

The Pseudo-Symmetry of Modulated Crystal Structures

BY P. M. DE WOLFF

Werkgroep Microstructuur, Laboratorium voor Technische Natuurkunde, Lorentzweg 1, Delft, Netherlands

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A modulated structure can be depicted as a section through a four-dimensional periodic structure. In the latter, each atom is represented by a string continuing endlessly in the overall direction (\mathbf{e}_4) of the normal to R_3 , R_3 being the hyperplane of the section. The strings have periodic bends or densifications for displacive and substitutional modulation respectively. Formulae for structure factors can be derived from this picture with little effort. The pseudo-symmetry of modulated structures can be described conveniently in this picture. Each four-dimensional space group to which the four-dimensional structure can belong is a possible MS_3 (modulated three-dimensional structure) group of pseudo-symmetry, and is called an MS_3 space group. It is shown that MS_3 point groups are reducible in the form $Q \oplus \varepsilon \cdot \mathbf{1}$, where $\mathbf{1}$ is the unit 2×2 matrix, and $\varepsilon = \pm 1$. A list is presented of these 31 groups written as black-and-white or colourless groups of three-dimensional symmetry. The MS_3 space groups are discussed briefly. As an example of the peculiar differentiations caused by \mathbf{e}_4 being a unique direction, the 23 MS_2 space groups are listed explicitly. Finally, it is shown that MS groups are essential for the description of MS symmetry, because very often the latter cannot be represented completely and unambiguously by the normal space group of an approximate superstructure.

1. Main reflexions and satellites

Certain crystals (*cf.* §5) have diffraction patterns consisting of sharp spots which cannot all be indexed in the usual way. Instead, four indices h_i and four reciprocal base vectors \mathbf{b}_i ($i=1 \dots 4$) have to be introduced so that the diffraction vector of each spot can be written as

$$h_1\mathbf{b}_1 + h_2\mathbf{b}_2 + h_3\mathbf{b}_3 + h_4\mathbf{b}_4 \quad (1)$$

with integer h_1, h_2, h_3 and h_4 .

Since the four vectors \mathbf{b}_i occur in three-dimensional space, one may write:

$$\mathbf{b}_4 = k_1\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3 \quad (2)$$

and the abnormal character of the pattern can be expressed by saying that at least one of the k_i is irrational. Translated into physics, this means that one k_i depends on, say, the temperature in a continuous manner. That, and not the measured k_i value, the rationality of which is undecidable, is the criterion which differentiates these crystals from superstructures. For an example see Fig. 1.

The diffraction image of these crystals shows a very conspicuous three-dimensional reciprocal lattice among the points (1). We shall call it B and characterize it by $h_4=0$ through a suitable choice of the base vectors $\mathbf{b}_1, \mathbf{b}_2$ and \mathbf{b}_3 . This lattice has the following properties.

(I) It has the same point-group symmetry as the entire diffraction image in reciprocal space, both geometrically and with regard to the intensities occurring in the latter and in B respectively.

(II) Together with the density it leads to an integer number of formula weights per unit cell.

(III) There is often a transition to another phase which retains only the reflexions belonging to this lat-

tice, whereas the other reflexions – the ‘satellites’, having $h_4 \neq 0$ – disappear at the transition point.

(IV) It is, among all three-dimensional lattices which could be chosen from the points (1), the one which has by far the biggest total diffraction intensity of its points.

We shall call the reflexions belonging to this lattice main reflexions.

The existence of a three-dimensional sublattice with the above properties can be explained on the basis of so-called modulated structures (§5). From a practical point of view, the properties (I) . . . (IV) could be used as criteria to find the lattice B . So far, however, main reflexions have invariably been so strong compared to satellites – at least at low angles – that there has never been any doubt about the lattice B .

Within the lattice B , there are the usual conventions for choosing base vectors $\mathbf{b}_1, \mathbf{b}_2$ and \mathbf{b}_3 . The vector \mathbf{b}_4 is not unique either, but it is natural to choose it within the first Brillouin zone of the B lattice.

2. The problem

The reciprocal lattice of main reflexions obviously corresponds to very dominating features of the structure. Consider the conjugate lattice A in real space, with base vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ reciprocal to $\mathbf{b}_1, \mathbf{b}_2$ and \mathbf{b}_3 . The A -lattice vectors cannot all be vectors of translation symmetry, or there would be no satellites. The prominence of the reciprocal lattice B nevertheless points to a pseudo-translation character of the A -lattice vectors, or at least of part of them, and the first goal is to specify that character.

Being devoid of three-dimensional periodicity, our crystal has of course lost all claims to belong to a three-dimensional space group. The second question then becomes: What kind of symmetry – if any – can be

assigned to these structures? Finally: To what extent is the result applicable to the symmetry of superstructures, or *vice versa*?

It needs hardly be said that the reason for solving these problems is the need to establish a foundation on which the analysis of the structures involved can be based. Just as for normal crystals, full knowledge of the symmetry is indispensable for modulated structures to be solved.

3. The four-dimensional structure

The difficulty with four base vectors is that there is no set of vectors reciprocal to it in three-dimensional space. As set out in the previous section, the lattice A reciprocal to B may be constructed – we shall call this the *pseudo-translation lattice* – but that leaves \mathbf{b}_4 to be dealt with. The way this may be done can be visualized if one looks at a layer of reflexions containing the direction of \mathbf{b}_4 , as in Fig. 2.

Such pictures strongly suggest that the rows of satellites do not lie in the plane of the figure, but that the latter constitutes a view in perspective of parallel rows which run in a direction oblique to the paper. Of course it is precisely the non-rationality of the k_i in (2) which allows one to uncouple \mathbf{b}_4 in this way from the main reflections.

We now extend this concept to the full reciprocal space instead of just one layer. The satellites are considered as projections onto three-dimensional space R_3 of lattice points of a four-dimensional lattice B' in four-dimensional space R_4 . Assuming the projection to be at right angles to R_3 , we find that the lattice B' can be based on vectors \mathbf{b}'_i , three of which lie in R_3 :

$$\mathbf{b}'_1 = \mathbf{b}_1 \quad \mathbf{b}'_2 = \mathbf{b}_2 \quad \mathbf{b}'_3 = \mathbf{b}_3 \quad \mathbf{b}'_4 = \mathbf{b}_4 + \mathbf{e}_4 \quad (3)$$

where \mathbf{e}_4 is a vector perpendicular to R_3 (see Fig. 3). We shall take \mathbf{e}_4 as the unit vector in that direction.

The advantage gained at the cost of an extra dimension is that we are now able to find a lattice A' in R_4 , reciprocal to B' . Moreover, a very useful four-dimensionally periodic structure can be based upon this lattice as follows:

Looking at Fig. 3, we observe that the points T are peaks in the Fourier transform of the actual electron density ρ in R_3 . We now assign the diffraction amplitude F of each point T to the corresponding point T' in reciprocal R_4 space. Then we perform the Fourier summation in R_4 to obtain the function ρ' , which is periodic in four coordinates in R_4 , and which has the translation lattice A' . Now what is the relation between ρ and ρ' ?

From the construction of ρ' we have (calling \mathcal{F}_n the Fourier transform in n dimensions).

$$\mathcal{F}_3(\rho) = \text{projection of } \mathcal{F}_4(\rho') \text{ along } \mathbf{e}_4.$$

Therefore $\rho =$ section of ρ' , obtained by intersecting ρ' with the space (hyperplane) R_3 perpendicular to \mathbf{e}_4 .

The situation may be visualized in three instead of four dimensions: Imagine a normal crystal (density ρ')

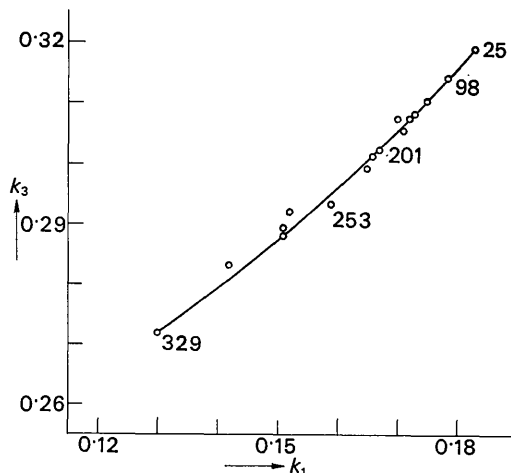


Fig. 1. The components k_1 vs. k_3 of the satellite vector \mathbf{b}_4 for Na_2CO_3 , for a range of temperatures as shown in degrees Celsius.

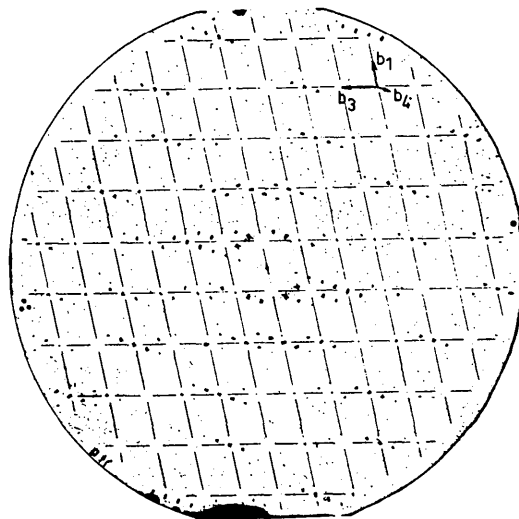


Fig. 2. Retigram of the layer $h3l$ of Na_2CO_3 , taken with $\text{Cu } K\alpha$ radiation.

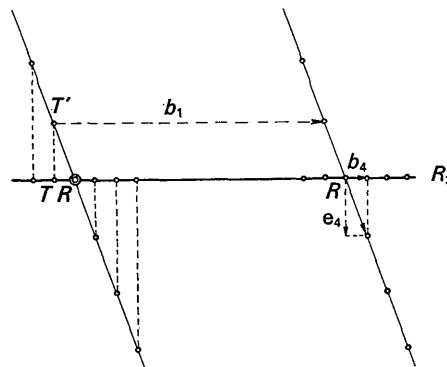


Fig. 3. Main reflexions (R) and satellites (T) in R_3 as a projection of points T' of a four-dimensional lattice.

intersected by a plane with irrational indices. The electron density ρ in the plane as a function of two coordinates is non-periodic. Its Fourier transform is ob-

tained from that of ρ' by the usual routine: project all points in reciprocal space along the plane normal onto the plane. Because the intensity always vanishes for sufficiently high indices, this projection remains a set of discrete points, which can be indexed by an expression like (1) with one term less. Therefore it is the exact two-dimensional analogue of the situation from which we started in §1.

4. The pseudo-translation lattice

The set of vectors \mathbf{a}'_i reciprocal to \mathbf{b}'_i in R_4 (that is, fulfilling the conditions $\mathbf{a}'_i \mathbf{b}'_j = \delta_{ij}$) expressed in the set \mathbf{a}_i reciprocal to \mathbf{b}_i in R_3 , and in \mathbf{e}_4 , is:

$$\begin{aligned} \mathbf{a}'_1 &= \mathbf{a}_1 - k_1 \mathbf{e}_4 & \mathbf{a}'_2 &= \mathbf{a}_2 - k_2 \mathbf{e}_4 \\ \mathbf{a}'_3 &= \mathbf{a}_3 - k_3 \mathbf{e}_4 & \mathbf{a}'_4 &= \mathbf{e}_4 \end{aligned} \quad (4)$$

This is verified as follows:

$$\begin{aligned} \mathbf{a}'_1 \mathbf{b}'_4 &= (\mathbf{a}_1 - k_1 \mathbf{e}_4) \cdot (\mathbf{b}_4 + \mathbf{e}_4) = \mathbf{a}_1 \cdot \mathbf{b}_4 - k_1 \\ &= \mathbf{a}_1 (k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 + k_3 \mathbf{b}_3) - k_1 = 0 \\ \mathbf{a}'_1 \mathbf{b}'_3 &= (\mathbf{a}_1 - k_1 \mathbf{e}_4) \cdot \mathbf{b}_3 = \mathbf{a}_1 \mathbf{b}_3 = 0 \\ \mathbf{a}'_1 \mathbf{b}'_1 &= (\mathbf{a}_1 - k_1 \mathbf{e}_4) \cdot \mathbf{b}_1 = \mathbf{a}_1 \mathbf{b}_1 = 1, \text{ etc.} \end{aligned}$$

The pseudo-translation character of the lattice A can now be interpreted more precisely. Each of its lattice vectors is the projection of a row of lattice points of A' , projected along \mathbf{e}_4 onto R_3 (e.g. $\mathbf{a}_1 = \mathbf{a}'_1 + k_1 \mathbf{e}_4$). The lattice vectors of A' in R_4 are true translation vectors of the function ρ' , of which the actual density ρ is a section as discussed above. A sketch of the situation reduced by two dimensions is given in Fig. 4. Accordingly, the pseudo-translation lattice A in R_3 is the projection of the true translation lattice A' in R_4 .

In this respect, the relation between A and A' is similar to that between the lattice B of main reflexions and the four-dimensional reciprocal lattice B' , which yields B when projected along \mathbf{b}'_4 . The important difference is that B is part of B' , whereas A' has no three-dimensional sublattice in R_3 . On the other hand, \mathbf{e}_4 is directed along a lattice vector of A' , but not of B' .

Let us call the coordinates in R_4 with respect to the base $\mathbf{a}'_1 \dots \mathbf{a}'_4$: $x_i (i=1 \dots 4)$. No primes are needed to distinguish the first three of these coordinates from those in R_3 with respect to $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$; they are identical since A is the projection of A' along \mathbf{a}'_4 . The hyperplane R_3 , perpendicular to $\mathbf{e}_4 = \mathbf{a}'_4$, is given by

$$\mathbf{e}_4 \cdot (x_1 \mathbf{a}'_1 + x_2 \mathbf{a}'_2 + x_3 \mathbf{a}'_3 + x_4 \mathbf{a}'_4) = 0$$

or, because of (4),

$$-k_1 x_1 - k_2 x_2 - k_3 x_3 + x_4 = 0 \quad (5)$$

It is convenient to introduce a new coordinate t in R_4

$$t = -k_1 x_1 - k_2 x_2 - k_3 x_3 + x_4 \quad (6)$$

so that R_3 is given by $t=0$.

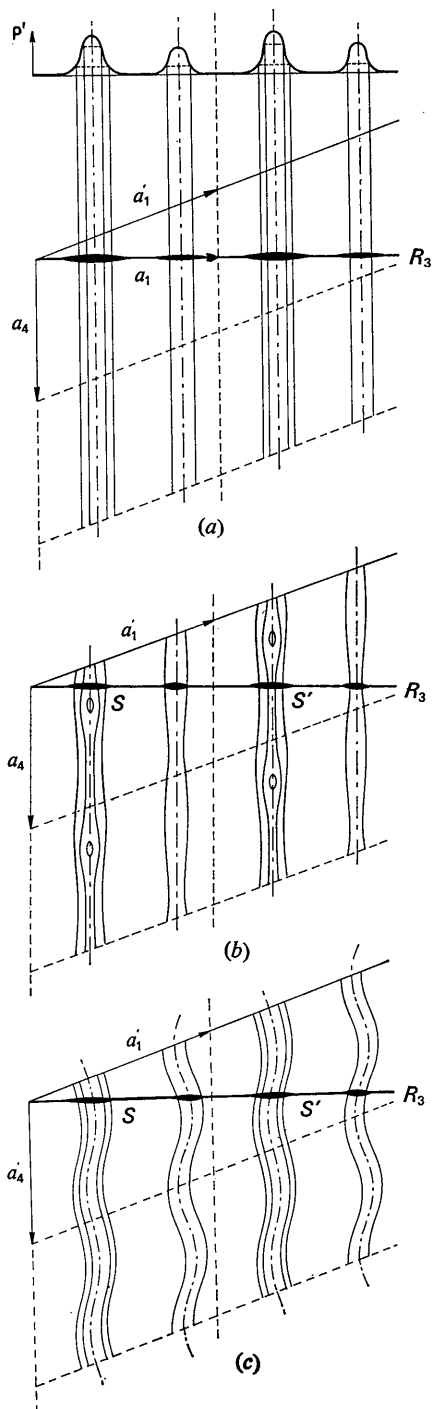


Fig. 4. Representation of structures by density ρ' in R_4 . Real atoms are indicated by bulging parts of the line representing R_3 . (a) Normal crystal. The top figure is a plot of the density in a cross section. (b) Structure with substitutional modulation. (c) Structure with displacive modulation.

5. Modulated crystal structures

So far, we have discussed in a rather abstract way a certain class of diffraction patterns, namely those with 'irrational' satellites. We shall show now that such patterns, as well as the properties of main reflexions mentioned in §2, can be explained by assuming the structure to be 'modulated' according to the following definition.

Modulated structures can be obtained from normal structures by modifying some parameter p of an atom at $(\bar{x}_1, \bar{x}_2, \bar{x}_3)$ (coordinates measured from the origin in a fixed unit cell) in such a way that it becomes a periodic function (not necessarily harmonic),

$$p(k_1\bar{x}_1 + k_2\bar{x}_2 + k_3\bar{x}_3)$$

with unit period. This function can be different for different atoms in the unit cell, but the constants k_i are the same for all atoms. The parameter p can be a fractional coordinate (displacive modulation), a magnetic moment (magnetic modulation), or an average occupational fraction in mixed or non-stoichiometric crystals (substitutional modulation). Several parameters can be modulated simultaneously as well. Such a crystal is a section through a four-dimensional structure of the type discussed before, provided each atom is represented in R_4 by a string in the overall direction of \mathbf{e}_4 . In each section $t = \text{constant}$ the string appears as an atom again. The value of its parameter p has to be

$$p(t + k_1\bar{x}_1 + k_2\bar{x}_2 + k_3\bar{x}_3)$$

in order to yield the above modulated structure in R_3 ($t=0$). According to equation (6) this is identical to $p(x_4)$, x_4 referring to the point in R_4 defined by the given values of t and \bar{x}_i .

Different types of modulation will now be discussed in some detail depending on the function p . Firstly, there is the trivial case in which p does not depend on x_4 at all [Fig. 4(a)]. There is no real modulation, and indeed the section $t=0$ is seen to be perfectly periodic.

A real case of modulation is that in which the atomic form factor of the μ th atom is given by a periodic function

$$f_\mu = f_\mu(x_4) \text{ or, in } R_3, f_\mu = f_\mu(k_1x_1 + k_2x_2 + k_3x_3) \quad (7)$$

but the fractional coordinates of each atom are fixed as in Fig. 4(b).

It has been shown to occur as *substitutional modulation* [e.g. by Jamieson, de Fontaine & Abrahams (1969) for $\text{Nd}_2(\text{MoO}_4)_3$; by Korekawa & Jagodzinski (1967) for labradorite]. The value of $f_\mu(x_4)$ must be understood as an average over a statistical distribution of two kinds of atoms in all unit cells in which the μ th atom has the same value of x_4 ; for instance, all cells connected by $q_2\mathbf{a}_2 + q_3\mathbf{a}_3$ (q_2, q_3 integer) if the vector \mathbf{b}_4 is parallel to \mathbf{b}_1 , while \mathbf{b}_2 and \mathbf{b}_3 are at right angles to \mathbf{b}_1 .

Helical magnetic structures too, can be described by equation (7). Here $f_\mu(x_4)$ is not an average; it is the actual factor by which the neutron scattering contribu-

tion is multiplied because of the local spin direction, and it is the same for all atoms with equal x_4 .

Finally, there is the case of *displacive modulation* as depicted in Fig. 4(c). Here it is assumed that the scattering factor is a constant for each atom, but the position is a periodic function of x_4 (cf. next section).

This kind of modulation has sometimes been assumed to occur as a corollary of substitutional modulation. Recently, however, several A_2BX_3 and A_2BX_4 compounds have been found to possess very pronounced satellites in their diffraction patterns (Dubbeldam & de Wolff, 1969; van den Berg, Tuinstra & Warczewski, 1972; Jacobi, 1973). In all these cases, only displacive modulation is possible.

The properties of the lattice B of main reflexions mentioned in §1 can be readily explained on the basis of the above types of modulation. They are all of them connected with the unique role of the \mathbf{a}'_4 base vector of the A' lattice, because this entails an equally unique role of the reciprocal lattice B conjugate to \mathbf{a}'_4 . The uniqueness of \mathbf{a}'_4 consists in that 'atoms' can be distinguished in the function q' as continuous strings, with periodic bends and/or densifications, but all of them continuing endlessly in the overall direction of \mathbf{a}'_4 , and each separated from all others.

The symmetry property (I) of B will be discussed in §7. Property (II), the integer unit cell content of the pseudo-translation lattice A , is a direct consequence of the string structure. The phase transitions [property (III)] are readily understood as transitions of q' from the types Fig. 4(b) or 4(c) to that of Fig. 4(a), making real translations from pseudotranslations. Property (IV), the conspicuously high intensities of main reflexions, can be understood if one realizes that their sum is proportional to the height of the origin peak in a Patterson map of the q' structure projected along \mathbf{a}'_4 . The string-like character of the 'atoms' in q' leads to high maxima in that projected density ρ_{av} (not to be confused with ρ , which is a section). This *average structure* is important in all attempts at structure analysis because it contains recognizable atom peaks.

In any other projection of q' , the density of a string is very much more smeared out. Only for exceptional displacements is the validity of property IV questionable. This could occur, e.g. if one were to describe helical-molecular crystals, such as ψ -sulphur (Tuinstra, 1967) as modulated structures.

6. Structure factor for modulated structures

As an example of the usefulness of the four-dimensional description, we shall derive the general formula for the structure factor. The formula for substitutional modulation as defined by equation (7) with $h_4 = m$:

$$F(h_1, h_2, h_3, m) = \sum_{\mu} \exp \{2\pi i(h_1x_1^{\mu} + h_2x_2^{\mu} + h_3x_3^{\mu})\} \cdot \int_0^1 f_{\mu}(x_4) \cdot \exp(2\pi imx_4) dx_4 \quad (8)$$

can be derived straightforwardly, but the dispersive type requires careful treatment.

The position of an atom P can be defined conveniently with respect to some average set of coordinates $\bar{x}_1, \bar{x}_2, \bar{x}_3$ so that for one 'string'

$$x_1 = \bar{x}_1 + u_1(\tau) \quad x_2 = \bar{x}_2 + u_2(\tau) \quad x_3 = \bar{x}_3 + u_3(\tau) \quad (9)$$

where u_1, u_2 and u_3 are functions of the x_4 coordinate τ of the undisplaced atom P_0 at the same value of t (Fig. 5).

From equation (6) we find:

$$\tau = x_4(P_0) = t + k_1\bar{x}_1 + k_2\bar{x}_2 + k_3\bar{x}_3 \quad (10)$$

and also

$$x_4(P) = t + k_1x_1 + k_2x_2 + k_3x_3 \\ = \tau + k_1u_1 + k_2u_2 + k_3u_3. \quad (11)$$

We are now ready to perform the Fourier transformation of q' . As a matter of fact, the contribution of an interval $d\tau$ of the string to the Fourier coefficient h_1, h_2, h_3, m is

$$fd\tau \cdot \exp \{2\pi i(h_1x_1 + h_2x_2 + h_3x_3 + mx_4)\}. \quad (12)$$

Again, we have replaced the satellite index h_4 by the more currently used symbol m .

Substitution of (9) and (11) in (12) yields

$$fd\tau \cdot \exp 2\pi i \{h_1\bar{x}_1 + h_2\bar{x}_2 + h_3\bar{x}_3 + (h_1 + mk_1)u_1 \\ + (h_2 + mk_2)u_2 + (h_3 + mk_3)u_3 + m\tau\}.$$

Performing the integration over τ , and recalling that only the u_i depend upon τ , we find the structure factor upon summing over the 'string index' μ

$$F(h_1, h_2, h_3, m) = \sum_{\mu} f_{\mu} \exp 2\pi i(h_1\bar{x}_1^{\mu} + h_2\bar{x}_2^{\mu} + h_3\bar{x}_3^{\mu}) \\ \times \int_0^1 d\tau \exp 2\pi i \left\{ \sum_1^3 (h_i + mk_i)u_i^{\mu} + m\tau \right\}. \quad (13)$$

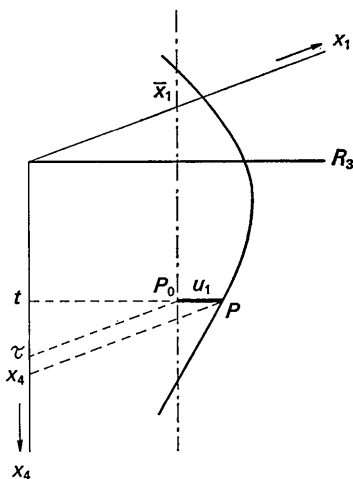


Fig. 5. Coordinates used in the derivation of the structure factor for dispersive modulation.

From this general equation, the well-known results for, e.g., sinusoidal displacements $u_i(\tau)$, can be readily obtained. If

$$u_i^{\mu} = U_i^{\mu} \sin(2\pi\tau - \alpha),$$

the integral in (13) equals

$$\exp \{im(\alpha + \pi)\} \cdot J_m[2\pi \sum_1^3 (h_i + mk_i)U_i^{\mu}].$$

7. Pseudo symmetry

Because of the unique rôle (explained in §5) of the vector \mathbf{a}'_4 , the direction of this vector must be invariant for all symmetry operations of the four-dimensional 'crystal' given by q' . Hence with respect to an orthonormal basis with \mathbf{e}_4 as the fourth vector, all operations of the point group assume the reduced form:

$$P' = \begin{pmatrix} P & 0 \\ 0 & \varepsilon \end{pmatrix} \quad (14)$$

with P a 3×3 matrix and $\varepsilon = \pm 1$.

Let us now look at the symmetry of diffraction intensities in reciprocal space. In R_4 , apart from the inversion centre created by Friedel's law, these intensities will have the point-group symmetry consisting of the operations (14). The main reflexions, situated on lattice B in the subspace R_3 , are imaged onto themselves by each P' , because R_3 is the hyperplane perpendicular to the invariant direction of \mathbf{a}'_4 . In R_3 , only the minor P of P' is effective. It follows that main reflexions have the matrices P plus inversion, if lacking, as their point group elements. The satellites can therefore only be permuted among themselves by each P , hence they have the same point group. Then the same holds for the entire diffraction image in R_3 , which explains property (I) of §1.

The actual crystal, though it has no three-dimensional periodicity, can have true symmetry elements and even true translations. In some cases, the ensuing group can be an adequate description of the symmetry in R_4 . For instance, if the latter is generated by a mirror hyperplane

$$\begin{pmatrix} 1 & & & \\ & -1 & & \\ & & 1 & \\ & & & 1 \end{pmatrix} \quad (15)$$

the actual crystal has a true mirror plane (and true translations perpendicular to it). An additional glide component of (15) is, however, enough to suppress the mirror plane. Also, if binary axes are added perpendicular to the mirror hyperplane, they have a chance zero to appear in any finite volume of R_3 . The same is true for the centres of symmetry, generated by (15) and the axes in R_4 . Therefore, the true symmetry of q in R_3 – if any – can also be a very poor residue of the full symmetry of q' in R_4 .

Accordingly, just as we have established a pseudo-translation character for the relation between atoms like S and S' in Fig. 4, we define pseudo-symmetry relations between atoms: such relations hold if the corresponding strings in ϱ' have a – true – symmetry relation in R_4 . In this way every symmetry operation of ϱ' in R_4 can be interpreted as a pseudo-symmetry relation of the atoms in R_3 . All these relations taken together can be called the ‘pseudo-symmetry’ of the modulated crystal, in the sense that they simplify its description – just as true crystal symmetry, they reduce the number of structure parameters. They also yield simple relations between symmetry-related structure factors.

Thus we find that point groups of (3+1)-reducible matrices like (14) may correspond to types of pseudo-symmetry of modulated crystals. According to a definition given by Janssen (1969), each (3+1)-reducible space group in R_4 corresponds to a generalized magnetic symmetry (GM group). In the following sections, we shall show that a much less simple relation exists between these space groups and ‘MS-groups’.

8. Modulated 3-dimensional structure (MS_3) point groups

We started from the condition that at least one k_i in (2) is irrational. As stated earlier, this means that:

(a) R_3 does not contain a three-dimensional sublattice of A' .

(b) \mathbf{e}_4 is not a lattice vector direction of B' .

Statements (a) and (b) are equivalent. According to a proposition by Janssen (1969, proposition 2), the vector representation of the four-dimensional point group has to be reducible as follows:

$$\left(\begin{array}{c|c} Q & 0 \\ \hline 0 & \varepsilon 0 \\ & 0 \varepsilon \end{array} \right) \quad (16)$$

with Q a 2×2 matrix and $\varepsilon = \pm 1$, in order to satisfy condition (a).

Thus only point groups with a ‘(2+2×1)-reducible’ vector representation can describe the symmetry of modulated structures. Instead of following the proof of the above generalized proposition, one may obtain this result more directly by using statement (b) in order to construct a point-group eigenvector different from \mathbf{e}_4 :

Introduce P'_+ and P'_- as symbols for point group elements (14) with, respectively, $\varepsilon = +1$ and $\varepsilon = -1$. Then the B' lattice vector \mathbf{b}'' :

$$\mathbf{b}'' = (\sum P'_+ - \sum P'_-) \mathbf{b}'_4$$

is an eigenvector of all the operators (14), because multiplication with any of them either leaves $\sum P'_+$ and $\sum P'_-$ the same or interchanges them. Now since $\mathbf{b}'_4 \mathbf{e}_4 = 1$, it follows from equation (14) that $\mathbf{b}'' \mathbf{e}_4$ is the order of the point group and therefore non-zero; so \mathbf{b}'' is not perpendicular to \mathbf{e}_4 . On the other hand \mathbf{b}'' cannot have the direction of \mathbf{e}_4 because of condition (b). There-

fore, for each point-group element, \mathbf{e}_4 and \mathbf{b}'' are different and non-perpendicular eigenvectors, so the corresponding eigenvalues must be the same: there exists an invariant plane containing $\mathbf{e}_4 = \mathbf{a}'_4$, as expressed by the form (16).

The point groups satisfying (16) can easily be enumerated since they correspond to the 31 colourless, grey or black-and-white plane point groups. It is much more convenient, however, to express them as colourless or black-and-white three-dimensional point groups (Table 1) as suggested by the matrix (14). These symbols at once yield the point group of the average structure by leaving out the primes, if any. They correspond to the 30 geometrical crystal classes belonging to systems I...VII in Table II of the report by Fast & Janssen (1968) and to systems 1, 2, 3, 4, 7, 8 and 9 in Table 1 of the paper by Wondratschek, Bülow & Neubüser (1971). For the first class of system III or 3, two different MS point groups are obtained, generated by

$$\begin{pmatrix} -1 & & & \\ & -1 & & \\ & & 1 & \\ & & & 1 \end{pmatrix} \text{ and by } \begin{pmatrix} 1 & & & \\ & 1 & & \\ & & -1 & \\ & & & -1 \end{pmatrix}$$

respectively.

Table 1. *The seven MS_3 systems and the 31 MS_3 point groups, expressed as three-dimensional colourless or black-and-white groups*

A prime (') added to a symmetry operation stands for simultaneous reversal of the sign of x_4 . The systems table contains: numbers according to FJ (Fast & Janssen, 1968) and to WBN (Wondratschek, Bülow & Neubüser, 1971); name as given by WBN; three-dimensional system of the average structure; k_i 's which do not vanish because of symmetry. The vector \mathbf{b}_4 is directed along the unique axis in system III (\mathbf{a}_3) and in the systems V, VI, VII, (\mathbf{a}_3). In system II it is perpendicular to the unique axis (\mathbf{a}_2), while in system IV it corresponds to the third place of the symbols in the point-group table.

System number	Name (WBN)	System of average structure	$k_i \neq 0$
FJ 1	Hexaclinic	Triclinic	k_1, k_2, k_3
II 2	Triclinic	Monoclinic	k_1, k_3
III 3	Diclinic	Monoclinic	k_2
IV 4	Monoclinic	Orthorhombic	k_3
V 9	Hexagonal monoclinic	Hexagonal	k_3
VI 8	Rhombohedral monoclinic	Trigonal	k_3
VII 7	Tetragonal monoclinic	Tetragonal	k_3

The following MS_3 -point-group symbols are identical with the point groups of the corresponding average structures, except for the primes ('), if any. Each point group is preceded by its FJ system number.

I 1	VI 3	III 2	VII 4	V 6
I 1'	VI 3'	III m'	VII 4'	V 6'
II 2'	VI 32'	III 2/m'	VII 4/m'	V 6/m'
II m	VI 3m	IV mm2	VII 4mm	V 6mm
II 2'/m	VI 3'm	IV m2'm'	VII 4'2'm	V 6'2'm
		IV 2'2'2	VII 42'2'	V 62'2'
		IV mmm'	VII 4/m'mm	V 6/m'mm

9. MS₃ space groups

The papers just mentioned also give details of Bravais lattices and of arithmetic classes (better known to crystallographers as the corresponding symmorphic space groups) of which they list a total of 76 for the above 30 point groups. The uniqueness of \mathbf{a}'_4 yields a considerable further differentiation, both in lattice types and in space groups.

Centring of a triclinic lattice in the point group generated by (15), for instance, can be performed by adding translations

$$\left(\frac{1}{2}\frac{1}{2}00\right) \text{ or } \left(0\frac{1}{2}0\frac{1}{2}\right). \quad (17)$$

In the context of four-dimensional symmetry groups, these two (and many other) types of centring are equivalent, just as *A*, *C* and *I* types of centring are equivalent in monoclinic lattices in *R*₃. For MS space groups, however, the shifts (17) cannot be regarded as equivalent since \mathbf{a}'_4 and \mathbf{a}'_1 have to be interchanged in order to transform the ensuing space groups into each other.

Similar arguments hold for translation components of space-group operations such as a glide added to the

mirror hyperplane (15). It is not the purpose of the present paper to enumerate all MS₃ space groups. By way of illustration we shall, however, give the complete list for the pseudo-symmetry groups of plane modulated structures.

10. The MS₂ space groups

The operations of pseudo-symmetry in plane modulated structures are 3 × 3 matrices of type (16), but with *Q* = ±1. This can be shown exactly as in §8. The ensuing point groups are those of the three-dimensional triclinic system and of the monoclinic system, five in all. Together, these groups yield 23 MS₂ space groups, cf. Table 2 and Fig. 6.*

Table 2. *The two MS₂ systems, the five MS₂ point groups and the 23 MS₂ space groups*

Each space group is given by the symbol of the corresponding three-dimensional symmetry, with *a* and *c* perpendicular to the binary axis or in the mirror plane, if any, and *c* as the unit vector *e*₃ of the extra (third) dimension. The groups in the last two columns are pairwise equivalent as normal space groups, but different as MS₂ space groups.

MS ₂ system	Plane system of average struct	<i>k</i> ₁ , <i>k</i> ₂	MS ₂ point group	
			Two-dimensional	Three-dimensional
Triclinic	Oblique	<i>k</i> ₁ , <i>k</i> ₂	1	1
			2'	I
Monoclinic	Orthogonal	<i>k</i> ₁	<i>m'</i> <i>b</i>	2
			<i>m</i> <i>a</i>	<i>m</i>
			<i>mm'</i>	2/ <i>m</i>

MS ₂ point group	MS ₂ space group	
1	<i>P</i> 1	
I	<i>P</i> I	
2	<i>P</i> 2, <i>P</i> 2 ₁	<i>A</i> 2 <i>C</i> 2
<i>m</i>	<i>P</i> <i>m</i>	<i>P</i> <i>a</i> <i>P</i> <i>c</i>
		<i>A</i> <i>m</i> <i>C</i> <i>m</i>
		<i>A</i> <i>a</i> <i>C</i> <i>c</i>
2/ <i>m</i>	<i>P</i> 2/ <i>m</i>	<i>P</i> 2/ <i>a</i> <i>P</i> 2/ <i>c</i>
	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> 2 ₁ / <i>m</i> <i>P</i> 2 ₁ / <i>c</i>
		<i>A</i> 2/ <i>m</i> <i>C</i> 2/ <i>m</i>
		<i>A</i> 2/ <i>a</i> <i>C</i> 2/ <i>c</i>

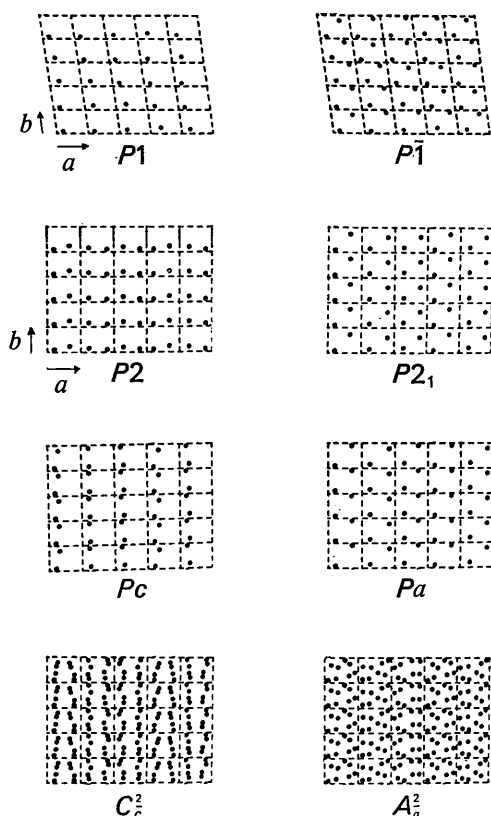


Fig. 6. Points in a general position in displacively modulated structures, illustrating some of the MS₂ space groups listed in Table 2. Note the difference between *Pa* and *Pc*, which are equivalent as three-dimensional space groups. For *P*1 and *P*I, *k*₁ = 0.194, *k*₂ = 0.252; for the others, *k*₁ = 0.382.

11. Modulated structures and superstructures

A modulated structure can approximately be described as a superstructure by substituting rational numbers for the irrational *k*_{*i*} (or *k*_{*i*}'s) in (2).† The question then arises whether such a description can account adequately for the pseudo-symmetry and pseudo-translations of the modulated structure.

The answer is that the superstructure has a wider scope with regard to pseudo-translations, but a nar-

* Programming, design and photography of Figs. 6 and 7 (oscilloscope displays of computer output) are due to Ir H. Overeijnder.

† Physical properties and symmetry of such superstructures have recently been treated by Aizu (1973) for the case of harmonic displacive modulation of a structure with space group *Pnam*.

lower range of symmetry groups. Looking at equation (5) in order to find the change in x_4 when going from a given atom in R_3 to a pseudo-translation-equivalent atom (*i.e.* with integers added to x_1 , x_2 and x_3), we observe that if the k_i are rational numbers, x_4 can change by multiples of a certain fraction only. This means that ϱ' [or $f_\mu(x_4)$ in (7), or $u_\mu^i(\tau)$ in (9)] need no longer be given as a continuous function of x_4 . Instead, it suffices to give its value at a finite number of x_4 values, separated by rational intervals. Thereby the continuity of the strings (which is the fundamental reason for the uniqueness of \mathbf{a}_4') is lost.

Successive values of the functions f_μ or u_μ^i can now be chosen without even a semblance of continuity. In this respect, one might say that superstructures offer wider possibilities than modulated structures. On the other hand, the range of available space groups is considerably smaller than that of MS_3 space groups. This is clearly illustrated by the case of plane modulated structures, *cf.* Table 2. Consider, for instance, a C -centred MS_2 space group. Since it occurs in the orthogonal system, there is just one non-zero k_i , say k_1 . In an approximative superstructure, k_1 will be replaced by a fraction ν/λ . Now the C centring of the MS group may reappear in the superstructure as a centred net (c_n). This requires that the centring translation ($\frac{1}{2}\frac{1}{2}0$) or one of its equivalents ($q_1 + \frac{1}{2}, q_2 + \frac{1}{2}, q_3$) lies in R_2 . Substitution in (5) yields:

$$(\nu/\lambda) (q_1 + \frac{1}{2}) = q_3$$

(here the extra dimension is the third, not the fourth). Since the q_i are integers, one finds the condition $\nu = \text{even}$ for $C \rightarrow c_n$.

The same reasoning yields the condition $\lambda = \text{even}$ for $A \rightarrow c_n$. Similarly, one finds that glide planes c or a in the MS_2 group can lead to glide lines g in the superstructure. Here the conditions for a glide component to lie in R_2 are $\lambda = \text{even}$ for $c \rightarrow g$; $\nu = \text{even}$ for $a \rightarrow g$. Accordingly, each symbol of the MS_2 group can be made to reappear in the superstructure by a judicious choice of λ and ν . The difference between A and C , or a and c , however, is lost. Moreover, MS_2 groups like Cc cannot be retrieved at all, because the parity conditions are contradictory (λ and ν cannot both be even), *cf.* Fig. 7.

Analogous situations occur when three-dimensional modulated structures are approximated by superstructures. The latter's space groups, again, are often ambiguous and/or incomplete portrayals of the actual pseudo-symmetry.

Conversely, MS groups could be helpful in describing certain features of superstructures not apparent from their space group.

12. Discussion

The present extension of the symmetry concept may appear sterile in view of the small number of satellite patterns discovered so far. Yet it has already been

applied successfully in order to explain special extinctions occurring in the diffraction pattern of Na_2CO_3 (de Wolff & van Aalst, 1972), which belongs to MS_3 point group $2'/m$ in system II (*cf.* Table 1). For K_2MoO_4 , the threefold \mathbf{b}_4 vector (van den Berg, Tuinstra and Warczewski, 1972) has recently been shown to be a result of twinning (Tuinstra & van Eldik, 1973). The actual modulated structure is not hexagonal; it belongs to system IV. For these and other compounds now under investigation, structure analysis would be next to impossible without the use of pseudo-symmetry groups. The number of examples is small indeed. However, there may exist many others yet unknown, seeing that some occur in a very narrow temperature interval, such as $163\text{--}164\frac{1}{2}^\circ\text{C}$ for the modulated phase of $NaNO_2$ (Hoshino & Motegi, 1967).

From a physical point of view, the static structure models proposed in this paper may seem unconvincing. However, one may also regard the artificial quantity t from §5 as time (as suggested to the author by Professor Janner), which makes \mathbf{a}_4' the time axis. Thereby the displacive modulation phenomenon becomes a wave very similar to a phonon, and each string-like atom in R_4 becomes the trajectory of an actual atom in space-time. In this concept, pseudo-translations and pseudo-symmetry operations are actual equivalence relations between atoms, *cf.* Janner (1972). Experiments are under way now to assess the existence of such a wave, the dynamic character of which cannot be expected to be observable by the usual methods of X-ray diffraction.

In this respect it should be remarked that thermal motion has expressly been disregarded in §§5 and 6. Work in progress on Na_2CO_3 has shown that thermal motion can be accounted for – at least in first approximation – by a Debye–Waller factor of the usual form. The fact that satellites usually vanish for rather small values of h_4 (Na_2CO_3 is an exception with some visible satellites up to $h_4 = 5$) probably has nothing to do with thermal motion. It can be explained just by assuming a

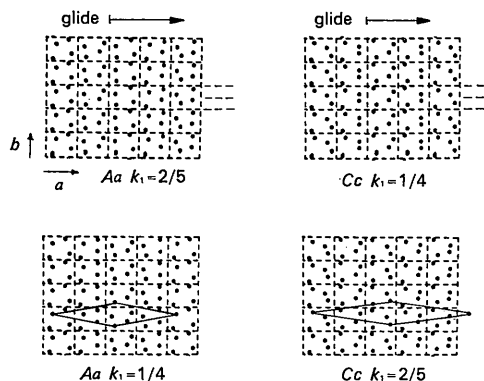


Fig. 7. Superstructures in two dimensions, obtained from MS_2 space groups Cc and Aa for $k_1 = \frac{1}{4}$ and for $k_1 = \frac{2}{5}$. These structures have either a centred net (lower figures) or a glide line (upper figures), but never the two together.

smooth nature of the modulation functions $f_u(x_4)$ or $u_i^u(\tau)$ from §5. As stated earlier, the continuity of these functions is an essential feature of modulated structures.

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The Symmetry of the Spin-Density Patterson Function

By D. B. LITVIN

Department of Physics, University of British Columbia, Vancouver, Canada

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Generalized space groups are defined to describe the symmetry of a spin-density Patterson function due to the spin-group (generalized magnetic group) symmetry of a spin arrangement. The information on spin arrangements obtainable from the generalized space-group symmetry of a spin-density Patterson function is discussed. It is shown that one cannot infer from the symmetry of the spin-density Patterson function the characteristic spin-group symmetry of a spiral spin arrangement, and an alternate method of doing so is given.

1. Introduction

The Spin-Density Patterson Function, abbreviated by SDPF, is defined as the Fourier transform of the intensity of unpolarized neutrons elastically scattered from a magnetic crystal (Wilkinson, 1968, 1973). This function has been used in determining the spin arrangements of Mn_2P (Yessik, 1968) and vivianite (Forsyth, Johnson, & Wilkinson, 1970). Wilkinson & Lisher (1973) have discussed the symmetry properties of the SDPF due to the magnetic-group symmetry of the spin arrangement and the information on spin arrangements obtainable from the SDPF. They have shown that for multi-domain crystals one may be unable to determine the orientation of the spins from the SDPF.

Spin symmetry groups have been defined to describe the symmetry of spin arrangements in magnetic crystals (Litvin, 1973; Litvin & Opechowski, 1974). The theory of spin symmetry groups is briefly reviewed in § 2. In § 3 we determine the symmetry of the SDPF due to the spin symmetry group of a spin arrangement. We show that space groups are inadequate to describe these symmetries of the SDPF and define a general-

ization of the space groups to do so. We then discuss the information on spin arrangements obtainable from the generalized space-group symmetry of the SDPF. In § 4 we discuss the information on spiral spin arrangements obtainable from the SDPF of single-domain magnetic crystals. We show that one cannot infer from the symmetry of the SDPF the characteristic spin symmetry of a spiral spin arrangement, and, as in the case of multi-domain crystals, one is unable to determine from the SDPF the orientation of the spins. An alternative method is given of determining the characteristic spin symmetry of a spiral spin arrangement from the SDPF. In § 5 we discuss the SDPF of multi-domain crystals and show that in general no symmetry information, neither magnetic space-group nor spin-group symmetry, on the spin arrangement can be inferred from the symmetry of the multi-domain SDPF.

2. Spin groups

Generalized magnetic groups called *spin groups* have been defined to describe the symmetry of spin arrangements in magnetic crystals (Litvin, 1973; Litvin &