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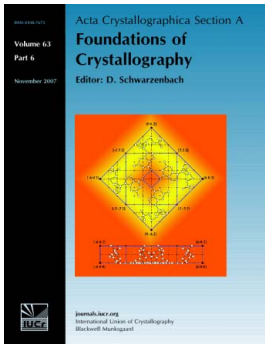

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Checklist for the Description of Incommensurate Modulated Crystal Structures

Report of the International Union of Crystallography Commission on Aperiodic Crystals†

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Abstract

One of the terms of reference published in 1992 (*Acta Cryst.* A**48**, 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 Leikeitio, 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.

This list specifies the information to be given in papers reporting analyses of incommensurate modulated structures. In general, nomenclature should follow the suggestions given in *International Tables for Crystallography* (1992), Vol. C, pp. 797–847. Dordrecht: Kluwer Academic Publishers.	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), B**50**, 333–343.
Crystal data	
Chemical formula.	$(C_3H_7NH_3)_2MnCl_4$
Formula weight.	316.98
Source of material.	Slow evaporation at room temperature of a stoichiometric aqueous solution of n-$C_3H_7NH_3Cl$ (Sigma) and $MnCl_2$ (Merck, >98%)
Crystal shape and size.	Platelet, {001} pinacoid [0.064 (4) mm thick], {111} orthorhombic dipyramid [base: 0.618 (4) × 0.612 (4) mm]
If observed, mention the existence of crystal faces associated to incommensurate modulation vectors.	The crystals were grown at room temperature at which the structure is commensurate

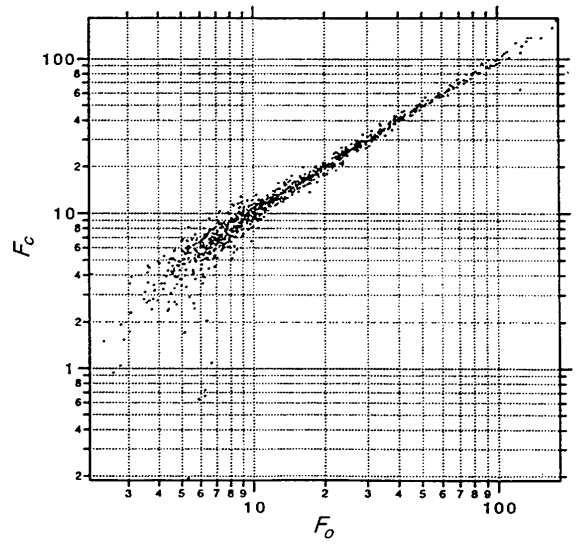
Crystal system of the incommensurate structure.	Orthorhombic
Superspace group [*International Tables for Crystallography* (1992). Vol. C, pp. 797–847 (Dordrecht: Kluwer Academic Publishers); de Wolff, Janner & Janssen (1981). *Acta Cryst.* A**37**, 625–636] or equivalent description of the symmetry of the incommensurate modulated structure.	*Abma*(*a*01)000 (No. 64.3)
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)+; $(0\frac{1}{2}\frac{1}{2}\frac{1}{2})+$ generate the full set of operations: $^{1,9}E$: $\{xyzt\}$ $^{5,13}I$: $\{\bar{x}\bar{y}\bar{z}\bar{t}\}$ $^{2,10}\sigma_x$: $\{\bar{x}+\frac{1}{2}yz+\frac{1}{2}\bar{t}\}$ $^{6,14}C_{2x}$: $\{x+\frac{1}{2}\bar{y}\bar{z}+\frac{1}{2}t\}$ $^{3,11}\sigma_y$: $\{x\bar{y}zt\}$ $^{7,15}C_{2y}$: $\{\bar{x}y\bar{z}\bar{t}\}$ $^{4,12}\sigma_z$: $\{x+\frac{1}{2}y\bar{z}+\frac{1}{2}t\}$ $^{8,16}C_{2z}$: $\{\bar{x}+\frac{1}{2}\bar{y}z+\frac{1}{2}\bar{t}\}$ Generators of the superlattice: $\{E\|1,0,0,0\}, \{E\|0,\frac{1}{2},\frac{1}{2},0\}, \{E\|0,-\frac{1}{2},\frac{1}{2},\frac{1}{2}\}, \{E\|0,0,0,1\}$
Diffraction symmetry (Laue symmetry, systematic absences) and possible superspace group(s) compatible with it.	*hklm*: $k+l+m=2n$ *hk*0*m*: $h=2n$ 0*kl*0: $k=2n$
Unit-cell dimensions (cell parameters and volume) of the average lattice deduced from main reflections; number and θ range of main reflections used for this measurement.	Lattice parameters (Å): $a = 7.414(2)$, $b = 7.289(2)$, $c = 26.803(7)$ V(Å^3): 1448(1) Number of main reflections: 1846; [$> 3\sigma(I)$]: 1331 $(\sin\theta/\lambda)_{max}$ (Å^{-1}): 0.53 for $\|m\| = 0, 1$ 0.37 for $\|m\| = 2$
Independent modulation wave vector(s) $\mathbf{q}_i$ (with standard deviations) with which diffraction vectors are indexed in the form $h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + \sum m_i\mathbf{q}_i$ ($\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$: 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.	$\mathbf{q}_i = 0.176(1)\mathbf{a}^*$
Z	4
Measured and calculated densities D_m and D_x	$D_x = 1.462$ Mg m^{-3}
Radiation and wavelength.	$\lambda_{Cu} = 1.54184$ (Å)
Linear absorption coefficient.	μ(Cu $K\alpha$) = 140.1 cm^{-1}
F(000)	652
Data collection	
Diffractometer used.	Syntex $P2_1$
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) $\mathbf{q}_i$.	Obtained by averaging the fractional parts of index h of ten accurately centered first-order satellites at $2\theta \simeq 50°$
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 FWHM (°, *hklm*): 0.60 (4000), 0.52 (0400), 0.48 (0080), 0.59 (0,4,13,$\bar{1}$), 0.52 (11$\bar{8}\bar{1}$)
Absorption correction applied (maximum and minimum transmission values).	0.638–0.053 (analytical correction method applied)
For each reflection class m ($= \sum \lvert m_i \rvert$): number of measured reflections; range of h, k, l; $\sin\theta/\lambda$ range; internal R value from merging equivalent reflections. Maximum value of θ. Number of independent reflections, total and for each reflection class. Criterion for recognizing unobserved reflections. Number of observed reflections, total and for each reflection class.	$\lvert m\rvert = 0$ / $\lvert m\rvert = 1$ / $\lvert m\rvert = 2$ / Total $R_{\rm int}$ (2θ: 3–70°, full sphere) with absorption correction: 0.063 / 0.067 / 0.083 / 0.064 without absorption correction: 0.137 / 0.186 / 0.134 / 0.144 Number of reflections: 1846 / 3820 / 897 / 6563 [$> 3\sigma(I)$]: 1331 / 2126 / 127 / 3584 Independent reflections: 524 / 1072 / 292 / 1888 [$> 3\sigma(I)$]: 369 / 627 / 60 / 1056
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; $2\bar{2}1\bar{1}$; $041\bar{1}$ Loss of intensity: ~30% within 216 h Equal decay for $\lvert m\rvert = 0, 1$
Thermal history of the sample(s). Temperature stability during the measurement.	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 $\mathbf{q}(T)$
Characteristics of diffuse scattering phenomena if any.	-
Refinement	
Brief outline of the refinement method used. Computer programs employed.	The average structure was solved first, followed by the incommensurate structure refinement. *SHELX* [Sheldrick (1978). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* University of Göttingen, Federal Republic of Germany] and *MSR* [Paciorek (1991). *Methods of Structural Analysis of Modulated Structures and Quasicrystals*, edited by J. M. Pérez-Mato, F. J. Zúñiga & G. Madariaga, pp. 268–279. Singapore: World Scientific] were used for the refinements of the structure
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), A**50**, 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.	$u_i^\mu(t) = \sum_{n>0}[c_{i,n}^\mu \cos(2\pi n t) + s_{i,n}^\mu \sin(2\pi n t)]$ with $t = \mathbf{q}(\mathbf{n} + \mathbf{r}^\mu) \bmod 1$, $\beta_{ij}^\mu(t) = \beta_{ij,2}^\mu \cos(4\pi t + \chi_{ij,2}^\mu)$ 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 μ within the unit cell $\mathbf{n}$ 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 $\mathbf{u}^{\lambda}(t) - \mathbf{R}\mathbf{u}^{\mu}[R_{44}(t-\tau_4)]$ and $\mathbf{T}^{\lambda}(t) - \mathbf{R}\mathbf{T}^{\mu}[R_{44}(t-\tau_4)]\mathbf{R}^t$, where μ and λ denote the properties before and after the transformation, **u** is a vector of the displacive modulation functions, **T** the DWF tensor, **R** and $\mathbf{R}^t$ the rotational part and its transpose of the standard space group and τ_4 the internal coordinate translation Wyckoff notation: 4(*a*); site symmetry: $(^2_1)_y/(^m_1)_y$; atom: Mn; 0 0 *x*1*s*1 0 *x*1*s*2 0 0 0 0 0 0 0 *x*3*s*1 0 *x*3*s*2 β^{11} ($\beta^{11}c1$) 0 $\beta^{11}c2$ 0 β^{22} ($\beta^{22}c1$) 0 ($\beta^{22}c2$) 0 β^{33} ($\beta^{33}c1$) 0 $\beta^{33}c2$ 0 0 0 0 0 0 β^{13} ($\beta^{13}c1$) 0 $\beta^{13}c2$ 0 0 0 0 0 0
Source of scattering factors.	Scattering factors for neutral atoms taken from *International Tables for X-ray Crystallography* (1974), Vol. IV (Birmingham: Kynoch Press)
Starting structural model. Parameters refined.	As starting parameters, the coordinates of the δ 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 5*a* 1058 reflections 80 parameters Model 5*b* 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. 5*a* harmonic displacive, Axe correction (global phason), $I > 3\sigma(I)$; No. 5*b* harmonic displacive, Axe correction (global phason), all observed reflections For all models: $\Delta_{max}/\sigma < 0.001$, goodness of fit $\simeq 2$, $OSR_{all} \simeq 0.99$, R values are multiplied by 100 R_{all}: $R_{MSR} = \frac{\Sigma\|F_{i,o}/S_i - F_c\|}{\Sigma F_{i,o}/S_i}$; R_w: $R_{w,MSR} = \left(\frac{\Sigma w(F_{i,o}/S_i - F_c)^2}{\Sigma w(F_{i,o}/S_i)^2}\right)^{1/2}$; OSR: $\sum F_c/\sum F_o$; N_p: number of parameters No. R_{all} $R_{w,all}$ $R_{w,main}$ $R_{w,sat}$ $R_{w,1}$ $R_{w,2}$ OSR_2 N_p $C^{Axe/Ove}$ 5*a* 5.22 3.93 3.1 6.8 6.5 11.9 0.91 80 0.17 (1) 5*b* 9.81 6.82 6.2 9.1 6.6 18.9 0.72 80 0.17 (1)
In the case of refinement restraints, an analog wR' and S' for the pseudo-observations is recommended.	-
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 $F_c^{corr} = F_c/(1 + 10^{-5}C_{ext}F_c^2/\sin\theta)^{1/4}$, $C_{ext} = 2.6\,(2)$

F$_o$ *versus* *F*$_c$ plots for the different reflection classes, or other plots for data and refinement quality assessment.

F$_c$ *vs* *F*$_o$ plot



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 $\beta^{ij}\mu$. 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 2π. The modulations are expressed by

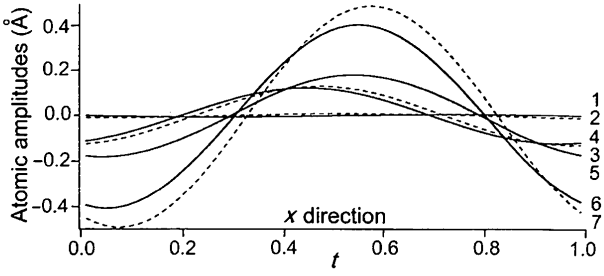
$$u_i^{\mu}(t) = \sum_{n>0} a_{i,n}^{\mu} \cos[2\pi(nt + \varphi_{i,n}^{\mu})]$$

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

x	0	a_x	8 (2)	φ_x	0.25
y	0	a_y	–	φ_y	–
z	0	a_z	139.5 (8)	φ_z	0.75
β^{11}	12.2 (4)	U^{11}	34 (1)	U^{11}_{av}	35 (2)
β^{22}	12.5 (4)	U^{22}	34 (1)	U^{22}_{av}	35 (2)
β^{33}	2.46 (4)	U^{33}	9.0 (1)	U^{33}_{av}	17.9 (3)
β^{12}	–	U^{12}	–	U^{12}_{av}	–
β^{13}	−0.10 (6)	U^{13}	−1.0 (1)	U^{13}_{av}	−3.6 (9)
β^{23}	–	U^{23}	–	U^{23}_{av}	–
		U_{eq}	5.3	$U_{eq,av}$	8.3

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 C1; 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).

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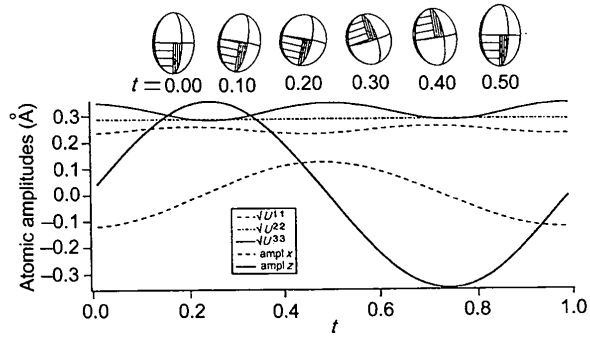
Selected geometrical data	
Average, *minimum and maximum interatomic distances and other pertinent geometrical parameters.*	Short selection of bond distances of model 5; d_{av}: average distance (Å), standard deviations are given in parentheses; d_{min}: minimum distance; d_{max}: maximum distance; Δ: difference between max. and min. N—C1 1.48 (2) 1.47 1.50 0.03 C1—C2 1.45 (3) 1.39 1.52 0.13 C1—C2 1.52 (3) 1.47 1.58 0.11
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^{33} 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.	See Doudin & Chapuis [*Acta Cryst.* (1990), B**46**, 175–180, 180–186]
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 $(h, k, l, m_1, \ldots, m_i, \ldots)$	h k l m F_o $\Delta F(=F_o-F_c)$ $\sigma(F)$ 0 0 1 −1 15.21 0.27 0.27 0 0 2 0 120.53 9.73 2.02 ...

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