finding differences from complete data sets with possible scaling errors.

Errors in assessing g values are probably not too critical in the sense that a sufficient number of reliably indicated values will usually be available. Any g not reliably estimated may simply be rejected. It will also be seen from Fig. 2 that even if the accuracy of $\Delta(\mathbf{h})$, $\Delta(\bar{\mathbf{h}})$ measurements is sufficient only to be in the correct quadrant of the diagram an error in θ [and hence in $\varphi(\mathbf{h})$] will result which will be quite acceptable by the standards of protein crystallography.

Although the determination of (g, θ) solutions has been explained in terms of the diagram in Fig. 2, in practice these can be deduced for any δ, $\Delta(\mathbf{h})$ and $\Delta(\bar{\mathbf{h}})$ from a simple computer program.

Tests need to be done to confirm or otherwise the effectiveness of this procedure. It is hoped to be able to report on such tests in due course.

Reference

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Dualistic Interpretation of the Symmetry of Incommensurate Structures

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Abstract

The symmetry of an incommensurately modulated structure may be described in terms of the basic structure (B) and the modulation pattern (M). This description contrasts with the superspace-group approach, in which the structure is defined in a space of dimension $3+d$, where d is the number of rationally independent modulation vectors. Space groups G_B and G_M are defined, consisting of symmetry operations of B and M which are simply interrelated. These groups together characterize the total symmetry; they lead to a classification which for $d = 1$ is equivalent to the superspace groups. With this dualistic approach, all symmetry operations can be based on symmetry elements in the space of the crystal, and the lattice types can be composed simply from those of G_B and G_M.

1. The dualistic approach

We shall exemplify the modulation phenomenon by a hypothetical two-dimensional compound OX, in which the X atoms are not modulated at all. The basic structure is orthogonal, plane group *pmm*, basic vectors a, b; $Z = 1$ (Fig. 1). We assume modulation of the O atoms with a wave vector $\beta\mathbf{b}^*$, where $\beta = b/\lambda$ is an irrational number, λ being the modulation wavelength. Then for a transverse displacive type of modulation, the crystal might look as in Fig. 2. The periodicity in the direction of $\mathbf{b}$ is lost – at least when 'periodicity' is taken in the usual sense. However, there is still perfect order in this direction – only there are two periods instead of one, *viz* b and λ.

The structure has, therefore, a dual character, being composed of the basic structure and a modulation pattern. The latter is indicated by the dashed wavy line in Fig. 2. Such a line becomes ambiguous as soon as a longitudinal component of the displacement is present (Fig. 3). In that case, a complete vector function is required, representing the displacement vector $\mathbf{u}$ as a periodic function of Y, the coordinate in the direction of $\mathbf{b}$. It is important to specify that $\mathbf{u}(Y_1)$ is the displacement of an atom which in the basic structure (not in the modulated one) has $Y = Y_1$.

In this way the modulated structure of Fig. 3, too, can be decomposed into two components: the basic structure and $\mathbf{u}(Y)$. Each of these is strictly periodic within the two-dimensional space considered here. Therefore the symmetry of the crystal can be

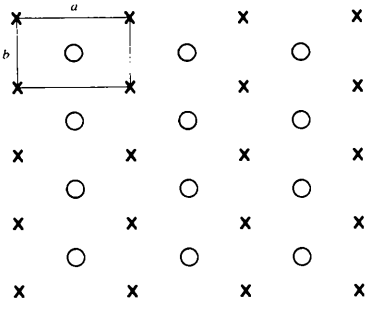

Fig. 1. Two-dimensional crystal XO, basic structure for the modulated structures in Figs. 2–5.

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described by the symmetry groups of the two components, both defined in the space of the crystal; this is what we mean by the dualistic approach.

2. Scope of dualistic *vs* superspace approach

The above dualistic description can be contrasted with a former approach (de Wolff, 1974; de Wolff, Janssen & Janner, 1981, referred to as I in this paper) in which a fully periodic representation of the structure is defined in a space of higher dimension, such that the actual modulated structure is a section through this 'supercrystal'. In the present example, the supercrystal is three dimensional and Fig. 2 or 3 is a plane section through it. A modulated crystal in three-dimensional space is the section made by that space (considered as a hyperplane in R_4) through a four-dimensional supercrystal or, if there are d independent modulation wave vectors, through a $(3+d)$-dimensional supercrystal. From the above-mentioned papers it follows that

(i) this supercrystal is an adequate representation of any kind whatsoever of a modulated structure yielding an incommensurate satellite-type diffraction pattern. Actually the structure factors of the diffracted reflections, indexed unambiguously by $3+d$ indices each, are the Fourier coefficients of the supercrystal's periodic density in $(3+d)$-dimensional space.

(ii) all conceivable symmetry operations of the modulated structure, including translations, correspond to elements of the supercrystal's full symmetry group in $(3+d)$-dimensional space. Accordingly the latter – the so-called superspace group – represents the full symmetry of the modulated crystal.

An explanation is called for with regard to the expression 'symmetry operation of the modulated structure' used in (ii). Consider for instance a 'lost' symmetry translation like **b** in Fig. 2. Such an operation can be retrieved as a symmetry operation if it is combined with a suitable shift of the modulation pattern. This pattern (the dashed line in Fig. 2 or the vector function in Fig. 3) simply has to be moved back over b in order to restore the original situation. An essential feature of incommensurate crystals is the fact that such a shift of the modulation pattern (not only by b but by any amount) leaves the structure virtually unaltered. In the superspace approach the shift is expressed by a change Δt of t, the modulation phase divided by 2π. In the above example this would amount to $\Delta t = b/\lambda = \beta$. The extra parameter t is in fact a coordinate defining the extra dimension used in that approach. If d modulation wave vectors are involved then also d extra parameters are required in accordance with the corresponding $(3+d)$-dimensional superspace groups. In the dualistic approach, on the other hand, the modulation pattern is considered separately from the basic structure; shift parameters, like the phase coordinate t, are not explicitly used. They enter only in the derivation of the key relation between corresponding symmetry operations of the two structural components (§ 5).

Both approaches deal with the same phenomenon, and it is the interpretation rather than the symmetry classification which differs. In particular, for $d = 1$,

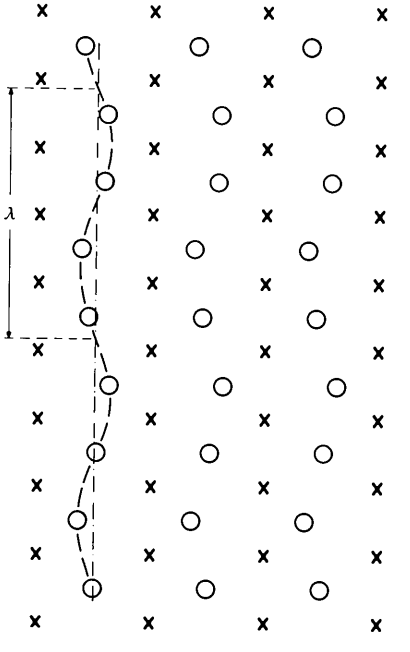

Fig. 2. Transverse displacive modulation of O atoms in XO. The modulation wavelength λ is shown at left.

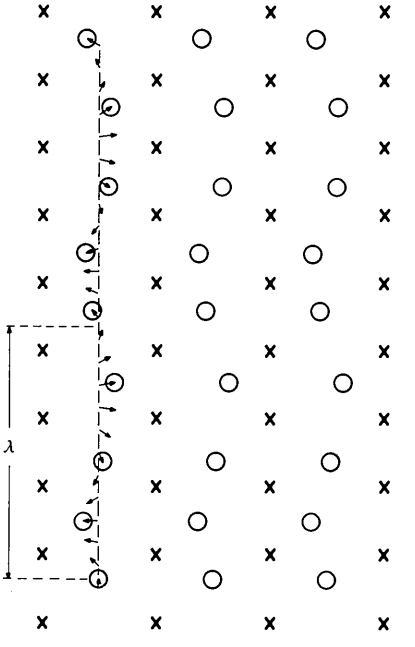

Fig. 3. General displacive modulation of O atoms in XO. The arrows indicate the modulation vector function $\mathbf{u}(Y)$, wavelength λ.

the dualistic classification is fully equivalent to the superspace groups. In § 10 we shall show that the dualistic interpretation is, to a certain extent, also applicable when $d = 2$ or 3. In view of the fact that the cases of modulation known so far have mostly $d = 1$, rarely $d = 2$, and very seldom $d = 3$, further examination of the dualistic approach seems worth while.

3. Axial modulation patterns

Let us assume that periodicity is 'lost' in just one dimension. In more exact terms, this means that periodicity of the modulated crystal still holds in one direction for a two-dimensional crystal, or in two directions (that is, in a plane) for a three-dimensional crystal. Moreover, we assume that this situation arises because of symmetry (for instance, in Fig. 2 both the basic structure and the modulation pattern have horizontal mirror lines; this leads to identical horizontal symmetry translations for both, which are valid for the actual structure as well). In that case we characterize it by the term 'axial modulation', and we define the direction perpendicular to the true translations as the axis of the modulation. In reciprocal space all reflections lie on a periodic array of lines parallel to this axis, and for the whole pattern the latter is an axis of rotational symmetry.

Because of the assumed symmetry, the axial direction is along a lattice vector of the basic structure. Modulation functions can, therefore, be defined on axial lines through rows of atoms, like the vertical ones in Fig. 2. We shall show now that the resulting *axial modulation patterns* are particularly useful in analysing the symmetry of an axially modulated crystal.

Modulation of incommensurate crystals is illustrated most clearly – without loss of generality as regards symmetry – when it affects a scalar quantity. Therefore, in Fig. 4 we show an occupation density modulation of the O atoms in our compound XO. The occupation density at a given atomic site is the value of the wave-like pattern at that site. The wave has been drawn in columns, though it could as well have been drawn as a wave covering the plane.

In Figs. 2–4, the difference between a full wave on the one hand and a set of identical functions defined on parallel lines on the other is utterly trivial. A striking aspect appears, however, when we look at Fig. 5. Here successive columns are shifted mutually by $\frac{1}{2}\lambda$, resulting in a centring of the modulation pattern's translation net. This centred rectangular net, symbol *oc*,* and the primitive (*op*) net of the basic structure together determine the translational properties of the modulated structure. In the superspace approach, the latter are expressed as a single-Bravais-lattice type in $(2+1)$-dimensional space. In dualistic terms, exactly the same properties are described by the ordered pair of the two-dimensional lattice types. This pair is written here as $^{op}_{oc}$, the upper line referring to the basic structure, and the lower one to the modulation pattern. The alternative *op/oc* will also be used.

In Fig. 5 it is seen that symmetry operations of the basic structure correspond to similar operations in the modulation pattern. Half of the vertical mirror lines are also present in the latter, while the other half become glide mirror lines. Horizontal mirror lines and centres of inversion are also present in both components, though of course they cannot coincide because of the incommensurability.

One more example will now be given, because the special positions of X and O in Figs. 2–5 prevent an adequate appreciation of the space-group relations. Fig. 6 shows a two-dimensional compound Xp_2 with space group *pgg*, all atoms X on inversion centres and atoms p in a general position. The axial modulation pattern corresponds to an occupation density modulation of p atoms only. The axis of modulation is vertical, so the pattern consists of vertical lines through p atoms, as well as a periodic modulation function on each line. These functions are of the most general asymmetric type. Thereby it is possible to

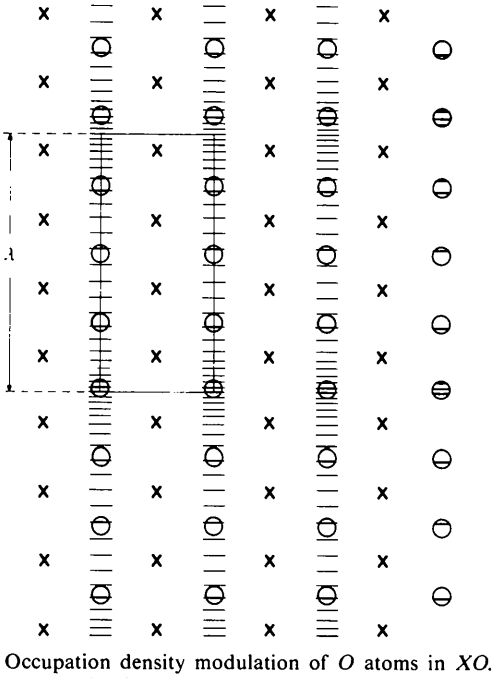

Fig. 4. Occupation density modulation of O atoms in XO. The scalar modulation function is indicated by the density of hatching on vertical strips, each of which represents an axial element of the modulation pattern. The actual function values at the sites of O atoms are shown at right in the same way. The rectangular unit cell of the modulation pattern has the edges a, λ.

* In these Bravais-lattice-type symbols, introduced in *International Tables for Crystallography* (1983), the usual centring letter (*p*, *c*, *P*, *C*, ...) is preceded by a letter indicating the crystal family as follows: *a*(triclinic), *m*(onoclinic, oblique), *o*(rthorhombic, rectangular), *t*(etragonal, square), *h*(exagonal) and *c*(ubic).

show that horizontal glide mirror lines occur not only in the basic structure but also in the modulation pattern, resulting in reversed scalar functions for b and d as compared with p and q. The reversal is necessary if a horizontal mirror is to be conserved as an element of the point group of the modulated structure as a whole, *cf.* § 5.

4. *q* equivalence

In Fig. 6 we observe that the vertical glide mirrors of the basic structure are replaced by mirror lines in the modulation pattern, which therefore has the space group *pmg*. As an alternative, one could think of vertical glide mirror lines in the modulation pattern. The latter would then assume the same symmetry, *pgg*, as the basic structure. It turns out, however, that the combined symmetries which we shall indicate provisionally (*cf.* § 7) by

$$\begin{matrix} pgg \\ pmg \end{matrix} \quad \text{and} \quad \begin{matrix} pgg \\ pgg \end{matrix} \tag{1}$$

(where again the upper line refers to the basic structure) are equivalent in a special sense which we shall indicate by the term *q equivalent.* The term applies to different pairs of space groups, like those in (1), which can describe the symmetry of exactly the same structure – though with different values of λ (or of the modulation vector $\mathbf{q}$, whence the name). For (1), q equivalence is shown as follows. In Fig. 6 the modulation functions for both p and q atoms can be written – because of the vertical mirrors in the modulation pattern – as the same Fourier series:

$$f(y) = \sum A_n \exp(2\pi niy/\lambda). \tag{2}$$

Supposing the p atoms to lie at $y = mb$, m integer, we obtain for them

$$f(mb) = \sum A_n \exp(2\pi nimb/\lambda) \tag{3}$$

and for the q atoms at $y = (m+\frac{1}{2})b$:

$$f(m+\tfrac{1}{2})b = \sum A_n \exp\{2\pi ni(m+\tfrac{1}{2})b/\lambda\}. \tag{4}$$

Now if we replace λ by λ' defined by

$$1/\lambda' = 1/\lambda - 1/b \tag{5}$$

while retaining the mirror lines, (3) is clearly not changed in value, but (4) becomes

$$\begin{aligned} &\sum A_n \exp\{2\pi ni(m+\tfrac{1}{2})b/\lambda'\} \\ &\quad = \sum A_n \exp\{2\pi ni(m+\tfrac{1}{2})b/\lambda - \pi ni\} \\ &\quad = f\{(m+\tfrac{1}{2})b - \lambda/2\}. \end{aligned} \tag{6}$$

This would also have been the result for q atoms if we had assumed a glide mirror in the original modulation pattern with wavelength λ. Hence we have shown that this glide mirror yields exactly the same structure as a true mirror for the pattern with wavelength λ'.

The same reasoning can be used to show that q equivalence may occur whenever a symmetry operation of the basic structure contains an intrinsic translation equal to half the axial repetition period, such as the translation $\frac{1}{2}\mathbf{b}$ contained in the glide reflections treated above. In three dimensions, fractional translations of $\frac{1}{4}$, $\frac{1}{3}$ or $\frac{1}{6}$ occur, and these can give rise to q equivalence as well.

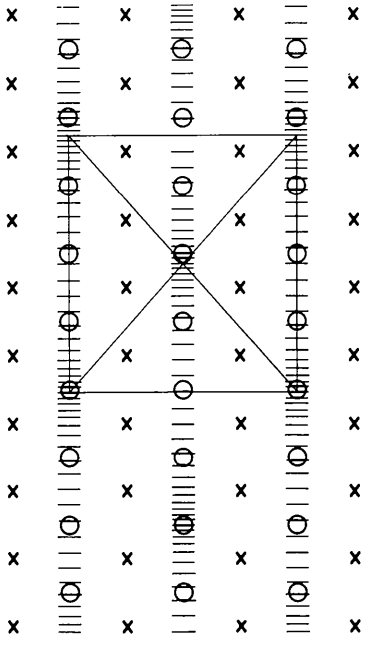

Fig. 5. As Fig. 4. but with shift of $\frac{1}{2}$ between successive axial elements, resulting in a centred lattice of the modulation pattern, as shown by its unit cell, edges $2a$, λ.

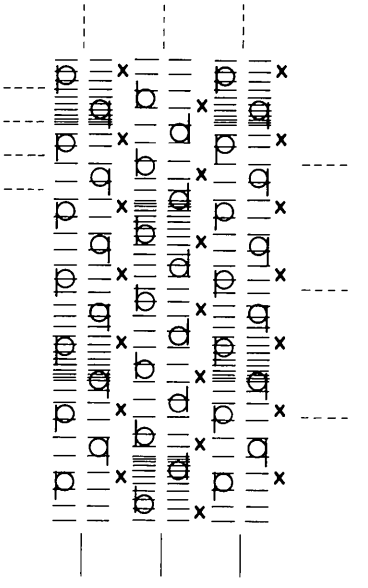

Fig. 6. Two-dimensional compound Xp_2. Basic structure: plane group *pgg*, glide lines indicated at left and at the top. Modulation pattern of axial scalar modulation: plane group *pmg*, *g* and *m* lines indicated at right and below.

Moreover, important cases of q equivalence arise when the Bravais lattice of the basic structure contains centring translations with a fractional component in the axial direction. This already occurs in two dimensions. Here a basic structure with a centred orthogonal lattice apparently gives rise to two different Bravais types

$$\begin{matrix} oc \\ op \end{matrix} \quad \text{and} \quad \begin{matrix} oc \\ oc \end{matrix} \tag{7}$$

but the equations (2–6) used above for atoms related in the basic structure by a glide reflection are equally valid for atoms related by the centring translation in (7). Hence the two types (7) are q equivalent. The mutual disposition of the unit cells is indicated schematically in Fig. 7; see also next section.

q equivalence is by no means restricted to the dualistic approach. In (I) it is mentioned in the definition of superspace-group types ('**q** is determined ... up to a reciprocal basic lattice vector', p. 630), and it has been one of the main equivalence criteria used in eliminating superfluous entries in (I), Table 2. It has been treated explicitly here because it is often encountered in practice, whereas it is more difficult to recognize than other causes of equivalence.

5. The two dualistic principles

With regard to axial modulation patterns in general, there is an apparent complication when the axial lines through two different atoms coincide, whereas the two modulation functions differ. For instance, if there had been horizontal mirror lines in Fig. 6, instead of glide lines, p and b atoms would sit on the same vertical line. In such cases the two coinciding axial lines, each with its own modulation function, must be considered as separate entities. We shall call a line plus the modulation function defined upon it an *axial element* of the modulation pattern. So, in the above case, p and b atoms still have different axial elements. Thereby we establish the first principle: that *each atom of the basic structure belongs to just one axial element of the modulation pattern.* (The reverse is not true: atoms can share the same axial element, though this happens only if in the basic structure they are related by an axial symmetry translation.)

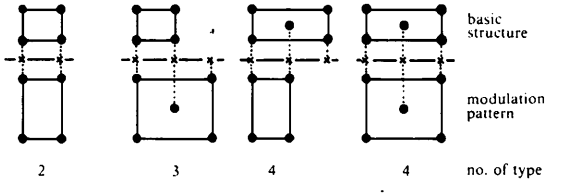

Fig. 7. Two-dimensional lattices of G_B and G_M showing identical projections (crosses) as required by (10). The numbers are those of the lattice types in Table 1*A* as well as *B*.

For the sake of simplicity, all considerations in this paper refer to point atoms (or spherically symmetrical atoms) only. However, they apply equally well to continuous charge distributions; in that case, volume elements in the basic unit cell take over the rôle of atoms and there is a separate density modulation function for each volume element.

Now we introduce the second principle. It is based upon the essential feature of incommensurate crystals mentioned in § 2, *viz* the fact that they are virtually invariant for any axial translation, t_i, applied to the modulation pattern. In this sense, any symmetry operation of the modulated crystal can be described as a symmetry operation g_B of the basic structure (but applied to the actual modulated structure!) supplemented by such a shift t_i of the modulation pattern alone. Since this combined operation is required to be a symmetry operation of the actual crystal, it also transforms the modulation pattern into itself. Therefore the latter has a symmetry operation of its own:

$$g_M = g_B t_i. \tag{8}$$

Here the index i(nvariant) refers to the invariance of the structure for t_i, in the above sense. It is used rather than a(xial), since exactly the same reasoning applies to planar and to spatial modulations. In the planar case, the translation t_i is parallel to the plane of the modulation just as here it is parallel to the axis; for spatial modulation, t_i is arbitrary.

The operations g_B for which (8) allows a corresponding g_M form a group G_B. They obviously belong to the basic structure's space group S_B, which can (but need not) be identical with G_B. Similarly, the operations g_M for which (8) is valid form the group $G_M \subseteq S_M$, S_M being the space group of the modulation pattern. Relation (8) requires that the operations g_B and g_M have identical point-group components. Accordingly, these form *identical point groups* $K_B = K_M = K$. All operations of K clearly must transform the axis of the modulation in itself.

Equation (8) remains valid – with a different t_i – if g_M is supplemented by any axial translation contained in G_M, or g_B by any axial translation of G_B. The groups T_λ and T_c formed by these axial translations $m\lambda$ and nb (m, n integers) are invariant subgroups of G_M and G_B, respectively; and it is T_c and its cosets in G_B which through (8) are related 1:1 to T_λ and its cosets in G_M.

To illustrate the fact that G_B need not contain all symmetry operations of the basic structure, it suffices to imagine that the latter has tetragonal symmetry in Figs. 2–5, with $a = b$. Then it has symmetry rotations over $\pi/2$, but these cannot occur in G_M since they do not conserve the axial direction. Hence such operations cannot fulfil (8). The full space groups S are not needed any further since the symmetry of the modulated crystal is determined completely by G_B and G_M.

Finally, it should be noted that the relation (8) is equivalent to relations like

$$p'(x) = p\{\varepsilon(x-\tau)\} \tag{9}$$

[equation (3.15) in (I), or equation (14) in de Wolff (1977)] describing the transformation of a scalar modulation function with unit period, $p(x)$, in terms of the parameters ε and τ of a superspace symmetry operation. Here τ is related directly to g_M, *cf.* § 7. The parameter ε is +1 or −1 for conservation or reversal of axial vectors; it does not appear in (8) because it is implicit in both g_B and g_M.

6. Lattice types for axial modulation

Since for axial modulation the groups G_B and G_M belong to the same geometric class defined by their common point group K, they also belong to the same system. We can therefore classify axially modulated three-dimensional structures as belonging to the monoclinic axial system, the orthorhombic axial system *etc.*, without ambiguity.

With regard to symmetry translations t_B and t_M contained in the lattices Γ_B and Γ_M of G_B and G_M and related by (8), projection in the direction of t_i yields

$$t_{Bi} = t_{Mi}, \tag{10}$$

$t_{Bi}(t_{Mi})$ being the projection of the translation vector of $t_B(t_M)$ along the modulation axis. Equation (10) amounts to saying that the lattices Γ_B and Γ_M, thus projected, coincide completely. This affords such a strong tie between Γ_B and Γ_M that most of their possible combinations are fully characterized by merely stating the Bravais type of each. Only for the orthorhombic system a further specification is needed, namely if single-face centring occurs.

In two dimensions, axial modulation occurs in the orthogonal system only. (The reason given in § 5 for excluding the quadratic one is also valid for the trigonal–hexagonal system. Oblique plane patterns can have planar modulation only, *cf.* § 8.) Of the four combinations allowed by the orthogonal net types *op* and *oc*, two are *q* equivalent as we saw in § 4. Fig. 7 gives the mutual disposition of the unit cells for each combination. It shows that the conventional basis vectors of Γ_B perpendicular to the modulation axis may differ from those of Γ_M. Also indicated in Fig. 7 is, for each combination, the lattice-type number listed together with the symbols in Table 1. The *q*-equivalent lattices belong to the same type, so in Fig. 7 they receive the same number.

In three dimensions, cubic symmetry of G_B is incompatible with axial modulation. Triclinic space groups G_B lead to spatial modulation, *cf.* § 8. The lattice types for the remaining systems are listed in Table 1. Within a given system all types may combine, except for the orthorhombic system. For instance, if the modulation axis is **c**, an orthorhombic C-centred lattice for G_B cannot be combined with a primitive lattice for G_M because the axial projections of these two lattices can never be made identical. Only if the type of the second is either *oC* as well or *oI* is coincidence of the projections possible, as indicated in Fig. 8. Within each of the five sets of lattice types shown in Fig. 8, all pairwise combinations occur in Table 1 except for *oP*/*oB* which is an obvious equivalent of *oP*/*oA*.

Some data from Table 1 of (I) and of Janssen, Janner & de Wolff (1980) are cited in our Table 1, in order to make reference easier. This also shows an advantage of the dualistic notation, *viz* the possiblity to derive the complete translational symmetry from the symbol. The capital prefixes used in (I), on the other hand, are often without meaning. From a dualistic point of view, some are confusing, *e.g.* *A* for a *B*-centred lattice of G_M and *vice versa*. Dualistic symbols for orthorhombic lattices can be adapted to any setting provided that the modulation axis label is specified.

7. Derivation of G_M from the superspace-group symbol for axial modulation

In (I), two-line superspace-group symbols have been defined. The upper contains the symbol of G_B. The axial direction can be derived from a clue contained in the lower line. Together with the capital prefix,

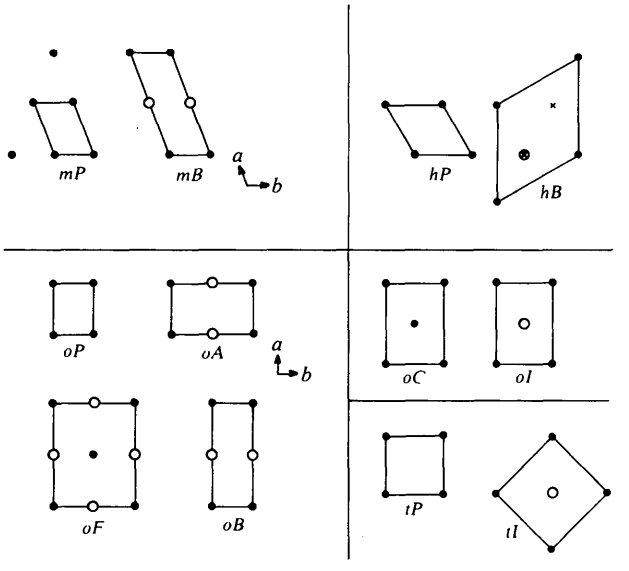

Fig. 8. Three-dimensional lattices with identical axial projections as required by (10), for axial modulation along **c**, perpendicular to the plane of the paper. (*a*) Monoclinic; (*b*) orthorhombic *P*, *A*, *B*, *F*; (*c*) orthorhombic *C*, *I*; (*d*) tetragonal; (*e*) hexagonal-trigonal. Open circles: lattice nodes at a level halfway between the levels of black circles; for *hR* the nodes at $\pm\frac{1}{3}$ are shown. Within each of the five groups, any pair of lattice types can combine so as to satisfy (10); this can be checked in Table 1.

Table 1. *Dualistic symbols for the lattice types of modulated crystals with* $d = 1$

Columns 1, 2, 3: *number, modulation vector (including rational centring components) and capital prefix of superspace symbol, as given in the reference in the sub-heading. Column* 4; *dualistic symbol as defined in* § 3; q-equivalent lattice types for G_M are shown between parentheses and the one-dimensional type by u. Column 5: crystal family of G_B, and type of modulation.

A	Two-dimensional crystals, *cf.* Janssen, Janner & de Wolff (1980), Table 1			
1	$\alpha\beta$	P	mp/u	oblique planar
2	0β	P	op/op	rectangular axial
3	$\frac{1}{2}\beta$	A	op/oc	
4	0β	P	$oc/op(c)$	
B	Three-dimensional crystals, *cf.* (I), Table 1			
1	$\alpha\beta\gamma$	P	aP/u	triclinic spatial
2	$\alpha\beta 0$	P	mP/op	monoclinic planar
3	$\alpha\beta\frac{1}{2}$	C	mP/ob	c unique
4	$\alpha\beta 0$	P	$mB/op(b)$	
5	00γ	P	mP/mP	monoclinic axial
6	$\frac{1}{2}0\gamma$	A	mP/mB	c unique
7	00γ	P	$mB/mP(B)$	
8	$0\frac{1}{2}\gamma$	B	mB/mA	
9	00γ	P	oP/oP	orthorhombic axial
10	$0\frac{1}{2}\gamma$	B	oP/oA	modulation axis: c
11	$\frac{1}{2}\frac{1}{2}\gamma$	W	oP/oF	
12	00γ	P	$oI/oC(I)$	
13	00γ	P	oC/oC	
14	100	L	oC/oI	
15	00γ	P	$oA/oP(A)$	
16	$\frac{1}{2}0\gamma$	A	$oA/oB(F)$	
17	00γ	P	$oF/oP(F)$	
18	10γ	L	$oF/oB(A)$	
19	00γ	P	tP/tP	tetragonal axial
20	$\frac{1}{2}\frac{1}{2}\gamma$	W	tP/tI	
21	00γ	P	$tI/tP(I)$	
22	00γ	P	$hR/hP(R)$	hexagonal axial
23	$\frac{1}{3}\frac{1}{3}\gamma$	R	hP/hR	
24	00γ	P	hP/hP	

these data can be used to find from Table 1 the lattice type of G_M. The clue just mentioned consists in looking at the generators in the upper-line G_B symbol below which the character $\bar{1}$ appears in the lower line. These generators reverse all axial vectors, as expressed by $\varepsilon = -1$ in (I); the others ($\varepsilon = +1$) conserve them, and together they indicate the direction of the modulation axis.

Now it may sometimes be desirable to derive the complete space group of G_M, the lattice type having been found already by the means just indicated. It suffices to find operations of G_M related by (8) to those of G_B that appear in the upper line. For a generator g_B with $\varepsilon = -1$, multiplication by t_i as required by (8) merely shifts the symmetry element but does not otherwise change the operation. Therefore it should be given the same character as in G_B, except when the non-axial basis vectors of G_B and G_M differ. In the latter case, the character must be determined by taking the mutual disposition of the two lattices into account (Fig. 8).

Generators g_B with $\varepsilon = +1$ are represented on the lower line of the superspace-group symbol by a character depending on τ, $\tau\lambda$ being the axial component of the intrinsic translation t_{int} contained in the corresponding generator of G_M. This character is 1, s, t, q or h for $\tau = 0, \frac{1}{2}, \frac{1}{3}, \frac{1}{4}$ or $\frac{1}{6}$. Because of (8), the other – transverse – component of t_{int} equals that of the intrinsic translation of the G_B generator. For instance, if that generator in G_B is an **a**-glide reflection in the a, c plane, the modulation axis being **c**, this transverse component is $\frac{1}{2}\mathbf{a}$. If, further, the letter s appears below the a, then $\tau = \frac{1}{2}$, so the axial component is $\frac{1}{2}\lambda$. The two components together define an n-glide reflection in the a, c plane in G_M, provided that **a** is a basis vector for G_M as well.

Once the group G_M is known as well as G_B, from their two symbols a dualistic two-line symbol of the superspace group could be composed as was done above, in (1). Such symbols are however, incomplete unless they include information about the orientation of the modulation axis. Example: for a modulation axis along **b**, $G_B = A2/m$ and $G_M = C2/m$, the superspace group might be described in a dualistic way as, for instance,

$$\begin{matrix} mA\ 2/m \\ yC\ 2/m, \end{matrix} \qquad (11)$$

writing yC instead of mC to indicate that the y axis is the modulation axis. However, the two space groups in (11) with their very unequal unit cells (*cf.* Fig. 9) are a serious risk when one deals with coordinate values. Therefore, symbols like (11) should be regarded as *ad hoc* symbols, to be used with great care.

8. Planar and spatial modulation, $d = 1$

The concept of axial modulation is useless in the case of *oblique two-dimensional* crystals, because these cannot have axial symmetry. Then one may as well consider the whole plane, plus the full modulation wave function defined upon it for a given atom, as the *planar element* assigned to that atom (and also to all translation-equivalent atoms). The modulation pattern now consists of all these overlapping planar elements. It has a one-dimensional lattice, of which there is only one type; hence, there is also just one lattice type in the oblique planar system in two

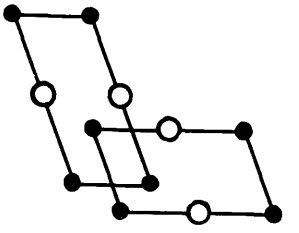

Fig. 9. The axial projections of the lattice mA for G_B, and mB for G_M in the symmetry group (11), to show the very different unit cells which may occur.

dimensions for $d = 1$. The two symmetry groups – with and without an inversion centre – are equally obvious.

In three dimensions planar modulation with $d = 1$ occurs in the *monoclinic planar system.* There is normal periodicity in the direction of the unique axis of the basic structure, and the planar element for a given atom is perpendicular to it, while it passes through the atomic site, see Fig. 10. It is shared by all translation-equivalent atoms lying in the plane of the element. The set of all these parallel planes, each with its one-dimensionally periodic modulation function, constitutes the modulation pattern. Since all 'ripples' are parallel, the pattern is two-dimensionally periodic and orthogonal, the basis vectors being directed along the wave normal and along the unique axis **c**. Therefore it can have either *op* or *ob* as its lattice type. Together with the types *mP* and *mB* allowed for the basic structure, we obtain four combinations, shown in Table 1. The mutual disposition is again given by Fig. 7, which now should be seen as a projection in a direction parallel to the ripples. This is so because the mutual disposition of the lattices Γ_B and Γ_M is still dictated by (10) since the key relation (8) remains valid. Only t_i now is some translation parallel to the plane of modulation; hence t_{Bi} and t_{Mi} are projections on the normal to that plane. Accordingly, the coincident projected lattices of G_M and G_B are one-dimensional, that is, they consist merely of equidistant points on that normal.

Planar modulation with $d = 1$ can occur in the above systems only. Likewise, *spatial modulation* with $d = 1$ occurs only in the *triclinic spatial system.* Strict periodicity now happens in no direction at all (except by chance), so the elements are one-dimensionally periodic functions defined in the full space, one function for every atom in the triclinic basic unit cell. The fact that they overlap completely must be interpreted in the same way as the overlap of lines which can happen for axial modulation, *cf.* § 5. There is again just one lattice type, and there are two symmetry groups (with and without inversion).

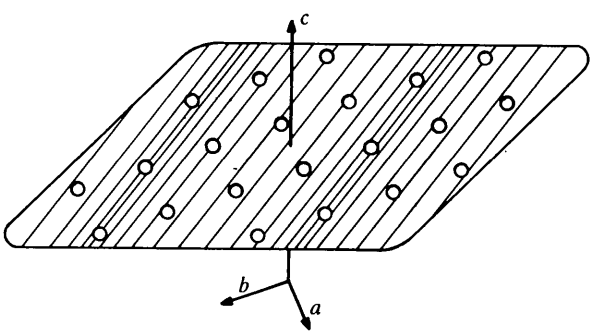

Fig. 10. Planar element for an atom in a monoclinic structure with planar modulation, $d = 1$. The modulation wave vector is perpendicular to **c**.

9. Planar and spatial modulation, $d = 2$ or 3

In both two and three dimensions planar modulation can occur also for $d = 2$. Then the planar element bears a modulation function periodic in two dimensions. The corresponding lattice types and symmetry groups for two-dimensional crystals have been listed (along with those for $d = 1$) by Janssen, Janner & de Wolff (1980) as superspace groups; their dualistic interpretation follows the lines set out in § 8. This will not be detailed here, but it should be mentioned that (8) still holds in the way described above for $d = 1$. For spatial modulation, t_i is arbitrary so then (8) merely expresses the identity of the point groups K_B and K_M; this holds also for $d = 1$.

No symmetry-group listing exists for three-dimensional crystals with either planar modulation and $d = 2$, or with spatial modulation and $d = 2$ or 3. Their lattice types can be derived from the comprehensive listing of superspace lattices by Janner, Janssen & de Wolff (1983). As we stated before, structures in these categories with $d > 1$ are not often met in practice. Nevertheless some do exist, such as the mineral wustite analyzed by Yamamoto (1982), where the symbol of a possible superspace group

$$P\begin{matrix} Fm3m \\ Pm3m \end{matrix}$$

could be written in the following dualistic way, analogous to (11):

$$\begin{matrix} cFm3m \\ xyzPm3m, \end{matrix}$$

using *xyz* to indicate the spatial character of the modulation.

10. Discussion

A dualistic interpretation of a given modulated structure in terms of two periodic component structures is not possible when $d > 3$, whereas it is always possible when $d = 1$. So the question remains to what extent that interpretation is applicable for a number $d = 2$ or 3 of independent modulation vectors. It can be answered by the statement that a dualistic interpretation in terms of the categories of § 9 exists provided that (*a*) no two modulation vectors are collinear; (*b*) no three are coplanar [disregarding any rational components, like $\frac{1}{2}$ in $\frac{1}{2}0\gamma$, as discussed in § 5 or (I)] because in these cases it is not possible to define the modulation pattern element as a periodic function on a line or plane or in space.

No such restrictions hold for the superspace approach. For example, three Bravais types in two dimensions for $d = 2$ (Janssen, Janner & de Wolff, 1980) violate condition (*a*) by having collinear modulation vectors. Nor is that condition always fulfilled in practice. The known exceptions occur for matrix structures with channels, penetrated by more than

one system of chains in the channels. If the chains are incommensurable both with the matrix and with each other, then there is a modulation vector for each system, and these vectors violate (*a*). In such cases, an interpretation similar to the dualistic one is possible only by allowing two or more modulation patterns – each of them periodic in space – to act on the same basic structure.

Nearly all known modulated structures, however, can straightforwardly be interpreted in a dualistic way. The type of modulation (displacement or scalar density variation) plays no role for the symmetry; displacements have to undergo the symmetry operations of G_M as vectors. Thus it is possible to visualize the symmetry of a modulated structure just as easily as that of a normal one. In particular, the lattice and all symmetry elements of G_M can be pinpointed in the direct space of the crystal. If a drawing is desired, it suffices to superimpose the symmetry element figures in *International Tables for X-ray Crystallography* (1969) for G_M and G_B. The graphic representation proposed earlier by the author (de Wolff, 1981) comes very close to such a superposition.

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Nomenclature and Generation of Three-Periodic Nets: the Vector Method

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Dedicated to Professors M. J. Buerger and A. F. Wells on the occasions of their 80*th and* 70*th birthdays*

Abstract

Three-periodic nets are connected graphs which permit embeddings having a threefold periodicity. To many crystal structures such nets can be meaningfully assigned and used to express the topology of the structures. It is shown that such a net can be fully characterized by a finite graph in which the edges are labelled in a suitable way. The reversal of the process of assigning a labelled finite graph to a given net can be used to generate nets of real and hypothetical crystal structures in a systematic fashion.

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1. Introduction

This exposition deals with the various ways in which the atoms in crystal structures may be connected to each other. For such a study it is convenient to use the language and the tools of graph theory. The relation between a crystal structure and a graph is established by identifying the atoms of the structure with the vertices of the graph and the chemical bonds with the edges. Such an assignment is straightforward for structures in which the bonds are largely covalent. For structures in which ionic, metallic or van der Waals bonds dominate, the method to be discussed may still be useful, but requires an assignment of

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