

## Molecular Geometry of Incommensurate Structures

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### Abstract

Molecular-geometry calculations in the superspace framework of incommensurate structure analysis are presented in detail. In particular, a method is described for attaching atoms to groups of others without the necessity of introducing further modulation functions. Modified structure-factor expressions are derived to simplify the application of constraints to modulation functions by introducing internal coordinate reference points in a more general way. The consequences of such changes are discussed. The results can be useful to improve the existing algorithms for incommensurate structure refinement and the analysis and presentation of results, especially for recently discovered incommensurate structures of large organic molecules. Some ambiguities still existing in the superspace approach related to molecular geometry are clarified. The results may also be useful for the compilation of a database describing incommensurate structures.

### 1. Introduction

Incommensurate (IC) structures are currently being studied in the framework of superspace-group symmetry and no working alternative seems as yet to exist. Most of them have been studied by means of so-called atomic models.

Although the structure refinement is sometimes rather difficult (Watkin, 1994), applications of techniques specific to large structures are sparse. The analysis and presentation of the results is rather limited, but some standard requirements have been formulated recently (Chapuis *et al.*, 1996).

As the size of the IC structure and the complexity of modulation (high anharmonicity) increases, more elaborate methods of controlling the structure refinement and the analysis of the results have to be developed. The latter should not only include typical plots of modulation functions (MF) but also much more elaborate techniques like graphical animation of the entire IC structure, visualization of snapshots of the structure for a given value of the internal coordinate and quick inspection of the modulation of any geometrical parameter to enumerate the most important features.

Another problem in the superspace framework concerns the extension of the existing methods of attaching light atoms (usually H atoms) to groups, which are explicitly refined. In IC structures of even moderate size, such a procedure can prevent an excessive increase in the number of refined parameters. This is justified as any omission of a number of atoms will significantly distort the final result. The MF parameters are usually very sensitive to any deficiency in the basic structure model.

In this paper, an attempt to solve some of these problems is reported. An extension of the basic molecular-geometry (MG) calculations to the superspace framework will be presented. The superspace symmetry is fully exploited. The procedures to attach light atoms in any desired coordination as well as other standard molecular-geometry calculations will be extended to IC structures. The important concept of the internal coordinate (or phase) reference point (RP) is presented. The modified structure-factor expressions to handle the RP are also given.

Our results have been implemented and used in the study of the complex IC structure of hexamethylene-tetramine suberate (Bussien Gaillard, Paciorek, Schenk & Chapuis, 1996), exhibiting both a high anharmonicity of the modulation and a large number of H atoms.

### 2. Basic molecular-geometry calculations

In our approach to the MG of IC structures, the algorithms have been derived in two steps. In the first step, the modulation has been neglected and all calculations have been tested on unmodulated crystals. The modulation has been added in the second step. In this section, all the procedures will be briefly described.

#### 2.1. Transformation to the Cartesian coordinates

In most of our computations, the first part is a sequence of transformations of the fractional coordinates of  $n$  selected atoms to Cartesian coordinates. To achieve a greater flexibility, a symmetry operation (usually identity) is associated with each atom. In this paper, this is the three-dimensional part of the superspace-group operation:

$$\mathbf{x}_j \leftrightarrow \{\mathbf{R}|\mathbf{v}\}_j, \quad j = 1, \dots, n. \quad (1)$$

The coordinates are first transformed according to the associated symmetry operations:

$$\mathbf{x}_j^f = \mathbf{R}_j \mathbf{x}_j + \mathbf{v}_j, \quad (2)$$

and the resulting vectors of the fractional coordinates are arranged in the following  $3 \times n$  matrix:

$$\mathbf{X}^f = [\mathbf{x}_1^f, \dots, \mathbf{x}_n^f]. \quad (3)$$

Subsequently, they are all transformed to the Cartesian coordinates

$$\mathbf{X}^c = \mathbf{C}\mathbf{X}^f \quad (4)$$

and stored in the final  $3 \times n$  matrix. A standard definition of the last transformation matrix has been adopted (see Dunitz, 1979).

### 2.2. Computation of the geometrical parameters

A useful convention is to consider any MG parameter as a scalar function of the matrix argument computed in the previous step:

$$f = \text{geom}(\mathbf{X}^c). \quad (5)$$

The partial derivatives are (optionally) calculated and arranged in the following matrix (Fréchet derivative):

$$[\mathbf{D}^c]_{ij} = \partial f / \partial x_{ij}^c. \quad (6)$$

They are then transformed back to derivatives with respect to fractional coordinates:

$$\mathbf{D}^f = \tilde{\mathbf{C}}^{-1} \mathbf{D}^c, \quad (7)$$

and subsequently all columns of the resulting matrix

$$\mathbf{D}^f = [\mathbf{d}_1^f, \dots, \mathbf{d}_n^f] \quad (8)$$

are transformed by the corresponding rotation matrices

$$\mathbf{d}_j = \tilde{\mathbf{R}}_j \mathbf{d}_j^f \quad (9)$$

to the desired partial derivatives of the geometrical quantity with respect to the coordinates of the initial atoms:

$$[\mathbf{D}]_{ij} = \partial f / \partial x_{ij}. \quad (10)$$

In all the above expressions, the tilde stands for matrix transposition. All standard quantities like interatomic distance, bond angle, dihedral angle, sin and cos functions of both kinds of angles have been implemented in our program.

### 2.3. Computation of the attached atom coordinates

As is well known, any molecule can be specified geometrically by the internal coordinates (interatomic distances, and bond and dihedral angles). Atoms can be attached sequentially to the previously specified part. Only two operations involving three atoms are required: elongation of the three-atom sequence or branching on the second atom. Such algorithms are common in all molecular-modeling programs.

Both operations require the Cartesian coordinates of three atoms and three parameters specifying the local geometry, as will be shown later. A general procedure has been implemented as a vector function of a  $3 \times 3$  matrix and three scalar arguments:

$$\mathbf{y}^c = \text{put}(\mathbf{X}^c, d, \phi, \psi), \quad (11)$$

where the matrix argument is the same as in §2.1. The scalar arguments are the bond length and two angles defined in §§3.3 and 3.4.

The result is the vector of Cartesian coordinates of the attached atom. A transformation to fractional coordinates is performed next:

$$\mathbf{y} = \mathbf{C}^{-1} \mathbf{y}^c. \quad (12)$$

In our implementation, the derivatives of the coordinates of the attached atom with respect to the coordinates of the defining atoms are not computed. Its contribution to the normal matrix is thus neglected. This can be a source of subtle numerical difficulties and we hope to remove this approximation in the future.

### 2.4. Symmetry transformation of the attached atom

In the structure refinement, attached atoms are considered as symmetrically independent. For other purposes, it might also be useful to obtain easily their coordinates transformed by any symmetry operation. Two approaches are possible.

The first is, of course, to apply the symmetry transformation to the resulting coordinates:

$$\mathbf{y}' = \mathbf{R}\mathbf{y} + \mathbf{t}. \quad (13)$$

This is satisfactory for unmodulated structures. In the presence of a modulation, this procedure leads to severe difficulties since the MFs of the attached atom are implicit. Thus, another approach is preferred.

The procedure described in the previous section can be modified to obtain directly the desired coordinates. The modification is to premultiply all the symmetry operations attached to the defining atoms and one of the angular parameters as follows:

$$\begin{aligned} \{\mathbf{R}|\mathbf{t}\}_j &\leftarrow \{\mathbf{R}|\mathbf{t}\}\{\mathbf{R}|\mathbf{t}\}_j, \\ \psi &\leftarrow \det(\mathbf{R})\psi. \end{aligned} \quad (14)$$

The computations are now performed without further modifications and the result yields the coordinates of the transformed attached atom.

### 3. Details of molecular-geometry calculations

More details on MG calculations will be given in the following sections. These calculations are greatly simplified in Cartesian coordinates. Vector algebra identities have been extensively used to simplify the computation of the derivatives, especially for the dihedral angle. Standard definitions of some quantities given by Dunitz (1979) have been used. The coordinates of the attached atom are computed by using modified algorithms given by Schlick (1987). Before extending our calculations to IC structures, some tests were performed by comparison with procedures given by Schlick (1989).

#### 3.1. Bond lengths and angles

Given any two vectors, their lengths and angle are easily calculated from the well known expressions

$$\begin{aligned} u &= |\mathbf{u}|, \\ v &= |\mathbf{v}|, \\ \cos \phi &= (\mathbf{u} \cdot \mathbf{v}) / (uv), \\ \sin \phi &= |\mathbf{u} \times \mathbf{v}| / (uv). \end{aligned} \quad (15)$$

In the last equation, the norm of the cross product is eliminated using

$$|\mathbf{u} \times \mathbf{v}|^2 = (uv)^2 - (\mathbf{u} \cdot \mathbf{v})^2. \quad (16)$$

The above expressions involve dot and cross products only. Partial derivatives of the vector functions are understood component-wise in the following useful relations:

$$\begin{aligned} \partial_x (\mathbf{u} \cdot \mathbf{v}) &= \partial_x \mathbf{u} \cdot \mathbf{v} + \mathbf{u} \cdot \partial_x \mathbf{v}, \\ \partial_x (\mathbf{u} \times \mathbf{v}) &= \partial_x \mathbf{u} \times \mathbf{v} + \mathbf{u} \times \partial_x \mathbf{v}. \end{aligned} \quad (17)$$

Both kinds of angle can be computed from the equations above.

Let us define the interatomic vector

$$\mathbf{r}_{kl} = \mathbf{x}_k - \mathbf{x}_l. \quad (18)$$

To obtain a bond angle, two interatomic vectors are required:

$$\begin{aligned} \mathbf{u} &= \mathbf{r}_{12}, \\ \mathbf{v} &= \mathbf{r}_{32}, \end{aligned} \quad (19)$$

and for a dihedral angle, two cross products:

$$\begin{aligned} \mathbf{u} &= \mathbf{r}_{21} \times \mathbf{r}_{32}, \\ \mathbf{v} &= \mathbf{r}_{32} \times \mathbf{r}_{43}. \end{aligned} \quad (20)$$

In both cases, the general expressions above enable us to compute the desired quantity. As in the case of the dihedral angle new cross products were introduced, further simplifications could be performed to facilitate the derivative calculation.

#### 3.2. More on dihedral angle

Let us introduce an index-free notation for interatomic vectors:

$$\begin{aligned} \mathbf{a} &= \mathbf{r}_{21}, \\ \mathbf{b} &= \mathbf{r}_{32}, \\ \mathbf{c} &= \mathbf{r}_{43} \end{aligned} \quad (21)$$

and define two further quantities:

$$\begin{aligned} \mathbf{n} &= \mathbf{b} / |\mathbf{b}|, \\ \eta^{-1} &= |\mathbf{a} \times \mathbf{b}| |\mathbf{b} \times \mathbf{c}|. \end{aligned} \quad (22)$$

The standard definition of the dihedral angle may then be written as

$$\begin{aligned} \cos \phi &= \eta (\mathbf{a} \times \mathbf{b}) \cdot (\mathbf{b} \times \mathbf{c}), \\ \mathbf{n} \sin \phi &= \eta (\mathbf{a} \times \mathbf{b}) \times (\mathbf{b} \times \mathbf{c}). \end{aligned} \quad (23)$$

The last quantity can be written in a more concise form:

$$\sin \phi = \eta b \mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}) = \eta b \det[\mathbf{a}, \mathbf{b}, \mathbf{c}], \quad (24)$$

which is very convenient for further calculations. Additional simplifications are achieved by using the identities

$$\begin{aligned} (\mathbf{a} \times \mathbf{b}) \cdot (\mathbf{b} \times \mathbf{c}) &= (\mathbf{a} \cdot \mathbf{b})(\mathbf{b} \cdot \mathbf{c}) - (\mathbf{a} \cdot \mathbf{c})(\mathbf{b} \cdot \mathbf{b}), \\ (\mathbf{a} \times \mathbf{b}) \times (\mathbf{b} \times \mathbf{c}) &= [\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})] \mathbf{b} = \det[\mathbf{a}, \mathbf{b}, \mathbf{c}] \mathbf{b}. \end{aligned} \quad (25)$$

Furthermore, the identity

$$\begin{aligned} \partial_x \det[\mathbf{a}, \mathbf{b}, \mathbf{c}] &= \det[\partial_x \mathbf{a}, \mathbf{b}, \mathbf{c}] + \det[\mathbf{a}, \partial_x \mathbf{b}, \mathbf{c}] \\ &\quad + \det[\mathbf{a}, \mathbf{b}, \partial_x \mathbf{c}] \end{aligned} \quad (26)$$

greatly simplifies the calculation of the derivatives. Most of them have been reduced to simple dot products and determinants.

#### 3.3. Position of a terminal atom

Given three atoms, the coordinates of a fourth are calculated such that the bond length to atom 3 is  $d$ , the bond angle in the 2-3-4 sequence is  $\theta_{234}$  and the dihedral angle of the 1-2-3-4 sequence is  $\tau_{1234}$ . The following calculations are performed:

$$\begin{aligned} \mathbf{u} &= \mathbf{x}_2 - \mathbf{x}_1, \\ \mathbf{v} &= \mathbf{x}_3 - \mathbf{x}_2, \end{aligned} \quad (27)$$

$$\begin{aligned} \mathbf{e}_1 &= \mathbf{v} / |\mathbf{v}|, \\ \delta &= \mathbf{u} \cdot \mathbf{e}_1, \\ \mathbf{e}_2 &= -(\mathbf{u} - \delta \mathbf{e}_1) / |\mathbf{u} - \delta \mathbf{e}_1|, \\ \mathbf{e}_3 &= \mathbf{e}_1 \times \mathbf{e}_2, \end{aligned} \quad (28)$$

$$d \equiv |\mathbf{x}_4 - \mathbf{x}_3|,$$

$$\alpha = d \cos \theta_{234},$$

$$\beta = d \sin \theta_{234} \cos \tau_{1234},$$

$$\gamma = d \sin \theta_{234} \sin \tau_{1234},$$

$$\mathbf{x}_4 = \mathbf{x}_3 - \alpha \mathbf{e}_1 + \beta \mathbf{e}_2 + \gamma \mathbf{e}_3. \quad (30)$$

If an additional transformation is required, the dihedral angle will be modified:

$$\tau_{1234} \leftarrow \det(\mathbf{R})\tau_{1234}. \quad (31)$$

This algorithm can be understood easily from the definition of the dihedral angle. The calculations are done in the local Cartesian coordinate system with the first axis along the 2-3 bond, as shown in Fig. 1.

### 3.4. Tetrahedral and trigonal arrangements

Given three atoms, the coordinates of a fourth are calculated in such a way that the bond length to atom 2 is  $d$  and the two angles  $\phi$  and  $\psi$  presented in Fig. 2 admit the given values. The following calculations are performed:

$$\mathbf{u} = \mathbf{x}_1 - \mathbf{x}_2,$$

$$\mathbf{v} = \mathbf{x}_3 - \mathbf{x}_2, \quad (32)$$

$$\mathbf{e}_2 = -(\mathbf{u} + \mathbf{v})/|\mathbf{u} + \mathbf{v}|,$$

$$\mathbf{e}_3 = -(\mathbf{u} \times \mathbf{v})/|\mathbf{u} \times \mathbf{v}|, \quad (33)$$

$$\mathbf{e}_1 = \mathbf{e}_2 \times \mathbf{e}_3,$$

$$d \equiv |\mathbf{x}_4 - \mathbf{x}_2|,$$

$$\alpha = d \cos \psi \sin \phi,$$

$$\beta = d \cos \psi \cos \phi, \quad (34)$$

$$\gamma = d \sin \psi,$$

$$\mathbf{x}_4 = \mathbf{x}_2 + \alpha \mathbf{e}_1 + \beta \mathbf{e}_2 + \gamma \mathbf{e}_3. \quad (35)$$

If an additional symmetry transformation is required, the

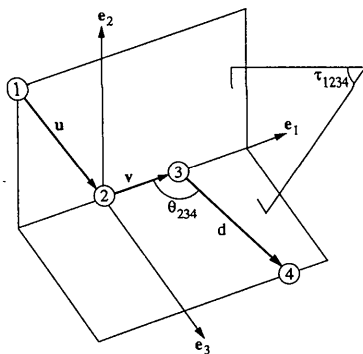


Fig. 1. Local geometry of the terminal atomic arrangement.

angle  $\psi$  is modified:

$$\psi \leftarrow \det(\mathbf{R})\psi. \quad (36)$$

This very flexible procedure includes, as a special case, two common arrangements. The tetrahedral arrangement is obtained if

$$\phi = 0, \quad \psi = \pm \Theta^{\text{Tet}}/2,$$

$$\Theta^{\text{Tet}} = \arccos(-1/3),$$

$$\mathbf{x}_4 = \mathbf{x}_2 + d \cos(\Theta^{\text{Tet}}/2)\mathbf{e}_2 \pm d \sin(\Theta^{\text{Tet}}/2)\mathbf{e}_3. \quad (37)$$

The sign change indicates that two atoms can be placed simultaneously. For the trigonal arrangement, the calculations reduce to

$$\phi = \psi = 0,$$

$$\mathbf{x}_4 = \mathbf{x}_2 + d\mathbf{e}_2. \quad (38)$$

The simplified forms are used most frequently, but it is the general form that has been implemented in order to let the user specify both angles.

## 4. Molecular geometry in superspace

When an IC structure has been solved and refined, a final validation of the model and presentation of the results is usually expected. For unmodulated structures, large data bases and numerous software tools are available. For IC structures, the situation is less favorable.

Some of the problems related to the interpretation of existing data of modulated structures will be exposed. To clarify the presentation, some basic concepts of the superspace approach have to be reviewed.

### 4.1. Incommensurate structure model

Some standard requirements for the unambiguous presentation of the results of IC structure analysis have been formulated recently. Apart from analogous requirements for conventional structures, a number of additional

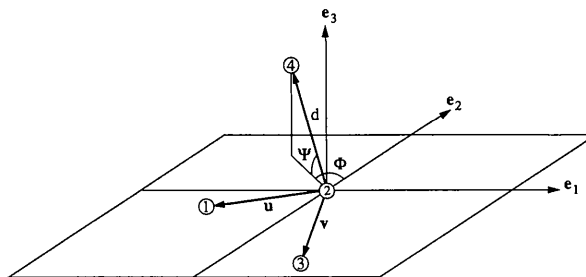


Fig. 2. Local geometry of the tetrahedral and trigonal atomic arrangements.

parameters and indications should be included. Only some of them will be studied in detail in order to check what kind of data are necessary to validate the geometry of the final model and present the relevant results in detail. We shall restrict ourselves to (3+1)-dimensional IC structures, since the vast majority belongs to this category.

The departure from classical crystallography consists in the presence of the so-called MF given for every coordinate of each atom:

$$x_i^\mu(x) = \bar{x}_i^\mu + u_i^\mu(x), \quad i = 1, 2, 3, \quad (39)$$

where  $\bar{x}_i^\mu$  is the average coordinate of the symmetry-independent atom  $\mu$ . These functions are real and periodic in one scalar variable:

$$u_i^\mu(x+1) = u_i^\mu(x), \quad (40)$$

and include a number of adjustable parameters. Usually, the analytic form of such a function is common to all atoms and all parameters. The strict meaning of the displacive modulation introduced above is then

$$u_i^\mu(x) \equiv u(p_{i,1}^\mu, \dots, p_{i,N}^\mu; x). \quad (41)$$

Its Fourier expansion reads

$$u(x) = \sum_{n=1}^M u_n \exp(2\pi i n x) + \text{c.c.} \quad (42)$$

(c.c. indicates the complex conjugate term) and the set of adjustable parameters can be just the set of expansion coefficients.

In practice, the trigonometric series expansion

$$u(x) = \sum_{n=1}^M [c_n \cos(2\pi n x) + s_n \sin(2\pi n x)] \quad (43)$$

or the equivalent amplitude/phase form

$$u(x) = \sum_{n=1}^M c_n \cos(2\pi n x + 2\pi \phi_n) \quad (44)$$

are preferred but other functions are occasionally used as well (see Petříček, Gao, Lee & Coppens, 1990; Petříček, van der Lee & Evain, 1995)

Finally, constraint equations (usually linear ones) may be applied to some parameters, for example,

$$p_{i,k}^\mu = A p_{j,l}^\nu + B, \quad (45)$$

where  $p$  is the generic name of any structural parameter (e.g. coordinate),  $i$  enumerates its components, if appropriate, and  $k$  enumerates the modulation-function parameters (index equal to zero usually refers to the

average value). The interpretation of these constraints will also be discussed.

The radical departure from classical crystallography lies in the use of a higher-dimensional space group to describe the symmetry properties. The superspace-group operator includes a part acting on the so-called internal coordinate, which may be identified with the independent variable of the MF. As expected, such a transformation is consistent (under some additional assumptions given later) with the standard mathematical definition of the function mapping induced by an independent variable transformation:

$$g(x) = f[R_{44}^{-1}(x - \tau_4)]. \quad (46)$$

The above notation suggests correctly that the complete symmetry operation can be considered as an element of a (3+1)-reducible four-dimensional space group with some additional properties. All these groups have been derived (de Wolff, Janssen & Janner, 1981).

#### 4.2. Lattices in superspace

The metric properties of the supercrystal, an artificial periodic structure in higher-dimensional space, should be well defined in order to interpret correctly MG quantities, defined in three-dimensional space only. In order to define all quantities to be used later, the construction of the supercrystal will be briefly presented.

The departure point is an unusual diffraction pattern, a combination of well known Bragg reflections and additional reflections called ‘satellites’. It is assumed that both sets can be separated and all reflections can be indexed by more than three integers.

From the set of ‘main’ reflections, the reciprocal basis can be constructed and the additional reflections are indexed by introducing the modulation vector. We will restrict ourselves to the case when one vector suffices and each reflection can be labeled by four indices only:

$$\mathbf{H} = \mathbf{K} + h_4 \mathbf{q}, \quad (47)$$

where the first vector points to a main reflection:

$$\mathbf{K} = \sum_{i=1}^3 h_i \mathbf{a}_i^* \quad (48)$$

and

$$\mathbf{q} = \sum_{i=1}^3 q_i \mathbf{a}_i^* \quad (49)$$

is the modulation vector. The important feature is the incommensurability: at least one component of the modulation vector should be incommensurate with the reciprocal lattice defined by the main reflections. Thus, the translational symmetry in three-dimensional space cannot be recovered by any basis transformation.

Using modern mathematical terminology, such a diffraction pattern has the structure of the following  $Z$ -module:

$$\begin{aligned} \mathbf{H} &\in M^*, \\ \dim(M^*) &= 3, \\ \text{rank}(M^*) &= 4. \end{aligned} \quad (50)$$

To make the rank equal to the dimension, *i.e.* convert the  $Z$ -module to the reciprocal lattice, an embedding is used. The vectors are augmented by additional components and uniquely mapped into lattice points:

$$\mathbf{H} \mapsto (\mathbf{H}, H_I) \in \Sigma^* \quad (51)$$

in the four-dimensional superspace with the direct sum structure

$$(\mathbf{r}, t) \in V_S = V \oplus V_I, \quad (52)$$

where the first component relates to physical space and the second is called the internal one. The vectors in the physical space and on any hyperplane parallel to it will be denoted in bold.

Of great importance is the definition of the split basis, first defined in reciprocal superspace:

$$\begin{aligned} a_{S_i}^* &= (\mathbf{a}_i^*, 0), \quad i = 1, 2, 3, \\ a_{S_4}^* &= (\mathbf{q}, 1). \end{aligned} \quad (53)$$

The direct lattice can be easily calculated as

$$\begin{aligned} a_{S_i} &= (\mathbf{a}_i, -q_i), \quad i = 1, 2, 3, \\ a_{S_4} &= (\mathbf{q}, 1) \end{aligned} \quad (54)$$

by using the standard relation, extended to four dimensions:

$$a_{S_i} \cdot a_{S_j}^* = \delta_{ij}, \quad i, j = 1, \dots, 4. \quad (55)$$

The diffraction pattern admits now a standard interpretation:

$$H_S \equiv (\mathbf{H}, H_I) = (\mathbf{K} + h_4 \mathbf{q}, h_4) = \sum_{i=1}^4 h_i a_{S_i}^* \quad (56)$$

as a set of points of some lattice. Note that in the split reciprocal basis the first three integer coordinates consist of main reflection indices only.

In direct space, any vector can be written as

$$r_S \equiv (\mathbf{r}, r_I) = (\mathbf{r}, t) = \sum_{i=1}^4 x_i a_{S_i}, \quad (57)$$

where

$$\begin{aligned} \mathbf{r} &= \sum_{i=1}^3 x_i \mathbf{a}_i, \\ x_4 &= \mathbf{q} \cdot \mathbf{r} + t. \end{aligned} \quad (58)$$

It is important to note that the first three fractional coordinates are the same in both three- and four-dimensional direct bases but the fourth is not. It is also easy to

verify that if  $t = 0$  the point  $r_S$  will be placed in the original physical space, now a specific three-dimensional hyperplane. Of great importance is the last relation between  $t$  and  $x_4$ , the additional coordinates in two bases.

The scalar product between the two vectors  $H_S$  and  $r_S$  above can be written in a variety of equivalent forms:

$$\begin{aligned} H_S \cdot r_S &\equiv (\mathbf{H}, H_I) \cdot (\mathbf{r}, r_I) \\ &= \mathbf{H} \cdot \mathbf{r} + H_I t \\ &= \mathbf{K} \cdot \mathbf{r} + h_4 x_4 \\ &= \sum_{i=1}^4 h_i x_i. \end{aligned} \quad (59)$$

This series of equivalences is the first source of ambiguities that we would like to clarify as the structure-factor expression, for example, depends mainly on this scalar product.

The above construction is called a standard embedding (see Fig. 3) and lies at the heart of the superspace approach to IC structures. Many results can be directly obtained from classical crystallographic techniques of structural analysis extended to higher dimensions. However, at first we have to gain a better insight into the contents of the direct supercell just constructed, as our former three-dimensional structure has been mapped into a higher-dimensional object.

### 4.3. Concept of supercrystal

From Fourier analysis (Bricogne, 1993), especially from the slice-projection theorem, it follows that the electron density in physical space is the inverse Fourier transform of the projection onto that hyperplane.

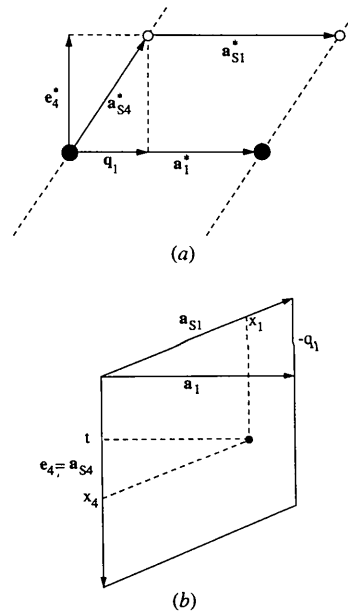


Fig. 3. (a) Reciprocal and (b) direct bases of the standard embedding.

As this section is central, but not principal, this density is in general non-periodic, even if by construction the supercrystal is periodic. Incommensurability excludes the possibility of making such a section central and principal by base transformation with integer coefficients.

In the absence of satellites, the same result is obtained for any section parallel to the physical hyperplane. Thus, a so-called basic structure is simply a continuously repeated image of the three-dimensional crystal along the internal coordinate. In particular, the atomic positions are represented by a set of straight lines parallel to the fourth basis vector in the superspace. For each atom, this line is defined as

$$\begin{aligned} \mathbf{r}^\mu &= \bar{x}_1^\mu \mathbf{a} + \bar{x}_2^\mu \mathbf{b} + \bar{x}_3^\mu \mathbf{c}, \\ \bar{x}_4^\mu &= \mathbf{q} \cdot \mathbf{r}^\mu + t, \quad t \in \mathbb{R}, \end{aligned} \quad (60)$$

which specifies the fractional coordinates of every point in the superspace basis. The commonly used notation introduced above suggests that the first three coordinates can result from an averaging over one period of the internal coordinate. The fourth coordinate is obviously continuous and the labeling is redundant. In some cases, it is even useful to reserve the fourth labeled coordinate symbol for special purposes, especially for

$$\bar{x}_4^\mu = \mathbf{q} \cdot \mathbf{r}^\mu, \quad (61)$$

an important quantity in the standard embedding called a ‘compensating shift’: a change in the internal coordinate caused by a translation in the physical space (here from the origin to the atom position).

The variable  $t$  has sometimes a different interpretation as the following (non-unique) mapping of all cells of the basic structure:

$$\mathbb{Z}^3 \ni \mathbf{n} \mapsto t = (\mathbf{q} \cdot \mathbf{n} \bmod Z) \in [0, 1). \quad (62)$$

For an IC modulation vector and an infinite crystal, a dense but countable set of points is obtained and the continuous approximation to any function of  $t$  can be properly constructed. Such a mapping of atomic

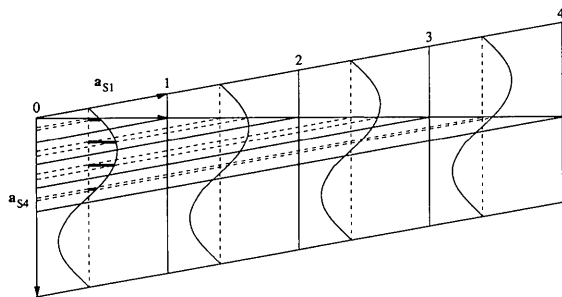


Fig. 4. Mapping of atomic displacements from physical space into the supercell.

displacements in physical space into the supercell is shown in Fig. 4.

#### 4.4. Interatomic vector as a modulation function

The presence of satellites indicates a breaking of the translational symmetry in any section parallel to the physical space. The supercrystal remains periodic in superspace. Conservation of translational symmetry is the main advantage of this approach. In particular, it is sufficient to investigate only one period of the basic structure distortion, *e.g.*, for a displacive modulation, only the functions that are added to the basic coordinates:

$$x_i^\mu(x) = \bar{x}_i^\mu + u_i^\mu(x). \quad (63)$$

Since all displacements take place in physical space, the following condition should always be fulfilled:

$$u_4^\mu(x) = \mathbf{q} \cdot \mathbf{u}^\mu(x). \quad (64)$$

The remaining problem is how to compute  $x$ , especially if more functions, belonging to different atoms, are required simultaneously, *e.g.* at the common  $t$  section. This is the case for all MG calculations.

In the first example, let us consider an interatomic vector defined as

$$\Delta x_i(t) = x_i^\mu(t_0^\mu + t) - x_i^\nu(t_0^\nu + t), \quad i = 1, 2, 3. \quad (65)$$

This vector should obviously be parallel to physical space. Furthermore, we have to guarantee that, for  $t = 0$ , *i.e.* in the physical hyperplane, the MF arguments take on correct values by definition equal to RP. This will add proper coordinate shifts to the basic values, a kind of ‘synchronization’ problem. In this case, we can use such a vector to compute correctly, for example, a distance equivalent to the three-dimensional quantity. Otherwise, the result has no physical meaning.

In general, we face the problem of computing the coordinates for all atoms of interest simultaneously from the expression

$$x_i^\mu(t_0^\mu + t) = \bar{x}_i^\mu + u_i^\mu(t_0^\mu + t), \quad (66)$$

which is the only one supplying the correct coordinates to all previously discussed procedures. The proper construction of the required interatomic vector in superspace is shown in Fig. 5. The problem is thus to infer the initial values of the internal coordinates for all atoms and to know where such information is ‘hidden’ when not given explicitly. This is the worst manifestation of the long-standing ‘shifted–unshifted’ dilemma, well known among practitioners.

In this contribution, an attempt is made to resolve this problem. In particular, a method will be given

to extract the relevant data from the structure-factor formula or take advantage of this extra flexibility during the structure refinement. This problem has been recently recognized by other authors as well (van Smaalen, 1995) and at least three different choices of RP were proposed and applied in practice:

$$t_0^\mu = \mathbf{q} \cdot \mathbf{r}^\mu, \quad (67a)$$

$$t_0^\mu = 0, \quad (67b)$$

$$t_0^\mu = \mathbf{q} \cdot \mathbf{g}^\mu. \quad (67c)$$

The first one is de Wolff's (1974) original choice and is the most frequently used. The second one was occasionally used in theoretical considerations, and at least twice used in structural studies (Kobayashi, 1974; Bussien Gaillard, Paciorek, Schenk & Chapuis, 1996).

The last is the most general case and was an inevitable choice to deal with a rigid-body approximation (Petříček, Coppens & Becker, 1985), an instance of the problem when one MF has to be assigned to several atoms simultaneously. The new vectors can be the centroids of the molecules, for example. The relation between the atomic coordinates and MF arguments is partially relaxed. Note also that the first two choices are special cases of the last one and, sometimes, the additional three-dimensional vectors are synonymously called the RP.

A simple consequence of this flexibility in our MG calculations is the structure of the final Jacobian transformation of the calculated derivatives. In all cases, the derivatives with respect to the modulation-function parameters will require a simple Jacobian matrix of the

form

$$\partial x_i^\mu / \partial p_{i,n}^\mu = \partial u_i^\mu / \partial p_{i,n}^\mu \quad (68)$$

for every atom and every coordinate when the atomic model is adopted. To compute the derivatives with respect to the basic coordinates, different expressions are required for each choice:

$$\partial x_i^\mu / \partial \bar{x}_j^\mu = \delta_{ij} + q_j \, du_i^\mu / dx, \quad (69a)$$

$$\partial x_i^\mu / \partial \bar{x}_j^\mu = \delta_{ij}, \quad (69b)$$

$$\partial x_i^\mu / \partial \bar{x}_j^\mu = \delta_{\mu\gamma} \delta_{ij} + \sum_{\nu} du_i^\mu / dx \sum_{k=1}^3 q_k \partial g_k^\mu / \partial \bar{x}_j^\mu. \quad (69c)$$

The first and last choices lead to the 'mixing' of derivatives within one atom or any number of them, respectively. This distinction has to be taken into account when computing restraints and e.s.d.s for coordinates.

#### 4.5. Constraints on modulation functions

The choice of the  $t_0$  value has a great influence on the physical meaning of the constraints on MF parameters. The simplest example is when it is desirable to have the same modulation refined on two independent atoms. This necessity is obviously motivated by some physical considerations and should first of all be fulfilled in physical space and on all hyperplanes parallel to it:

$$p^\nu(t_0^\nu + t) = p^\mu(t_0^\mu + t), \quad t \in \mathbb{R}. \quad (70)$$

The natural solution is to introduce the following simplest set of constraint equations:

$$p_n^\nu = p_n^\mu, \quad n = 1, \dots, N, \quad (71)$$

equating all MF parameters on the target atom to the corresponding values of the refined one. A good example is the occupational type of modulation. Unfortunately, the effect of this constraint depends on the  $t_0$  values, as shown in Fig. 6. In the three cases depicted, the MF parameters of atoms 1 and 3 are constrained to the MF parameters of the reference atom 2 by applying equality constraints (71). In Fig. 1(a), the RP are chosen according to (67a). Note that the atomic displacements are different on any section parallel to the physical hyperplane but equal on any principal section of the supercell (one of them is shown). We are not aware of any useful application of such constraints. Usually, it is desired to maintain the equality of the displacements or other modulations on every physical hyperplane. It is thus obvious that, in the second choice (Fig. 6b), where (67b) is used to define RP, these constraints are appropriate for every MF. To achieve our requirement in the former choice, severe complications arise. The effect of our constraint should be that the target MF fulfils the condition

$$\tilde{p}^\nu(t_0^\nu + \Delta) = p^\mu(t_0^\mu), \quad (72)$$

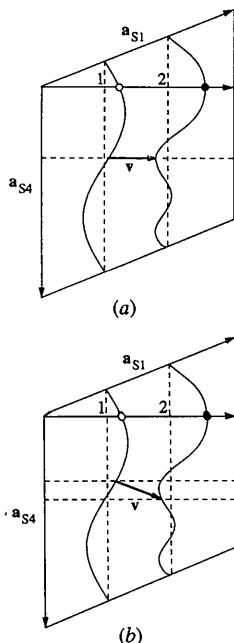


Fig. 5. Physically (a) proper and (b) improper interatomic vectors in superspace. The wrong RP in the MF leads to non-zero components along the internal coordinate.



where

$$\Delta = \mathbf{q} \cdot (\mathbf{r}^\mu - \mathbf{r}^\nu), \quad (73)$$

which is equivalent to a change of RP. In other words, we have to 'simulate' such a change by using only parameters that are at our disposal. The solution depends on what these parameters are.

If the complex Fourier coefficients are refined, the solution is to apply the shift theorem and obtain the following set of constraints:

$$\begin{aligned} |p_n^\nu| &= |p_n^\mu|, \\ \phi_n^\nu &= \phi_n^\mu + n\Delta. \end{aligned} \quad (74)$$

The same approach is valid for any MF with the phase refined. If trigonometric series are used, this simple approach is virtually impossible since the constraint equations become nonlinear. The drawback of this ap-

proach (apart from forcing the user to select a particular form of MF) is that, in most cases, the basic coordinates are also refined and some constraint parameters in (74) need to be recomputed after each refinement cycle.

The exact solution is thus to leave the user a choice of RP, at least between the first and the second case. This freedom helps solve the problem above exactly and for any MF. In the third case (Fig. 6c), which corresponds to RP given by (67c), it is sufficient to assign the same value (not necessarily equal to zero) to both subject atoms and the reference atom.

All results presented so far can be applied to commensurate structures. The only difference is that one gets a discrete set of values for any modulation function and MG quantity rather than a continuous one. The RP is always explicitly included in all expressions, including structure-factor formulae (Parisi, 1994).

## 5. Structure-factor formulae

A supercrystal is a periodic structure and, as such, exhibits a discrete diffraction pattern. The diffraction spots coincide with the reciprocal superlattice. By construction, the diffraction pattern is the projection of the former onto the physical three-dimensional space. The incommensurability property implies a one-to-one correspondence between both sets of points.

Of great practical importance is that the structure factor of an IC structure is equal to that calculated in superspace. This identity can be verified by deriving this expression in superspace by taking into account translational symmetry, and in three-dimensional space, where such a symmetry is absent. Similar calculations have been done even before the advent of the superspace approach in order to explain the presence of satellite reflections for some simple models (Böhm, 1975).

However, to fully exploit the superspace-group symmetry, more elaborate expressions have been derived and are now commonly used in IC structure analysis, mainly for the structure refinement. Unlike in unmodulated structures, these expressions are usually at least briefly mentioned in most structural studies of IC structures. There is more flexibility in this expression and in some cases it is difficult to interpret the results without knowing explicitly which formula has been used in the structure refinement. An alternative is to provide some additional indications on the modulation functions.

The first source of ambiguities lies in the choice of the analytical form of the MF since no commonly accepted standard exists. We shall also focus on another rarely mentioned flexibility: the choice of RP and its consequences. In particular, it will be shown that, by using a slightly different, but permissible, expression, one can get a numerically different, but physically equivalent, description of the same IC structure. This extra flexibility will also be proved useful to achieve some additional requirements.

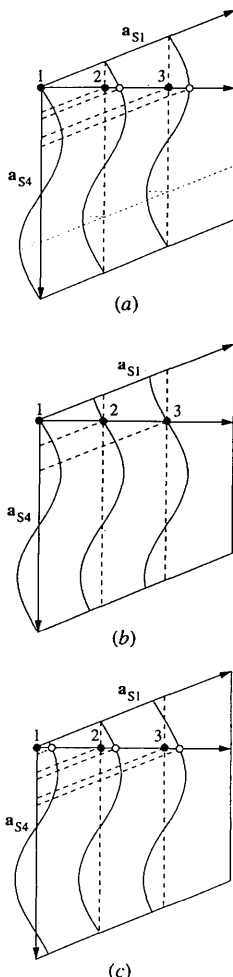


Fig. 6. Influence of the choice of the internal coordinate reference point on equality constraints applied to the parameters of the modulation functions. (a) de Wolff's choice, (b) Kobayashi's choice, (c) arbitrary choice.

### 5.1. Structure factor of a supercrystal

The most frequently used expression was derived by Yamamoto (1982). It is a straightforward extension of de Wolff's original formula that incorporates into one concise formula of striking simplicity various types of modulation and  $(3+d)$ -dimensional superspace-group symmetry. Restricting ourselves to one-dimensional modulations and neglecting only the temperature factors, we obtain the expression

$$F_{\mathbf{H}} = \sum_{\mu, s} f_{\mathbf{H}}^{\mu} \int_0^1 d\bar{x}_4^{\mu} \tilde{p}^{\mu}(\bar{x}_4^{\mu}) \times \exp\left\{2\pi i \sum_{i=1}^4 [h_i^s x_i^{\mu}(\bar{x}_4^{\mu}) + h_i \tau_i^s]\right\}. \quad (75)$$

This form differs slightly from the original writing since some simplifications have been achieved (Paciorek & Kucharczyk, 1985). In particular, rotations were applied to reflection indices rather than atomic coordinates. Let us define

$$h_i^s = \sum_{j=1}^4 R_{ji}^s h_j, \quad i = 1, \dots, 4, \quad (76)$$

$$H_i^s = h_i^s + h_4^s q_i, \quad i = 1, 2, 3.$$

The last equation results from the condition below, which is fulfilled by all superspace-group symmetry operations when applied to the irrational part of the modulation vector:

$$R\mathbf{q} = R_{44}\mathbf{q}, \quad (77)$$

and is sometimes called the compatibility condition.

Characteristic of this approach is the consequent use of higher-dimensional notation and fractional coordinates only, even if some quantities are redundant, as will be shown later. Special attention should be paid to the fourth coordinate. This quantity is considered as a continuous variable but atomic indices and other 'decorations' are retained, probably to achieve a simple expression for symmetry conditions.

All four atomic coordinates are augmented by MF:

$$x_i^{\mu}(\bar{x}_4^{\mu}) = \bar{x}_i^{\mu} + \tilde{u}_i^{\mu}(\bar{x}_4^{\mu}), \quad i = 1, \dots, 4. \quad (78)$$

Symmetry-generated atom parameters (both average and MF) are computed by using the following set of equations:

$$\bar{x}_i^{\nu} = \sum_{j=1}^4 R_{ij}^s \bar{x}_j^{\mu} + \tau_i^s, \quad (79)$$

$$\tilde{u}_i^{\nu}(\bar{x}_4^{\nu}) = \sum_{j=1}^4 R_{ij}^s \tilde{u}_j^{\mu}(\bar{x}_4^{\mu}),$$

$$\tilde{p}^{\nu}(\bar{x}_4^{\nu}) = \tilde{p}^{\mu}(\bar{x}_4^{\mu}).$$

In the last equation, a symmetry condition is given for a scalar MF. In IC structures, such a function

possesses non-trivial transformation properties owing to the presence of internal coordinates. No analogy to this phenomenon exists in normal crystals and this parameter is simply the same for all symmetry-equivalent atoms.

The price for a full higher-dimensional notation is that some quantities are obviously redundant. For example, displacements take place in physical space only and the additional component is calculated from the equation

$$\tilde{u}_4^{\mu}(\bar{x}_4^{\mu}) = \sum_{i=1}^3 q_i \tilde{u}_i^{\mu}(\bar{x}_4^{\mu}) \quad (80)$$

at every value of the argument. The same is observed for anisotropic temperature factors (not discussed here). This is the place where the compatibility condition for superspace-group symmetry operations is necessary.

The actual MF parameters are coefficients of the following Fourier series, usually truncated to a very few terms:

$$\tilde{u}_i^{\mu}(\bar{x}_4^{\mu}) = \sum_{n \geq 0} \tilde{u}_{i,n}^{\mu} \exp(2\pi i n \bar{x}_4^{\mu}) + \text{c.c.}, \quad i = 1, 2, 3, \quad (81)$$

$$\tilde{p}^{\mu}(\bar{x}_4^{\mu}) = \sum_{n \geq 0} \tilde{p}_n^{\mu} \exp(2\pi i n \bar{x}_4^{\mu}) + \text{c.c.}$$

Sometimes, the zero-order terms are excluded, especially from displacive MFs.

The use of the labeled symbol for the integration variable, the 'fourth' atomic coordinate, in (75) is somewhat confusing. The justification lies only in the symmetry property of that variable: together with the remaining true atomic coordinates, it transforms according to the superspace-group symmetry operation as a higher-dimensional vector component.

In (75), only the symmetrically independent atoms are required for the evaluation of the structure factor. The contribution of a symmetrically equivalent atom does not require an explicit evaluation of its MF. This resembles the evaluation of an ordinary structure factor. This is possible because several conditions are fulfilled simultaneously:

- (a) the structure factor is a sum of contributions from individual atoms;
- (b) it is an integral of a periodic function over one period;
- (c) the internal coordinate is the integration variable;
- (d) the symmetry transformation of the internal coordinate is linear.

It is easy to show that in the simplest case of a purely occupational modulation the following identity holds:

$$\int_0^1 dx p[R_{44}^{-1}(x - \tau_4)] \exp(2\pi i h_4 x) = \int_0^1 dx p(x) \exp[2\pi i h_4 (R_{44} x + \tau_4)]. \quad (82)$$

The same is true for the general case of modulations and this identity is the main simplification leading to the above structure-factor formula. It has a great numerical advantage when evaluating such an expression by use of any numerical integration method because MFs of symmetry-independent atoms can be precomputed at the required values of the arguments and subsequently used for all reflections. More elaborate methods have also been investigated (Paciorek & Chapuis, 1992, 1994).

In the simpler case of internal coordinate translation only, not necessarily related to the symmetry transformation, one gets

$$\begin{aligned} & \int_0^1 dx p(x - \tau) \exp(2\pi i h_4 x) \\ &= \exp(2\pi i h_4 \tau) \int_0^1 dx p(x) \exp(2\pi i h_4 x) \end{aligned} \quad (83)$$

and again, if other MFs of a given atom undergo such a common transformation, the integral is multiplied by the exponential factor above. This relation is of great practical importance as an internal coordinate translation affects only the geometrical part of the structure factor.

### 5.2. The structure factor in vector notation

Nowadays, IC structures are no longer exotic and a detailed exposition of the underlying concepts and methods has recently been presented in *International Tables for Crystallography* (Janssen, Janner, Looijenga-Vos & de Wolff, 1992). The superspace groups have been tabulated for (3+1) dimensions only due to space limitations and many related concepts of higher-dimensional crystallography relevant to this topic have been clarified.

In particular, the structure-factor expressions have been given and the concept of MFs and their symmetries have been explained. To our surprise, the expressions are in a different form and those used in practice are rarely mentioned. The most general expression has been given in the form

$$\begin{aligned} F_{\mathbf{H}} &= \sum_{\mu} f_{\mathbf{H}}^{\mu} \int_{\Omega_I} dt p^{\mu}(t) \\ & \times \exp\{2\pi i(\mathbf{H}, \mathbf{H}_I) \cdot (\mathbf{r}^{\mu} + \mathbf{u}^{\mu}(t), t)\} \end{aligned} \quad (84)$$

and it is valid for a general (3+d)-dimensional IC structure. The integration above is over a d-dimensional hypercube, the internal space counterpart of the unit cell. The modulation of the temperature factors is omitted. Surprisingly, no attempt has been made to accommodate symmetry operations in the above expression. On the contrary, the discussion of the symmetry properties of the MF has been separated and the summation is over all atoms. It suggests that in order to use such an expression we are forced first to evaluate the MF parameters for all atoms, a kind of ‘expand’ procedure. This is sometimes

feasible, but rarely used, if the structure factor is to be calculated together with all partial derivatives, even in unmodulated structures.

Since we are mainly concerned with one-dimensional modulations, let us first rewrite the above expression for that case. One gets

$$\begin{aligned} F_{\mathbf{H}} &= \sum_{\mu} f_{\mathbf{H}}^{\mu} \int_0^1 dt p^{\mu}(t) \\ & \times \exp[2\pi i(\mathbf{H}, H_I) \cdot (\mathbf{r}^{\mu} + \mathbf{u}^{\mu}(t), t)] \end{aligned} \quad (85)$$

and can extract the factor independent of the integration variable:

$$\begin{aligned} F_{\mathbf{H}} &= \sum_{\mu} f_{\mathbf{H}}^{\mu} \exp(2\pi i \mathbf{H} \cdot \mathbf{r}^{\mu}) \\ & \times \int_0^1 dt p^{\mu}(t) \exp[2\pi i(\mathbf{H} \cdot \mathbf{u}^{\mu}(t) + h_4 t)]. \end{aligned} \quad (86)$$

This form is more and more frequently used and the integral, possibly multiplied by an atomic scattering factor, is sometimes called an atomic modulation factor and is given a new symbol (Pérez-Mato, Madariaga, Zúñiga & Garcia Arribas, 1987). The expression (86) is getting even closer to that for unmodulated structures.

The conditions for real-valued MFs take the form

$$\begin{aligned} \mathbf{u}^{\mu}(t) &= \sum_n \mathbf{u}_n^{\mu} \exp(2\pi i n t), \quad \mathbf{u}_{-n}^{\mu} = \mathbf{u}_n^{\mu*}, \\ p^{\mu}(t) &= \sum_n p_n^{\mu} \exp(2\pi i n t), \quad p_{-n}^{\mu} = p_n^{\mu*}, \end{aligned} \quad (87)$$

where the complex vector notation is used for a dispersive modulation.

The simplest expression one can get for a purely occupational modulation is

$$F_{\mathbf{H}} = \sum_{\mu} f_{\mathbf{H}}^{\mu} \exp(2\pi i \mathbf{H} \cdot \mathbf{r}^{\mu}) \int_0^1 dt p^{\mu}(t) \exp(2\pi i h_4 t) \quad (88)$$

and, furthermore, an analytical solution can be found to the integral

$$F_{\mathbf{H}} = \sum_{\mu} f_{\mathbf{H}}^{\mu} \exp(2\pi i \mathbf{H} \cdot \mathbf{r}^{\mu}) p_{-h_4}^{\mu}. \quad (89)$$

It is interesting to compare this expression with (75). At first, let us neglect the symmetry and recover the vector notation partially,

$$\begin{aligned} F_{\mathbf{H}} &= \sum_{\mu} f_{\mathbf{H}}^{\mu} \exp(2\pi i \mathbf{K} \cdot \mathbf{r}^{\mu}) \int_0^1 d\bar{x}_4^{\mu} \tilde{p}^{\mu}(\bar{x}_4^{\mu}) \\ & \times \exp(2\pi i h_4 \bar{x}_4^{\mu}), \end{aligned} \quad (90)$$

and then recast it into the final form:

$$F_{\mathbf{H}} = \sum_{\mu} f_{\mathbf{H}}^{\mu} \exp(2\pi i \mathbf{K} \cdot \mathbf{r}^{\mu}) \tilde{p}_{-h_4}^{\mu}. \quad (91)$$

The result is apparently different since the dot product in the geometrical complex factor now involves the main reflection indices only.

Using both expressions in the structure refinement, one can get different parameters of the MF from the experimental data of the same structure. But comparing the results more carefully, one can easily find that parameters of the MF, in our case, the complex Fourier coefficients, are related by the equation

$$\tilde{p}_n^\mu \exp(2\pi i n \mathbf{q} \cdot \mathbf{r}^\mu) = p_n^\mu \quad (92)$$

and this is equivalent to the translation of the scalar function along its independent variable. Such a translation has been achieved by a small change in the geometrical part of the structure factor, without any explicit modification of the MF expression.

### 5.3. The structure factor with internal coordinate reference points

The two forms of the structure-factor expression differ in the use of two different integration variables, which are related by the equation

$$\mathbf{K} \cdot \mathbf{r}^\mu + h_4(\mathbf{q} \cdot \mathbf{r}^\mu + t) = \sum_{i=1}^4 h_i \bar{x}_4^i. \quad (93)$$

It is easy to show that, by integrating the rather long expression

$$F_{\mathbf{H}} = \sum_{\mu} f_{\mathbf{H}}^{\mu} \exp(2\pi i \mathbf{K} \cdot \mathbf{r}^\mu) \int_0^1 dt \tilde{p}^\mu(\mathbf{q} \cdot \mathbf{r}^\mu + t) \times \exp\{2\pi i h_4(\mathbf{q} \cdot \mathbf{r}^\mu + t)\}, \quad (94)$$

one obtains exactly the same result using either of them. To recover Yamamoto's formula, it is sufficient to perform a trivial change of the integration variable. The explicit relation between MFs can be written as

$$\begin{aligned} \tilde{p}^\mu(\mathbf{q} \cdot \mathbf{r}^\mu + t) &= \sum_n \tilde{p}_n^\mu \exp[2\pi i n(\mathbf{q} \cdot \mathbf{r}^\mu + t)] \\ &= \sum_n p_n^\mu \exp(2\pi i n t) \\ &= p(t). \end{aligned} \quad (95)$$

It is obvious that, in the numerical calculations, the use of the right-hand side of (95) has some advantages. As this is just a standard Fourier expansion, the basis functions (simple exponentials) are the same for all atoms and all MFs. It is desirable to retain this form whenever possible.

Let us leave the argument of the MF unchanged and modify only the geometrical part of the structure factor in front of the integral:

$$F_{\mathbf{H}} = \sum_{\mu} f_{\mathbf{H}}^{\mu} \exp(2\pi i \mathbf{H} \cdot \mathbf{r}^\mu) \int_0^1 dt \tilde{p}^\mu(\mathbf{q} \cdot \mathbf{r}^\mu + t) \times \exp(2\pi i h_4 t). \quad (96)$$

This form indicates directly the RP of the MF and resembles an expression used in deriving structure factors directly in three-dimensional space. The integral was a by-product of the summation over all unit cells of the basic structure.

This form is a suitable starting point for introducing an arbitrary RP. The best method is to replace the atomic coordinates in the MF argument above by an arbitrary vector. This is equivalent to a new choice of MF. First, one can write a new expression:

$$F_{\mathbf{H}} = \sum_{\mu} f_{\mathbf{H}}^{\mu} \exp(2\pi i \mathbf{H} \cdot \mathbf{r}^\mu) \int_0^1 dt \hat{p}^\mu(\mathbf{q} \cdot \mathbf{g}^\mu + t) \times \exp(2\pi i h_4 t), \quad (97)$$

and then change the integration variable:

$$F_{\mathbf{H}} = \sum_{\mu} f_{\mathbf{H}}^{\mu} \exp\{2\pi i(\mathbf{H} \cdot \mathbf{r}^\mu - h_4 \mathbf{q} \cdot \mathbf{g}^\mu)\} \times \int_0^1 dx \hat{p}^\mu(x) \exp(2\pi i h_4 x). \quad (98)$$

Assuming that the new MF has the Fourier expansion

$$\hat{p}^\mu(x) = \sum_n \hat{p}_n^\mu \exp(2\pi i n x), \quad (99)$$

we arrive at the more general final result:

$$F_{\mathbf{H}} = \sum_{\mu} f_{\mathbf{H}}^{\mu} \exp\{2\pi i(\mathbf{H} \cdot \mathbf{r}^\mu - h_4 \mathbf{q} \cdot \mathbf{g}^\mu)\} \hat{p}_{-h_4}^\mu. \quad (100)$$

To solve easily the equality constraint problem discussed in §4.5 by using this expression, it is more convenient to rewrite it in the equivalent form

$$F_{\mathbf{H}} = \sum_{\mu} f_{\mathbf{H}}^{\mu} \exp\{2\pi i[\mathbf{K} \cdot \mathbf{r}^\mu + h_4 \mathbf{q} \cdot (\mathbf{r}^\mu - \mathbf{g}^\mu)]\} \hat{p}_{-h_4}^\mu \quad (101)$$

and compare it with the requirement on the phases of MFs discussed before. The additional exponential phase factor contains precisely the required phase difference when the newly introduced vector is replaced by the atomic position vector of the required reference atom. The solution to this problem is exact, independent of the form of the analytic form of the MF and requires a trivial set of equality constraints.

Finally, a relationship between the two MFs can be established by comparing their Fourier coefficients:

$$\hat{p}_n^\mu \exp(2\pi i n \mathbf{q} \cdot \mathbf{g}^\mu) = p_n^\mu. \quad (102)$$

This is the most general relationship and it is easy to see that the two other forms discussed above are special cases, in some sense extreme ones. The choice of RP by using atomic coordinates or the null vector leads to the original formulae of de Wolff and Kobayashi's result, respectively. The most general form has been used by Petříček in his expression to accommodate a modulation of a rigid molecule.

#### 5.4. Contribution from attached atoms

In IC structures, the procedures discussed above give us directly the coordinates of the attached atoms on a given physical section of superspace. It is virtually impossible to split such a coordinate into MFs and average coordinates. They can eventually be calculated numerically from the expression

$$\langle \mathbf{r}^\mu \rangle = \int_0^1 dt \mathbf{r}^\mu(t) \quad (103)$$

in order to compare an attached-atom modulation with others by evaluating the following differences:

$$\mathbf{u}^\mu(t) = \mathbf{r}^\mu(t) - \langle \mathbf{r}^\mu \rangle, \quad (104)$$

in order to make, for example, some plots. These functions as well as attached-atom coordinates are given by an algorithm rather than an analytical expression. Furthermore, the number of relevant harmonics included in these functions is unpredictable and can be much higher than in the defining atoms (usually rather limited). In this case, the problem of RP also arises.

Let us write the structure-factor expression of a purely displacive modulated structure in the form

$$F_{\mathbf{H}} = \sum_{\mu} f_{\mathbf{H}}^{\mu} \int_0^1 dt \exp[2\pi i(\mathbf{H} \cdot \mathbf{r}^\mu(t) + h_4 t)], \quad (105)$$

where the distinction between average coordinates and MFs has been abandoned. This expression is essentially equivalent to the case when zero-order harmonics have been included in the MF and basic atomic coordinates are zero. The choice of RP has a natural solution, as both extreme cases discussed before lead to the same result, namely zero. For the defining atoms, we have of course room for choice. In Fig. 7, part of an IC structure with attached H atoms is shown. Both arrangements have been used to compute the desired atomic coordinates.

In some cases, the structure factor can be evaluated analytically. Unfortunately, this is not possible when

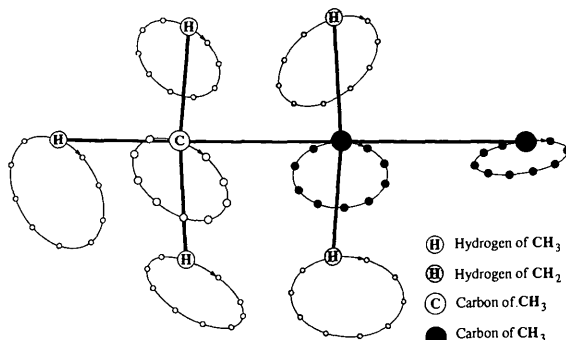


Fig. 7. Part of an IC structure with attached H atoms. Only C atoms have refined displacive MFs. For every  $t$ , all H atoms are located in a predefined arrangement without adding any further MFs and restraints.

attached atoms are included. The complete structure-refinement program also has to provide an algorithm to evaluate such an expression by numerical integration. The coordinates of the attached atoms have to be calculated for every value of the internal coordinate required by the chosen numerical integration method. It requires some additional memory space but is generally quite efficient.

#### 5.5. Recovering superspace-group symmetry

In our above considerations, the superspace-group symmetry was not fully utilized. To achieve the former simplicity and efficiency, we have to include the symmetry in all expressions in the most economic and efficient way. Fortunately, only minor changes to the structure-factor formula are required to take into account the contribution from attached atoms and the definition of the phase reference point.

Let us begin with the expression for a scalar MF of the atom transformed by a symmetry operation when the target value of the physical section in the superspace is to be specified. Such an expression reads

$$p^\nu(\mathbf{q} \cdot \mathbf{g}^\nu + t) = p^\mu[R_{44}^{-1}(\mathbf{q} \cdot \mathbf{g}^\mu - \tau_4 + t)] \quad (106)$$

and it is easy to see that this operation requires also the evaluation of the target value of RP. Even if the MF is scalar, we have to exploit fully the superspace-group transformation defined as

$$\begin{aligned} \mathbf{g}^\nu &= \mathbf{R}\mathbf{g}^\mu + \mathbf{s}, \\ t' &= R_{44}t + \tau_4 - \mathbf{q} \cdot \mathbf{s}, \end{aligned} \quad (107)$$

where, in the case of (3+1)-dimensional IC structures,

$$R_{44} = R_{44}^{-1} = \pm 1, \quad (108)$$

which allows some further simplifications.

The compatibility relation reads

$$R_{44}\mathbf{q} \cdot \mathbf{R}\mathbf{g}^\mu = \mathbf{q} \cdot \mathbf{g}^\mu \quad (109)$$

and, after some straightforward algebra, we arrive at the equivalent expression:

$$p^\nu(\mathbf{q} \cdot \mathbf{g}^\nu + t) = p^\mu[\mathbf{q} \cdot \mathbf{g}^\mu + R_{44}^{-1}(\mathbf{q} \cdot \mathbf{s} - \tau_4 + t)], \quad (110)$$

which has a great computational advantage since a transformation of the RP is not required. All quantities on the right-hand side are limited to the symmetrically independent atom only.

In our approach to present results, the above expression is extensively used to plot all MFs or even an entire modulated structure on the physical sections of

the superspace. All plots are of the form

$$f^\mu(t) = p^\mu(\mathbf{q} \cdot \mathbf{g}^\mu + t), \quad t \in [0, 1], \quad (111)$$

which makes the RP choice transparent.

Our next concern is to include the symmetry operations in the structure-factor formulae in the most efficient way. Only essential steps of the derivation will be presented here and it is recommended that the very intuitive approach given by de Wolff (1974) should be studied.

To accommodate an atom with explicitly refined displacive MFs and a given RP, our departure point is the expression for its coordinates transformed by a superspace-group operation when the target  $t$  section is prescribed:

$$\mathbf{r}^\nu(t) = \mathbf{r}^\nu + \mathbf{u}^\nu(\mathbf{q} \cdot \mathbf{g}^\nu + t) = \mathbf{R}\mathbf{r}^\mu + \mathbf{s} + \mathbf{R}\mathbf{u}^\mu(x), \quad (112)$$

where the new internal coordinate is

$$x = \mathbf{q} \cdot \mathbf{g}^\mu + R_{44}^{-1}(\mathbf{q} \cdot \mathbf{s} - \tau_4 + t). \quad (113)$$

Then, the inverse transformation reads

$$t = R_{44}x - R_{44}\mathbf{q} \cdot \mathbf{g}^\mu - \mathbf{q} \cdot \mathbf{s} + \tau_4. \quad (114)$$

The point on the string representing the new atom in superspace has been defined. Its contribution to the structure factor can be written as

$$F_{\mathbf{H}}^\nu = f_{\mathbf{H}}^\mu \int_0^1 dt \exp[2\pi i \mathbf{H} \cdot \mathbf{r}^\nu(t) + h_4 t], \quad (115)$$

and then transformed to the form below, which is better suited to numerical evaluation:

$$F_{\mathbf{H}}^\nu = f_{\mathbf{H}}^\mu \Omega_{\mathbf{H}}^s \exp[2\pi i (\mathbf{H}^s \cdot \mathbf{r}^\mu - h_4^s \mathbf{q} \cdot \mathbf{g}^\mu)] \times \int_0^1 dx \exp[2\pi i (\mathbf{H}^s \cdot \mathbf{u}^\mu(x) + h_4^s x)]. \quad (116)$$

In the expression above, all parameters are now related to the symmetrically independent atom only. Other quantities are defined as

$$\begin{aligned} \mathbf{H}^s &= \tilde{\mathbf{R}}\mathbf{H}, \\ h_4^s &= R_{44}h_4 \end{aligned} \quad (117)$$

and

$$\Omega_{\mathbf{H}}^s = \exp[2\pi i (\mathbf{K} \cdot \mathbf{s} + h_4 \tau_4)] = \exp\left(2\pi i \sum_{i=1}^4 h_i \tau_i\right), \quad (118)$$

where the tilde means matrix transposition. The last equation is the factor related to the non-primitive translations of the superspace-group operation, which always adopts this particular form.

To include attached atoms and their symmetrically equivalent ones another, but equivalent, form of the superspace-symmetry transformation can be used. Our departure point is now a discrete set of coordinates (not modulation functions) calculated at values of the integration variable required for the numerical integration:

$$\mathbf{r}^\nu(x_k) = \mathbf{R}\mathbf{r}^\mu(t_k) + \mathbf{s}, \quad k = 1, \dots, M, \quad (119)$$

where the transformed internal coordinates are

$$x_k = R_{44}t_k + \tau_4 - \mathbf{q} \cdot \mathbf{s}. \quad (120)$$

The transformed points appear on other sections in superspace but in this calculation it is irrelevant since the required value is the integral of periodic functions taken over the whole period. The contribution to the structure factor of the new atom is

$$F_{\mathbf{H}}^\nu \simeq f_{\mathbf{H}}^\mu \sum_{k=1}^M w_k \exp[2\pi i (\mathbf{H} \cdot \mathbf{r}^\nu(x_k) + h_4 x_k)], \quad (121)$$

which can, without difficulties, be transformed to the final form:

$$F_{\mathbf{H}}^\nu \simeq f_{\mathbf{H}}^\mu \Omega_{\mathbf{H}}^s \sum_{k=1}^M w_k \exp[2\pi i (\mathbf{H}^s \cdot \mathbf{r}^\mu(t_k) + h_4^s t_k)]. \quad (122)$$

In both above expressions, weights are chosen according to the integration method and no attempt has been made to simplify further the result as the coordinates are computed by algorithms, not by analytical expressions.

Even if simpler equations were available, in which all quantities related to the internal coordinates would disappear, there is one place in all the expressions above where the superspace-group symmetry manifests itself. This is the simple exponential factor (118) due to the non-primitive translations, visibly higher-dimensional ones. Our system possesses a higher-dimensional space-group symmetry with all the crystallographic consequences.

### 5.6. Toward future improvements

As mentioned before, the preceding results have been applied to the IC structure of hexamethylenetetramine suberate. The final result can be summarized as follows:

Chemical formula:  $\text{C}_6\text{H}_{12}\text{N}_4 \cdot (\text{CH}_2)_6(\text{COOH})_2$ .

Superspace group:  $P2_1(\alpha 0 \gamma)$ .

Reflections: 4969.

Parameters/harmonics: 1364/8, 431/4.

Geometrical restraints: 99.

H atoms attached to C and N atoms: 24.

Divisions in numerical integration: 64.

CPU time/cycle: 15 min on SG Indigo-2.

Discrepancy indices:  $R = 0.079$ ,  $wR = 0.07$ ,  $\text{GOF} = 3.77$ .

A short synopsis of our first unsuccessful attempts to refine this structure will be given.

(i) The H atoms constitute about 16% of the electron density and their omission leads to serious deficiencies of the model. This is also observed in the basic structure refinement using conventional techniques.

(ii) Most of the refined parameters are related to displacive MFs. Our attempts to find an occupational modulation model failed.

(iii) Adding all H atoms almost triples the number of refined parameters. Even by adding all necessary geometrical restraints (pseudo-observations), it was not possible to obtain a reasonable observations/parameters ratio. The refinement became very unstable and time consuming.

We reconsidered the whole procedure and developed a new approach to handle at least H atoms. The crucial observation was that the atomic model has a serious limitation if the nature of the modulation is orientational rather than displacive.

Let us consider a simple two-dimensional rotation:

$$\begin{pmatrix} c & s \\ -s & c \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} x' \\ y' \end{pmatrix}, \quad (123)$$

where

$$c = \cos \phi, \quad s = \sin \phi. \quad (124)$$

Assume that the rotation angle is a proper MF and restrict ourselves to the harmonic case:

$$\phi = \alpha \sin(t). \quad (125)$$

The objective is to convert this orientational modulation to the atomic model, *i.e.* to find the MF for every coordinate. The result is

$$x'(t) = J_0(\alpha)x + Ax + By, \quad (126)$$

$$y'(t) = J_0(\alpha)y + Ay - Bx, \quad (127)$$

where known Fourier-series expansions are

$$A = 2 \sum_{n=1}^{\infty} J_{2n}(\alpha) \cos(2nt), \quad (128)$$

$$B = 2 \sum_{n=1}^{\infty} J_{2n-1}(\alpha) \sin[(2n-1)t]. \quad (129)$$

Thus, even the simplest harmonic modulation of the rotation angle leads to the infinite Fourier-series expansion for each displacive MF. The same holds in the three-dimensional case (modulation of Euler angles).

Our current software is limited to atomic MFs expressed as Fourier series and thus requires the use of rather long expansions to reproduce rotations with large amplitudes. This approach is not exact and does not take

into account the rotation of the thermal ellipsoids. The number of parameters is also growing rapidly.

We conclude that significant improvements are necessary to deal with similar IC structures. The exact solution of the rotational modulation is our current concern. We are considering the application of quaternions to handle these problems.

## 6. Conclusions

The main motivation for this study was to extend the IC structure refinement procedure to accommodate a class of crystals containing a large number of atoms in the unit cells. The atomic model with MFs refined for each atom can be very difficult or even impossible to compute. It is necessary to find means to reduce the number of refined parameters without sacrificing the precision of the final model. An analog of the so-called 'riding refinement' has been proposed, in which a number of atoms has to faithfully follow groups of others, while maintaining some given geometrical constraints. Such a procedure has been extended here to (3+1)-dimensional IC structures.

In the course of these studies, we encountered also a number of related problems concerning the effective and unambiguous use and interpretation of constraints and restraints. Our results are included above along with a short review of the relevant concepts and formulae of higher-dimensional crystallography. Some proposals regarding a more precise presentation of the results are included.

We hope that our considerations will be helpful in ongoing projects to build a structural database of solved IC structures, especially to build a suitable dictionary of all relevant items making further studies of IC structures possible, unambiguous and easier.

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