
<td>1.45 (3)</td>
</tr>
<tr>
<td>C1—C2</td>
<td>1.52 (3)</td>
</tr>
</tbody>
</table>

Graphical representation of a selection of pertinent geometrical parameters along the internal coordinate(s).

Atomic modulation functions of Cl2. For this atom, the positional parameters $x$ and $z$ are modulated (first harmonic) as well as the Debye–Waller terms $U^{11}$, $U^{22}$ and $U^{13}$ (second harmonic). For six values of $t$ (internal coordinate), ORTEP plots of Cl2 are given (projection parallel to b) showing the rotation of the thermal ellipsoid as a function of $t$ due to Debye–Waller-factor modulation.

If possible, comparison of the modulation with those in related compounds.


If possible, comparison with other phases, commensurate and incommensurate of the same compound: structure and space-group relations, atomic modulations.

Mentioned in the Discussion

In the material to be deposited, the list of structure factors should include their N-dimensional indexing $(h, k, l, m_1, \ldots, m_i, \ldots)$

<table>
<thead>
<tr>
<th>$h$</th>
<th>$k$</th>
<th>$l$</th>
<th>$m$</th>
<th>$F_o$</th>
<th>$\Delta F (= F_o - F_i)$</th>
<th>$\sigma(F)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
<td>-1</td>
<td>15.21</td>
<td>0.27</td>
<td>0.27</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>120.53</td>
<td>9.73</td>
<td>2.02</td>
</tr>
</tbody>
</table>

We thank Dr W. Paciorek and M. Meyer of the University of Lausanne for their criticisms and constructive remarks during the elaboration of the Checklist.