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

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

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

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

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

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

Hence,

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

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

$$\Delta(\mathbf{H}) = \sum_{h_1h_2h_3}\delta\left(\mathbf{H} - \sum_{i=1}^{3} h_i\mathbf{a}_i^*\right).$$

Consequently, the diffraction peaks occur at positions $\mathbf{H}$ given by (9.8.1.7). For a simple sinusoidal modulation [$m=\pm1$ in (9.8.1.29)], there are only main reflections and first-order satellites ($m=\pm1$). One may introduce an additional coordinate t and generalize (9.8.1.27) to

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

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 *IT* A 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

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

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.

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

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 *IT* B (1993, p. 241, Subsection 2.3.4.1).

references