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(9.8.4.13). It is then faithfully represented by integral matrices that are of the form indicated in (9.8.4.17) and (9.8.4.18).

9.8.4.3.2. *Crystallographic systems*

Definition 5. A *crystallographic system* is a set of lattices having geometrically equivalent holohedral point groups.

In this way, a given holohedral point group (and even each crystallographic point group) belongs to exactly one system. Two lattices belong to the same system if there are orthonormal bases in V and in V_I, respectively, such that the holohedral point groups of the two lattices are represented by the same set of matrices.

9.8.4.3.3. *Bravais classes*

Definition 6. Two lattices belong to the same *Bravais class* if their holohedral point groups are arithmetically equivalent.

This means that each of them admits a lattice basis of standard form such that their holohedral point group is represented by the same set of integral matrices.

9.8.4.4. *Superspace groups*

9.8.4.4.1. *Symmetry elements*

The elements of a $(3 + d)$-dimensional superspace group are pairs of Euclidean transformations in 3 and d dimensions, respectively:

$$g_s = (\{R|\mathbf{v}\}, \{R_I|\mathbf{v}_I\}) \in E(3) \times E(d), \qquad (9.8.4.28)$$

i.e. are elements of the direct product of the corresponding Euclidean groups. The elements $\{R|\mathbf{v}\}$ form a three-dimensional space group, but the same does not hold for the elements $\{R_I|\mathbf{v}_I\}$ of $E(d)$. This is because the internal translations $\mathbf{v}_I$ also contain the 'compensating' transformations associated with the corresponding translation $\mathbf{v}$ in V [see (9.8.4.32)]. In other words, a basis of the lattice Σ does not simply split into one basis for V and one for V_I.

As for elements of a three-dimensional space group, the translational component $\upsilon_s = (\mathbf{v}, \mathbf{v}_I)$ of the element g_s can be decomposed into an intrinsic part υ_s^o and an origin-dependent part υ_s^a:

$$(\upsilon, \upsilon_I) = (\mathbf{v}^o, \mathbf{v}_I^o) + (\mathbf{v}^a, \mathbf{v}_I^a),$$

with

$$(\mathbf{v}^o, \mathbf{v}_I^o) = \frac{1}{n} \sum_{m=1}^{n} (R^m \mathbf{v}, R_I^m \mathbf{v}_I), \qquad (9.8.4.29)$$

where n denotes the order of the element R. In particular, for $d = 1$ the intrinsic part $\mathbf{v}_I^o$ of $\mathbf{v}_I$ is equal to $\mathbf{v}_I$ if $R_I = \varepsilon = +1$ and vanishes if $\varepsilon = -1$. The latter means that for $d = 1$ there is always an origin in the internal space such that the internal shift $\mathbf{v}_I$ can be chosen to be zero for an element with $\varepsilon = -1$.

The internal part of the intrinsic translation can itself be decomposed into two parts. One part stems from the presence of a translation in the external space. The lattice of the $(3 + d)$-dimensional space group has basis vectors

$$(\mathbf{a}_i, \mathbf{a}_{Ii}), (0, \mathbf{d}_j), \quad i = 1, 2, 3, \quad j = 1, \ldots, d. \qquad (9.8.4.30)$$

The internal part of the first three basis vectors is

$$\mathbf{a}_{Ii} = -\Delta \mathbf{a}_i = -\sum_{j=1}^{d} \sigma_{ji} \mathbf{d}_j \qquad (9.8.4.31)$$

according to equation (9.8.4.20). The three-dimensional translation $\mathbf{v} = \sum_i \upsilon_i \mathbf{a}_i$ then entails a d-dimensional translation $-\Delta \mathbf{v}$ in V_I given by

$$\Delta \mathbf{v} = \Delta \left(\sum_{i=1}^{3} \upsilon_i \mathbf{a}_i \right) = \sum_{i=1}^{3} \upsilon_i \Delta \mathbf{a}_i. \qquad (9.8.4.32)$$

These are the so-called compensating translations. Hence, the internal translation $\mathbf{v}_I$ can be decomposed as

$$\mathbf{v}_I = -\Delta \mathbf{v} + \boldsymbol{\delta}, \qquad (9.8.4.33)$$

where $\boldsymbol{\delta} = \sum_{j=1}^{d} \upsilon_{3+j} \mathbf{d}_j$.

This decomposition, however, does still depend on the origin. Consider the case $d = 1$. Then an origin shift $\mathbf{s}$ in the three-dimensional space changes the translation $\mathbf{v}$ to $\mathbf{v} + (1 - R)\mathbf{s}$ and its internal part $-\Delta \mathbf{v} = -\mathbf{q} \cdot \mathbf{v}$ to $-\mathbf{q} \cdot \mathbf{v} - \mathbf{q} \cdot (1 - R)\mathbf{s}$. This implies that for the case that $\varepsilon = 1$ the part δ changes to $\delta + \mathbf{q} \cdot (1 - R)\mathbf{s} = \delta + \mathbf{q}^r \cdot (1 - R)\mathbf{s}$, because $\mathbf{q}^i$ is invariant under R. Therefore, δ changes, in general. The internal translation

$$\tau = \delta - \mathbf{q}^r \cdot \mathbf{v}, \qquad (9.8.4.34)$$

however, is invariant under an origin shift in V.

Definition 7. Equivalent superspace groups. Two superspace groups are equivalent if they are isomorphic and have point groups that are arithmetically equivalent.

Another definition leading to the same partition of equivalent superspace groups considers equivalency with respect to affine transformations among bases of standard form.

This means that two equivalent superspace groups admit standard bases such that the two space groups are represented by the same set of $(4 + d)$-dimensional affine transformation matrices. We recall that an n-dimensional Euclidean transformation $g_s = \{R_s | v_s\}$ if referred to a basis of the space can be represented isomorphically by an $(n + 1)$-dimensional matrix, of the form

$$A(g_s) = \begin{pmatrix} R_s & v_s \\ 0 & 1 \end{pmatrix} \qquad (9.8.4.35)$$

with R_s an $n \times n$ matrix and v_s an n-dimensional column matrix, all with real entries.

9.8.4.4.2. *Equivalent positions and modulation relations*

A $(3 + d)$-dimensional space group that leaves a function invariant maps points in $(3 + d)$-space to points where the function has the same value. The atomic positions of a modulated crystal represent such a pattern, and the superspace group leaving the crystal invariant leads to a partition into equivalent atomic positions. These relations can be formulated either in $(3 + d)$-dimensional space or, equally well, in three-dimensional space. As a simple case, we first consider a crystal with a one-dimensional occupation modulation: this implies $d = 1$. Again, as in §9.8.1.3.2, we omit to indicate the basis vectors $\mathbf{d}_1$ and $\mathbf{d}_1^*$ and give only the corresponding components.

An element of the $(3 + 1)$-dimensional superspace group is a pair

$$g_s = (\{R|\mathbf{v}\}, \{\varepsilon|\upsilon_I\}) \qquad (9.8.4.36)$$

of Euclidean transformations in V and V_I, respectively. This element maps a point located at $r_s = (\mathbf{r}, t)$ to one at $(R\mathbf{r} + \mathbf{v}, \varepsilon t + \upsilon_I)$. Suppose the probability for the position $\mathbf{n} + \mathbf{r}_j$ to be occupied by an atom of species A is given by

$$P_A(\mathbf{n}, j, t) = p_j[\mathbf{q} \cdot (\mathbf{n} + \mathbf{r}_j) + t], \qquad (9.8.4.37)$$

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where $p_j(x) = p_j(x+1)$. By g_s, the position $\mathbf{n} + \mathbf{r}_j$ is transformed to the equivalent position $\mathbf{n}' + \mathbf{r}_{j'} = R\mathbf{n} + R\mathbf{r}_j + \mathbf{v}$. As the crystal is left invariant by the superspace group, the occupation probability on equivalent points has to be the same:

$$P_A(\mathbf{n}', j', t) = P_A[\mathbf{n}, j, \varepsilon(t - \upsilon_I)]. \qquad (9.8.4.38)$$

This implies that for the structure in the three-dimensional space one has the relation

$$P_A(\mathbf{n}', j', 0) = P_A(\mathbf{n}, j, -\varepsilon\upsilon_I). \qquad (9.8.4.39)$$

In terms of the modulation function p_j this means

$$p_{j'}[\mathbf{q} \cdot (\mathbf{n}' + \mathbf{r}_{j'})] = p_j[\mathbf{q} \cdot (\mathbf{n} + \mathbf{r}_j) - \varepsilon\upsilon_I]. \qquad (9.8.4.40)$$

In the same way, one derives the following property of the modulation function:

$$p_{j'}(x) = p_j[\varepsilon(x - \delta) + \mathbf{K} \cdot (\mathbf{r}_{j'} - \mathbf{v})], \quad \text{where } R\mathbf{q} = \varepsilon\mathbf{q} + \mathbf{K}. \qquad (9.8.4.41)$$

Analogously, for a displacive modulation, the position $\mathbf{n} + \mathbf{r}_j$ with displacement $\mathbf{u}_j(t_o)$, where $t_o = \mathbf{q} \cdot (\mathbf{n} + \mathbf{r}_j)$, is transformed to $\mathbf{n}' + \mathbf{r}_{j'}$ with displacement

$$\mathbf{u}_{j'}(t_o') = R\mathbf{u}_j(t_o - \varepsilon\upsilon_I). \qquad (9.8.4.42)$$

To be invariant, the displacement function has to satisfy the relation

$$\mathbf{u}_{j'}(x) = R\mathbf{u}_j[\varepsilon x - \varepsilon\delta + \mathbf{K} \cdot (\mathbf{r}_{j'} - \mathbf{v})], \quad \text{where } R\mathbf{q} = \varepsilon\mathbf{q} + \mathbf{K}. \qquad (9.8.4.43)$$

The expressions for $d > 1$ are straightforward generalizations of these.

9.8.4.4.3. *Structure factor*

The scattering from a set of atoms at positions $\mathbf{r}_n$ is described in the kinematic approximation by the structure factor:

$$S_\mathbf{H} = \sum_n f_n(\mathbf{H}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_n), \qquad (9.8.4.44)$$

where $f_n(\mathbf{H})$ is the atomic scattering factor. For an incommensurate crystal phase, this structure factor $S_\mathbf{H}$ is equal to the structure factor S_{H_s} of the crystal structure embedded in $3 + d$ dimensions, where $\mathbf{H}$ is the projection of H_s on V_E. This structure factor is expressed by a sum of the products of atomic scattering factors f_n and phase factors $\exp(2\pi i H_s \cdot r_{sn})$ over all particles in the unit cell of the higher-dimensional lattice. For an incommensurate phase, the number of particles in such a unit cell is infinite: for a given atom in space, the embedded positions form a dense set on lines or hypersurfaces of the higher-dimensional space. Disregarding pathological cases, the sum may be replaced by an integral. Including the possibility of an occupation modulation, the structure factor becomes (up to a normalization factor)

$$S_\mathbf{H} = \sum_A \sum_j \int_\Omega d\mathbf{t}\, f_A(\mathbf{H}) P_{Aj}(\mathbf{t})$$
$$\times \exp\{2\pi i(\mathbf{H}, \mathbf{H}_I) \cdot [\mathbf{r}_j + \mathbf{u}_j(\mathbf{t}), \mathbf{t}]\}, \qquad (9.8.4.45)$$

where the first sum is over the different species, the second over the positions in the unit cell of the basic structure, the integral over a unit cell of the lattice spanned by $\mathbf{d}_1, \ldots, \mathbf{d}_d$ in V_I; f_A is the atomic scattering factor of species A, $P_{Aj}(\mathbf{t})$ is the probability of atom j being of species A when the internal position is $\mathbf{t}$.

In particular, for a given atomic species, without occupational modulation and a sinusoidal one-dimensional displacive modulation

$$P_j(t) = 1; \quad \mathbf{u}_j(t) = \mathbf{U}_j \sin[2\pi(\mathbf{q} \cdot \mathbf{r}_j + t + \varphi_j)]. \qquad (9.8.4.46)$$

According to (9.8.4.45), the structure factor is

$$S_\mathbf{H} = \sum_j \int_0^1 dt\, f_j(\mathbf{H}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_j) \exp(2\pi i m t)$$
$$\times \exp[2\pi i \mathbf{H} \cdot \mathbf{U}_j \sin 2\pi(\mathbf{q} \cdot \mathbf{r}_j + t + \varphi_j)]. \qquad (9.8.4.47)$$

For a diffraction vector $\mathbf{H} = \mathbf{K} + m\mathbf{q}$, this reduces to

$$S_\mathbf{H} = \sum_j f_j(\mathbf{H}) \exp(2\pi i \mathbf{K} \cdot \mathbf{r}_j) J_{-m}(2\pi \mathbf{H} \cdot \mathbf{U}_j)$$
$$\times \exp(-2\pi i m \varphi_j). \qquad (9.8.4.48)$$

For a general one-dimensional modulation with occupation modulation function $p_j(t)$ and displacement function $\mathbf{u}_j(t)$, the structure factor becomes

$$S_\mathbf{H} = \sum_j \int_0^1 dt\, f_j(\mathbf{H}) p_j(\mathbf{q} \cdot \mathbf{r}_j + t + \psi_j) \exp[2\pi i(\mathbf{H} \cdot \mathbf{r}_j + mt)]$$
$$\times \exp[2\pi i \mathbf{H} \cdot \mathbf{u}_j(\mathbf{q} \cdot \mathbf{r}_j + t + \varphi_j)]. \qquad (9.8.4.49)$$

Because of the periodicity of $p_j(t)$ and $\mathbf{u}_j(t)$, one can expand the Fourier series:

$$p_j(\mathbf{q} \cdot \mathbf{r}_j + t + \psi_j) \exp[2\pi i \mathbf{H} \cdot \mathbf{u}_j(\mathbf{q} \cdot \mathbf{r}_j + t + \varphi_j)]$$
$$= \sum_k C_{j,k}(\mathbf{H}) \exp[2\pi i k(\mathbf{q} \cdot \mathbf{r}_j + t)], \qquad (9.8.4.50)$$

and consequently the structure factor becomes

$$S_\mathbf{H} = \sum_j f_j(\mathbf{H}) \exp(2\pi i \mathbf{K} \cdot \mathbf{r}_j) C_{j,-m}(\mathbf{H}), \quad \text{where } \mathbf{H} = \mathbf{K} + m\mathbf{q}. \qquad (9.8.4.51)$$

The diffraction from incommensurate crystal structures has been treated by de Wolff (1974), Yamamoto (1982a,b), Paciorek & Kucharczyk (1985), Petricek, Coppens & Becker (1985), Petříček & Coppens (1988), Perez-Mato *et al.* (1986, 1987), and Steurer (1987).

9.8.5. Generalizations

9.8.5.1. *Incommensurate composite crystal structures*

The basic structure of a modulated crystal does not always have space-group symmetry. Consider, for example, composite crystals (also called intergrowth crystals). Disregarding modulations, one can describe these crystals as composed of a finite number of subsystems, each with its own space-group symmetry. The lattices of these subsystems can be mutually incommensurate. In that case, the overall symmetry is not a space group, the composite crystal is incommensurate and so also is its basic structure. The superspace approach can also be applied to such crystals. Let the subsystems be labelled by an index ν. For the subsystem ν, we denote the lattice by Λ_ν with basis vectors $\mathbf{a}_{\nu i}$ ($i = 1, 2, 3$), its reciprocal lattice by Λ_ν^* with basis vectors $\mathbf{a}_{\nu i}^*$ ($i = 1, 2, 3$), and the space group by G_ν. The atomic positions of the basic structure are given by

$$\mathbf{n}_\nu + \mathbf{r}_{\nu j}, \qquad (9.8.5.1)$$

where $\mathbf{n}_\nu$ is a lattice vector belonging to Λ_ν. In the special case that the subsystems are mutually commensurate, there are three basis vectors $\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$ such that all vectors $\mathbf{a}_{\nu i}^*$ are integral linear combinations of them. In general, however, more than three basis vectors are needed, but never more than three times the number of subsystems. Suppose that the vectors $\mathbf{a}_i^*$ ($i = 1, \ldots, n$)