

9. BASIC STRUCTURAL FEATURES

that two such groups are arithmetically equivalent if there is a basis transformation for the reciprocal-vector module, which transforms main reflections into main reflections and satellites into satellites and which transforms one of the matrix groups into the other. The arithmetic classes are determined by the arithmetic equivalence class of the three-dimensional group K_E [*i.e.* by $\Gamma_E(K)$] and by the components of the modulation wavevector with respect to the corresponding reciprocal-lattice basis. This is because the elements ε are fixed by the relation

$$R\mathbf{q} \equiv \varepsilon\mathbf{q} \text{ (modulo reciprocal-lattice vectors of the basic structure).} \quad (9.8.1.22)$$

Note that these $(3 + 1)$ -dimensional equivalence classes are not simply those one obtains in four-dimensional crystallography, as the relation between the higher-dimensional space V_s and the three-dimensional physical space V plays a fundamental role.

The embedded structures in four dimensions have lattice periodicity. So the symmetry groups are four-dimensional space groups, called *superspace groups*. The new name has been introduced because of the privileged role played by the three-dimensional subspace V . A superspace-group element g_s consists of a point-group transformation (R, ε) and a translation (\mathbf{v}, Δ) . The action of such an element on the four-dimensional space is then given by

$$g_s r_s = \{(R, \varepsilon)|(\mathbf{v}, \Delta)\}(\mathbf{r}, t) = (R\mathbf{r} + \mathbf{v}, \varepsilon t + \Delta). \quad (9.8.1.23)$$

It is important to realize that a superspace-group symmetry of an embedded crystal induces three-dimensional transformations leaving the original modulated structure invariant. Corresponding to (9.8.1.23), one obtains the following relations [cf. (9.8.1.13)]:

$$\mathbf{u}_{j'}[\mathbf{q} \cdot (\mathbf{n}' + \mathbf{r}_{j'})] = R\mathbf{u}_j[\mathbf{q} \cdot (\mathbf{n} + \mathbf{r}_j) - \varepsilon\Delta] \quad (9.8.1.24)$$

with

$$\mathbf{n}' + \mathbf{r}_{j'} = R(\mathbf{n} + \mathbf{r}_j) + \mathbf{v}.$$

These are purely three-dimensional symmetry relations, but of course not Euclidean ones.

In three-dimensional Euclidean space, the types of space-group transformation are translations, rotations, rotoinversions, reflections, central inversion, screw rotations, and glide planes. Only the latter two transformations have intrinsic non-primitive translations. For superspace groups, the types of transformation are determined by the point-group transformations. By an appropriate choice of the basis in V_s , each of the latter can be brought into the form

$$\begin{pmatrix} \cos \varphi & -\sin \varphi & 0 & 0 \\ \sin \varphi & \cos \varphi & 0 & 0 \\ 0 & 0 & \delta & 0 \\ 0 & 0 & 0 & \varepsilon \end{pmatrix}; \quad \varepsilon, \delta = \pm 1. \quad (9.8.1.25)$$

By a choice of origin, each translational part can be reduced to its intrinsic part, which in combination with the point-group element (R, ε) gives one of the transformations in V indicated above together with the inversion, or the identity, or a shift in V_I . So, for phase inversion (when $\varepsilon = -1$), the intrinsic shift in V_I vanishes. When $\varepsilon = +1$, the intrinsic shift in V_I is given by τ . It will be shown in Subsection 9.8.3.3 that the value of τ is one of

$$0, \frac{1}{2}, \frac{\pm 1}{3}, \frac{\pm 1}{4}, \frac{\pm 1}{6}. \quad (9.8.1.26)$$

Therefore, a superspace-group element can be denoted by a symbol that consists of a symbol for the three-dimensional part following the conventions given in Volume A of *International*

Tables for Crystallography, a symbol that determines ε , and one for the corresponding intrinsic internal translation τ .

9.8.1.4.4. Generalized nomenclature

In Section 9.8.4, the theory is extended to structures containing d modulations, with $d \geq 1$. In this case, each point-group transformation in internal space is given by R_I and the associated internal translation by the (d -dimensional) vector \mathbf{v}_I . Thus,

$$g_s = \{(R, R_I)|(\mathbf{v}, \mathbf{v}_I)\}.$$

The transformations R and R_I are represented by the matrices $\Gamma_E(R)$ and $\Gamma_I(R)$, respectively. In the following discussion, this nomenclature (but with v_I rather than \mathbf{v}_I) is sometimes also applied for the $(3 + 1)$ -dimensional case. The usual formulae are obtained by replacing R_I by ε and v_I by Δ .

9.8.1.4.5. Four-dimensional space groups

Four-dimensional space groups were obtained in the $(3 + 1)$ -reducible case by Fast & Janssen (1969) and in the general case by Brown, Bülow, Neubüser, Wondratschek & Zassenhaus (1978). The groups were determined on the basis of algorithms developed by Zassenhaus (1948), Janssen, Janner & Ascher (1969), Brown (1969), and Fast & Janssen (1971). In the book by Brown, Bülow, Neubüser, Wondratschek & Zassenhaus, quoted above, a mathematical characterization of the basic crystallographic concepts is given together with corresponding tables for the dimensions one, two, three, and four. One finds there, in particular, a full list of four-dimensional space groups. The list by Fast & Janssen is restricted to space groups with $(3 + 1)$ -reducible point groups. The four-dimensional groups in the work of Brown *et al.* are labelled by numbers. For these same groups, alternative symbols have been developed by Weigel, Phan, Veyssseyre and Grebille generalizing the principles of the notation adopted by *International Tables for Crystallography*, Volume A, for the three-dimensional space groups (Weigel, Phan & Veyssseyre, 1987; Veyssseyre & Weigel, 1989; Grebille, Weigel, Veyssseyre & Phan, 1990).

The difference in the listing of four-dimensional crystallographic groups one finds in Brown *et al.* and in Weigel *et al.* with respect to that in the present tables is not simply a matter of notation. In the first place, here only those groups appear that can occur as symmetry groups of one-dimensional incommensurate modulated phases (there are 371 such space groups). Furthermore, as already mentioned, a finer equivalence relation has been considered that reflects the freedom one has in embedding a three-dimensional modulated structure in a four-dimensional Euclidean space. Instead of 371, one then obtains 775 inequivalent groups for which the name superspace group has been introduced. A $(3 + 1)$ -dimensional superspace group is thus a four-dimensional space group having some additional properties. In Section 9.8.4, the precise definitions are given.

In the commensurate one-dimensionally modulated case, 3833 four-dimensional space groups may occur, out of which 320 already belong to the previous 371. The corresponding additional $(3 + 1)$ -dimensional superspace groups are also present in the listing by Fast & Janssen (1969) and have been considered again (and applied to structure determination) by van Smaalen (1987). The Bravais classes for the commensurate $(3 + 1)$ -dimensional case are given in Table 9.8.3.2(b).

The relation between modulated crystals and the superspace groups is treated in a textbook by Opechowski (1986). That between the superspace-group symbols of the present tables and those of Weigel *et al.* is discussed in Grebille *et al.* (1990).

Note that no new names have been introduced for the underlying crystallographic concepts like Bravais classes, geometric and arithmetic crystal classes, even if in those cases also the equivalence relation is not simply that of four-dimensional Euclidean crystallography, an explicit distinction always being possible by specifying the dimension as $(3 + 1)$ instead of four.

9.8.1.5. Occupation modulation

Another type of modulation, the occupation modulation, can be treated in a way similar to the displacive modulation. As an example consider an alloy where the positions of the basic structure have space-group symmetry, but are statistically occupied by either of two types of atoms. Suppose that the position \mathbf{r} is occupied by an atom of type A with probability $p(\mathbf{r})$ and by one of type B with probability $1 - p(\mathbf{r})$ and that p is periodic. The probability of finding an A atom at site $\mathbf{n} + \mathbf{r}_j$ is

$$P_A(\mathbf{n} + \mathbf{r}_j) = p_j[\mathbf{q} \cdot (\mathbf{n} + \mathbf{r}_j)], \quad (9.8.1.27)$$

with $p_j(x) = p_j(x + 1)$. In this case, the structure factor becomes

$$S_{\mathbf{H}} = \sum_{\mathbf{n}} \sum_j [(f_A p_j[\mathbf{q} \cdot (\mathbf{n} + \mathbf{r}_j)] + f_B \{1 - p_j[\mathbf{q} \cdot (\mathbf{n} + \mathbf{r}_j)\}]) \times \exp[2\pi i \mathbf{H} \cdot (\mathbf{n} + \mathbf{r}_j)]], \quad (9.8.1.28)$$

where f_A and f_B are the atomic scattering factors. Because of the periodicity, one has

$$p_j(x) = \sum_m w_{jm} \exp(2\pi i m x). \quad (9.8.1.29)$$

Hence,

$$S_{\mathbf{H}} = \sum_j \left\{ f_B \Delta(\mathbf{H}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_j) + (f_A - f_B) \sum_m \Delta(\mathbf{H} + m\mathbf{q}) w_{jm} \times \exp[2\pi i (\mathbf{H} + m\mathbf{q}) \cdot \mathbf{r}_j] \right\}, \quad (9.8.1.30)$$

where $\Delta(\mathbf{H})$ is the sum of δ functions over the reciprocal lattice of the basic structure:

$$\Delta(\mathbf{H}) = \sum_{h_1 h_2 h_3} \delta \left(\mathbf{H} - \sum_{i=1}^3 h_i \mathbf{a}_i^* \right).$$

Consequently, the diffraction peaks occur at positions \mathbf{H} given by (9.8.1.7). For a simple sinusoidal modulation [$m = \pm 1$ in (9.8.1.29)], there are only main reflections and first-order satellites ($m = \pm 1$). One may introduce an additional coordinate t and generalize (9.8.1.27) to

$$P_A(\mathbf{n} + \mathbf{r}_j, t) = p_j[\mathbf{q} \cdot (\mathbf{n} + \mathbf{r}_j) + t], \quad (9.8.1.31)$$

which has $(3 + 1)$ -dimensional space-group symmetry. Generalization to more complex modulation cases is then straightforward.

9.8.2. Outline for a superspace-group determination

In the case of a modulated structure, the diffraction pattern consists of main reflections and satellites. The main reflections span a reciprocal lattice generated by \mathbf{a}_1^* , \mathbf{a}_2^* , \mathbf{a}_3^* . Considerations are here restricted for simplicity to the one-dimensional modulated case, *i.e.* to the $n = 4$ case. Extension to the more general $n = 3 + d$ case is conceptually not difficult and does not modify the general procedure outlined here.

(1) *The first step* is the determination of the *Laue group* P_L of the diffraction pattern: it is the point group in three dimensions

that transforms every diffraction peak into a peak of the same intensity.†

As P_L leaves invariant the subset of main reflections, this Laue group belongs to one of the 11 Laue symmetry classes. Accordingly, the Laue group determines a three-dimensional holohedral point group which determines a crystallographic system.

(2) *The second step* consists of choosing a basis according to the conventions of *ITA* for the main reflections and choosing a modulation wavevector.

From the centring extinctions, one can deduce to which Bravais class the main reflections belong. This is one of the 14 three-dimensional Bravais classes. Notice that the cubic Bravais classes do not occur because a one-dimensional (incommensurate) modulation is incompatible with cubic symmetry. For this same reason, only the nine non-cubic Laue-symmetry classes occur in the one-dimensional incommensurate case.

The main reflections are indexed by $hkl0$ and the satellite reflections by $hklm$. The Fourier wavevector of a general reflection $hklm$ is given by

$$\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}. \quad (9.8.2.1)$$

Note that this step involves a choice because the system of satellite reflections is only defined modulo the main reflections. When a satellite is in the vicinity of a main reflection, it is reasonable to assign it to that reflection. But one has, especially when deciding whether or not situations are equivalent, to be aware of the fact that each satellite may be assigned to an arbitrary main reflection. It is even possible to assign a satellite to an extinct main reflection. One takes by preference the \mathbf{q} vector along a symmetry axis or in a mirror plane. According to equation (9.8.2.1), the fourth basis vector \mathbf{a}_4^* is equal to the chosen \mathbf{q} , the modulation wavevector.

(3) In the *third step*, one determines the space group of the *average structure* (from the main reflections).

The average structure is unique but possibly involves split atoms. The space group of the average structure is often the symmetry group of the undistorted phase. That helps to make a good choice for the basic structure and also gives an insight as to how the satellite reflections split from the main reflections at the phase transition.

(4) *Step four* is the identification of the $(3 + 1)$ -dimensional Bravais lattice type. In superspace also, centring gives rise to *centring extinctions*, and that corresponds to making the choice of a *conventional unit cell* in $(3 + 1)$ dimensions.

The previous three steps establish \mathbf{a}^* , \mathbf{b}^* , \mathbf{c}^* , the three-dimensional Bravais class and $\mathbf{q} = \alpha\mathbf{a}^* + \beta\mathbf{b}^* + \gamma\mathbf{c}^*$, where the components α , β , and γ are given with respect to the three-dimensional conventional basis.

$$\alpha = \mathbf{q} \cdot \mathbf{a}, \quad \beta = \mathbf{q} \cdot \mathbf{b}, \quad \gamma = \mathbf{q} \cdot \mathbf{c}. \quad (9.8.2.2)$$

The $(3 + 1)$ -dimensional Bravais class is fixed by that three-dimensional Bravais class and the components α , β , γ of \mathbf{q} .

Just as for three-dimensional lattices, a conventional cell can be chosen for $(3 + 1)$ -dimensional lattices. To this end, the

† Except for deviations from Friedel's law caused by dispersion; see *ITB* (1993, p. 241, Subsection 2.3.4.1).