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Chapter 2

Crystal Math

2.1 Classification of Crystalline Structures

Crystallography is the classification of spatially periodic structures according to their translational and rotational symmetries. It is a mature field[1], and the possible crystalline symmetries of two and three dimensional structures have been exhaustively classified. We shall not endeavor to prove, *e.g.*, that there are precisely 230 three-dimensional space groups. Rather, our proximate goal is to economically describe the most relevant aspects of the classification scheme, so that we may apply methods of group theory to analyze experimentally relevant physical processes in crystals.

2.1.1 Bravais Lattices

A Bravais lattice $\mathcal{L}$ in d space dimensions is defined by a set of linearly independent vectors $\{\boldsymbol{a}_j\}$ with $j \in \{1, \ldots, d\}$ which define a *unit cell*. A general point $\boldsymbol{R}$ in the Bravais lattice is written as $\boldsymbol{R} = \sum_j n_j \boldsymbol{a}_j$, where each $n_j \in \mathbb{Z}$. The unit cell volume is given by

$$\Omega = \epsilon_{\mu_1 \cdots \mu_d}\, a_1^{\mu_1} \cdots a_d^{\mu_d} \quad , \tag{2.1}$$

and is by definition positive[2]. The choice of the vectors $\{\boldsymbol{a}_j\}$ is not unique, for one can always replace $\boldsymbol{a}_i$ with $\boldsymbol{a}_i + \boldsymbol{a}_j$ for any $j \neq i$, and, due to the antisymmetry of the determinant, Ω is unchanged. It is then conventional to choose the $\{\boldsymbol{a}_j\}$ so that they have the shortest possible length, though even this prescription is not necessarily unique. The lattice of points $\{\boldsymbol{R}\}$ is called the *direct lattice*, and the $\{\boldsymbol{a}_j\}$ are the *elementary* (or *primitive*) *direct lattice vectors*.

One can then define the elementary (primitive) *reciprical lattice vectors*,

$$b_k^\nu \equiv \frac{2\pi}{\Omega}\, \epsilon_{\mu_1 \cdots \mu_{k-1}\, \nu\, \mu_{k+1} \cdots \mu_d}\, a_1^{\mu_1} \cdots a_{k-1}^{\mu_{k-1}}\, a_{k+1}^{\mu_{k+1}} \cdots a_d^{\mu_d} \quad , \tag{2.2}$$

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[1] Crystallography has enjoyed something of a resurgence in its relevance to recent theories of topological classification of electronic band structures. The interplay between symmetry and topology leads to a new classification for materials known as crystalline topological insulators, for example.

[2] One can always reorder the $\boldsymbol{a}_j$ so that $\Omega > 0$.

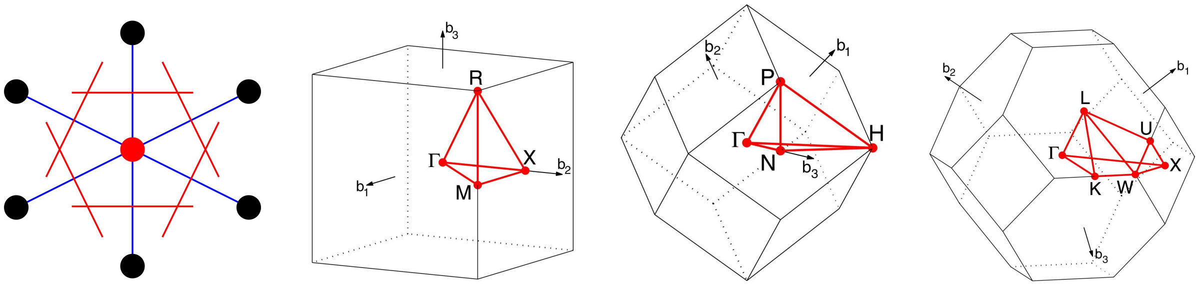

Figure 2.1: First panel shows construction of the first Wigner-Seitz cell or first Brillouin zone for the triangular lattice. Second, third, and fourth panels show first Brillouin zones for the simple cubic, body-centered cubic, and face-centered cubic direct lattices, respectively, with high symmetry points identified. Image credit: *Wikipedia* and Setyawan and Curtarolo, DOI: 10.1016/j.commatsci.2010.05.010.

which satisfy $\boldsymbol{a}_i \cdot \boldsymbol{b}_j = 2\pi\,\delta_{ij}$. Indeed, we must have

$$\sum_{\mu=1}^{d} a_i^\mu\, b_j^\mu = 2\pi\,\delta_{ij} \qquad , \qquad \sum_{j=1}^{d} a_j^\mu\, b_j^\nu = 2\pi\,\delta_{\mu\nu} \quad , \tag{2.3}$$

because if the square matrices $A_{j,\mu} \equiv a_j^\mu$ and $B^{\mathsf{T}}_{\mu,j} \equiv b_j^\mu$ are inverses, they are each other's right as well as left inverse. For example, with $d = 3$ we have $\Omega = \boldsymbol{a}_1 \cdot \boldsymbol{a}_2 \times \boldsymbol{a}_3$ and

$$\boldsymbol{b}_1 = \frac{2\pi}{\Omega}\,\boldsymbol{a}_2 \times \boldsymbol{a}_3 \quad , \quad \boldsymbol{b}_2 = \frac{2\pi}{\Omega}\,\boldsymbol{a}_3 \times \boldsymbol{a}_1 \quad , \quad \boldsymbol{b}_3 = \frac{2\pi}{\Omega}\,\boldsymbol{a}_1 \times \boldsymbol{a}_2 \quad . \tag{2.4}$$

The set of vectors $\boldsymbol{K} = \sum_{j=1}^{d} m_j\, \boldsymbol{b}_j$, with each $m_i \in \mathbb{Z}$, is called the *reciprocal lattice*, $\hat{\mathcal{L}}$. The reciprocal lattice is therefore also a Bravais lattice, though not necessarily the same Bravais lattice as the direct lattice. For example, while the reciprocal lattice of a simple cubic lattice is also simple cubic, the reciprocal lattice of a body-centered cubic lattice is face-centered cubic. Constructing the reciprocal lattice of the reciprocal lattice, one arrives back at the original direct lattice. The unit cell volume of the reciprocal lattice is

$$\hat{\Omega} = \epsilon_{\mu_1\cdots\mu_d}\, b_1^{\mu_1} \cdots b_d^{\mu_d} = \frac{(2\pi)^d}{\Omega} \quad . \tag{2.5}$$

The repeating unit cells in the direct and reciprocal lattices may be written as the collection of points $\boldsymbol{r}$ and $\boldsymbol{k}$, respectively, where

$$\boldsymbol{r} = \sum_{j=1}^{d} x_j\, \boldsymbol{a}_j \qquad , \qquad \boldsymbol{k} = \sum_{j=1}^{d} y_j\, \boldsymbol{b}_j \quad , \tag{2.6}$$

where each $x_j, y_j \in [0,1]$. The symmetries of the direct and reciprocal lattices are more fully elicited by shifting each $\boldsymbol{r}$ and $\boldsymbol{k}$ point by a direct or reciprocal lattice vector so that it is as close as possible to the origin. Equivalently, sketch all the nonzero shortest direct/reciprocal lattice vectors emanating from the origin[3], and bisect each such vector with a perpendicular plane. The collection of points lying within

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[3] There may be more than d shortest direct/reciprocal lattice vectors. For example, the triangular lattice is two-dimensional, but it has six nonzero shortest direct/reciprocal lattice vectors.

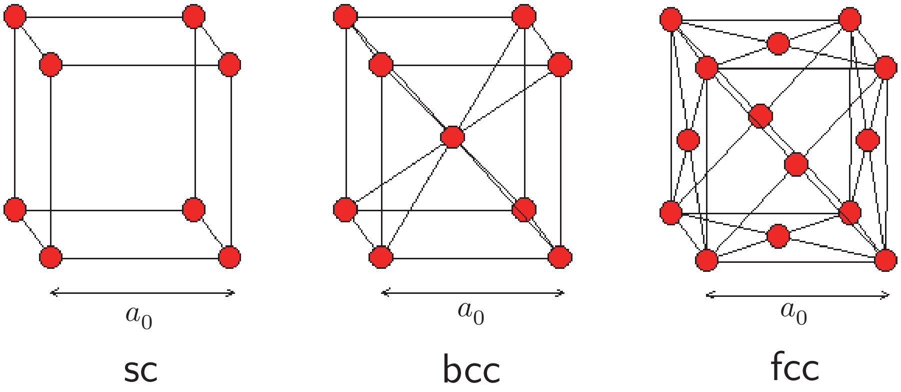

Figure 2.2: Simple cubic (sc), body-centered cubic (bcc), and face-centered cubic (fcc) lattices.

all the planes will form the first *Wigner-Seitz cell* of the direct lattice, and the first *Brillouin zone* of the reciprocal lattice.

Finally, we cannot resist mentioning the beautiful and extremely important application of the Poisson summation formula to Bravais lattice systems:

$$\sum_{\boldsymbol{K}} e^{i\boldsymbol{K}\cdot\boldsymbol{r}} = \Omega \sum_{\boldsymbol{R}} \delta(\boldsymbol{r}-\boldsymbol{R}) \quad , \quad \sum_{\boldsymbol{R}} e^{i\boldsymbol{k}\cdot\boldsymbol{R}} = \hat{\Omega} \sum_{\boldsymbol{K}} \delta(\boldsymbol{k}-\boldsymbol{K}) \quad . \tag{2.7}$$

Example: fcc and bcc lattices

The primitive direct lattice vectors for the fcc structure may be taken as

$$\boldsymbol{a}_1 = \frac{a}{\sqrt{2}}\,(0,1,1) \quad , \quad \boldsymbol{a}_2 = \frac{a}{\sqrt{2}}\,(1,0,1) \quad , \quad \boldsymbol{a}_3 = \frac{a}{\sqrt{2}}\,(1,1,0) \quad . \tag{2.8}$$

The unit cell volume is $\Omega = \boldsymbol{a}_1 \cdot \boldsymbol{a}_2 \times \boldsymbol{a}_3 = 2a^3$. Note that $|\boldsymbol{a}_j| = a$. Each FCC lattice point has twelve nearest neighbors, located at $\pm\boldsymbol{a}_1$, $\pm\boldsymbol{a}_2$, $\pm\boldsymbol{a}_3$, $\pm(\boldsymbol{a}_1-\boldsymbol{a}_2)$, $\pm(\boldsymbol{a}_2-\boldsymbol{a}_3)$, and $\pm(\boldsymbol{a}_3-\boldsymbol{a}_1)$. The corresponding primitive reciprocal lattice vectors are

$$\boldsymbol{b}_1 = \frac{b}{\sqrt{3}}\,(-1,1,1) \quad , \quad \boldsymbol{b}_2 = \frac{b}{\sqrt{3}}\,(1,-1,1) \quad , \quad \boldsymbol{b}_3 = \frac{b}{\sqrt{3}}\,(1,1,-1) \, , \tag{2.9}$$

with $b = \sqrt{6}\,\pi/a$. These primitive vectors form a bcc structure, in which each site has eight nearest neighbors, located at $\pm\boldsymbol{b}_1$, $\pm\boldsymbol{b}_2$, $\pm\boldsymbol{b}_3$, and $\pm(\boldsymbol{b}_1+\boldsymbol{b}_2+\boldsymbol{b}_3)$. The simple, body-centered, and face-centered cubic structures are depicted in Fig. 2.2.

Be forewarned that in some texts, distances are given in terms of the side length of the cube. In the fcc lattice, if the cube has side length a_0, then the fcc lattice constant, *i.e.* the distance between nearest neighbor sites, is $a = a_0/\sqrt{2}$. Similarly, for the bcc case, if the cube has side length b_0, the corresponding bcc lattice constant is $b = \sqrt{3}\,b_0/2$.

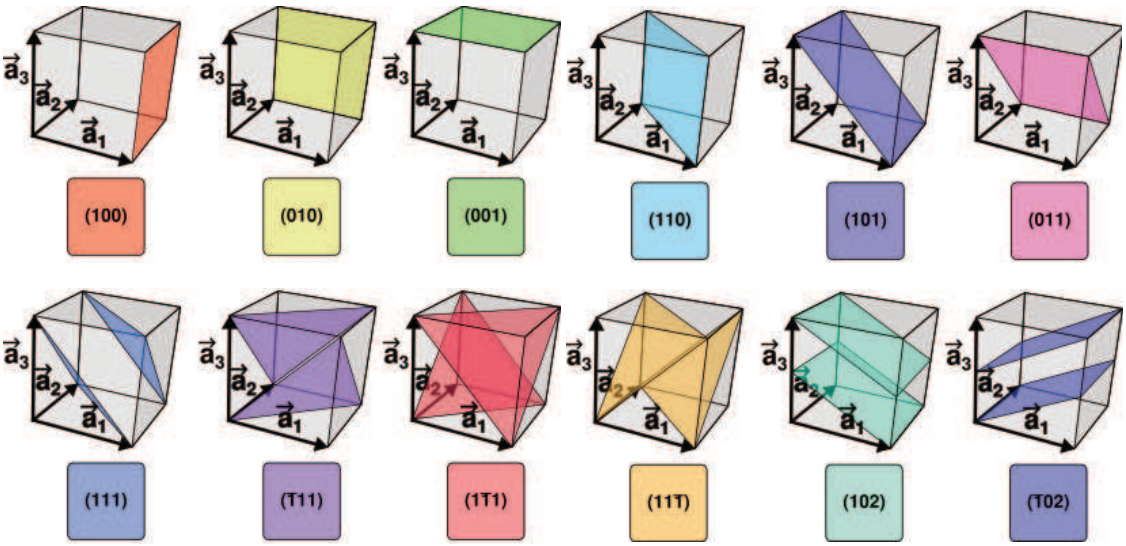

Figure 2.3: Examples of Miller planes. Image credit: Wikipedia.

In Fig. 2.1, the two rightmost panels show the first Brillouin zones corresponding to the bcc and fcc direct lattices, respectively. It follows that the same shapes describe the first Wigner-Seitz cells for the fcc and bcc lattices, respectively.

2.1.2 Miller indices

This eponymous notation system, first introduced by the British minerologist William H. Miller in 1839, provides a convenient way of indexing both directions and planes of points in a Bravais lattice. Briefly,

- $[\,h\,k\,l\,]$ represents a direction in the direct lattice given by the vector $h\boldsymbol{a}_1 + k\boldsymbol{a}_2 + l\boldsymbol{a}_3$. For negative numbers, one writes, *e.g.*, $\bar{2}$ instead of -2. Thus, $[\,1\,\bar{2}\,0\,]$ is the direction parallel to $\boldsymbol{a}_1 - 2\boldsymbol{a}_2$. Only integers are used, so the direction parallel to $\frac{1}{4}\boldsymbol{a}_1 + \frac{1}{2}\boldsymbol{a}_2 - \frac{1}{3}\boldsymbol{a}_3$ is written as $[\,3\,6\,\bar{4}\,]$.
- $\langle\,h\,k\,l\,\rangle$ denotes the set of all directions which are related to $[\,h\,k\,l\,]$ by a rotational symmetry.
- $(\,h\,k\,l\,)$ represents a set of *lattice planes* which lie perpendicular to the vector $h\boldsymbol{b}_1 + k\boldsymbol{b}_2 + l\boldsymbol{b}_3$. Again, only integers are used, and any negative numbers are written with bars rather than minus signs.
- $\{\,h\,k\,l\,\}$ denotes all families of lattice planes related to $(\,h\,k\,l\,)$ by a rotational symmetry.

We can think of the Miller planes in terms of plane waves, *i.e.* as sets of points of constant phase $\phi(\boldsymbol{r}) = \boldsymbol{K}_{hkl} \cdot \boldsymbol{r}$, where $\boldsymbol{K}_{hkl} = h\boldsymbol{b}_1 + k\boldsymbol{b}_2 + l\boldsymbol{b}_3$ is a reciprocal lattice vector. If we write $\boldsymbol{R} = r\boldsymbol{a}_1 + s\boldsymbol{a}_2 + t\boldsymbol{a}_3$, we have $\phi(r,s,t) = 2\pi(hr + ks + lt) \equiv 2\pi N$, and thus the intersection of this plane with the $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, and $\boldsymbol{a}_3$ axes, which in general are not mutually orthogonal, lie at $N\boldsymbol{a}_1/h$, $N\boldsymbol{a}_2/k$, and $N\boldsymbol{a}_3/l$, respectively. In this way, one can identify the Miller indices of any lattice plane by taking the inverses of the respective coefficients and inverting them, then multiplying by the least common denominator if the results turn

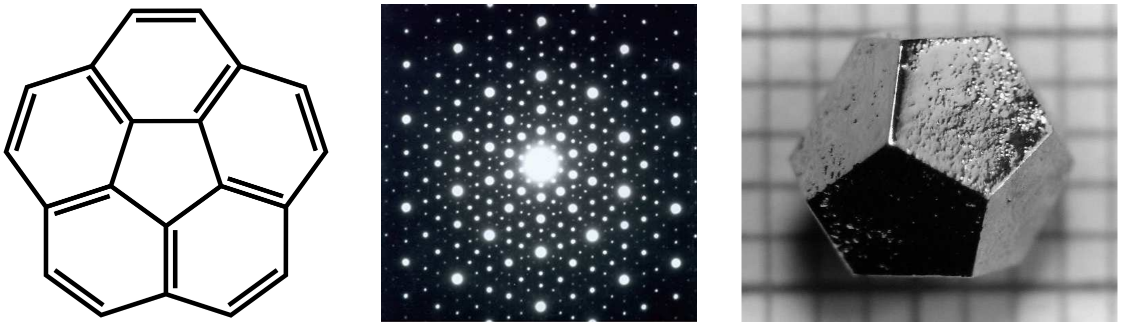

Figure 2.4: Left: Molecular structure of corannulene, $C_{20}H_{10}$. Center: Tenfold-symmetric diffraction pattern from a quasicrystalline alloy of aluminum, copper, and iron. Right: A Ho-Mg-Zn icosahedral quasicrystal forms a beautiful pentagonal dodecahedron (20 sites, 12 pentagonal faces, 30 edges, 3-fold coordinated), a structure dual to the icosahedron (12 sites, 20 triangular faces, 30 edges, 5-fold coordinated). Image credits: Wikipedia.

out to be fractional. From the formula $\exp(i\boldsymbol{K}\cdot\boldsymbol{r}) = 1$, we also see that the distance between consecutive Miller planes is $2\pi/|\boldsymbol{K}|$.

Cubic and hexagonal systems

For cubic systems, it is conventional to index the lattice planes based on the underlying simple cubic Bravais lattice. The bcc lattice is then viewed as a simple cubic lattice with a two element basis (see §2.1.5 below), and the fcc lattice as simple cubic with a four element basis. In hexagonal systems, typically one chooses the primary direct lattice vectors $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ to subtend an angle of $120°$, in which case $\boldsymbol{b}_1$ and $\boldsymbol{b}_2$ subtend an angle of $60°$. Then defining $\boldsymbol{b}_0 \equiv \boldsymbol{b}_2 - \boldsymbol{b}_1$, we have that $\boldsymbol{b}_0$ is rotationally equivalent to $\boldsymbol{b}_1$ and $\boldsymbol{b}_2$. Thus, if we define $i \equiv -(h+k)$, then we have the following rotations:

$$\begin{aligned} h\,\boldsymbol{b}_1 + k\,\boldsymbol{b}_2 &= R_{120°}\big(k\,\boldsymbol{b}_1 + i\,\boldsymbol{b}_2\big) = R_{240°}\big(i\,\boldsymbol{b}_1 + h\,\boldsymbol{b}_2\big) \\ &= R_{60°}\big(\bar{i}\,\boldsymbol{b}_1 + \bar{h}\,\boldsymbol{b}_2\big) = R_{180°}\big(\bar{h}\,\boldsymbol{b}_1 + \bar{k}\,\boldsymbol{b}_2\big) = R_{300°}\big(\bar{k}\,\boldsymbol{b}_1 + \bar{i}\,\boldsymbol{b}_2\big) \quad . \end{aligned} \tag{2.10}$$

To reveal this rotational symmetry, the redundant fourth index i is used, and the Miller indices are reported as $(\,h\,k\,i\,l\,)$. The fourth index is always along the c-axis. The virtue of this four index notation is that it makes clear the relations between, *e.g.*, $(\,1\,1\,\bar{2}\,0\,) \equiv (\,1\,1\,0\,)$ and $(\,1\,\bar{2}\,1\,0\,) \equiv (\,1\,\bar{2}\,0\,)$, and in general

$$(\,h\,k\,i\,l\,) \;\to\; (\,\bar{i}\,\bar{h}\,\bar{k}\,l\,) \to\; (\,k\,i\,h\,l\,) \;\to\; (\,\bar{h}\,\bar{k}\,\bar{i}\,l\,) \;\to\; (\,i\,h\,k\,l\,) \;\to\; (\,\bar{k}\,\bar{i}\,\bar{h}\,l\,) \;\to (\,h\,k\,i\,l\,) \tag{2.11}$$

gives the full sixfold cycle.

2.1.3 Crystallographic restriction theorem

Consider a Bravais lattice and select one point as the origin. Now consider a general rotation $R \in \mathsf{SO}(3)$ and ask how the primary direct lattice vectors transform. If the Bravais lattice is symmetric under the operation R, then each $\boldsymbol{a}_j$ must transform into another Bravais lattice vector, *i.e.*

$$R_{\mu\nu}\, a_i^\nu = K_{ij}\, a_j^\mu \quad , \tag{2.12}$$

where K_{ij} is a matrix composed of integers. Now multiply both sides of the above equation by b_i^ρ and sum on the index i. From Eqn. 2.3, we have $a_i^\nu\, b_i^\rho = 2\pi\delta_{\nu\rho}$, hence $2\pi R_{\mu\rho} = K_{ij}\, a_j^\mu\, b_i^\rho$. Now take the trace over the indices μ and ρ, again invoking Eqn. 2.3, to get $\mathsf{Tr}\ R = \mathsf{Tr}\ K$. Now the trace of any matrix is invariant under similarity transformation, and in $d = 3$ dimensions, and if $R = R(\xi, \hat{\boldsymbol{n}})$ we can always rotate $\hat{\boldsymbol{n}}$ so that it lies along $\hat{\boldsymbol{z}}$, in which case

$$S\, R(\xi, \hat{\boldsymbol{n}})\, S^{-1} = \begin{pmatrix} \cos\xi & -\sin\xi & 0 \\ \sin\xi & \cos\xi & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad , \tag{2.13}$$

in which case $\mathsf{Tr}\ R = 2\cos\xi + 1$. In $d = 2$ we have $\mathsf{Tr}\ R = 2\cos\xi$ for proper rotations. Thus, $\mathsf{Tr}\ R \in \mathbb{Z}$ is possible only for $\xi = 2\pi/n$ where $n = 1, 2, 3, 4$, or 6. Fivefold, sevenfold, *etc.* symmetries are forbidden! Note that it is perfectly possible to have a fivefold symmetric molecule, such as $\mathrm{C}_{20}\mathrm{H}_{10}$, also known as corannulene. But when we insist on having both rotational as well as translational symmetries, the former are strongly restricted. Remarkably, there exists a family of three-dimensional structures, called *quasicrystals*, which exhibit forbidden fivefold or tenfold rotational symmetries. They elude the restriction theorem by virtue of not being true crystals, *i.e.* they are *quasi*periodic structures. See Fig. 2.4.

The result $\mathsf{Tr}\ R = \mathsf{Tr}\ K \in \mathbb{Z}$ is valid in all dimensions and does impose restrictions on the possible rotational symmetries. However, rotations in higher dimensions are in general not planar. Consider that it takes $d - 1$ angles to specify an axis in d dimensions, but the dimension of $\mathsf{SO}(d)$ is $\frac{1}{2}d(d-1)$, so an additional $\frac{1}{2}(d-1)(d-2)$ parameters in addition to specifying an axis are required to fix an element of $\mathsf{SO}(d)$. For example, the four-dimensional F_4 lattice is a generalization of the three-dimensional bcc structure, consisting of two interpenetrating four-dimensional hypercubic lattices, and exhibits 12-fold rotational symmetries.

2.1.4 Enumeration of two and three-dimensional Bravais lattices

The complete classification of two and three Bravais lattices is as follows[4]. In two dimensions, there are four *lattice systems*: square, oblique, hexagonal, and rectangular. Of these, the rectangular system supports a subvariety called center rectangular, resulting in a total of five distinct two-dimensional Bravais lattices, shown in Fig. 2.5.

In three dimensions, there are seven lattice systems: triclinic, monoclinic, orthorhombic, tetragonal, trigonal, hexagonal, and cubic[5]. Of these, monoclinic supports two subvarieties or *types* (simple and base-centered), orthorhombic four subvarieties (simple, base-centered, body-centered, and face-centered), and cubic three subvarieties (simple, face-centered, and body-centered), amounting to a grand total of 14 three-dimensional Bravais lattices:

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[4] To reinforce one's memory, there is even a song: `https://ww3.haverford.edu/physics/songs/bravais.htm.`

[5] The systematic enumeration of three-dimensional lattices based on symmetry was first done by M. L. Frankenheim in 1842. Frankenheim correctly found there were 32 distinct crystal classes, corresponding to the 32 distinct three-dimensional point groups, but he erred in counting 15 rather than 14 distinct lattices. A. L. Bravais, in 1845, was the first to get to 14, and for this he was immortalized. The identity of Frankenheim's spurious 15th lattice remains unclear.

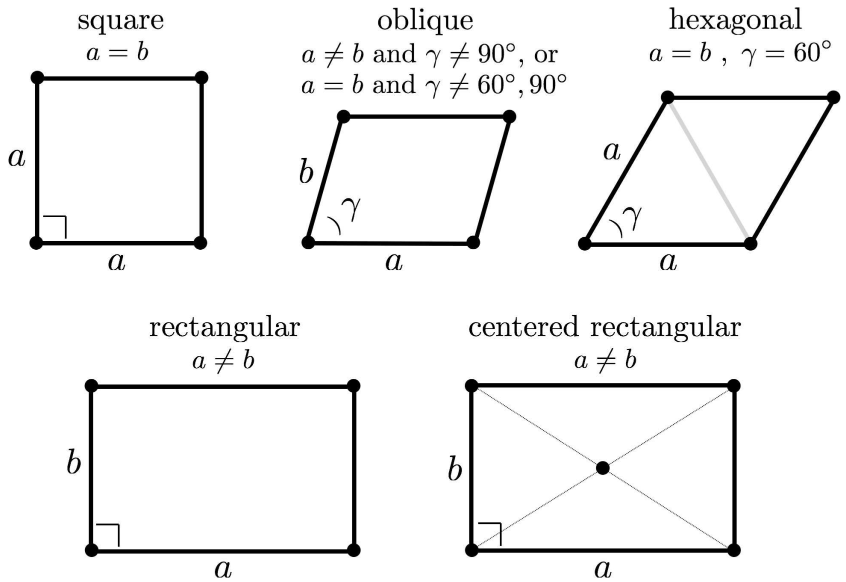

Figure 2.5: The five two-dimensional Bravais lattices.

(i) *Cubic* : this system is the most symmetric, with symmetry group $O_h \cong S_4 \times \mathbb{Z}_2$, which has 48 elements[6]. The $\mathbb{Z}_2$ factor arises from the *inversion* symmetry exhibited by all Bravais lattices. Recall inversion takes (x, y, z) to $(-x, -y, -z)$. The three cubic subvarieties (simple, body-centered, and face-centered) are depicted in the first three panels of 2.6.

(ii) *Tetragonal* : Lowering the cubic symmetry by stretching or compressing along one of the axes, one arrives at the tetragonal system, whose unit cell is a cubic rectangle with side lengths $a = b \neq c$. There are two sub-varieties: simple and body-centered, depicted in the left two panels of Fig. 2.8. Why is there not a face-centered subvariety as well? Because it is equivalent to the body-centered case[7]. The symmetry group is $D_{4h} \cong \mathbb{Z}_4 \times \mathbb{Z}_2 \times \mathbb{Z}_2$.

(iii) *Orthorhombic* : Further lowering the symmetry by stretching or compressing in along a second axis, we obtain the orthorhombic system. The only rotational symmetries are the three perpendicular mirror planes bisecting each of the unit cell sides, resulting in a $D_{2h} = \mathbb{Z}_2 \times \mathbb{Z}_2 \times \mathbb{Z}_2$ symmetry. There are four subvarieties, depicted in Fig. 2.7: simple, base-centered, body-centered, and face-centered.

(iv) *Monoclinic* : Take an orthorhombic lattice and shear it so that the c-axis is no longer along $\hat{\boldsymbol{z}}$, but lies in the (y, z) plane at an angle $\beta \neq 90°$ with respect to the horizontal. There are two distinct subvarieties, simple and base-centered, which are shown in the third and fourth panels of Fig. 2.8. The only remaining symmetries are reflection in the (y, z) plane and inversion, hence the symmetry group is $\mathbb{Z}_2 \times \mathbb{Z}_2$.

(v) *Triclinic* : Shearing in a second direction, one obtains the triclinic system, depicted in the right

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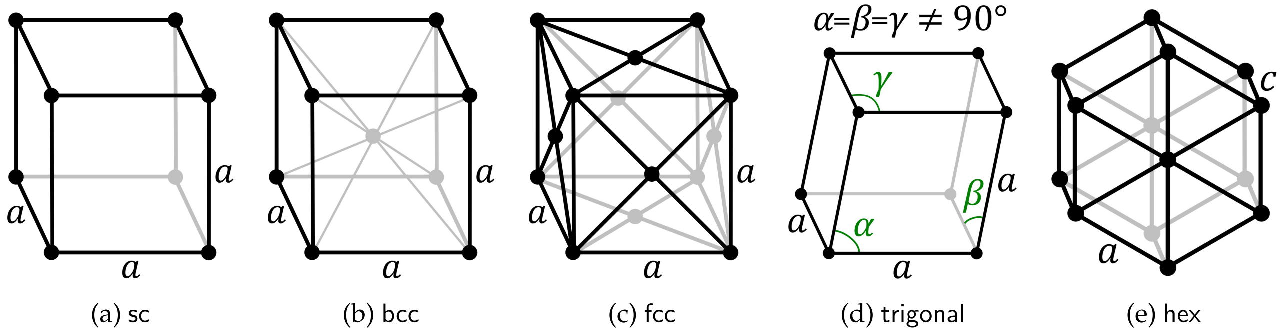
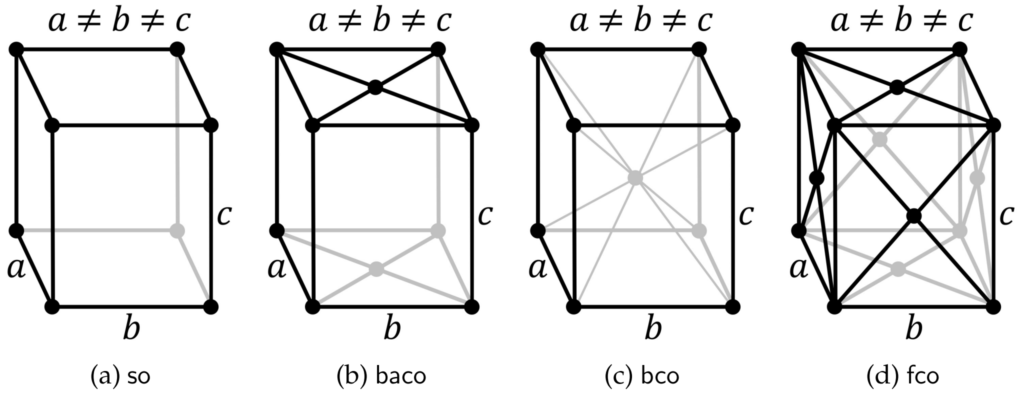
[6] Why is the symmetry group of the cube called O (or O_h with inversion)? Because the cube and the octahedron have the same symmetries. Hence O is sometimes called the octahedral group.

[7] See Ashcroft and Mermin, *Solid State Physics*, pp. 116-118.



(a) sc (b) bcc (c) fcc (d) trigonal (e) hex

Figure 2.6: Simple cubic, body-centered cubic, face-centered cubic, trigonal, and hexagonal Bravais lattices. Image credits: Wikipedia.



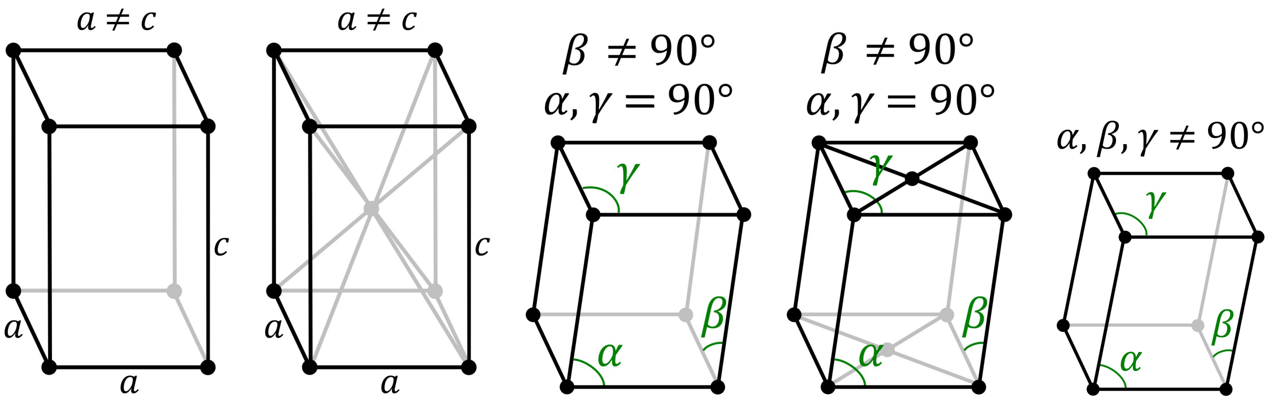
(a) so (b) baco (c) bco (d) fco

Figure 2.7: (Simple orthorhombic, base-centered orthorhombic, body-centered orthorhombic, and face-centered orthorhombic Bravais lattices. Image credits: Wikipedia.

panel of Fig. 2.8. At least two of the angles $\vartheta_{ij} = \cos^{-1}\big(\hat{\boldsymbol{a}}_i \cdot \hat{\boldsymbol{a}}_j\big)$ are not 90°, and all the axes are of unequal lengths. The only remaining symmetry is inversion, so the symmetry group is $\mathbb{Z}_2$.

(vi) *Trigonal*: Starting with the cubic system, rather than squashing it along one of its three orthogonal axes, imagine stretching it along the cube's diagonal. The resulting Bravais lattice is generated by three nonorthogonal primitive vectors which make the same angle with respect to one another, as depicted in the fourth panel of Fig. 2.6. The stretched cube diagonal becomes a threefold axis, and the symmetry group is D_{3d}, which is of order 12.

(vii) *Hexagonal*: Finally, we come to the hexagonal system, which is unrelated to the cube. The simple hexagonal lattice, depicted in the last panel of Fig. 2.6, is its only representative. Two of the primitive direct lattice vectors are of equal length a and subtend a relative angle of 60° or 120°. The third lies perpendicular to the plane defined by the first two, with an independent length c. The symmetry group is D_{6h}, which has 24 elements.



(a) st (b) bct (c) sm (d) bacm (e) tri

Figure 2.8: Simple tetragonal, body-centered tetragonal, monoclinic, base-centered monoclinic, and triclinic Bravais lattices. Image credits: Wikipedia.

2.1.5 Crystals

A Bravais lattice is a tiling of space with empty unit cells. We are in the position of a painter staring at a beautifully symmetric but otherwise empty canvas. The art with which we fill our canvas is the *crystalline unit cell*, and it consists of a number r of atoms or ions, where ions of species j are located at positions $\boldsymbol{\delta}_j$ relative to any given direct lattice point $\boldsymbol{R}$, with $j \in \{1, \ldots, r\}$. If the direct lattice points $\boldsymbol{R}$ themselves represent the positions of a class of ion, we write $\boldsymbol{\delta}_1 \equiv 0$. The set of vectors $\{\boldsymbol{\delta}_j\}$ is called a *basis*, and without loss of generality, we restrict the basis vectors so they do not lie outside the unit cell.

- ⋆ *In a crystal, ions of species j are located at positions $\boldsymbol{R} + \boldsymbol{\delta}_j$, where $\boldsymbol{R}$ is a Bravais lattice vector and $\boldsymbol{\delta}_j$ is a basis vector. All basis vectors are taken to lie within a single unit cell of the Bravais lattice.*

Obviously the existence of a basis, unless it is one of spherical symmetry with respect to each Bravais lattice point, will have consequences for the allowed rotational symmetries of the crystal, in general reducing them to a subgroup of the symmetry group of the Bravais lattice itself. A vivid illustration of this is provided in Fig. 2.9 for the cubic lattice. When our canvas is completely blank, the cube is entirely white, and the symmetry group is O_h, with 48 elements, as shown in the middle bottom panel of the figure. If one of the reflection generators is broken, but all other generators are preserved, the symmetry is reduced from O_h to O, which has 24 elements. By breaking different symmetry operations, O_h can be reduced to the tetrahedral groups T_d and T_h, which also have 24 elements. Finally, each of O, T_d, and T_h may be broken down to the 12 element tetrahedral group T, depicted in the upper left panel. It all depends on how we paint the canvas.

As an example of a filled canvas, consider Fig. 2.10, which shows the unit cells of four high temperature cuprate superconductors. It is a good exercise to verify the stoichiometry in at least one example. Consider the unit cell for LSCO. The blue Cu ions at the top and bottom of the cell are each shared by eight of these cubic rectangular cells, so the eight Cu ions at the corners amount to one per cell. The Cu ion in the center belongs completely to this cell, so we have a total of two Cu per cell. Each of the eight green La/Sr ions lying along the vertical columns at the cell edges is shared by four cells, so they amount to a

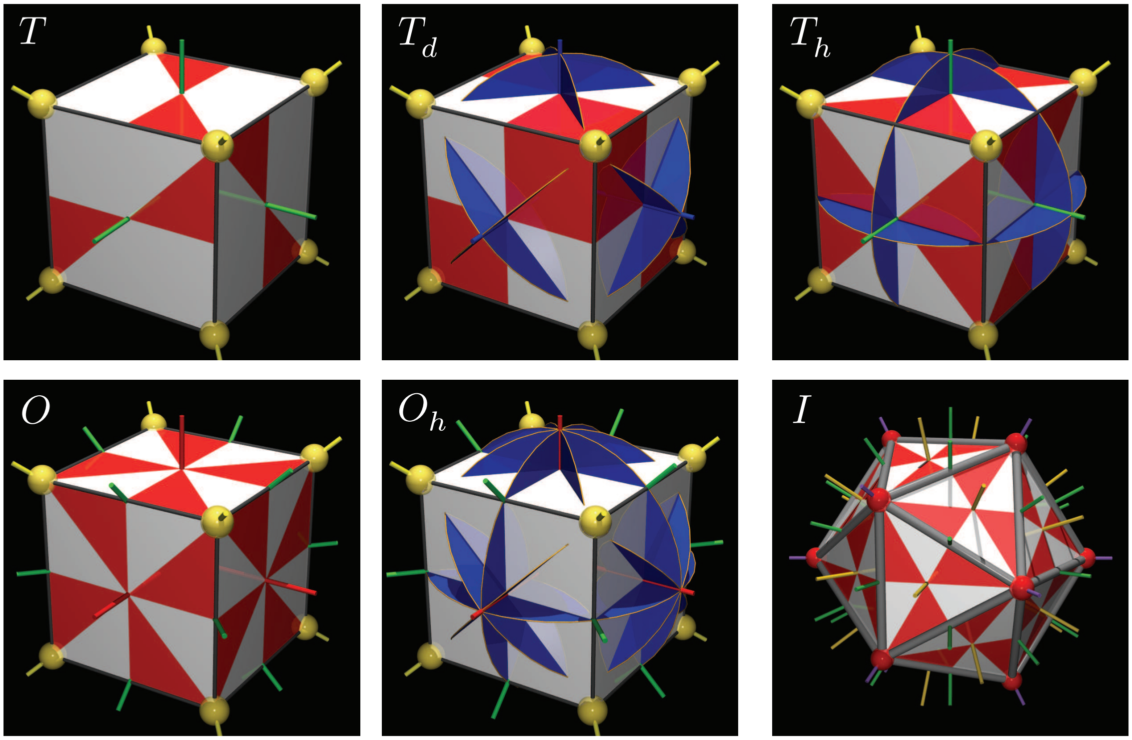


Figure 2.9: Tetrahedral, cubic, and icosahedral group symmetry operations. Twofold, threefold, fourfold, and sixfold axes are shown. The blue fins extend into discs, slicing the cube in two along reflection planes. Image credits: `http://azufre.quimica.uniovi.es/d-MolSym/`.

total of two per cell. The two La/Sr ions within the cell toward the top and bottom each count as one, for a total of four La/Sr per cell. Lastly, we come to the oxygen ions, shown in red. Each of the O ions along any of the 12 edges of the cell is shared by four cells. There are 16 such O sites, thus accounting for four O per cell. If you think about the periodic repetition of the cell, you should realize that each Cu ion is surrounded by six O ions arranged in an octahedron. There is also such an octahedron in the center of the cell, on which we now focus. Two of its O ions are displaced vertically with respect to the central Cu ion, and are therefore wholly part of our cell. The other four each lie in the center of a face, and are each shared by two cells. Thus, this central octahedron accounts for an additional four O ions, for a grand total of 8 per cell. Our final tally: two Cu, four La/Sr, and eight O per cell, which is to say $La_{2-x}Sr_xCuO_4$. In the three other compounds, the oxygen stoichiometry is given as $4+\delta$ (Hg1201) or $6+\delta$ (YBCO and Ti2201). The deviation of δ from an integer value (either 0 or 1) accounts for the presence of oxygen vacancies[8].

In an electron diffraction experiment, an incident beam of electrons with wavevector $\boldsymbol{q}$ is scattered from a crystal, and the scattering intensity $I(\boldsymbol{k})$ as a function of the *wavevector transfer* $\boldsymbol{k}=\boldsymbol{q}'-\boldsymbol{q}$ is measured. If the scattering is elastic, $|\boldsymbol{q}'|=|\boldsymbol{q}|$, which means k is related to the scattering angle $\vartheta=\cos^{-1}(\hat{\boldsymbol{q}}\cdot\hat{\boldsymbol{q}}')$ by

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[8] It is a good exercise to determine the stoichiometry of these compounds based on the figures.

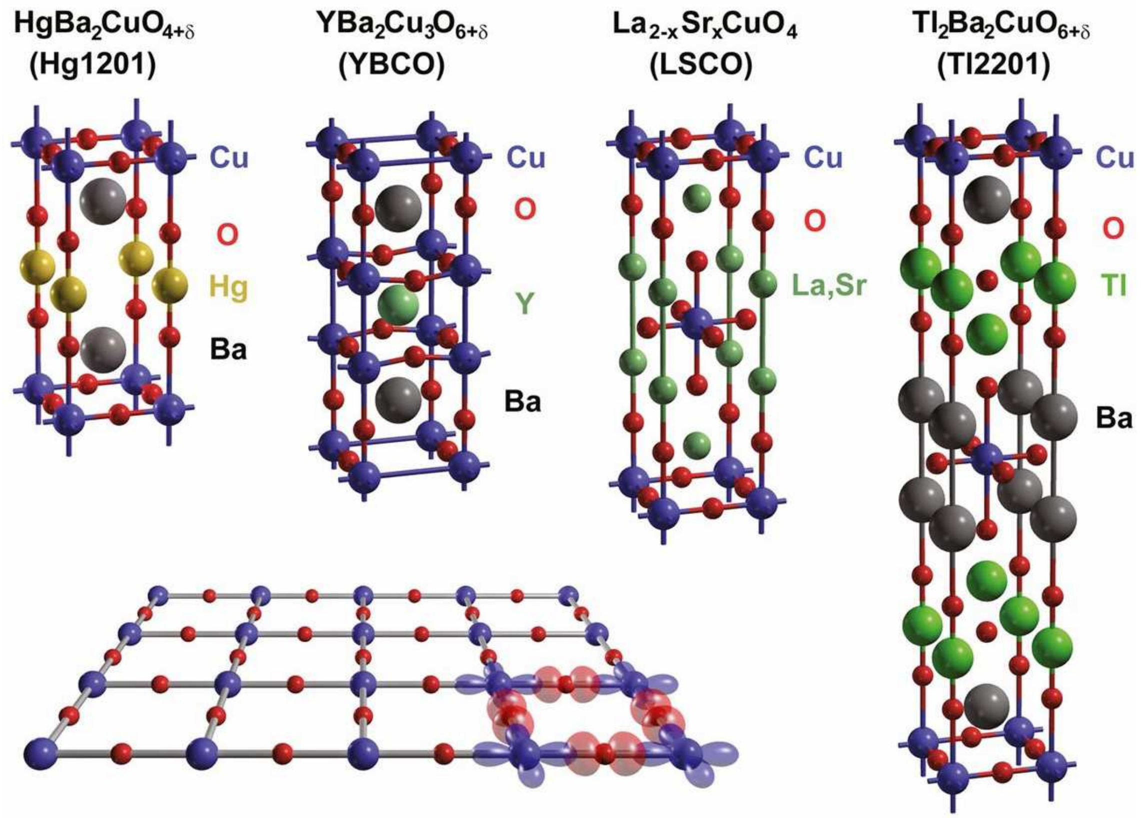

Figure 2.10: Unit cells of four high temperature cuprate superconductors. Lower left shows a sketch of the active electronic orbitals in the Cu-O planes. Image credit: N. Barišić *et al.*, *Proc. Nat. Acad. Sci.* **110**, 12235 (2013).

$k=2q\sin(\frac{1}{2}\vartheta)$. Let us model the $T=0$ density[9] of the crystal $\rho(\boldsymbol{r})$ as

$$\rho(\boldsymbol{r})=\sum_{\boldsymbol{R}}\sum_j c_j\,\delta(\boldsymbol{r}-\boldsymbol{R}-\boldsymbol{\delta}_j) \quad , \tag{2.14}$$

where c_j is the weight for ionic species j. The total scattering intensity $I(\boldsymbol{k})$ is proportional to $|\hat{\rho}(\boldsymbol{k})|^2/N$, where $\hat{\rho}(\boldsymbol{k})$ is the Fourier transform of $\rho(\boldsymbol{r})$ and N is the total number of unit cells in the crystal. Choosing units where the prefactor is unity, we have

$$\begin{aligned} I(\boldsymbol{k})&=\frac{1}{N}\,\big|\hat{\rho}(\boldsymbol{k})\big|^2=\frac{1}{N}\sum_{\boldsymbol{R},\boldsymbol{R}'}e^{-i\boldsymbol{k}\cdot(\boldsymbol{R}-\boldsymbol{R}')}\sum_{j,j'}c_j\,c_{j'}\,e^{-i\boldsymbol{k}\cdot(\boldsymbol{\delta}_j-\boldsymbol{\delta}_{j'})}\\ &=F(\boldsymbol{k})\sum_{\boldsymbol{R}}e^{-i\boldsymbol{k}\cdot\boldsymbol{R}}=\hat{\Omega}\sum_{\boldsymbol{K}}F(\boldsymbol{K})\,\delta(\boldsymbol{k}-\boldsymbol{K}) \quad , \end{aligned} \tag{2.15}$$

where we have invoked the Poisson summation formula of Eqn. 2.7, and where we have defined the

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[9] What matters for electron diffraction is the electron density.

form factor

$$F(\boldsymbol{K}) = \left| \sum_{j=1}^{r} c_j \, e^{-i\boldsymbol{K}\cdot\boldsymbol{\delta}_j} \right|^2 \quad . \tag{2.16}$$

Thus we expect δ-function *Bragg peaks* in the scattering intensity at values of the wavevector transfer equal to any reciprocal lattice vector $\boldsymbol{K}$. The form factor $F(\boldsymbol{K})$ modifies the intensity and can even lead to systematic *extinctions* of certain reciprocal lattice vectors. Consider, for example, a one-dimensional lattice with lattice spacing a and basis elements $\delta_1 = 0$ and $\delta_2 = \frac{1}{2}a$. If $c_1 = c_2 \equiv c$, the form factor is

$$F(K) = |c|^2 \left|1 + e^{iKa/2}\right|^2 \quad . \tag{2.17}$$

This vanishes for $K = 2\pi j/a$ whenever j is odd. So the lesson here is that the $T = 0$ scattering intensity from a crystal is given by a sum of δ-functions and is singular whenever the wavevector transfer is equal to a reciprocal lattice vector. The presence of a basis modifies each Bragg peak by the form factor $F(\boldsymbol{K})$, which in some cases can even extinguish the peak completely[10].

2.1.6 Trigonal crystal system

While the trigonal point group D_{3d} is a normal subgroup of the hexagonal point group D_{6h}, the trigonal Bravais lattice does not result from an infinitesimal distortion of the simple hexagonal lattice. Contrast this situation with that for, *e.g.*, tetragonal *vis-a-vis* cubic, where a tetragonal lattice is obtained by an infinitesimal stretching along one of the principal axes of the cubic lattice. Any trigonal lattice, however, can be expressed as a hexagonal lattice with a three element basis. To see this, define the vectors

$$\boldsymbol{s}_1 = \tfrac{1}{\sqrt{3}}\, a\big(\tfrac{\sqrt{3}}{2}\,\hat{\boldsymbol{x}} - \tfrac{1}{2}\hat{\boldsymbol{y}}\big) \quad , \quad \boldsymbol{s}_2 = \tfrac{1}{\sqrt{3}}\, a\hat{\boldsymbol{y}} \quad , \quad \boldsymbol{s}_3 = \tfrac{1}{\sqrt{3}}\, a\big(-\tfrac{\sqrt{3}}{2}\,\hat{\boldsymbol{x}} - \tfrac{1}{2}\hat{\boldsymbol{y}}\big) \quad . \tag{2.18}$$

Then $\boldsymbol{a}_1 \equiv \boldsymbol{s}_1 - \boldsymbol{s}_3 = a\hat{\boldsymbol{x}}$ and $\boldsymbol{a}_2 \equiv \boldsymbol{s}_2 - \boldsymbol{s}_3 = a\big(\frac{1}{2}\hat{\boldsymbol{x}} + \frac{\sqrt{3}}{2}\hat{\boldsymbol{y}}\big)$ are primitive DLVs for a two-dimensional hexagonal lattice. The vectors $\boldsymbol{d}_j \equiv \boldsymbol{s}_j + \frac{1}{3}c\hat{\boldsymbol{z}}$ for $j = 1, 2, 3$ then constitute three primitive DLVs for the trigonal lattice, each of length $d = \frac{1}{3}\sqrt{3a^2 + c^2}$. They also correspond to a three element basis within the first Wigner-Seitz cell of the simple hexagonal lattice. Conventionally, and equivalently, the three element basis may be taken to be $\boldsymbol{\delta}_1 = 0$, $\frac{1}{3}\boldsymbol{a}_1 + \frac{1}{3}\boldsymbol{a}_2 + \frac{1}{3}c\hat{\boldsymbol{z}}$, and $\frac{2}{3}\boldsymbol{a}_1 + \frac{2}{3}\boldsymbol{a}_3 + \frac{2}{3}c\hat{\boldsymbol{z}}$, all of which are associated with the hexagonal unit cell spanned by vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, and $c\hat{\boldsymbol{z}}$. Note that this is not a Wigner-Seitz cell, and its projection onto the (x, y) plane is a rhombus rather than a hexagon. Although describing the trigonal Bravais lattice as a hexagonal Bravais lattice with a three element basis might seem an unnecessary complication, in fact it proves to be quite convenient because two pairs of axes in the hexagonal system are orthogonal. Similarly, it is convenient to describe the bcc and fcc cubic lattices as simple cubic with a two and four element basis, respectively, to take advantage of the mutually orthogonal primitive direct lattice vectors of the simple cubic structure.

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[10] It is a good exercise to compute $I(\boldsymbol{k})$ for the bcc and fcc structures when they are described in terms of a simple cubic lattice with a two or four element basis. The resulting extinctions limit the Bragg peaks to those wavevectors which are in the bcc or fcc reciprocal lattice.

CRYSTALLOGRAPHY	$d = 2$	$d = 3$
systems	4	7
lattices	5	14
point groups	10	32
space groups	17	230
symmorphic	13	73
non-symmorphic	4	157

Table 2.1: True Facts about two and three-dimensional crystallography.

2.1.7 Point groups, space groups and site groups

A group $\mathcal{P} \subset \mathsf{O}(3)$ of symmetry operations of a structure which leaves one point fixed is known as a *point group*[11]. The point group $\mathcal{P}_{\mathcal{L}}$ of a Bravais lattice is the group of rotational symmetries which fix any of the the Bravais lattice sites. This group is shared by all lattices in the same lattice system, and is known as the *holohedry* of the lattice.

In crystals, not every lattice site is equivalent. This may be due to the fact that different ions occupy different sites, but it is also the case for certain monatomic crystals, such as diamond, which consists of two interpenetrating fcc lattices that are not related by Bravais lattice translation. That is, the diamond structure is an fcc Bravais lattice with a two element basis. The full symmetry group of a crystal consists of both rotations and translations and is called the *space group* $\mathcal{S}$. A space group is a subgroup of the Euclidean group: $\mathcal{S} \subset \mathsf{E}(3)$, and a general space group operation $\{\, g \,|\, \boldsymbol{t} \,\}$ acts as

$$\{\, g \,|\, \boldsymbol{t} \,\}\, \boldsymbol{r} = g\, \boldsymbol{r} + \boldsymbol{t} \quad , \tag{2.19}$$

where $g \in \mathsf{O}(3)$. The identity element in $\mathcal{S}$ is $\{\, E \,|\, 0 \,\}$, where E is the identity in $\mathsf{O}(3)$, and the inverse is given by

$$\{\, g \,|\, \boldsymbol{t} \,\}^{-1} = \{\, g^{-1} \,|\, -g^{-1}\boldsymbol{t} \,\} \quad . \tag{2.20}$$

In order that $\mathcal{S}$ be a group, we must have that

$$\begin{aligned} \{\, g_2 \,|\, \boldsymbol{t}_2 \,\}\{\, g_1 \,|\, \boldsymbol{t}_1 \,\}\, \boldsymbol{r} &= \{\, g_2 \,|\, \boldsymbol{t}_2 \,\}(g_1\, \boldsymbol{r} + \boldsymbol{t}_1) \\ &= g_2\, g_1\, \boldsymbol{r} + g_2\, \boldsymbol{t}_1 + \boldsymbol{t}_2 = \{\, g_2\, g_1 \,|\, g_2\, \boldsymbol{t}_1 + \boldsymbol{t}_2 \,\}\, \boldsymbol{r} \quad , \end{aligned} \tag{2.21}$$

is also in $\mathcal{S}$. This requires that the matrices g themselves form a group, called the *crystallographic point group* $\mathcal{P}$. For a Bravais lattice, $\mathcal{P} = \mathcal{P}_{\mathcal{L}}$, but in general a crystal is of lower symmetry than its underlying Bravais lattice, and the crystallographic point group is a subgroup of the holohedry: $\mathcal{P} \subset \mathcal{P}_{\mathcal{L}}$. Note that $\mathcal{S} \not\cong \mathcal{P} \times \mathcal{T}$, *i.e.* the space group is not simply a direct product of the point group and the translation group, because multiplication of $(g, \boldsymbol{t}) \in \mathcal{P} \times \mathcal{T}$ satisfies $(g_2, \boldsymbol{t}_2)\,(g_1, \boldsymbol{t}_1) = (g_2\, g_1, \boldsymbol{t}_2 + \boldsymbol{t}_1)$. The abelian group $\mathcal{T} \cong \mathbb{Z}^d$ of Bravais lattice translations $\{\, E \,|\, \boldsymbol{R} \,\}$ forms an invariant subgroup of $\mathcal{S}$. If all the symmetry operations of a particular crystal can be written as $\{\, g \,|\, \boldsymbol{R} \,\}$, the crystal's space group is then said to be

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[11] Mathy McMathstein says that a point group is a group of *linear isometries* which have a common fixed point. An isometry is a distance-preserving transformation on a metric space.

symmorphic and we write $\mathcal{S} = \mathcal{P} \rtimes \mathcal{T}$, where the symbol $\rtimes$ indicates a *semi-direct product* of two groups. *In a symmorphic crystal, one may choose an origin about which all point group symmetries are realized.*

However, it turns out that many crystals have space group elements $\{\, g \,|\, \boldsymbol{t} \,\}$ where $g \in \mathcal{P}$ but $\boldsymbol{t} \notin \mathcal{T}$. Rather, for these symmetry operations, $\boldsymbol{t}$ is a fraction of a Bravais lattice translation. In some cases, with a different choice of origin, these operations can be expressed as a rotation followed by Bravais lattice translation[12]. For crystals with *nonsymmorphic* space groups, however, there is no possible choice of origin about which all elements of $\mathcal{S}$ can be decomposed into a point group operation followed by a Bravais lattice translation. Two examples are shown in Fig. 2.11: the three-dimensional hexagonal close packed (hcp) structure, and the two-dimensional Shastry-Sutherland lattice. An hcp crystal is a simple hexagonal lattice with a two element basis. It occurs commonly in nature and describes, for example, the low temperature high pressure phase of ^{4}He just above its melting curve (about 25 atmospheres at $T = 0\,\text{K}$). The primitive direct lattice vectors of the hcp structure are

$$\boldsymbol{a}_1 = \big(\tfrac{1}{2}\hat{\boldsymbol{x}} - \tfrac{\sqrt{3}}{2}\hat{\boldsymbol{y}}\big)a \quad , \quad \boldsymbol{a}_2 = \big(\tfrac{1}{2}\hat{\boldsymbol{x}} + \tfrac{\sqrt{3}}{2}\hat{\boldsymbol{y}}\big)a \quad , \quad \boldsymbol{a}_3 = c\hat{\boldsymbol{z}} \quad , \tag{2.22}$$

with $c = \sqrt{\frac{8}{3}}\,a$. The basis vectors are $\boldsymbol{\delta}_1 = 0$ and $\boldsymbol{\delta}_2 = \frac{1}{3}\boldsymbol{a}_1 + \frac{2}{3}\boldsymbol{a}_2 + \frac{1}{2}\boldsymbol{a}_3$. In the figure, A sublattice sites are depicted in red and B sublattice sites in blue. Note that the B sites lie in the centers of the up-triangles in each A sublattice plane, and displaced by half a unit cell in the $\hat{\boldsymbol{z}}$ diraction. The nonsymmorphic operation in the hcp point group is known as a *screw axis* and it involves a rotation by 60° about the $\hat{\boldsymbol{z}}$ axis through the centers of the A sublattice down triangles, followed by a translation by $\frac{1}{2}\boldsymbol{a}_3$.

The second example is that of the Shastry-Sutherland lattice, which describes the CuBO_3 layers in the magnetic compound $\text{SrCu}_2(\text{BO}_3)_2$. Here we have four sublattices, and the nonsymmorphic operation is known as a *glide mirror*, which involves translation along a plane (or a line in two dimensions) by a half unit cell, followed by a reflection in the plane. See if you can spot the nonsymmorphic symmetry.

A third example is that of diamond, which consists of two interpenetrating fcc lattices, and has a zincblende structure shown in Fig. 2.16. Diamond possesses both a fourfold (4_1) screw axis as well as a glide mirror. While the point group is O_h, there is no point in the diamond lattice about which all operations in O_h are realized. The maximum symmetry at any site is T_d.

In a symmorphic crystal, it is always possible to find some origin within the structural unit cell about which all point group symmetries are realized. In a Bravais lattice, this is true with respect to every lattice point, but obviously it is possible to choose an origin about which the group of rotational symmetries is reduced. For example, the point group of the square lattice is C_{4v}, but by choosing an origin in the center of one of the links the symmetry is reduced to C_{2v}. It is sometimes convenient to speak of the group of rotational symmetries with respect to a specific point $\boldsymbol{r}$ in the crystal structure. We call this the *site group* $\mathcal{P}(\boldsymbol{r})$. When $\boldsymbol{r} = \boldsymbol{R} + \boldsymbol{\delta}_j$ is a site in the crystal, *i.e.* a location of one of the ions, we may denote the site group as $\mathcal{P}(\boldsymbol{R}, j)$.

In a nonsymmorphic crystal, in general *no* sites will realize the symmetry of the point group $\mathcal{P}$. Consider, for example, the Shastry-Sutherland lattice in Fig. 2.11. Choosing the origin as the center of the magenta square unit cell, the site group is $\mathcal{P}(\boldsymbol{0}) = C_{2v}$. But the crystallographic point group for this structure is

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[12] In such cases, the putative nonsymmorphic operation is called *removable*. Otherwise, the nonsymmorphic operation is *essential*.

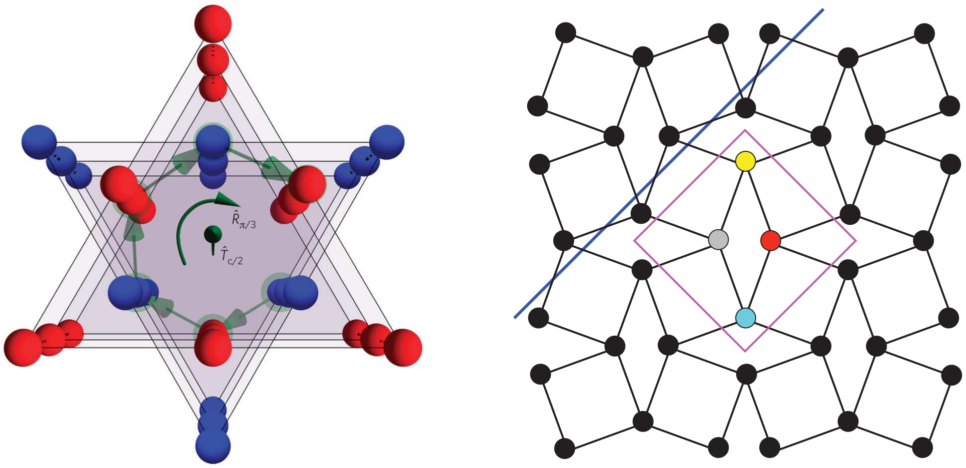

Figure 2.11: Two nonsymmorphic crystal lattices. Left: The hexagonal close packed lattice (space group $P6_3/mmc$) has a two site unit cell (red and blue) and a screw axis symmetry, given by a rotation by 60° followed by a translation of $\frac{1}{2}\boldsymbol{a}_3$ along the c-axis. The underlying Bravais lattice is simple hexagonal. Right: The Shastry-Sutherland lattice (space group $p4g$) has a four site unit cell (shown in center) and a glide mirror (blue line). Translation by half a unit cell along the mirror line followed by a mirror reflection is a lattice symmetry. The underlying Bravais lattice is square.

C_{4v}. Since $\mathcal{P}$ is the group of all rotational symmetries about all possible origins, necessarily $\mathcal{P}(\boldsymbol{r}) \subset \mathcal{P}$ for all sites $\boldsymbol{r}$.

Our crystallographer forbears have precisely tabulated for us all the possible lattices, point groups, and space groups in two and three dimensions (see Tab. 2.1). Proving these results is quite tedious, so we shall be content to take them as received wisdom. Note that a bit more than two thirds (157 out of 230) of the three-dimensional space groups are nonsymmorphic. Of those, all but two involve either a screw axis or a glide plane[13].

2.2 More on Point Groups

2.2.1 Standard notation for point group operations

A list of point group operations is provided in Tab. 2.2. We'll also start to use C_n to denote a group element, *i.e.* a rotation by $2\pi/n$ about a primary axis. If we need to distinguish this element from the cyclic group, which we've thus far also called C_n, we'll instead refer to the group as $\mathcal{C}_n$. Note that inversion can be written as $I = S_2$, and that I commutes with all elements of the point group $\mathcal{P}$, *i.e.* $I \in Z(\mathcal{P})$ is in the center of $\mathcal{P}$.

Any improper operation $g \in \mathsf{O}(3)$ has $\det(g) = -1$. This entails that g must have an eigenvalue $\lambda = -1$,

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[13] Space groups no. 24 (also known as $I2_12_12_1$) and no. 199 ($I2_13$) have removable screw axes, but nevertheless there is no single origin about which every symmetry operation can be expressed as $\{\, g \,|\, \boldsymbol{t} \,\}$ with $g \in \mathcal{P}$ and $\boldsymbol{t} \in \mathcal{T}$.

SYMBOL	OPERATION
E	identity
C_n	rotation through $2\pi/n$ about primary axis $\hat{\boldsymbol{n}}$; operator equivalent: $e^{-2\pi i \hat{\boldsymbol{n}}\cdot\boldsymbol{J}/n\hbar}$ where $\boldsymbol{J}=\boldsymbol{L}+\boldsymbol{S}$
I	inversion ($\boldsymbol{r}\to-\boldsymbol{r}$) ; leaves spinor coordinates invariant and commutes with all other point group operations
σ	C_2 rotation followed by reflection in plane perpendicular to the axis of rotation ; equivalent to IC_2 or $C_2\,I$
σ_h	reflection in a 'horizontal' plane perpendicular to a primary axis
σ_v	reflection in a 'vertical' plane which contains a primary axis
σ_d	reflection in a 'diagonal' plane containing the primary axis of symmetry and which bisects the angle between neighboring twofold axes perpendicular to the primary axis
S_n	rotoreflection: $S_n=\sigma_h^{-1}\,C_n$, *i.e.* rotation by $2\pi/n$ followed by reflection in the perpendicular plane (note $I=S_2$)
$\bar{E}$	spinor rotation through 2π ; $\bar{E}=e^{-2\pi i\hat{\boldsymbol{n}}\cdot\boldsymbol{S}}$ ($S=\frac{1}{2}$) ; leaves spatial coordinates (x,y,z) invariant
$\bar{g}$	any point group operation g followed by $\bar{E}$

Table 2.2: Standard notation for point group operations.

and the corresponding eigenvector $\hat{\boldsymbol{m}}$, for which $g\hat{\boldsymbol{m}}=-\hat{\boldsymbol{m}}$, is known as a *reversal axis*. It also follows in all odd dimensions that if g is proper, *i.e.* if $\mathsf{det}(g)=+1$, then g has an eigenvalue $\lambda=+1$, and the corresponding eigenvector $\hat{\boldsymbol{n}}$ which satisfies $g\hat{\boldsymbol{n}}=\hat{\boldsymbol{n}}$ is an *invariant axis*. Improper elements of $\mathsf{O}(n)$ can be written as $Ig(\xi,\hat{\boldsymbol{n}})$, where I is the inversion operator. In even dimensions, the inversion I is equivalent to C_2, but one can form improper rotations via a reflection σ.

The rotoreflection operation is $S_n=\sigma_h^{-1}\,C_n=C_n\,\sigma_h^{-1}$. The reason we write σ_h^{-1} rather than σ_h has to do with what happens when we account for electron spin, in which case $\sigma_h^{-1}=\overline{E}\,\sigma_h$, where $\overline{E}$ is spinor reversal, *i.e.* rotation of the spinor component through 2π. Without spin, we have $\sigma_h^{-1}=\sigma_h$, and for n odd, one then has $(S_n)^n=\sigma_h$ and $(S_n)^{n+1}=C_n$, which says that if $S_n\in\mathcal{P}$ then so are both σ_h and C_n . If, on the other hand, n is even, this may not be the case.

2.2.2 Proper point groups

A proper point group $\mathcal{P}$ is a subgroup of $\mathsf{SO}(3)$[14]. The following are the proper point groups:

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[14] Two-dimensional point groups are much simpler to classify as they always involve at most a single rotation axis and/or a planar reflection. They form a subset of the three-dimensional point groups.

(i) *Cyclic groups* : The cyclic group C_n (order n) describes n-fold rotations about a fixed axis. The restriction theorem limits crystallographic cyclic groups to the cases $n = 1, 2, 3, 4$, and 6. Again, molecules, which have no translational symmetries, are not limited by the restriction theorem.

(ii) *Dihedral groups* : The group D_n (order $2n$) has a primary n-fold axis and n twofold axes perpendicular to the primary axis. Note that if one started with only one such perpendicular twofold axis, the C_n operations would generate all the others. For n even, the alternating twofold axes break up into two conjugacy classes, whereas for n odd there is only one such class.

(iii) *Tetrahedral, octahedral, and icosahedral groups* : When there is more than one n-fold axis with $n > 2$, the rotations about either axis will generate new axes. Geometrically, this process run to its conclusion traces out a regular spherical polygon when one traces the intersections of the successively-generated axes on the unit sphere. There are only five possible such regular polyhedra: tetrahedron, cube, octahedron, dodecahedron, and icosahedron. The second two have the same symmetry operations, as do the last two, so there are only three such groups: T, O, and I.

  (iiia) *Tetrahedral group* : T is the symmetry group of proper rotations of the tetrahedron. Embedding the tetrahedron in a cube, as in Fig. 2.12, there are three two-fold axes through the cube faces, plus four threefold axes through the cube diagonals, for a total of 12 operations including the identity. Note $T \cong A_4$, the alternating group on four symbols.

  (iiib) *Octahedral group* : O consists of all the symmetry operations from T plus 12 more, arising from six new twofold axes running through the centers of each edge, not parallel to any face, and six more operations arising from extending the twofold axes through the faces to fourfold axes (see Fig. 2.9). So, 24 elements in all, shown in Fig. 2.12. Note $O \cong S_4$, the symmetric group on four symbols.

  (iiic) *Icosahedral group* : I is the symmetry group of the dodecahedron or icosahedron. There are six fivefold axes, ten threefold axes, and 15 twofold axes, so including the identity there are $1 + 6 \cdot (5 - 1) + 10 \cdot (3 - 1) + 15 \cdot (2 - 1) = 60$ elements. We also have $I \cong A_5$, the alternating group on five symbols.

2.2.3 Commuting operations

The following operations commute:[15]

- Rotations about the same axis.
- Reflections in mutually perpendicular planes. In general the product of reflections in two planes which intersect at an angle α is $\sigma_v \, \sigma_{v'} = C(2\alpha)$, where the rotation is about the axis defined by their intersection line in the direction from the v' plane to the v plane. Thus $\sigma_{v'} = \sigma_v \, C(2\alpha)$.
- Rotations about perpendicular twofold axes: $C_2 \, C_2' = C_2' \, C_2 = C_2''$, where the resulting rotation is about the third perpendicular axis.
- A rotation C_n and a reflection σ_h in a plane perpendicular to the n-fold axis.

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[15] See M. Lax, *Symmetry Principles in Solid State and Molecular Physics*, p. 54.

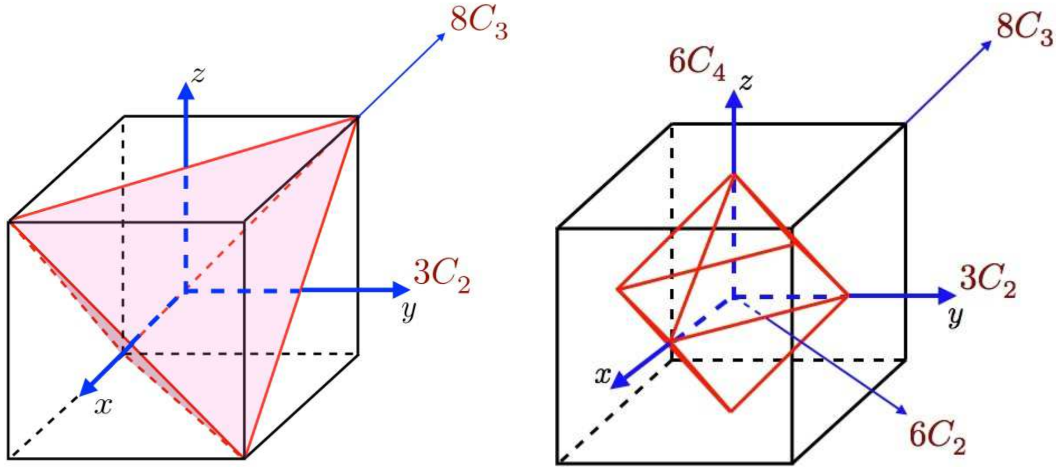

Figure 2.12: Left: Proper rotational symmetries of the tetrahedron, forming the group T. Right: Proper rotational symmetries of the octahedron (or cube), forming the group O.

- Inversion I and any point group operation g (with g a rotation relative to the inversion point)
- A twofold rotation C_2 and a reflection σ_v in a plane containing the rotation axis.

2.2.4 Improper point groups

First, some notation. Since we will start to use C_n to denote the generator of rotations about the primary axis, we'll write $\mathcal{C}_n$ to denote the cyclic group with n elements. Similarly we'll use $\mathcal{S}_{2n}$ to denote the rotoreflection group. In addition to the proper point group $\mathcal{C}_2 = \{E, C_2\} \cong \mathbb{Z}_2$, we will also define two improper $\mathbb{Z}_2$ clones: $\mathcal{C}_i = \{E, I\}$, containing the identity and the inversion operation, and $\mathcal{C}_s \equiv \{E, \sigma_h\}$ containing the identity and the horizontal reflection σ_h. All will play a role in our ensuing discussion.

In §2.10 of Lax, the relations between proper and improper point groups are crisply discussed. Suppose a group G contains both proper and improper elements. We write $G = H \cup M$ where $H \triangleleft G$ is a normal subgroup containing all the proper elements, and M, which is not a group (no identity!) contains all the improper elements. Let $m \in M$ be any of the improper operations. Then $mH = M$ since multiplying any proper element by an improper one yields an improper element, and we conclude that H and M contain the same number of elements. Thus $G \cong H \cup mH$ and only one improper generator is needed. Since the inversion operator commutes with all elements of $\mathsf{O}(3)$, we can always form an improper group which contains I by constructing $G = H \cup IH = H \otimes \mathcal{C}_i$. If $G = H \cup mH$ does not contain the inversion operator I, we can always form a *proper* group $\widetilde{G} = H \cup mIH$ which is isomorphic to G. Consider the case of the improper point group $G = \mathcal{C}_{3v}$, where $H = \mathcal{C}_3 = \{E\,,\, C_3\,,\, C_3^{-1}\}$ and $m = \sigma_v$ is a vertical reflection plane containing the threefold axis[16]. Then $\tilde{G} = D_3$, which is proper, and which is isomorphic to C_{3v}. Finally, if G is proper, and if it contains an index two subgroup, *i.e.* a subgroup $H \subset G$ such that $N_G = 2N_H$,

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[16] Acting with C_3 generates the additional vertical reflections: $C_3\,\sigma_v = \sigma_{v'}$ and $C_3\,\sigma_{v'} = \sigma_{v''}$.

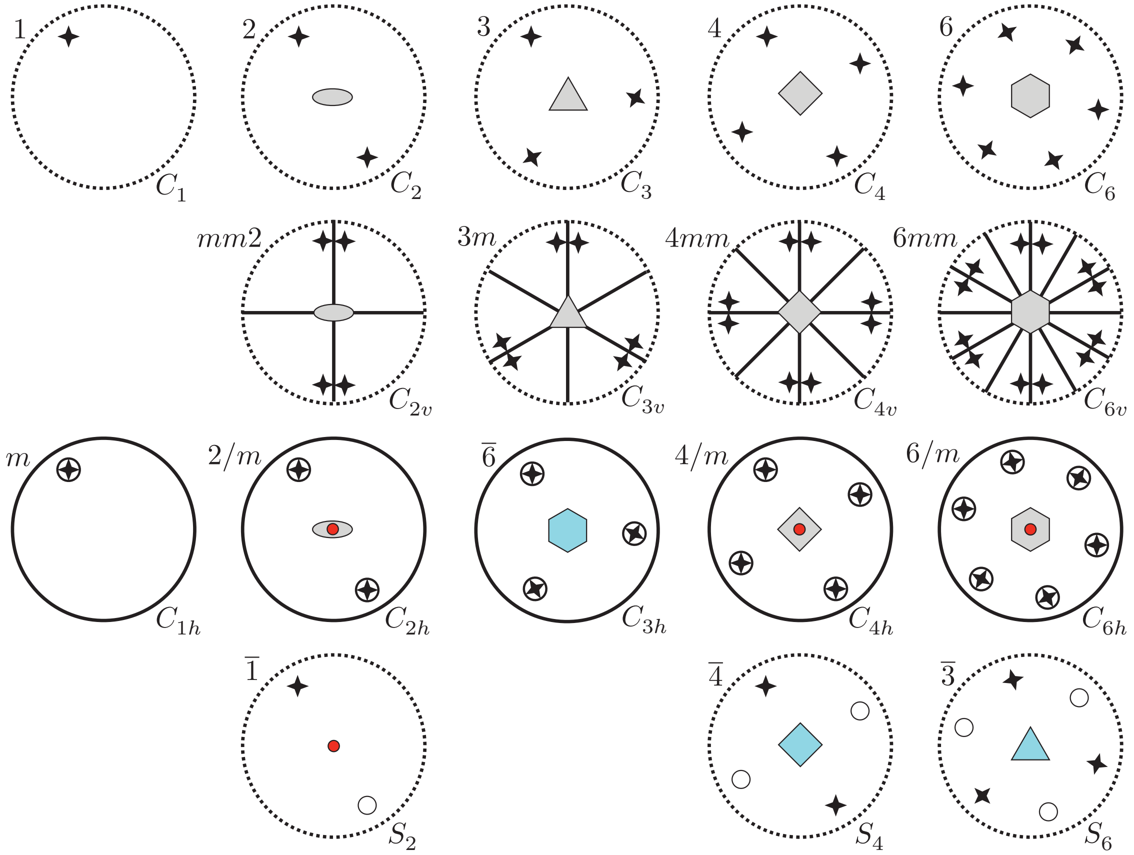

Figure 2.13: Stereographic projections of simple point groups C_n , C_{nv} , C_{nh} , and S_n. Dark lines correspond to reflection planes. C_{6v} looks like what I found the last time I sliced open a kiwi. Note $S_1 \cong C_{1h}$ and $S_3 \cong C_{3h}$. Adapted from Table 4.2 of M. Tinkham, *Group Theory and Quantum Mechanics*.

then we can construct $\tilde{G} = H \cup I\,(G\backslash H)$, where $G\backslash H$ is G with the elements from H removed. Then $\tilde{G}$ is an improper group with no inversion operation.

OK let's finally meet the improper point groups:

$\mathcal{S}_{2n}$: The rotoreflection group $\mathcal{S}_{2n}$ is a cyclic group of order $2n$ generated by $S_{2n} \equiv \sigma_h^{-1}\, C_{2n}$. In the absence of spin, $\sigma^{-1} = \sigma$ for any reflection. Then for n odd, $(S_{2n})^n = \sigma_h\, C_2 = I$, hence $\mathcal{S}_n \cong \mathcal{C}_n \otimes \mathcal{C}_i$.

$\mathcal{C}_{nh}$: The $2n$ element group $\mathcal{C}_{nh} \cong \mathcal{C}_n \otimes \mathcal{C}_s$ has two commuting generators, C_n and σ_h. For n odd, $\mathcal{C}_{nh}$ is cyclic and is generated by the single element $\sigma_h\, C_n$.

$\mathcal{C}_{nv}$: The $2n$ element group $\mathcal{C}_{nv}$ has two noncommuting generators, C_n and σ_v, where σ_v is a reflection in a plane containing the n-fold axis. Repeated application of C_n creates $(n-1)$ additional vertical reflection planes. One has $\mathcal{C}_{nv} \cong D_n$.

D_{nh} : Adding a horizontal reflection plane to D_n, one obtains $D_{nh} \cong D_n \otimes \mathcal{C}_s$. For n even, one also has $D_{nh} \cong D_n \otimes \mathcal{C}_i$. The group has $4n$ elements.

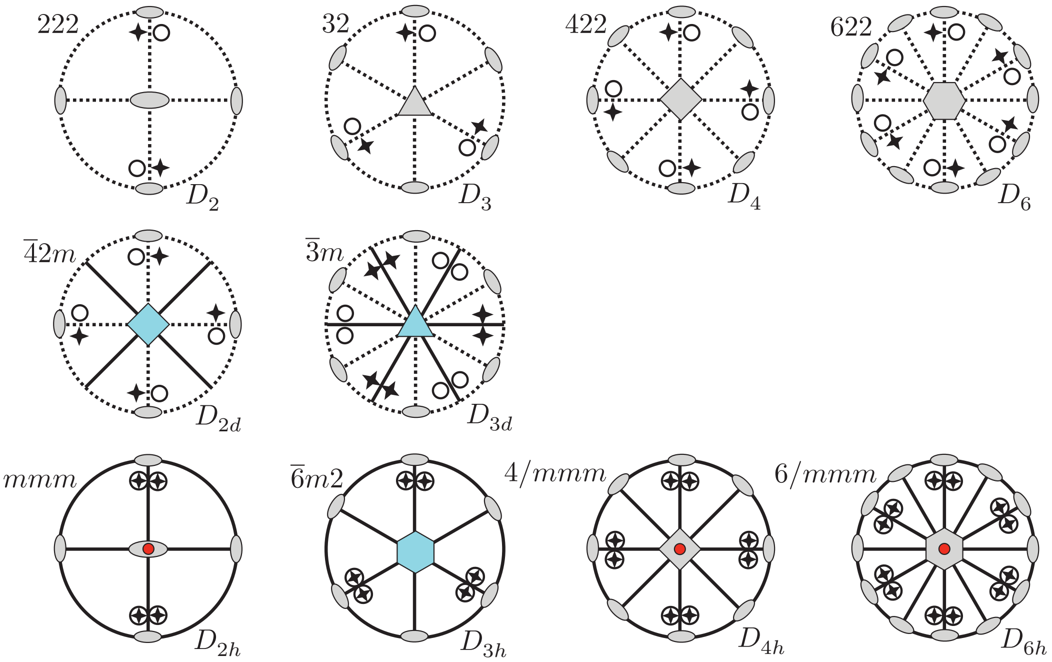

Figure 2.14: Stereograms of simple point groups D_n , D_{nd} , and D_{nh}. Dark lines correspond to reflection planes. Dashed lines correspond to 2-fold rotation axes. Adapted from Table 4.2 of M. Tinkham, *Group Theory and Quantum Mechanics*.

D_{nd} : If instead of adding a horizontal reflection σ_h we add a 'diagonal' reflection σ_d in a plane which bisects the angle between neighboring twofold axes, we arrive at D_{nd}, which also has $4n$ elements.

T_d : Adding a reflection plane passing through one of the edges of the tetrahedron, we double the size of the tetrahedral group from 12 to 24. In Fig. 2.12, such a reflection might permute the vertices 3 and 4. Thus while $T \cong A_4$, we have $T_d \cong S_4$.

T_h : Adding inversion to the proper rotational symmetries of the tetrahedron, we obtain $T_h \cong T \otimes \mathcal{C}_i$, which has 24 elements.

O_h : Adding inversion to the proper rotational symmetries of the cube, we obtain $O_h \cong O \otimes \mathcal{C}_i$, which has 48 elements.

I_h : Adding inversion to the proper rotational symmetries of the icosahedron, we obtain $I_h \cong I \otimes \mathcal{C}_i$, which has 60 elements.

Stereographic projections of the simple point groups are depicted in Figs. 2.13 and 2.14. The subgroup structure of the point groups, which tells us the hierarchy of symmetries, is shown in Fig. 2.17.

Why don't we consider the rotoreflection groups $\mathcal{S}_n$ for n odd? Because for n odd, $\mathcal{S}_n \cong C_{nh}$. For n odd, both S_n and S_{2n} generate cyclic groups of order $2n$. It is perhaps instructive to consider the simplest

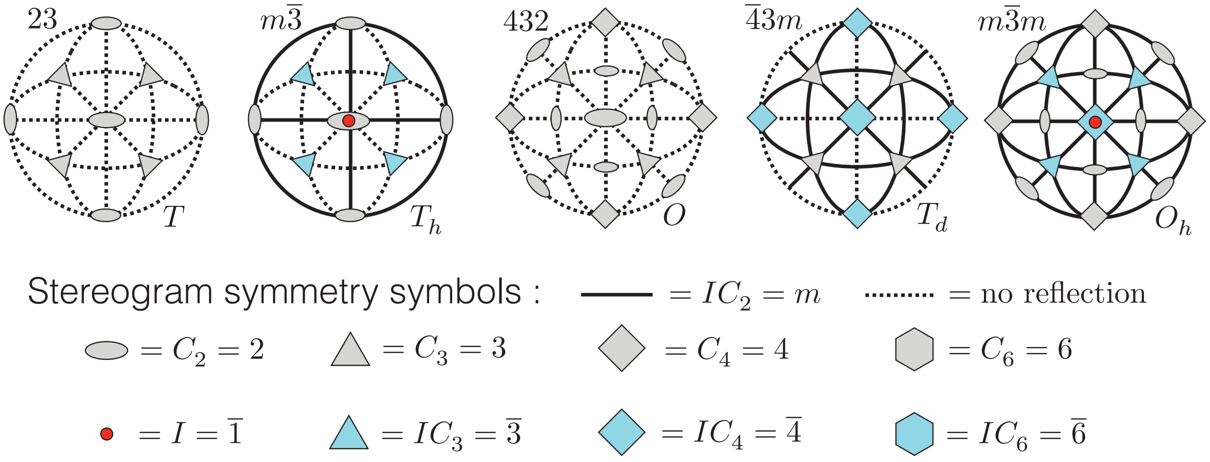

Figure 2.15: Stereograms of tetrahedral and cubic point groups and legend for symbols.

nontrivial case, $n = 3$:

$$\begin{aligned} \mathcal{S}_3 &= \{E \,,\, \sigma_h C_3 \,,\, C_3^{-1} \,,\, \sigma_h \,,\, C_3 \,,\, \sigma_h C_3^{-1}\} \\ \mathcal{S}_6 &= \{E \,,\, \sigma_h C_6 \,,\, C_3 \,,\, \sigma_h C_2 \,,\, C_3^{-1} \,,\, \sigma_h C_6^{-1}\} \quad . \end{aligned} \tag{2.23}$$

We see that $\mathcal{C}_{3h}$, which is generated by the pair $(C_3 \,,\, \sigma_h)$, contains the same elements as $\mathcal{S}_3$. This result holds for all odd n, because in those cases $\sigma_h \in \mathcal{S}_n$.

2.2.5 The ten two-dimensional point groups

There are ten two-dimensional point groups, listed in Tab. 2.3. As the only allowed elements are 2, 3, 4, and 6-fold rotations about the z-axis, plus vertical (line) mirrors, the only possible groups are C_1 , C_2 , C_3 , C_4 , C_6 and their mirrored extensions C_{1v} , C_{2v} , C_{3v} , C_{4v} , and C_{6v}. Note that the group C_{1v} is equivalent to C_{1h} , since in $d = 3$ both have a single reflection plane.

LATTICE SYSTEM	POINT GROUPS			
oblique	C_1	C_2		
rectangular	C_{1h}	C_{2v}		
centered rectangular	C_{1h}	C_{2v}		
square	C_4	C_{4v}		
hexagonal	C_3	C_{3v}	C_6	C_{6v}

Table 2.3: The ten two-dimensional point groups. Note $C_{1h} \cong C_{1v}$.

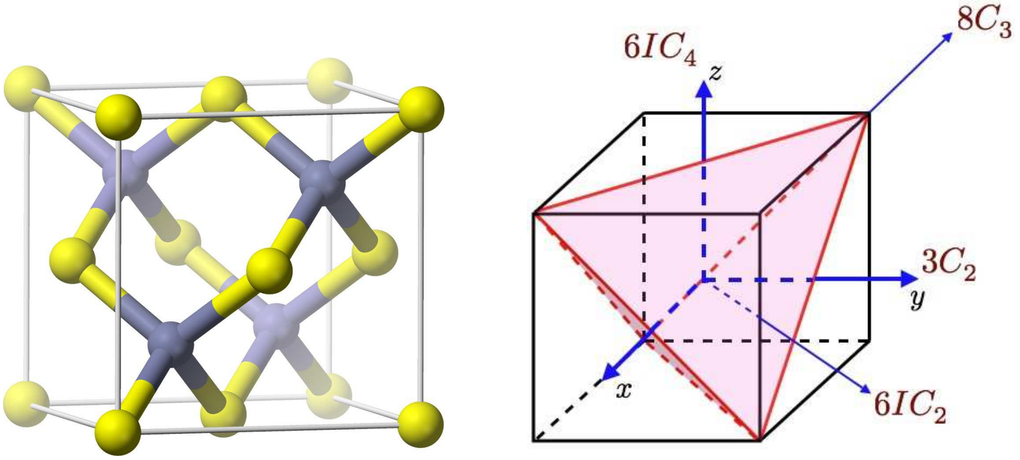

Figure 2.16: Left: The zincblende structure. Right: Proper and improper elements of the group T_d.

2.2.6 The achiral tetrahedral group, T_d

Many materials such as GaAs occur in an AB zincblende structure, which consists of two interpenetrating fcc lattices A and B, separated by $(\frac{a}{4}, \frac{a}{4}, \frac{a}{4})$, where a is the side length of the cube; see Fig. 2.16. As the figure shows, the B sublattice sites within the cube form a tetrahedron. The crystallographic point group for this structure is T_d, the achiral tetrahedral group. A noteworthy feature is that the zincblende structure has no center of inversion symmetry, hence $I \notin T_d$.

If all the atoms are identical, *i.e.* $\text{A} = \text{B}$, then we get the diamond structure, which is the structure of silicon and of course carbon diamond. The diamond lattice is inversion symmetric, with the point of inversion halfway between the A and B sublattice sites. The point group for diamond is the cubic group O_h. This might be surprising upon staring at the structure for a time, because it doesn't possess a cubic symmetry. However, the space group for diamond is non-symmorphic – it has a glide plane.

The group T_d has 24 elements; these are listed in Tab. 2.5. Its character table is provided in Tab. 2.4. These are arranged in five group *classes*. One class is the identity, E. Another class consists of three 180°

T_d	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	-1	1
T_2	3	0	-1	1	-1

Table 2.4: Character table for the group T_d.

class	x	y	z	$g \in \mathsf{O}(3)$	class	x	y	z	$g \in \mathsf{O}(3)$
E	x	y	z	1	$6\sigma_d$	$-y$	$-x$	z	$IR_{[110]}(\pi)$
$3C_2$	x	$-y$	$-z$	$R_{[100]}(\pi)$		y	x	z	$IR_{[1\bar{1}0]}(\pi)$
	$-x$	y	$-z$	$R_{[010]}(\pi)$		$-z$	y	$-x$	$IR_{[101]}(\pi)$
	$-x$	$-y$	z	$R_{[001]}(\pi)$		z	y	x	$IR_{[\bar{1}01]}(\pi)$
$8C_3$	z	x	y	$R_{[111]}(+\frac{2\pi}{3})$		x	$-z$	$-y$	$IR_{[011]}(\pi)$
	y	z	x	$R_{[111]}(-\frac{2\pi}{3})$		x	z	y	$IR_{[01\bar{1}]}(\pi)$
	z	$-x$	$-y$	$R_{[1\bar{1}1]}(+\frac{2\pi}{3})$	$6S_4$	$-x$	z	$-y$	$IR_{[100]}(+\frac{\pi}{2})$
	$-y$	$-z$	x	$R_{[1\bar{1}1]}(-\frac{2\pi}{3})$		$-x$	$-z$	y	$IR_{[100]}(-\frac{\pi}{2})$
	$-z$	x	$-y$	$R_{[11\bar{1}]}(+\frac{2\pi}{3})$		$-z$	$-y$	x	$IR_{[010]}(+\frac{\pi}{2})$
	y	$-z$	$-x$	$R_{[11\bar{1}]}(-\frac{2\pi}{3})$		z	$-y$	$-x$	$IR_{[010]}(-\frac{\pi}{2})$
	$-z$	$-x$	y	$R_{[1\bar{1}\bar{1}]}(+\frac{2\pi}{3})$		y	$-x$	$-z$	$IR_{[001]}(+\frac{\pi}{2})$
	$-y$	z	$-x$	$R_{[1\bar{1}\bar{1}]}(-\frac{2\pi}{3})$		$-y$	x	$-z$	$IR_{[001]}(-\frac{\pi}{2})$

Table 2.5: Table of elements and classes for T_d.

rotations about the $\hat{\boldsymbol{x}}$, $\hat{\boldsymbol{y}}$, and $\hat{\boldsymbol{z}}$ axes, respectively. A third class, with eight elements, consists of rotations by ±120° about each of the four body diagonals. This amounts to 12 group operations, all of which are proper rotations. The remaining 12 elements involve the inversion operator, I, which takes (x, y, z) to $(-x, -y, -z)$, and are therefore improper rotations, with determinant -1.[17] These elements fall into two classes, one of which consists of $180°$ rotations about diagonals parallel to one of the sides of the cube (*e.g.* the line $y = x$, $z = 0$), followed by inversion. The last class consists of rotations by $\pm 90°$ about $\hat{\boldsymbol{x}}$, $\hat{\boldsymbol{y}}$, and $\hat{\boldsymbol{z}}$, also followed by an inversion.

2.2.7 Tetrahedral *vs.* octahedral symmetry

In the case of the octahedral group, O, the inversion operation is not included in the last two classes, and they are written as $6C_2$ and $6C_4$, respectively. The symmetry operations of O are depicted in fig. 2.12. The groups O and T_d are isomorphic. Both are *enantiomorphic* (*i.e.* chiral), and completing either of them by adding in the inversion operator I results in the full cubic group, O_h, which has 48 elements.

While the groups T_d and O are isomorphic, the symmetry of their basis functions in general differs. Consider, for example, the function $\psi = xyz$. It is easy to see from table 2.5 that every element of T_d leaves ψ invariant. Within O, however, the classes $6\sigma_d$ and $6S_4$ are replaced by $6C_2$ and $6C_4$ when the inversion operation is removed. Each element of these classes then takes ψ to $-\psi$. Thus, within T_d, the function $\psi = xyz$ is indistinguishable from unity, and it transforms according to the trivial A_1 representation. Within O, however, ψ is distinguishable from 1 because ψ reverses sign under the operation of all group elements in classes $6C_2$ and $6C_4$.

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[17] Note that I itself is not an element of T_d.

Γ	d_Γ	basis functions ψ^Γ_μ for T_d	basis functions ψ^Γ_μ for O
A_1	1	1 or xyz	1
A_2	1	$x^4(y^2-z^2)+y^4(z^2-x^2)+z^4(x^2-y^2)$	xyz
E	2	$\big\{\sqrt{3}\,(x^2-y^2)\,,\,2z^2-x^2-y^2\big\}$	$\big\{\sqrt{3}\,(x^2-y^2)\,,\,2z^2-x^2-y^2\big\}$
T_1	3	$\big\{x\,(y^2-z^2)\,,\,y\,(z^2-x^2)\,,\,z\,(x^2-y^2)\big\}$	$\{x\,,\;y\,,\;z\}$
T_2	3	$\{x\,,y\,,z\}$	$\{yz\,,zx\,,xy\}$

Table 2.6: Irreducible representations and basis functions for T_d and O.

In O, the triplets of basis functions $\{x, y, z\}$ and $\{yz, zx, xy\}$ belong to different representations (T_1 and T_2, respectively). In T_d, however, they must belong to the same representation, since one set of functions is obtained from the other by dividing into xyz: $x = (xyz)/(yz)$, *et. cyc.* But xyz transforms as the identity, so 'polar' and 'axial' vectors belong to the same representation of T_d.

Finally, let's think about how O differs from O_h. Consider the function

$$\psi = xyz \cdot \Big\{x^4\,(y^2-z^2)+y^4\,(z^2-x^2)+z^4\,(x^2-y^2)\Big\}\,. \tag{2.24}$$

One can check that this function is left invariant by every element of O. It therefore transforms according to the A_1 representation of O. But it reverses sign under parity, so within the full cubic group O_h, it transforms according to separate one-dimensional representation. Note that ψ transforms according to the A_2 representation of T_d.

LATTICE SYSTEM	POINT GROUPS						
cubic	O_h	O	T_h	T_d	T		
hexagonal	D_{6h}	D_{3h}	C_{6v}^*	D_6	C_{6h}	C_{3h}	C_6^*
trigonal	D_{3d}	C_{3v}^*	D_3	S_6	C_3^*		
tetragonal	D_{4h}	D_{2d}	C_{4v}^*	D_4	C_{4h}	S_4	C_4^*
orthorhombic	D_{2h}	C_{2v}^*	D_2				
monoclinic	C_{2h}	C_s^*	C_2^*				
triclinic	C_i	C_1^*					

Table 2.7: The 32 three-dimensional crystallographic point groups. Color scheme: centrosymmetric, non-centrosymmetric, enantiomorphic (*i.e.* chiral). Polar point groups are marked with an asterisk *. For each lattice system, the most highest symmetry point groups are toward the left.

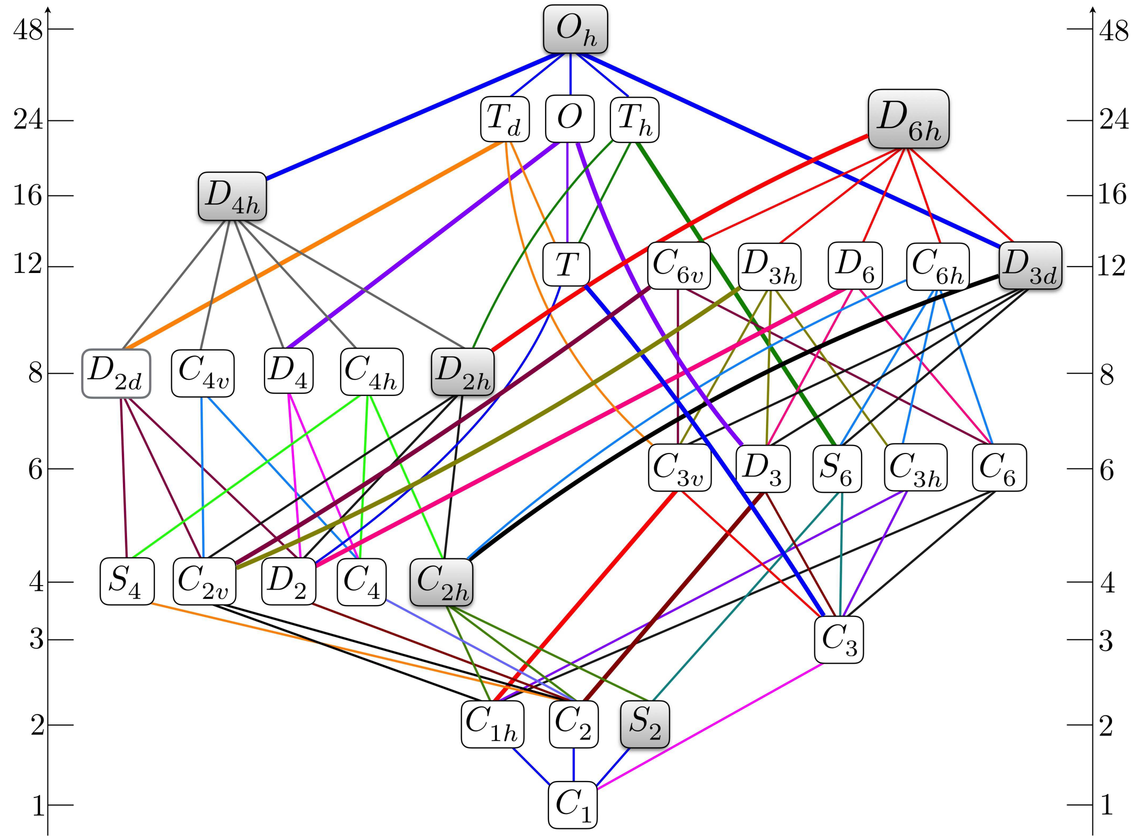

Figure 2.17: The 32 crystallographic point groups, their orders, and their subgroup structure. If the subgroup is not invariant (normal), the line is heavy. Gray boxes indicate holohedral groups, *i.e.* point groups of maximal symmetry within a given lattice system, corresponding to the symmetry of the underlying Bravais lattice itself. (See Tab. 6.1.6 of Lax, or Tab. 5 of Koster *et al.*)

2.2.8 The 32 crystallographic point groups

Tab. 2.7 lists all possible point group symmetries for three-dimensional crystals. The largest possible symmetry group within a given lattice system is the rightmost point group, corresponding to the symmetry of the underlying Bravais lattice. The point groups may be classified as being *centrosymmetric* (*i.e.* including the inversion operation I), *non-centrosymmetric*, or *enantiomorphic*. A centrosymmetric crystal has an inversion center. Enantiomorphic structures are non-centrosymmetric; they have only rotation axes and include no improper operations. They are intrinsically chiral and not superposable on their mirror image. In addition, a point group may be *polar*, meaning every symmetry operation leaves more than one point fixed (*i.e.* those points along the high symmetry *polar axis*). Thus, a group with more than one axis of rotation or with a mirror plane which does not contain the primary axis cannot be polar. A polar axis is only possible in non-centrosymmetric structures. Ferroelectricity and piezoelectricity can only occur in polar crystals.

2.2.9 Hermann-Mauguin (international) notation

The notation with which we have thus far identified point groups and their operations (C_{nv}, T_d, σ_h, *etc.*) is named for the German mathematician A. M. Schoenflies (1853-1928). A more informative system, originally due to German crystallographer C. Hermann and subsequently improved by the French minerologist C.-V. Mauguin, goes by the name *Hermann-Mauguin* (HM) or *international* notation. Since most physics publications today use the international notation, we pause to review it and to explain the method to its madness.

HM notation is defined for both point groups as well as their elements. For the individual symmetry operations, the HM symbols are as follows:

(i) n : rotation by $2\pi/n$ about a primary axis (Schoenflies C_n)

$$\begin{array}{ccccc} 2 = C_2 & 3 = C_3 & 4 = C_4 & 5 = C_5 & 6 = C_6 \\ & 3_2 = C_3^{-1} & 4_3 = C_4^{-1} & 5_4 = C_5^{-1} & 6_5 = C_6^{-1} \end{array} \tag{2.25}$$

(ii) m : reflection in a plane (σ)

- m_h : reflection in a plane perpendicular to the primary axis $\hat{\boldsymbol{n}}$ (σ_h)
- m_v : reflection in a plane containing the primary axis (σ_v)
- m_d : reflection in a plane containing the primary axis and bisecting the angle between two perpendicular 2-fold axes (σ_d)

(iii) $\overline{n}$: rotoinversion IC_n (note $\overline{1}$ is inversion, $\overline{2} = m_h$ is horizontal reflection)

$$\begin{array}{cccc} \overline{3} = S_6^{-1} & \overline{4} = S_4^{-1} & \overline{5} = S_{10}^{-1} & \overline{6} = S_3^{-1} \\ \overline{3}_2 = S_6 & \overline{4}_3 = S_4 & \overline{5}_4 = S_{10} & \overline{6}_5 = S_3 \end{array} \tag{2.26}$$

(iv) $\widetilde{n}$: rotoreflection $\sigma_h^{-1} C_n = S_n$

The number assignments associated with rotoinversion look strange at first. Pray tell, why do we have $\overline{3} = S_6^{-1}$ but $\overline{4} = S_4^{-1}$ and $\overline{6} = S_3^{-1}$? Well, since you asked so nicely, I will explain, but it will help if you consult Fig. 2.13. The issue here is that the Schoenflies groups $\mathcal{S}_n$ are generated by the *rotoreflection* operation $S_n \equiv \sigma_h^{-1} C_n$ while the HM symbol $\overline{n}$ denotes *rotoinversion* IC_n. The relation between the two

$\mathbb{Z}_2$ clones	$\{E, C_2\}$	$\{E, I\}$	$\{E, \sigma_h\}$
Schoenflies	$\mathcal{C}_2$	$\mathcal{C}_i$	$\mathcal{C}_s$
HM	2	$\overline{1}$	m

Table 2.8: Two element point group notation.

Schoenflies	HM	2	3	4	5	6	$\mathcal{G}$ (HM)	order
$\mathcal{C}_n$	n	2	3	4	5	6	n	n
$\mathcal{S}_n$ (n odd)	$\overline{(2n)}$		$\bar{6}$		$\overline{10}$		$\overline{(2n)}$	$2n$
$\mathcal{S}_n$ ($n = 4k$)	$\bar{n}$			$\bar{4}$			$\bar{n}$	n
$\mathcal{S}_n$ ($n = 4k + 2$)	$\overline{(n/2)}$	$\bar{1}$				$\bar{3}$	$\bar{n}$	n
$\mathcal{C}_{nv}$ (n even)	nmm	$2mm$		$4mm$		$6mm$	n, m_v	$2n$
$\mathcal{C}_{nv}$ (n odd)	nm		$3m$		$5m$		n, m_v	$2n$
$\mathcal{C}_{nh}$ (n even)	$\frac{n}{m}$	$\frac{2}{m}$		$\frac{4}{m}$		$\frac{6}{m}$	n, m_h	$2n$
$\mathcal{C}_{nh}$ (n odd)	$\overline{(2n)}$		$\bar{6}$		$\overline{10}$		n, m_h	$2n$
D_n (n even)	$n22$	222		422		622	$n, 2$	$2n$
D_n (n odd)	$n2$		32		52		$n, 2$	$2n$
D_{nd} (n even)	$\overline{(2n)}\,2m$	$\bar{4}2m$		$\bar{8}2m$		$\overline{12}\,2m$	$n, 2, m_d$	$4n$
D_{nd} (n odd)	$\bar{n}\,\frac{2}{m}$		$\bar{3}\,\frac{2}{m}$		$\bar{5}\,\frac{2}{m}$		$n, 2, m_d$	$4n$
D_{nh} (n even)	$\frac{n}{m}\frac{2}{m}\frac{2}{m}$	$\frac{2}{m}\frac{2}{m}\frac{2}{m}$		$\frac{4}{m}\frac{2}{m}\frac{2}{m}$		$\frac{6}{m}\frac{2}{m}\frac{2}{m}$	$n, 2, m_h$	$4n$
D_{nh} (n odd)	$\overline{(2n)}\,m2$		$\bar{6}m2$		$\overline{10}\,m2$		$n, 2, m_h$	$4n$

Table 2.9: Schoenflies and Hermann-Mauguin (international) notation for simple crystallographic point groups. The last columns list the generators $\mathcal{G}$ and the number of elements. Note $\mathcal{S}_n = \mathcal{C}_{nh}$ for n odd, and that $\overline{(2n)}\,2m = \overline{(2n)}\,m2$.

is as follows. Let $C(\alpha)$ denote counterclockwise rotation through an angle α. Then $S(\alpha) = I\,C(\alpha - \pi)$. In other words, $S_n = I\,C_2^{-1}\,C_n$. According to this definition,

$$S_2 = I \quad , \quad S_3 = I\,C_6^{-1} \quad , \quad S_4 = I\,C_4^{-1} \quad , \quad S_6 = I\,C_3^{-1} \quad . \tag{2.27}$$

Note that $S_5 = I\,C_5^{-3}$, which produces a ten-fold pattern. In general, for n odd, S_n generates a $2n$-fold pattern.

Now let's talk about the HM symbols for the point groups themselves. The basic idea is to identify symmetry-inequivalent axes and reflection planes. For a single n-fold axis, the Schoenflies group is $\mathcal{C}_n$ and the HM symbol is n. If we add a vertical mirror σ_v to $\mathcal{C}_n$, forming $\mathcal{C}_{nv}$, the HM symbol is nm if n is odd and nmm is n is even. The reason for the difference is that for n even, the alternating vertical reflections break into two classes, whereas for n odd there is only one class (check the character tables!). If we instead we had added a horizontal mirror σ_h to form $\mathcal{C}_{nh}$, the HM symbol would be $\frac{n}{m}$. However,

Schoenflies	T	T_h	T_d	O	O_h	I	I_h
HM	23	$\frac{2}{m}\overline{3}$	$\overline{4}3m$	432	$\frac{4}{m}\overline{3}\frac{2}{m}$	532	$\frac{2}{m}\overline{3}\,\overline{5}$
generators	$3, 2$	$3, 2, m_h$	$3, 2, m_d$	$4, 3, 2$	$4, 3, 2, m_h$	$5, 3, 2$	$5, 3, 2, m_h$
order	12	24	24	24	48	60	120

Table 2.10: Schoenflies and Hermann-Mauguin notation for multi-axis point groups. Indices for generators refer to distinct (though not necessarily orthogonal) axes.

when n is odd, $\mathcal{C}_{nh}$ is generated by the single rotoinversion $\overline{(2n)}$, and the convention is to use that symbol rather than the equivalent $\frac{n}{m}$ because the operation $\overline{(2n)}$ generates a pattern with more points than either n or m_h (though combined of course they generate the same group). For the dihedral groups D_n, the HM symbol is $n22$ if n is even and $n2$ if n is odd, for reasons similar to those for $\mathcal{C}_{nv}$. In general, for groups with a single primary axis, HM symbols can have up to three positions, which are assigned as follows:

- The first position indicates the rotational symmetry n of the primary axis, or $\overline{n}$ if the symmetry is rotoinversion. It can also be $\frac{n}{m}$ in the case of an n-fold axis plus a horizontal reflection plane.
- The second position indicates symmetry of a secondary axis or plane, and can be 2, m, or $\frac{2}{m}$.
- The third position indicates symmetry of a tertiary axis or plane, and can be 2, m, or $\frac{2}{m}$.

Thus, the HM symbol for D_{nd} is $\overline{n}\,\frac{2}{m}$ if n is odd but is $\overline{(2n)}m$ if n is even, while the HM symbol for D_{nh} is $\overline{n}m2$ if n is odd and $\frac{n}{m}\frac{2}{m}\frac{2}{m}$ if n is even. Notation for two element point groups is given in Tab. 2.8

Finally we come to the tetrahedral, octahedral, and icosahedral groups, all of which have more than one high order ($n > 2$) axis. For the tetrahedral group T, the HM symbol is 23 because the 2-fold axes are oriented parallel to the axes of the cube containing the tetrahedron, as shown in Figs. 2.9 and 2.12. The octahedral group O is written 432 in HM notation, because the fourfold axes are parallel to the cube axes, there are secondary threefold axes along the cube diagonals, and tertiary twofold axes running through the centers of the cube edges. The HM symbol for the icosahedral group I is 532. There are primary fivefold axes, through the vertices, secondary threefold axes through the face centers, and tertiary twofold axes through the edge centers (once again, see Fig. 2.9). Now add an improper element: inversion or a mirror plane. For the pyritohedral group T_h, we start with T and then add mirror planes perpendicular to the twofold axes, turning the threefold axes into inversion axes[18]. Consequently the HM symbol is $\frac{2}{m}\overline{3}$. For the achiral tetrahedral group T_d, we add mirrors perpendicular to the diagonal threefold axes, resulting in fourfold inversion axes and the symbol $\overline{4}3m$. When it comes to the cubic group O, we may add either a mirror or inversion. Since they are equivalent, consider the mirror, which bisects the fourfold axes, turning the threefold axes into inversion axes, and generating new mirrors perpendicular to the teriary twofold axes. The HM symbol is then $\frac{4}{m}\overline{3}\frac{2}{m}$. Finally, adding a mirror to the icosahedron turns I into I_h, with HM symbol $\overline{5}\,\overline{3}\,\frac{2}{m}$.

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[18] The seams of a volleyball have pyritohedral symmetry.

No.	HM short	HM full	Schoenflies	No.	HM short	HM full	Schoenflies
1	1	1	C_1	17	$\bar{3}$	$\bar{3}$	$C_{3i}\ (S_6)$
2	$\bar{1}$	$\bar{1}$	$C_i\ (S_2)$	18	32	32	D_3
3	2	2	C_2	19	$3m$	$3m$	C_{3v}
4	m	m	$C_s\ (C_{1h})$	20	$\bar{3}m$	$\bar{3}\frac{2}{m}$	D_{3d}
5	$2/m$	$\frac{2}{m}$	C_{2h}	21	6	6	C_6
6	222	222	$D_2\ (V)$	22	$\bar{6}$	$\bar{6}$	C_{3h}
7	$mm2$	$mm2$	C_{2v}	23	$6/m$	$\frac{6}{m}$	C_{6h}
8	mmm	$\frac{2}{m}\frac{2}{m}\frac{2}{m}$	$D_{2h}\ (V_h)$	24	622	622	D_6
9	4	4	C_4	25	$6mm$	$6mm$	C_{6v}
10	$\bar{4}$	$\bar{4}$	S_4	26	$\bar{6}m2$	$\bar{6}m2$	D_{3h}
11	$4/m$	$\frac{4}{m}$	C_{4h}	27	$6/mmm$	$\frac{6}{m}\frac{2}{m}\frac{2}{m}$	D_{6h}
12	422	422	D_4	28	23	23	T
13	$4mm$	$4mm$	C_{4v}	29	$m\bar{3}$	$\frac{2}{m}\bar{3}$	T_h
14	$\bar{4}2m$	$\bar{4}2m$	$D_{2d}\ (V_d)$	30	432	432	O
15	$4/mmm$	$\frac{4}{m}\frac{2}{m}\frac{2}{m}$	D_{4h}	31	$\bar{4}3m$	$\bar{4}3m$	T_d
16	3	3	C_3	32	$m\bar{3}m$	$\frac{4}{m}\bar{3}\frac{2}{m}$	O_h

Table 2.11: HM and Schoenflies notation for the 32 crystallographic point groups.

2.2.10 Double groups

The group operations act on electron wavefunctions, which are spinor functions of the spatial coordinates $\boldsymbol{r} = (x, y, z)$:

$$\vec{\psi}(\boldsymbol{r}) = \begin{pmatrix} \psi_\uparrow(\boldsymbol{r}) \\ \psi_\downarrow(\boldsymbol{r}) \end{pmatrix} \ . \tag{2.28}$$

Rotations by an angle θ about an axis $\hat{\boldsymbol{n}}$ are represented by the unitary operator $U(\theta;\hat{\boldsymbol{n}}) = e^{-i\theta\hat{\boldsymbol{n}}\cdot\boldsymbol{J}/\hbar}$, where $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$ is the sum of orbital ($\boldsymbol{L}$) and intrinsic spin ($\boldsymbol{S}$) angular momenta. For crystallographic point groups, $\theta = 2\pi/n$ where $n = 1$, 2, 3, 4, or 6.

When spin is neglected, we have the point groups we have studied. With spin, we must deal with the fact that $\mathsf{SU}(2)$ gives us a *projective representation* of $\mathsf{SO}(3)$. Recall that $\hat{D}(G)$ is a projective representation of G if

$$\hat{D}(g)\,\hat{D}(h) = \omega(g,h)\,\hat{D}(gh) \tag{2.29}$$

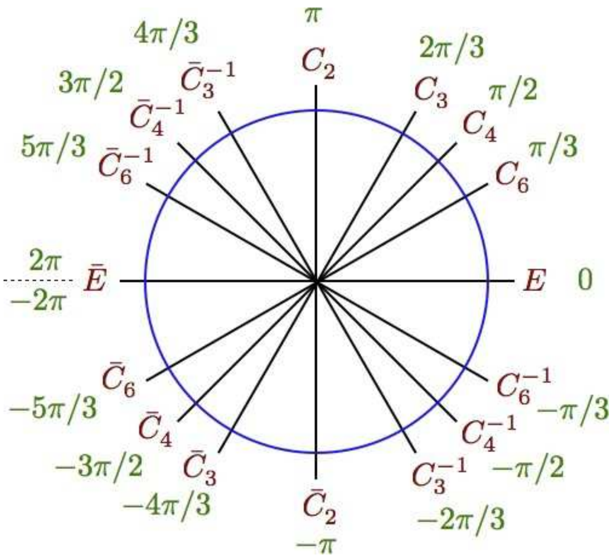

Figure 2.18: Schematic diagram of (common axis) double group rotation generators. Based on Fig. 1 of Koster *et al.* (1963). Note that $C_1 = \overline{E}$, *i.e.* a rotation by 2π.

where associativity imposes the following condition on the cocycle $\omega(g,h)$:

$$\frac{\omega(g,h)}{\omega(h,k)} = \frac{\omega(g,hk)}{\omega(gh,k)} \quad . \tag{2.30}$$

In our case, $G = \mathsf{SO}(3)$ and $\hat{D}\big(R(\xi,\hat{\boldsymbol{n}})\big) = \exp(-i\xi\hat{\boldsymbol{n}}\cdot\hat{\boldsymbol{J}})$ where $\hat{\boldsymbol{J}} = \hat{\boldsymbol{L}} + \hat{\boldsymbol{S}}$ and $S = \frac{1}{2}$. For example, any C_2 operation has $\xi = \pi$, hence $(C_2)^2 = C_1 = \exp(-2\pi i\hat{\boldsymbol{n}}\cdot\hat{\boldsymbol{S}}) = -1$, which is to say spinor inversion, *i.e.* $\begin{pmatrix} u \\ v \end{pmatrix} \to -\begin{pmatrix} u \\ v \end{pmatrix}$. *For any point group $\mathcal{P}$, the multiplication table for the projective representation $\hat{D}(\mathcal{P})$ looks exactly like that for $\mathcal{P}$, except some entries get multiplied by -1. I.e.* all the cocycles $\omega(g,h)$ are ±1. We can *lift* this projective representation to an enlarged point group, called the *double group*, $\mathcal{P}'$, by introducing a generator $\overline{E}$, representing spinor inversion, with $\overline{E}^2 = E$. To each element $g \in \mathcal{P}$, there corresponds a counterpart $\bar{g} \equiv g\overline{E}$. Thus, $N_{\mathcal{P}'} = 2N_{\mathcal{P}}$. Note that $\overline{E}$ leaves $\boldsymbol{r}$ unchanged, and that the bar of g^{-1} is the inverse of $\bar{g}$. A schematic illustration of proper rotations within a double group is shown in Fig. 2.18. *Do not confuse the barring operation in double groups with the HM symbol for rotoinversion!*

Remarks about double group multiplication

Some noteworthy aspects regarding multiplication of double group elements:

- ◇ The element $\overline{E}$ is given by $\overline{E} = C_1 = C(\pm2\pi)$. Note $C(4\pi) = E$.
- ◇ For any group element g, whether barred or unbarred, $gg^{-1} = E$.
- ◇ For the inversion operator I, $I^2 = \bar{I}^2 = E$ and $I\bar{I} = \bar{I}I = \overline{E}$.

- Any reflection σ obeys $\sigma^2 = \overline{E}$. This is because we can always write $\sigma = IC_2$ where C_2 is a twofold rotation about an axis normal to the reflection plane, whence $\sigma^2 = I^2\, C_2^2 = C_1 = \overline{E}$.

- For $n > 2$, we define $C_n \equiv \hat{R}(2\pi/n)$ to be a counterclockwise rotation by $2\pi/n$ and $C_n^{-1} \equiv \hat{R}(-2\pi/n)$ to be the inverse operation, *i.e.* clockwise rotation by $2\pi/n$. Then $C_2^2 = C_1 = \overline{E}$, hence $C_2^{-1} = \overline{C}_2$. More fully, according to Fig. 2.18, we have

$$\begin{array}{ccc}
C_2\, C_3^{-1} = C_6 & C_2\, C_4^{-1} = C_4 & C_2\, C_6^{-1} = C_3 \\
C_2\, C_6 = \overline{C}_3^{-1} & C_2\, C_4 = \overline{C}_4^{-1} & C_2\, C_3 = \overline{C}_6^{-1} \\
C_2\, \overline{C}_3^{-1} = \overline{C}_6 & C_2\, \overline{C}_4^{-1} = \overline{C}_4 & C_2\, \overline{C}_6^{-1} = \overline{C}_3 \\
C_2\, \overline{C}_6 = C_3^{-1} & C_2\, \overline{C}_4 = C_4^{-1} & C_2\, \overline{C}_3 = C_6^{-1} \quad ,
\end{array} \tag{2.31}$$

where all rotations are about the same axis.

- To compute the product of σ_h with a rotation, recall the definition of the rotoreflection operation $S_n \equiv \sigma_h^{-1}\, C_n = I\, C_2^{-1}\, C_n$, which entails $S_n^{-1} = \sigma_h\, C_n^{-1} = I\, C_2\, C_n^{-1}$. One then has

$$\sigma_h\, C_n = \overline{S}_n \quad , \quad \sigma_h\, \overline{C}_n^{-1} = \overline{S}_n^{-1} \quad , \quad \sigma_h\, \overline{C}_n = S_n \quad , \quad \sigma_h\, C_n^{-1} = S_n^{-1} \quad . \tag{2.32}$$

- We may then apply σ_h to Eqns. 2.31 and 2.32 to obtain results such as

$$C_2\, S_3^{-1} = \overline{S}_6 \quad , \quad C_2\, S_6 = S_3^{-1} \quad , \quad \sigma_h\, S_n = C_n \quad , \quad \sigma_h\, S_n^{-1} = \overline{C}_n^{-1} \quad . \tag{2.33}$$

- What about σ_v ? If $\{\sigma_v\,, \sigma_{v'}\,, \sigma_{v''}\}$ denote vertical reflection planes oriented at angles 0, $2\pi/3$, and $4\pi/3$, respectively, then we should have either $C_3\, \sigma_v = \sigma_{v'}$ or $C_3\, \sigma_v = \overline{\sigma}_{v'}$. Which is it? If we apply C_3 twice, for either initial case we obtain $C_3^2\, \sigma_v = \sigma_{v''}$. Applying C_3 yet again yields $C_3\, \sigma_{v''} = \overline{\sigma}_v$. Thus we have

$$C_3\, \sigma_v = \overline{\sigma}_{v'} \quad , \quad C_3\, \sigma_{v'} = \overline{\sigma}_{v''} \quad , \quad C_3\, \sigma_{v''} = \overline{\sigma}_v \quad . \tag{2.34}$$

  Note then that $\sigma_{v'}\, \sigma_v = C_3$ and $\sigma_v\, \sigma_{v'} = C_3^{-1}$, *et. cyc.*

To summarize, let $C(\alpha)$ denote counterclockwise rotation through an angle α, and let $C_n = C(\alpha_n)$ *etc.* with $\alpha_n = 2\pi/n$. Then

$$\overline{C}(\alpha) = C(\alpha - 2\pi) \quad , \quad S(\alpha) = I\, C(\alpha - \pi) \quad , \quad \overline{S}(\alpha) = I\, C(\alpha + \pi) \tag{2.35}$$

and

$$\sigma = I\, C(\pi) \quad , \quad \overline{\sigma} = I\, C(-\pi) \quad . \tag{2.36}$$

T_d'	E	$\overline{E}$	$8C_3$	$8\overline{C}_3$	$3C_2$ $3\overline{C}_2$	$6\sigma_d$ $6\overline{\sigma}_d$	$6S_4$	$6\overline{S}_4$
Γ_1 (A_1)	1	1	1	1	1	1	1	1
Γ_2 (A_2)	1	1	1	1	1	-1	-1	-1
Γ_3 (E)	2	2	-1	-1	2	0	0	0
Γ_4 (T_1)	3	3	0	0	-1	-1	1	1
Γ_5 (T_2)	3	3	0	0	-1	1	-1	-1
Γ_6	2	-2	1	-1	0	0	$\sqrt{2}$	$-\sqrt{2}$
Γ_7	2	-2	1	-1	0	0	$-\sqrt{2}$	$\sqrt{2}$
Γ_8	4	-4	-1	1	0	0	0	0

Table 2.12: Character table for the double group of T_d.

Character tables for double groups

One might at first suspect that any conjugacy class $\mathcal{C}$ of the point group $\mathcal{P}$ spawns two classes within the double group $\mathcal{P}'$, *i.e.* $\mathcal{C}$ and $\overline{\mathcal{C}} \equiv \overline{E}\,\mathcal{C}$. This is always true provided the elements of C don't square to the identity. But for twofold axes C_2 and reflections σ, a theorem due to Opechowski (1940) guarantees:

- For proper twofold operations, C_2 and $\bar{C}_2$ adjoin to the same class if either
  - there exists a second twofold axis perpendicular to the initial axis, or
  - there exists a reflection plane containing the initial axis.
- For improper twofold operations, σ and $\bar{\sigma}$ adjoin to the same class if either
  - there exists a second reflection plane perpendicular to the initial one, or
  - there exists a twofold axis lying within the initial plane.

In these cases, the resulting total number of classes in $\mathcal{P}'$ is less than twice that for $\mathcal{P}$. As an example, consider the tetrahedral group T_d. There are three twofold axis: $\hat{\boldsymbol{x}}$, $\hat{\boldsymbol{y}}$, and $\hat{\boldsymbol{z}}$. All are bilateral because a rotation by π about $\hat{\boldsymbol{x}}$ reverses the direction of both $\hat{\boldsymbol{y}}$ and $\hat{\boldsymbol{z}}$, *etc.* Accordingly, in the character table Tab. 2.12 for the double group of T_d, the classes C_2 and $\bar{C}_2$ are adjoined, as are σ_d and $\bar{\sigma}_d$.

With the exception of those twofold operations satisfying the conditions in Opechowski's theorem, the classes $\mathcal{C}$ and $\overline{\mathcal{C}}$ are distinct in the double group. Any IRREP of $\mathcal{P}$ will be an IRREP of $\mathcal{P}'$ with $\chi(\overline{\mathcal{C}}) = \chi(\mathcal{C})$. But since the number of elements is doubled in $\mathcal{P}'$, there must be new IRREPs specific to the double group. For these additional IRREPs, one has $\chi(\overline{\mathcal{C}}) = -\chi(\mathcal{C})$, hence if $\mathcal{C}$ and $\overline{\mathcal{C}}$ adjoin to $\mathcal{C} \cup \overline{\mathcal{C}}$ by Opechowski, one must have $\chi(\mathcal{C} \cup \overline{\mathcal{C}}) = 0$. Checking Tab. 2.12, we see that in the extra IRREPs $\Gamma_{6,7,8}$, $\chi(\overline{\mathcal{C}}) = -\chi(\mathcal{C})$ except in the case of the adjoined classes, for which $\chi(\mathcal{C} \cup \overline{\mathcal{C}}) = 0$.

We can understand that twofold rotations and reflections are special in this regard from the result we obtained for SU(2) characters,

$$\chi^{(j)}(\xi)=\frac{\sin\,(j+\frac{1}{2})\xi}{\sin\frac{1}{2}\xi} \tag{2.37}$$

for rotation by an angle ξ about any axis. Thus $\chi^{(j)}(\alpha+2\pi)=(-1)^{2j}\chi^{(j)}(\alpha)$. For $j=\frac{1}{2}$, or indeed for any half odd integer j, we have $\chi(\pi)=\chi(3\pi)=0$. Thus C_2 and $\overline{C}_2$ have the same character. A similar result holds for reflections, because $\sigma=IC_2$ and $\overline{\sigma}=I\overline{C}_2$. Therefore the classes C_2 and $\overline{C}_2$ are not distinguished by character, nor are σ and $\overline{\sigma}$. This is true in any IRREP in which $\chi(\overline{E})=-\chi(E)$.

2.2.11 The three amigos : D_4, C_{4v}, D_{2d}

Let's try to apply some of what we've just learned to the groups D_4, C_{4v}, and D_{2d}. All these eight-element groups are isomorphic to each other. The character table for all three is given in Tab. 2.13. Although they are all isomorphic, they include different sets of symmetry operations, and therefore they will have different basis representations.

Let's now discuss all the classes of these three groups. Recall that

$$R(\xi,\hat{\boldsymbol{n}})_{ab}=n^a n^b+\big(\delta^{ab}-n^a n^b\big)\cos\xi-\epsilon_{abc}\,n^c\sin\xi \quad . \tag{2.38}$$

- C_2 : This class is present in all three groups. It consists of a single element which is rotation by π about the $\hat{\boldsymbol{z}}$ axis, and represented by the 3×3 matrix

$$R^\pi_z\equiv R(\pi,\hat{\boldsymbol{z}})=\begin{pmatrix}-1&0&0\\0&-1&0\\0&0&1\end{pmatrix} \quad . \tag{2.39}$$

- $2C_4$: Present in D_4 and C_{4v}. Contains the elements

$$R^{\pi/2}_z\equiv R(\tfrac{\pi}{2},\hat{\boldsymbol{z}})=\begin{pmatrix}0&-1&0\\1&0&0\\0&0&1\end{pmatrix} \quad , \quad R^{-\pi/2}_z\equiv R(-\tfrac{\pi}{2},\hat{\boldsymbol{z}})=\begin{pmatrix}0&1&0\\-1&0&0\\0&0&1\end{pmatrix} \quad . \tag{2.40}$$

  These elements are inverses of each other.

- $2S_4$: Present only in D_{2d}. These are rotoreflections, *i.e.* $2C_4$ followed by $z\to-z$:

$$S^{\pi/2}_z\equiv S(\tfrac{\pi}{2},\hat{\boldsymbol{z}})=\begin{pmatrix}0&-1&0\\1&0&0\\0&0&-1\end{pmatrix} \quad , \quad S^{-\pi/2}_z\equiv S(-\tfrac{\pi}{2},\hat{\boldsymbol{z}})=\begin{pmatrix}0&1&0\\-1&0&0\\0&0&-1\end{pmatrix} \quad . \tag{2.41}$$

  These two are also inverses within O(3). In general we have $S(\alpha)=IC(\alpha-\pi)$, in which case $S^{\pi/2}_z=IR^{-\pi}_zR^{\pi/2}_z$ and $S^{-\pi/2}_z=IR^{-\pi}_zR^{-\pi/2}_z$. Why do we distinguish R^π_z and $R^{-\pi}_z$ when they are represented by the same matrix? This will be important when we construct the corresponding matrix representation for the double groups[19].

D_4	E	$2C_4$	C_2	$2C_2'$	$2C_2''$			
C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$			
D_{2d}	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$	D_4 basis	C_{4v} basis	D_{2d} basis
A_1	1	1	1	1	1	x^2+y^2	x^2+y^2 or z	x^2+y^2
A_2	1	1	1	-1	-1	L_z or z	L_z	L_z
B_1	1	-1	1	1	-1	x^2-y^2	x^2-y^2	x^2-y^2
B_2	1	-1	1	-1	1	xy	xy	xy or z
E	2	0	-2	0	0	$\{x\,,\,y\}$	$\{x\,,\,y\}$	$\{x\,,\,y\}$

Table 2.13: Character table for the point groups D_4, C_{4v}, and D_{2d}.

- $2C_2'$: Present in D_4 and D_{2d}, this class consists of twofold rotations about $\hat{\boldsymbol{x}}$ and $\hat{\boldsymbol{y}}$:

$$R_x^\pi \equiv R(\pi,\hat{\boldsymbol{x}}) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad , \quad R_y^\pi \equiv R(\pi,\hat{\boldsymbol{y}}) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad . \tag{2.42}$$

- $2\sigma_v$: This occurs only in C_{4v} and corresponds to reflections $x \to -x$ and $y \to -y$:

$$\varSigma_x \equiv I R_x^\pi = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad , \quad \varSigma_y \equiv I R_y^\pi = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad . \tag{2.43}$$

- $2C_2''$: Occurring only in D_4, these operations are twofold rotations about the diagonal axes $y = x$ and $y = -x$:

$$R_{xy}^\pi \equiv R\big(\pi, \tfrac{\hat{\boldsymbol{x}}+\hat{\boldsymbol{y}}}{\sqrt{2}}\big) = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad , \quad R_{x\overline{y}}^\pi \equiv R\big(\pi, \tfrac{\hat{\boldsymbol{x}}-\hat{\boldsymbol{y}}}{\sqrt{2}}\big) = \begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad . \tag{2.44}$$

- $2\sigma_d$: Occurring in C_{4v} and D_{2d}, this class of reflections is equivalent to IC_2'', hence

$$\varSigma_{xy} \equiv I R_{xy}^\pi = \begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad , \quad \varSigma_{x\overline{y}} \equiv I R_{x\overline{y}}^\pi = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad . \tag{2.45}$$

I apologize for the loose notation where we are using the same symbols to refer to group elements as well as their 3×3 matrix representations. Notice that all the matrices representing elements of C_{4v} have a block-diagonal structure with an upper left 2×2 block and a lower right 1×1 block, where the latter

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[19] See the explanation of Eqn. 2.32.

is always 1. This is because we never need to speak of the z-direction when we talk about C_{4v} as all its operations involve x and y alone.

Now let's talk about the basis functions. The projectors onto the various representations are given by

$$\Pi^{\Gamma} = \frac{d_\Gamma}{N_G} \sum_{g \in G} \chi^{\Gamma^*}(g)\, D(g) \quad , \tag{2.46}$$

where $N_G = 8$ for the three amigos. It should be clear how the basis functions in Tab. 2.13 are eigenfunctions of these projectors, but let's note the following to obviate any confusion. First of all, what do we mean by L_z as a basis function of the A_2 IRREP in the case of C_{4v} and D_{2d}? We mean the angular momentum operator, $L_z = xp_y - yp_x$. We know that $L_\alpha = \varepsilon_{\alpha\beta\gamma} r^\beta p^\gamma$ transforms as a vector under proper rotations, however it is known as an *axial vector* because it transforms differently under improper rotations. That is, under the operation σ_h (which, *nota bene* is present in none of our three groups), z is odd but L_z is even. Similarly, under either of the σ_v operations, z is even but L_z is odd. For D_4, the basis function $f(z) = z$ corresponds to the A_2 IRREP because it is even under E, $2C_4$, and C_2 and odd under $2C_2'$ and $2C_2''$. But in C_{4v}, whose operations all leave z invariant, $f(z) = z$ transforms as the A_1 IRREP. And for D_{2d}, where $2S_4$ and $2C_2'$ reverse z but $2\sigma_d$ does not, $f(z) = z$ transforms as the B_2 IRREP! Note that other valid choices of basis functions are possible. For example, rather than the pair $\{x\,,\,y\}$, we could have chosen $\{L_x\,,\,L_y\}$ as basis functions for the E IRREP.

Double group matrices and projectors

Now let's tackle the corresponding double groups. We will need the 2×2 matrices representing the various point group operations. Recall for a rotation by ξ about $\hat{\boldsymbol{n}}$,

$$\exp(-i\xi\hat{\boldsymbol{n}}\cdot\boldsymbol{\sigma}/2) = \cos(\tfrac{1}{2}\xi) - i\sin(\tfrac{1}{2}\xi)\,\hat{\boldsymbol{n}}\cdot\boldsymbol{\sigma} \quad . \tag{2.47}$$

We'll write the elements of $D^{(1/2)}(G)$ as $U(g)$. We then have

$$U(R_z^\pi) = \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix} \quad , \quad U(R_z^{\pi/2}) = \begin{pmatrix} e^{-i\pi/4} & 0 \\ 0 & e^{i\pi/4} \end{pmatrix} \quad , \quad U(R_z^{-\pi/2}) = \begin{pmatrix} e^{i\pi/4} & 0 \\ 0 & e^{-i\pi/4} \end{pmatrix} \quad . \tag{2.48}$$

For the rotoreflections,

$$U(S_z^{\pi/2}) = \begin{pmatrix} e^{i\pi/4} & 0 \\ 0 & e^{-i\pi/4} \end{pmatrix} \quad , \quad U(S_z^{\pi/2}) = \begin{pmatrix} -e^{-i\pi/4} & 0 \\ 0 & -e^{i\pi/4} \end{pmatrix} \quad . \tag{2.49}$$

Note that $U(S_z^{\pm\pi/2}) = I\,U(R_z^{-\pi})\,U(R_z^{\pm\pi/2})$, where $R_z^{-\pi} = -R_z^\pi$ and that I acts as the identity matrix on spinors. Note that $U(S_z^{\pi/2}) = U(R_z^{-\pi/2})$. Next, we need

$$U(\Sigma_x) = U(R_x^\pi) = \begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix} \quad , \quad U(\Sigma_y) = U(R_y^\pi) = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \quad . \tag{2.50}$$

Since the only difference between the twofold rotations and the corresponding reflections in the planes perpendicular to their axes is the inversion I, their representations in $D^{1/2}(G)$ are identical. The remaining matrices are

$$U(\Sigma_{xy}) = U(R_{xy}^\pi) = \begin{pmatrix} 0 & -e^{i\pi/4} \\ e^{-i\pi/4} & 0 \end{pmatrix} \quad , \quad U(\Sigma_{x\overline{y}}) = U(R_{x\overline{y}}^\pi) = \begin{pmatrix} 0 & e^{-i\pi/4} \\ -e^{i\pi/4} & 0 \end{pmatrix} \quad . \tag{2.51}$$

D'_4	E	$\overline{E}$	$2C_4$	$2\overline{C}_4$	$C_2 \cup \overline{C}_2$	$2C'_2 \cup 2\overline{C}'_2$	$2C''_2 \cup 2\overline{C}''_2$	
C'_{4v}	E	$\overline{E}$	$2C_4$	$2\overline{C}_4$	$C_2 \cup \overline{C}_2$	$2\sigma_v \cup 2\overline{\sigma}_v$	$2\sigma_d \cup 2\overline{\sigma}_d$	
D'_{2d}	E	$\overline{E}$	$2S_4$	$2\overline{S}_4$	$C_2 \cup \overline{C}_2$	$2C'_2 \cup 2\overline{C}'_2$	$2\sigma_d \cup 2\overline{\sigma}_d$	basis
Γ_1	1	1	1	1	1	1	1	$x^2 + y^2$
Γ_2	1	1	1	1	1	-1	-1	L_z
Γ_3	1	1	-1	-1	1	1	-1	$x^2 - y^2$
Γ_4	1	1	-1	-1	1	-1	1	xy
Γ_5	2	2	0	0	-2	0	0	$\{x\,,\,y\}$ or $\{L_x\,,\,L_y\}$
Γ_6	2	-2	$\sqrt{2}$	$-\sqrt{2}$	0	0	0	$\{\lvert\uparrow\rangle\,,\,\lvert\downarrow\rangle\}$
Γ_7	2	-2	-$\sqrt{2}$	$\sqrt{2}$	0	0	0	$\Gamma_3 \times \Gamma_6$ or $\Gamma_4 \times \Gamma_6$

Table 2.14: Character table for the double groups of D_4 , C_{4v} , and D_{2d} .

Note that their product is $U(\Sigma_{x\overline{y}})\,U(\Sigma_{xy}) = U(R^\pi_z)$. Note also that $\det U(g) = 1$ since each $U(g) \in \mathsf{SU}(2)$.

Appealing to the character table in Tab. 2.14, we can now construct the double group projectors. We write the projectors as

$$\Pi^\Gamma = \frac{d_\Gamma}{N_G} \sum_{g\in G} \chi^{\Gamma^*}(g)\, D(g) \otimes U(g) \quad . \tag{2.52}$$

where G is any of D'_4 , C'_{4v} , and D'_{2d} , and $N_G = 16$, since each of the double groups of the three amigos has 16 elements. For the IRREPs $\{\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4, \Gamma_5\}$ we may use the basis functions $\psi^\Gamma_\mu(\boldsymbol{r})$ from the proper point groups. *I.e.* we can simply ignore all the U-matrices and pretend there is no spin component. More correctly, we can consider the spin component of each basis function to be a *singlet*,

$$|\,\mathrm{S}\,\rangle = \frac{1}{\sqrt{2}}\Big(|\uparrow\rangle \otimes |\downarrow\rangle - |\downarrow\rangle \otimes |\uparrow\rangle\Big) \quad . \tag{2.53}$$

One can check that $U(g)\,|\,\mathrm{S}\,\rangle = |\,\mathrm{S}\,\rangle$ for all g, which follows from $\det U(g) = 1$. For Γ_6 and Γ_7 , though, the projectors annihilate any basis function of the form $f(\boldsymbol{r})\,|\,\mathrm{S}\,\rangle$. However, a basis function of the form $|\uparrow\rangle$ or $|\downarrow\rangle$ (*i.e.* with no spatial dependence) does the trick. In spinor notation, we have

$$\begin{gathered}\frac{2}{16}\Big[\chi^{\Gamma_6}(E)\,U(E) + \chi^{\Gamma_6}(\overline{E})\,U(\overline{E})\Big]\begin{pmatrix}u\\v\end{pmatrix} = \frac{1}{2}\begin{pmatrix}u\\v\end{pmatrix}\\ \frac{2}{16}\Big[\chi^{\Gamma_6}(2C_4) + \chi^{\Gamma_6}(2\overline{C}_4)\,\overline{E}\Big]\Big[U(R^{\pi/2}_z) + U(R^{-\pi/2}_z)\Big]\begin{pmatrix}u\\v\end{pmatrix} = \frac{1}{2}\begin{pmatrix}u\\v\end{pmatrix} \quad .\end{gathered} \tag{2.54}$$

Thus, $\begin{pmatrix}u\\v\end{pmatrix}$ is an eigenfunction of the projector Π^{Γ_6}. In order to keep this spinor from being annihilated by Π^{Γ_7}, we need to multiply it by a scalar function $\psi(\boldsymbol{r})$ which reverses the sign from the characters of the classes $2C_4$ and $2\overline{C}_4$. According to Tab. 2.13, the basis function from either the B_1 or the B_2 IRREPs will work. This explains the basis functions in Tab. 2.14[20]. Other valid choices of basis functions are of course possible.

Do we always need the double group?

Although electrons carry spin $S = \frac{1}{2}$, we usually don't need to invoke the double group formalism if the spin-orbit coupling is sufficiently weak. That is, we may use $\boldsymbol{L}$ rather than $\boldsymbol{J}$ as the generator of rotations, since $\big[\hat{H}, L^\alpha\big] = 0$. Each electronic energy level is of course doubly degenerate due to the spin, which just "comes along for the ride". In the presence of significant spin-orbit coupling, $\big[\hat{H}, L^\alpha\big] \neq 0$ but $\big[\hat{H}, J^\alpha\big] = 0$. Thus we must use the total angular momentum $\boldsymbol{J}$ as the generator of rotations, which entails the double point group symmetries.

2.3 Space Groups

The full group of symmetry operations of an n-dimensional crystal is called its *space group*, $\mathcal{S}$. Any crystallographic space group is a subgroup of the Euclidean group: $\mathcal{S} \subset \mathsf{E}(n)$. Space groups are infinite discrete groups. Two-dimensional space groups are called *wallpaper groups*. An accounting of the total number of lattices, point groups, and space groups for two and three dimensional crystals is provided in Tab. 2.1.

2.3.1 Space group elements and their properties

Each element $\{\, g \,|\, \boldsymbol{t} \,\} \in \mathcal{S}$ represents a compounded operation of rotation by a rotation g (either proper or improper) and a translation $\boldsymbol{t}$. When $g = E$, the space group operations are pure translations, and are all of the form $\{\, E \,|\, \boldsymbol{R} \,\}$, where $\boldsymbol{R} \in \mathcal{L}$ is a vector in the underlying Bravais lattice. As discussed in §2.1.7, the operations $\{\, g \,|\, \boldsymbol{t} \,\}$ form a group, with

$$\begin{aligned} \{\, g \,|\, \boldsymbol{t} \,\}\{\, g' \,|\, \boldsymbol{t}' \,\} &= \{\, gg' \,|\, g\boldsymbol{t}' + \boldsymbol{t} \,\} \\ \{\, g \,|\, \boldsymbol{t} \,\}^{-1} &= \{\, g^{-1} \,|\, -g^{-1}\boldsymbol{t} \,\} \quad . \end{aligned} \tag{2.55}$$

We see that the rotations g must themselves form a group, which is the *point group* $\mathcal{P}$ of the crystal. Pure translations $\{\, E \,|\, \boldsymbol{R} \,\}$ by a direct lattice vector are part of the space group, and indeed form a normal subgroup thereof: $\{\, g \,|\, \boldsymbol{t} \,\}^{-1}\{\, E \,|\, \boldsymbol{R} \,\}\{\, g \,|\, \boldsymbol{t} \,\} = \{\, E \,|\, g^{-1}\boldsymbol{R} \,\}$. Thus, $g^{-1}\boldsymbol{R} \in \mathcal{L}$ for any $g \in \mathcal{P}$, which means, as noted above in §2.1.7, that the point group $\mathcal{P}$ of any crystal is a subgroup of the point group $\mathcal{P}_{\mathcal{L}}$ of its underlying Bravais lattice (*i.e.* the holohedry).

Fom Eqn. 2.55, we have the group conjugation property

$$\{\, h \,|\, \boldsymbol{s} \,\}^{-1}\{\, g \,|\, \boldsymbol{t} \,\}\{\, h \,|\, \boldsymbol{s} \,\} = \{\, h^{-1}gh \,|\, h^{-1}g\boldsymbol{s} - h^{-1}\boldsymbol{s} + h^{-1}\boldsymbol{t} \,\} \equiv \{\, g' \,|\, \boldsymbol{t}' \,\} \quad , \tag{2.56}$$

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[20] The spin component of the basis functions for the $\varGamma_1$ through $\varGamma_5$ IRREPs should be considered to be the singlet $|\,\mathrm{S}\,\rangle$.

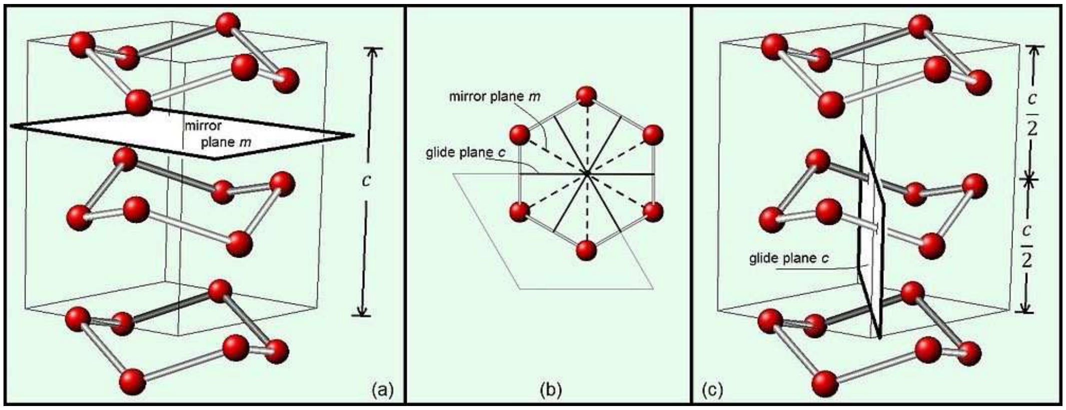


Figure 2.19: Structure of hexagonal H_2O ice, with red spheres showing location of oxygen atoms. The space group is $P6_3/mmc$. The 6_3 symbol indicates a sixfold screw axis. The first two m symbols indicate mirror planes perpendicular and parallel to the c-axis. The c symbol indicates a glide plane where the translation is along the c-axis. (Image credit: *Wikipedia*).

for which the rotation is $g' = h^{-1}gh$ and the translation is $\boldsymbol{t}' = h^{-1}g\boldsymbol{s} - h^{-1}\boldsymbol{s} + h^{-1}\boldsymbol{t}$. When $h = E$, we have $g' = g$ and

$$\boldsymbol{t} - \boldsymbol{t}' = (E - g)\,\boldsymbol{s} \quad . \tag{2.57}$$

Suppose we further demand $\boldsymbol{t}' = 0$, *i.e.* that the conjugated operation is equivalent to a pure rotation, with no translation, about a different choice of origin. We see that this is possible if we choose $\boldsymbol{s}$ such that $\boldsymbol{t} = (E - g)\,\boldsymbol{s}$.

Now it was noted in §2.2.1 that when the dimension n of space is odd, $g \in \mathsf{O}(n)$ always preserves some axis, meaning it has an eigenvalue $\lambda = 1$. The other two eigenvalues may be written as $e^{\pm i\alpha}$ where $\alpha = 2\pi/n$ with $n = 2$, 3, 4, or 6. (The case $n = 1$ corresponds to the identity E.) A mirror reflection, which is an improper operation, has an inversion axis corresponding to an eigenvalue $\lambda = -1$, with all remaining eigenvalues $\lambda = +1$. Proper rotations therefore have an *invariant axis*, while mirror reflections have an *invariant plane*. Thus we can write

$$\begin{aligned} \text{proper rotation}: \quad & r = |\,\hat{\boldsymbol{e}}_1\,\rangle\langle\,\hat{\boldsymbol{e}}_1\,| + e^{i\alpha}\,|\,\hat{\boldsymbol{e}}_2\,\rangle\langle\,\hat{\boldsymbol{e}}_2\,| + e^{-i\alpha}\,|\,\hat{\boldsymbol{e}}_3\,\rangle\langle\,\hat{\boldsymbol{e}}_3\,| \\ \text{mirror reflection}: \quad & m = -|\,\hat{\boldsymbol{e}}_1\,\rangle\langle\,\hat{\boldsymbol{e}}_1\,| + |\,\hat{\boldsymbol{e}}_2\,\rangle\langle\,\hat{\boldsymbol{e}}_2\,| + |\,\hat{\boldsymbol{e}}_3\,\rangle\langle\,\hat{\boldsymbol{e}}_3\,| \quad . \end{aligned} \tag{2.58}$$

We now see that if $g = r$ is a proper rotation, $\boldsymbol{t} = (E - r)\,\boldsymbol{s}$ cannot be solved for $\boldsymbol{s}$ if $\boldsymbol{t}$ has any component along the invariant axis $\hat{e}_1$. Similarly, if $g = m$ is a mirror, $\boldsymbol{t} = (E - m)\,\boldsymbol{s}$ cannot be solved for $\boldsymbol{s}$ if $\boldsymbol{t}$ has any component in the invariant plane spanned by $\{\hat{e}_2, \hat{e}_3\}$. Space group operations $\{\,r\,|\,\boldsymbol{t}\,\}$ for which $\boldsymbol{t}$ is parallel to the invariant axis of r are called *screws*, while those for which $\boldsymbol{t}$ is parallel to an invariant plane of m are called *glides*. As we shall see, the possible values of $\boldsymbol{t}$ are strongly constrained in either case. Screws and glides may be considered *intrinsic translations* because they cannot be removed simply by a new choice of origin.

Next we note that if $\{\,g\,|\,\boldsymbol{t}\,\} \in \mathcal{S}$, we can always choose the translation component $\boldsymbol{t}$ to either be in the direct lattice or to lie within the first Wigner-Seitz (WS) cell[21]. If $\boldsymbol{t} \equiv \boldsymbol{\tau} \notin \mathcal{T}$, then it must be unique for a

---

[21] A translation $\boldsymbol{t}$ which is not a direct lattice vector can always be brought into the first WS cell by a direct lattice translation.

Nos.	lattice	$\mathcal{P}^{(\mathrm{Sch})}$	$\mathcal{P}^{(\mathrm{HM})}$	order	$\mathcal{S}$ (sym)	$\mathcal{S}$ (n-sym)
1	oblique	C_1	1	1	$p1$	
2	oblique	C_2	2	2	$p2$	
3 - 4	rectangular	C_{1v}	m	2	pm	pg
5 - 6	rectangular	C_{2v}	$2mm$	4	pmm	pmg
7	centered rectangular	C_{1v}	m	2	cm	
8 - 9	centered rectangular	C_{2v}	$2mm$	2	cmm	pgg
10	square	C_4	4	4	$p4$	
11 - 12	square	C_{4v}	$4mm$	8	$p4m$	$p4g$
13	hexagonal	C_3	3	3	$p3$	
14 - 15	hexagonal	C_{3v}	$3m$	6	$p3m1$, $p31m$	
16	hexagonal	C_6	6	6	$p6$	
17	hexagonal	C_{6v}	$6mm$	12	$p6m$	

Table 2.15: The 17 wallpaper groups and their short notation.

given g, because if both $\{\, g \,|\, \boldsymbol{\tau} \,\}$ and $\{\, g \,|\, \boldsymbol{\tau}' \,\}$ are in $\mathcal{S}$, then so is $\{\, g \,|\, \boldsymbol{\tau}' \,\}^{-1} \{\, g \,|\, \boldsymbol{\tau} \,\} = \{\, E \,|\, g^{-1}(\boldsymbol{\tau} - \boldsymbol{\tau}') \,\}$, which means that $g^{-1}(\boldsymbol{\tau} - \boldsymbol{\tau}') \in \mathcal{T}$ and therefore $\boldsymbol{\tau} - \boldsymbol{\tau}' \in \mathcal{T}$. Since by assumption both $\boldsymbol{\tau}$ and $\boldsymbol{\tau}'$ lie within the first WS cell, we must have $\boldsymbol{\tau}' = \boldsymbol{\tau}$. Thus, all space group elements are of the form $\{\, g \,|\, \boldsymbol{R} + \boldsymbol{\tau}_g \,\}$, where $\boldsymbol{\tau}_g$ may either be zero or a unique nonzero vector within the first WS cell. Now the point group $\mathcal{P}$ is of finite order, so each element $g \in \mathcal{P}$ satisfies $g^n = E$ where n is finite and taken to be the smallest positive integer which satisfies this relation. Therefore

$$\{\, g \,|\, \boldsymbol{\tau}_g \,\}^n = \{\, g^n \,|\, \boldsymbol{\tau}_g + g\boldsymbol{\tau}_g + \ldots + g^{n-1}\boldsymbol{\tau}_g \,\} \quad , \tag{2.59}$$

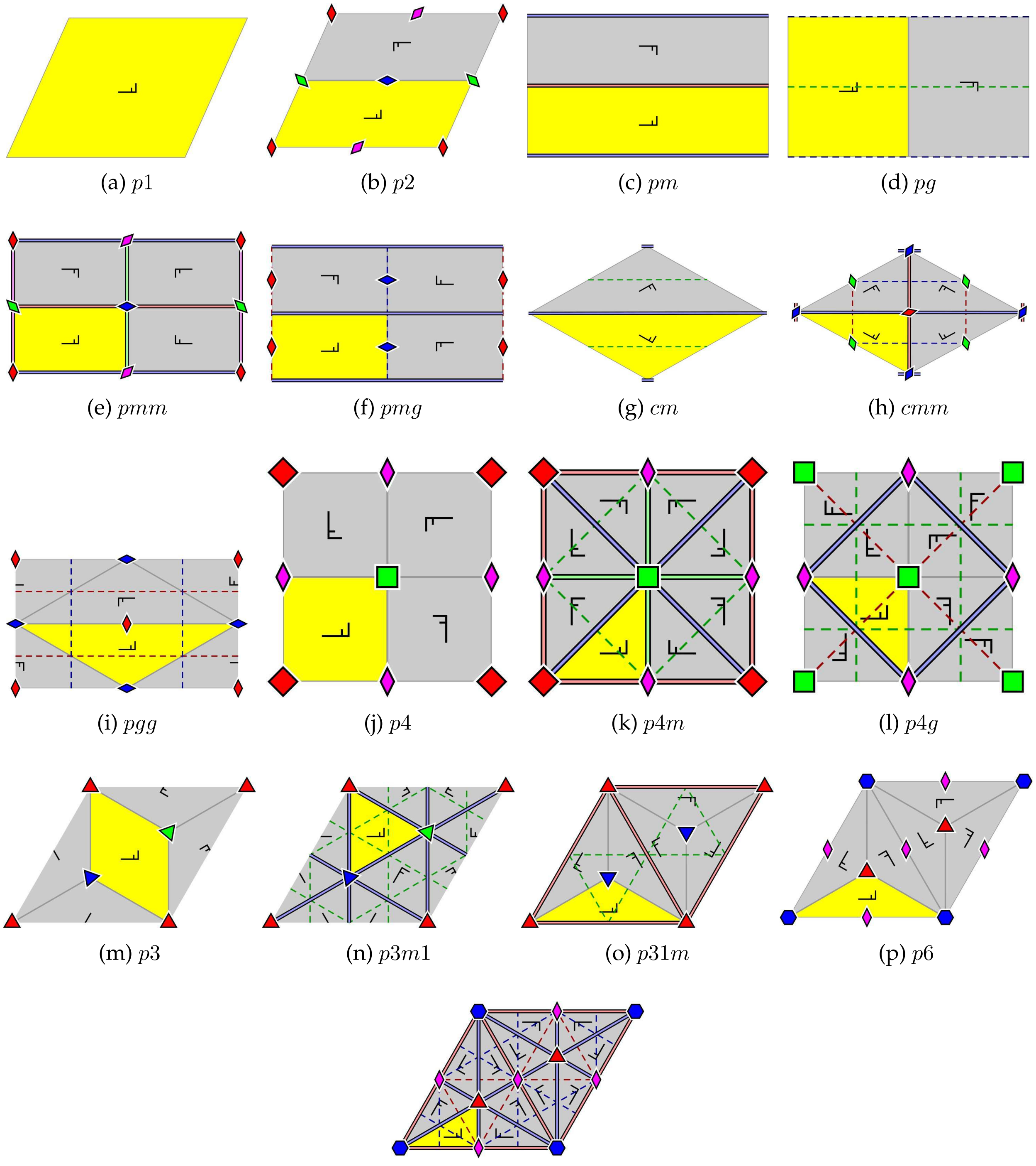
and since $g^n = E$, we must have that $\boldsymbol{\tau}_g + g\boldsymbol{\tau}_g + \ldots + g^{n-1}\boldsymbol{\tau}_g = \boldsymbol{R}$ is a direct lattice vector. Note that for $g = r$ we can have $n = 2, 3, 4$, or 6, while for $g = m$ we necessarily have $n = 2$.

According to Eqn. 2.58, we have

$$E + g + g^2 + \ldots + g^{n-1} = n\, P_{\parallel}(g) \quad , \tag{2.60}$$

where $P_{\parallel}(r) \equiv |\, \hat{\boldsymbol{e}}_1 \,\rangle\langle\, \hat{\boldsymbol{e}}_1 \,|$ is the projector onto the invariant axis of r, and $P_{\parallel}(m) \equiv |\, \hat{\boldsymbol{e}}_2 \,\rangle\langle\, \hat{\boldsymbol{e}}_2 \,| + |\, \hat{\boldsymbol{e}}_3 \,\rangle\langle\, \hat{\boldsymbol{e}}_3 \,|$ the projector onto the invariant plane of m. Thus we conclude $n\, P_{\parallel}(g)\, \boldsymbol{\tau}_g = \boldsymbol{R}$, which is to say that the nonremovable part of the translation $\boldsymbol{\tau}_g$, *i.e.* its projection onto the rotation axis or mirror plane, is equal to $\boldsymbol{R}/n$. Note also that in $d = 2$, there is no preserved rotation axis, since it would be orthogonal to the (x, y) plane. Therefore two dimensional point groups can at most have glides and no screws.

We may now identify all possible screws with the symbols 2_1, 3_1, 4_1, 4_2, 6_1, 6_2, and 6_3, as well as their enantiomorphous counterparts 3_2, 4_3, 6_4, and 6_5. Glide planes are denoted by the symbols a, b, c, n, and



(a) $p1$ (b) $p2$ (c) pm (d) pg

(e) pmm (f) pmg (g) cm (h) cmm

(i) pgg (j) $p4$ (k) $p4m$ (l) $p4g$

(m) $p3$ (n) $p3m1$ (o) $p31m$ (p) $p6$

(q) $p6m$

Figure 2.20: Unit cells for the 17 two-dimensional space groups (wallpaper groups). (Image credit: *Wikipedia*.)

d, depending on the direction of the translation component. Let the symmetry axes of the crystal be $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$. Then

- For a glides, $\boldsymbol{\tau} = \frac{1}{2}\boldsymbol{a}$.
- For b glides, $\boldsymbol{\tau} = \frac{1}{2}\boldsymbol{b}$.
- For c glides, $\boldsymbol{\tau} = \frac{1}{2}\boldsymbol{c}$.
- For n glides, $\boldsymbol{\tau} = \frac{1}{2}(\boldsymbol{a}+\boldsymbol{b})$, $\frac{1}{2}(\boldsymbol{b}+\boldsymbol{c})$, $\frac{1}{2}(\boldsymbol{a}+\boldsymbol{c})$, or $\frac{1}{2}(\boldsymbol{a}+\boldsymbol{b}+\boldsymbol{c})$.
- For d glides, $\boldsymbol{\tau} = \frac{1}{4}(\boldsymbol{a}+\boldsymbol{b})$, $\frac{1}{4}(\boldsymbol{b}+\boldsymbol{c})$, $\frac{1}{4}(\boldsymbol{a}+\boldsymbol{c})$, or $\frac{1}{4}(\boldsymbol{a}+\boldsymbol{b}+\boldsymbol{c})$.

The d-glide is called the *diamond glide* and is present in the diamond lattice.

Be forewarned that it is possible for a *symmorphic* space group to include screw and glide operations provided they are *removable* by choosing a different origin. Such nonsymmorphic operations are called *inessential*. In other words, if $\mathcal{S}$ contains nonsymmorphic operations (screws or glides), but there exists some $\rho \equiv \{\, h \,|\, \boldsymbol{s} \,\}$ such that all elements of $\rho^{-1}\mathcal{S}\rho$ are of the form $\{\, g \,|\, \boldsymbol{R} \,\}$, then $\mathcal{S}$ is symmorphic. A nonsymmorphic space group contains *essential* (*i.e.* unremovable) screws or glides[22].

2.3.2 Factor groups

In the dim and distant past – specifically, in §1.3.1 – we discussed the concept of a *factor group*. Recall that if $H \subset G$ is a subgroup, there is a unique *left coset decomposition* of G as $G = \bigcup_i r_i\, H$ where $i \in \{1, \ldots, N_G/N_H\}$. If $H \lhd G$ is a normal subgroup, meaning $gHg^{-1} \in H$ for all $g \in G$, the cosets $r_i\, H$ form a group under multiplication, called the *factor group* G/H.

Since the abelian group $\mathcal{T}$ of Bravais lattice translations is a normal subgroup of the space group, we can decompose $\mathcal{S}$ as

$$\mathcal{S} = \bigcup_g \{\, g \,|\, \boldsymbol{\tau}_g \,\}\, \mathcal{T} = \mathcal{T} + \{\, g_2 \,|\, \boldsymbol{\tau}_{g_2} \,\}\, \mathcal{T} + \ldots + \{\, g_{N_\mathcal{P}} \,|\, \boldsymbol{\tau}_{g_{N_\mathcal{P}}} \,\}\, \mathcal{T} \quad . \tag{2.61}$$

This says that the space group $\mathcal{S}$ is generated by all Bravais lattice translations $\{\, E \,|\, \boldsymbol{R} \,\}$ and all operations $\{\, g \,|\, \boldsymbol{\tau}_g \,\}$. If, as in §2.3.5 below, we impose periodic boundary conditions, so that space is compactified into a three-dimensional torus of $N_1 \times N_2 \times N_3$ unit cells, then the translation group $\mathcal{T}$ is of finite order $|\mathcal{T}| = N_1 N_2 N_3$, and the order of the space group is $|\mathcal{S}| = |\mathcal{P}| \cdot |\mathcal{T}|$.

The set of operations $\{\, g \,|\, \boldsymbol{\tau}_g \,\}$ is thus the factor group $\mathcal{F} \equiv \mathcal{S}/\mathcal{T}$. While there exists a bijective map $\{\, g \,|\, \boldsymbol{\tau}_g \,\} \longleftrightarrow \{\, g \,|\, \boldsymbol{0} \,\}$ between the factor group $\mathcal{F}$ and the point group $\mathcal{P}$, multiplication within the factor group is always modulo $\mathcal{T}$. Group multiplication of the factor group elements results in a projective representation of the point group,

$$\{\, g \,|\, \boldsymbol{\tau}_g \,\}\{\, h \,|\, \boldsymbol{\tau}_h \,\} = \{\, E \,|\, \boldsymbol{R}_{g,h} \,\}\{\, gh \,|\, \boldsymbol{\tau}_{gh} \,\} \quad , \tag{2.62}$$

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[22] As noted above, there are two nonsymmorphic space groups which contain neither screws nor glides, but for which one can nevertheless not write $\mathcal{S} = \mathcal{P} \rtimes \mathcal{T}$.

crystal system	type	symmorphic space groups
triclinic	P	$P1\,,\ P\bar{1}$
monoclinic	P	$P2\,,\ Pm\,,\ P2/m$
	A/C	$C2\,,\ Cm\,,\ C2/m$
orthorhombic	P	$P222\,,\ Pmm2\,,\ Pmmm$
	A/C	$C222\,,\ Cmm2\,,\ Cmmm\,,\ Amm2$
	I	$I222\,,\ Imm2\,,\ Immm$
	F	$F222\,,\ Fmm2\,,\ Fmmm$
tetragonal	P	$P4\,,\ P\bar{4}\,,\ P4/m\,,\ P422\,,\ P4mm$
		$P\bar{4}2m\,,\ P\bar{4}m2\,,\ P4/mmm$
	I	$I4\,,\ I\bar{4}\,,\ I4/m\,,\ I422\,,\ I4mm$
		$I\bar{4}2m\,,\ I\bar{4}m2\,,\ I4/mmm$
trigonal	P	$P3\,,\ P\bar{3}\,,\ P321\,,\ P3m1\,,\ P\bar{3}m1$
		$P312\,,\ P31m\,,\ P\bar{3}1m$
(rhombohedral)	R	$R3\,,\ R\bar{3}\,,\ R32\,,\ R3m\,,\ R\bar{3}m$
hexagonal	P	$P6\,,\ P\bar{6}\,,\ P6/m\,,\ P622\,,\ P6mm$
		$P\bar{6}m2\,,\ P\bar{6}2m\,,\ P6/mmm$
cubic	P	$P23\,,\ Pm3\,,\ P432\,,\ P\bar{4}3m\,,\ Pm\bar{3}m$
	I	$I23\,,\ Im3\,,\ I432\,,\ I\bar{4}3m\,,\ Im\bar{3}m$
	F	$F23\,,\ Fm3\,,\ F432\,,\ F\bar{4}3m\,,\ Fm\bar{3}m$

Table 2.16: The 73 symmorphic three-dimensional space groups and their short notation. Bravais lattice types are primitive (P), base-centered (A/C), body-centered (I), and face-centered (F). Space groups printed in red indicate cases where there are two inequivalent $\mathcal{P}$-invariant space lattice orientations.

and one can *lift* the projective representation of $\mathcal{P}$ to its *central extension*, which is to say $\mathcal{S}$. Here

$$\boldsymbol{R}_{g,h} = \boldsymbol{\tau}_g + g\boldsymbol{\tau}_h - \boldsymbol{\tau}_{gh} \tag{2.63}$$

must be in the Bravais lattice. Note that the cocycles here are actually translation operators rather than actual phases. Below we shall see how by diagonalizing the translation part of the space group, the cocycles become phases.

The case of diamond

Diamond is a rather typical nonsymmorphic space group. Recall the primitive direct lattice vectors for the fcc Bravais lattice,

$$\boldsymbol{a}_1 = \tfrac{1}{2}a_0\,(0,1,1) \quad , \quad \boldsymbol{a}_2 = \tfrac{1}{2}a_0\,(1,0,1) \quad , \quad \boldsymbol{a}_3 = \tfrac{1}{2}a_0\,(1,1,0) \quad , \tag{2.64}$$

where a_0 is the side length of the simple cubic lattice whose four element basis describes the fcc structure. The space group of diamond is $\mathcal{S} = Fd\overline{3}m$, this the point group is $m\overline{3}m$, which is O_h. Thus there are 48 cosets in the factor group $\mathcal{F}$, which is the order of O_h. These cosets break up into two collections. One consists of operations of the form $\{\, h \,|\, \mathbf{0} \,\}\, \mathcal{T}$ where $h \in T_d$. The other consists of operations of the form $\{\, I \,|\, \boldsymbol{\tau} \,\}\, \{\, h \,|\, \mathbf{0} \,\}\, \mathcal{T}$ where I is the inversion operator and $\boldsymbol{\tau} = \frac{1}{4}\boldsymbol{a}_1 + \frac{1}{4}\boldsymbol{a}_2 + \frac{1}{4}\boldsymbol{a}_3 = \frac{1}{4}a_0\,(1,1,1)$. The elements from the first collection thus constitute a group in their own right, which is the zincblende space group $\widetilde{\mathcal{S}} = F\overline{4}3m$. This is a normal subgroup of $\mathcal{S}$ of index two, *i.e.* $\mathcal{S}/\widetilde{\mathcal{S}} \cong \mathbb{Z}_2$. Explicitly, we then have $\mathcal{S} = \widetilde{\mathcal{S}} \cup \{\, I \,|\, \boldsymbol{\tau} \,\}\, \widetilde{\mathcal{S}}$.

2.3.3 How to make a symmorphic space group

The simplest recipe:

(i) Start with a lattice system.

(ii) Choose a point group consistent with the lattice system.

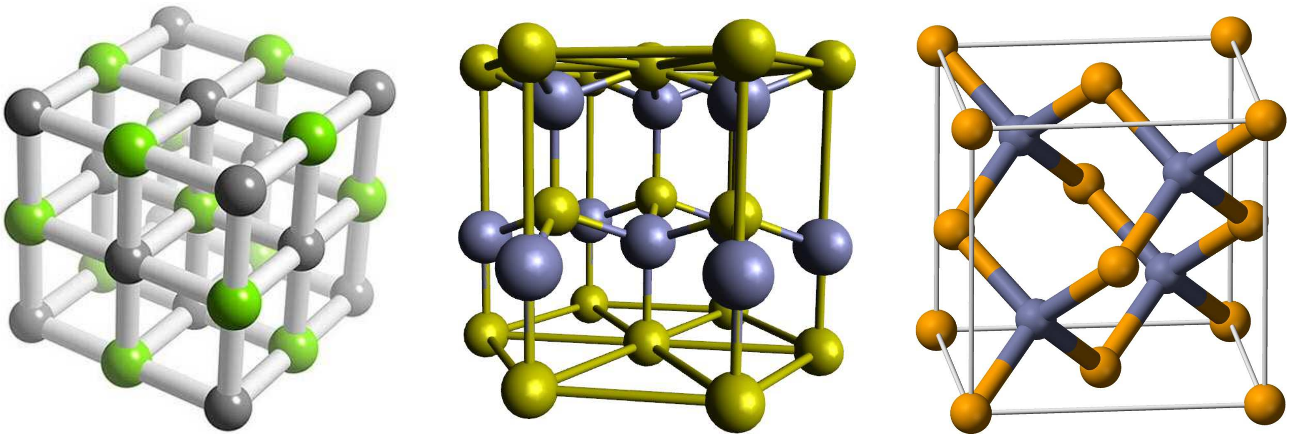
(iii) Choose an allowed lattice type (*i.e.* centering).

(iv) Congratulations, you've just specified a symmorphic point group.

To see this method in practice, let's try it out in two dimensions, where there 13 of the 17 space (wallpaper) groups are symmorphic. There are four crystal systems (oblique, rectangular, square, hexagonal), and the rectangular system can either have a primitive or a centered unit cell. For oblique lattices the allowed point groups are C_1 and C_2, so two possibilities. For rectangular lattices, the allowed point groups are C_{1v} and C_{2v}. There are two possible centerings, for a total of four possibilities. For square lattices, $\mathcal{P}$ can be either C_4 or C_{4v} – another two. For hexagonal, either C_3, C_{3v}, C_6, or C_{6v}, so four total. We arrive at 12 so we are missing a space group. The reason is there can be two inequivalent orientations of the space lattice which the point group leaves invariant, thereby leading to another space group. This happens in the case of the hexagonal lattice with C_{3v} ($3m$) point group symmetry. There are two space groups, called $p3m1$ and $p31m$.

A table of the 17 wallpaper groups is provided in Tab. 2.15, and sketches of the unit cells of each of them are depicted in Fig. 2.20. Study the nonsymmorphic cases pg, pmg, pgg, and $p4g$ to see if you can identify the glide mirrors. Note also how the naming convention works: the leading p or c character stands for primitive or centered. Information about the point group is contained in the space group label. Finally, the symbol g is used to indicate the presence of a glide mirror.

The naming convention for three-dimensional space groups is somewhat more complex, but the procedure is as described in the above recipe. There are seven distinct crystal systems, and Bravais lattice types are either primitive (P), base-centered (A/C), body-centered (I), or face-centered (F). Consider an fcc lattice with point group O_h ($m\overline{3}m$ in HM short notation). The corresponding symmorphic space group is $Fm\overline{3}m$, the full symbol for which is $F\frac{4}{m}\overline{3}\frac{2}{m}$. Proceeding in this way, accounting for all the crystal systems, their allowed point groups, and possible centerings, one obtains 66 symmorphic space groups. As in the two-dimensional case, when inequivalent orientations of the space lattice are both



(a) Rocksalt, $Fm\bar{3}m$ (b) Wurzite, $P6_3mc$ (c) Zincblende, $F\bar{4}3m$

Figure 2.21: Some common AB crystal structures and their space groups.

preserved by the point group, we get an extra space group. Such cases are indicated in red in Tab. 2.16. For example, for the case $C_{2v} = mm2$, the A and C centering types lead to different space groups, $Amm2$ and $Cmm2$, respectively. They are distinct space groups because in the latter case the centering is along a twofold axis, while in the former it is not.

2.3.4 Nonsymmorphic space groups

Returning to our example space group $F\frac{4}{m}\bar{3}\frac{2}{m}$, a check of the tables[23] reveals that there are a total of four space groups generated from the fcc lattice and point group $O_h = \frac{4}{m}\bar{3}\frac{2}{m}$. The other three are $F\frac{4}{m}\bar{3}\frac{2}{c}$, $F\frac{4_1}{d}\bar{3}\frac{2}{m}$, and $F\frac{4_1}{d}\bar{3}\frac{2}{c}$; their short names are $Fm\bar{3}c$, $Fd\bar{3}m$, and $Fd\bar{3}c$, respectively. These three space groups are all nonsymmorphic and involve either screws (4_1), glides (c, d), or both. The second of these three corresponds to carbon diamond. Schoenflies' names for the four point groups generated from fcc and O_h were O_h^5, O_h^6, O_h^7, and O_h^8, respectively, which convey little information other than the order in which he derived them from the point group O_h.[24]

Of the 230 three-dimensional space groups, 157 are nonsymmorphic and contain operations $\{\, g \,|\, \boldsymbol{\tau}_g \,\}$ where $\boldsymbol{\tau}_g \notin \mathcal{T}$ is not in the direct lattice, and no single change of origin can reduce all the $\boldsymbol{\tau}_g$ to zero or to a direct lattice vector.

Some of the nonsymmorphic space groups with screw axes have mirror images, and together are known as *enantiomorphic pairs*. For example, space groups $(P4_1\,,\, P4_3)$ form such a pair, as do $(P4_12_12\,,\, P4_32_12)$, $(P3_112\,,\, P3_212)$, $(P6_222\,,\, P6_422)$, *etc.*

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[23] See `http://www.wikiwand.com/en/List_of_space_groups`.

[24] Schoenflies' O_h^1 through O_h^4 correspond to primitive cubic lattices, and O_h^9 and O_h^{10} to bcc lattices.

system	$\mathcal{P}^{(\mathrm{Sch})}$	$\mathcal{P}^{\mathrm{HM}}$	$N_{\mathcal{P}}$	nonsymmorphic space groups
triclinic	C_1	1	1	none
	C_i	$\bar{1}$	2	none
monoclinic	C_2	2	2	$P2_1$
	C_s	m	2	Pc , Cc
	C_{2h}	$2/m$	4	$P2_1m$, $P2/c$, $P2_1/c$, $C2/c$
orthorhombic	D_2	222	4	$P222_1$, $P2_12_12$, $P2_12_12_1$, $C222_1$, $I2_12_12_1$
	C_{2v}	$mm2$	4	$Pmc2_1$, $Pcc2$, $Pma2$, $Pca2_1$, $Pnc2$, $Pmn2_1$, $Pba2$,
				$Pna2_1$, $Pnn2$
				$Cmc2_1$, $Ccc2$, $Abm2$, $Ama2$, $Aba2$, $Fdd2$, $Iba2$, $Ima2$
	D_{2h}	mmm	8	$Pnnn$, $Pccm$, $Pban$, $Pmma$, $Pnna$, $Pmna$, $Pcca$, $Pbam$,
				$Pccm$, $Pbcm$, $Pnnm$, $Pmmn$, $Pbcn$, $Pbca$, $Pnma$
				$Cmcm$, $Cmca$, $Cccm$, $Cmma$, $Ccca$, $Fddd$, $Ibam$, $Ibcm$, $Imma$
tetragonal	C_4	4	4	$P4_1$, $P4_2$, $P4_3$, $I4_1$
	S_4	$\bar{4}$	4	none
	C_{4h}	$4/m$	8	$P4_2/m$, $P4/n$, $P4_2/n$, $I4_1/a$
	D_4	422	8	$P42_12_1$, $P4_122$, $P4_12_12$, $P4_222$, $P4_22_12$, $P4_322$, $P4_32_12$, $I4_122$
	C_{4v}	$4mm$	8	$P4bm$, $P4_2cm$, $P4_2nm$, $P4cc$, $P4nc$, $P4_2mc$, $P4_2bc$
				$I4cm$, $I4_1md$, $I\bar{4}2d$
	D_{2d}	$\bar{4}2m$	8	$P\bar{4}2c$, $P\bar{4}2_1m$, $P\bar{4}2_1c$, $P\bar{4}c2$, $P\bar{4}c2$, $P\bar{4}n2$, $I\bar{4}c2$, $I\bar{4}2d$
	D_{4h}	$4/mmm$	16	$P4/mcc$, $P4/nbm$, $P4/nnc$, $P4/mbm$, $P4/mnc$, $P4/nmm$,
				$P4/ncc$, $P4_2/mmc$, $P4_2/mcm$, $P4_2/nbc$, $P4_2/nnm$, $P4_2/mbc$,
				$P4_2/mnm$, $P4_2/nmc$, $P4_2/ncm$
				$I4/mcm$, $I4_1/amd$, $I4_1/acd$
trigonal	C_3	3	3	$P3_1$, $P3_2$
	S_6	$\bar{3}$	3	none
	D_3	32	6	$P3_112$, $P3_121$, $P3_212$, $P3_221$
	C_{3v}	$3m$	6	$P31c$, $P3c1$, $R3c$
	D_{3d}	$\bar{3}m$	12	$P\bar{3}1c$, $P\bar{3}c1$, $R\bar{3}c$
hexagonal	C_6	6	6	$P6_1$, $P6_2$, $P6_3$, $P6_4$, $P6_5$
	C_{3h}	$\bar{6}$	6	none
	C_{6h}	$6/m$	12	$P6_3/m$
	D_6	622	12	$P6_122$, $P6_222$, $P6_322$, $P6_422$, $P6_522$
	C_{6v}	$6mm$	12	$P6cc$, $P6_3cm$, $P6_3mc$
	D_{3h}	$\bar{6}m2$	12	$P\bar{6}c2$, $P\bar{6}2c$
	D_{6h}	$6/mmm$	24	$P6/mcc$, $P6_3/mcm$, $P6_3/mmc$
cubic	T	23	12	$P2_13$, $I2_13$
	T_h	$m\bar{3}$	24	$Pn\bar{3}$, $Pa\bar{3}$, $Fd\bar{3}$, $Ia\bar{3}$
	O	432	24	$P4_132$, $P4_232$, $P4_332$, $I4_132$, $F4_132$
	T_d	$\bar{4}3m$	24	$P\bar{4}3n$, $F\bar{4}3c$, $I\bar{4}3d$
	O_h	$m\bar{3}m$	48	$Pn\bar{3}n$, $Pm\bar{3}n$, $Pn\bar{3}n$, $Fm\bar{3}c$, $Fd\bar{3}m$, $Fd\bar{3}c$, $Ia\bar{3}d$

Table 2.17: The 157 nonsymmorphic three-dimensional space groups.

2.3.5 Translations and their representations

The set of translations $\mathcal{T}$ is a subgroup of $\mathcal{S}$, consisting of the elements $\{\, E \,|\, \boldsymbol{R} \,\}$, where $\boldsymbol{R} = \sum_{j=1}^{d} m_j \, \boldsymbol{a}_j$ is a sum over the primitive direct lattice vectors with integer coefficients. It is convenient to work with discrete groups of finite order, so to this end we invoke periodic boundary conditions, which places our system on a d-dimensional torus extending for N_j unit cells in the $\boldsymbol{a}_j$ direction for each $j \in \{1, \ldots, d\}$. This means that $\boldsymbol{R}$ is equivalent to $\boldsymbol{R} + \sum_{j=1}^{d} l_j \, \boldsymbol{L}_j$ with $L_j = N_j \, \boldsymbol{a}_j$ and each $l_j \in \mathbb{Z}$. Our Bravais lattice translation group $\mathcal{T}$ now has $N = \prod_{j=1}^{d} N_j$ elements, which is the total number of unit cells in the real space torus.

Next we ask about irreducible representations of $\mathcal{T}$. Since $\mathcal{T}$ is an abelian group, all its IRREPs are one-dimensional. If $\psi(\boldsymbol{r})$ is a basis function for a unitary one-dimensional IRREP of $\mathcal{T}$, then

$$\{\, E \,|\, \boldsymbol{R} \,\} \, \psi(\boldsymbol{r}) = \psi\big(\{\, E \,|\, \boldsymbol{R} \,\}^{-1} \boldsymbol{r}\big) = \psi(\boldsymbol{r} - \boldsymbol{R}) = e^{-i\omega(\boldsymbol{R})} \, \psi(\boldsymbol{r}) \quad . \tag{2.65}$$

In order that the group multiplication law be satisfied, we must have $e^{-i\omega(\boldsymbol{R})} \, e^{-i\omega(\boldsymbol{R}')} = e^{-i\omega(\boldsymbol{R}+\boldsymbol{R}')}$, which tells us that $\omega(\boldsymbol{R})$ is linear in $\boldsymbol{R}$, *i.e.*

$$\omega(m_1 \, \boldsymbol{a}_1 + \ldots + m_d \, \boldsymbol{a}_d) = m_1 \, \omega(\boldsymbol{a}_1) + \ldots + m_d \, \omega(\boldsymbol{a}_d) \tag{2.66}$$

to within an additive multiple of 2π. We may define $\omega(\boldsymbol{a}_j) \equiv \theta_j$, in which case the IRREP is labeled by the set of angles $\boldsymbol{\theta}$. Furthermore, we must have $\omega(\boldsymbol{R}) = \omega(\boldsymbol{R} + \boldsymbol{L}_j)$ for all $j \in \{1, \ldots, d\}$, which says that $N_j \, \theta_j$ is congruent to zero modulo 2π, *i.e.* $\theta_j = 2\pi l_j / N_j$, where $l_j \in \{1, \ldots, N_j\}$. So the θ_j values are quantized and there are $N = \prod_j N_j$ distinct values of the vector $\boldsymbol{\theta} = (\theta_1, \ldots, \theta_d)$.

Recall the definition of the reciprocal lattice vectors $\boldsymbol{b}_j$ which satisfy $\boldsymbol{a}_i \cdot \boldsymbol{b}_j = 2\pi \, \delta_{ij}$. Then if we define the wavevector $\boldsymbol{k} \equiv \sum_{j=1}^{d} \theta_j \, \boldsymbol{b}_j / 2\pi$, we then have $\omega(\boldsymbol{R}) = \boldsymbol{k} \cdot \boldsymbol{R}$, and our basis functions may be written as $\psi_{\boldsymbol{k}}(\boldsymbol{r}) = u(\boldsymbol{r}) \, e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$ where $u(\boldsymbol{r} - \boldsymbol{R}) = u(\boldsymbol{r})$ for all $\boldsymbol{R} \in \mathcal{L}$ is a periodic *cell function*. Any cell function may be expanded as a discrete Fourier series, *viz.*

$$u(\boldsymbol{r}) = \sum_{\boldsymbol{K}} C_{\boldsymbol{K}} \, e^{i\boldsymbol{K}\cdot\boldsymbol{r}} \quad , \tag{2.67}$$

where $\boldsymbol{K} = \sum_{j=1}^{d} n_j \, \boldsymbol{b}_j$ is a reciprocal lattice vector, which satisfies $\exp(i\boldsymbol{K} \cdot \boldsymbol{R}) = 1$ for all direct lattice vectors $\boldsymbol{R}$, and the $\{C_{\boldsymbol{K}}\}$ are a set of coefficients. What we have just shown is known as *Bloch's theorem*, which says that the eigenfunctions of any Hamiltonian $\hat{H}$ which commutes with all Bravais lattice translations may be written in the form $\psi_{\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \, u(\boldsymbol{r})$, where $u(\boldsymbol{r})$ is a cell function and $\boldsymbol{k}$ lies within the first Brillouin zone of the reciprocal lattice. The reason that $\boldsymbol{k}$ is confined to this region is that $\boldsymbol{k} \to \boldsymbol{k} + \boldsymbol{K}$ amounts to a change of the cell function $u(\boldsymbol{r}) \to u(\boldsymbol{r}) \, e^{i\boldsymbol{K}\cdot\boldsymbol{r}}$. Note that quantization of $\boldsymbol{\theta}$ entails quantization of $\boldsymbol{k}$ to one of N possible values.

The character of the space group element $\{\, E \,|\, \boldsymbol{R} \,\}$ in the $\boldsymbol{k}$ IRREP is thus $\chi^{(\boldsymbol{k})}(\boldsymbol{R}) = e^{-i\boldsymbol{k}\cdot\boldsymbol{R}}$, in suitably abbreviated notation. The great orthogonality and completeness theorems then tell us

$$\sum_{\boldsymbol{R}} e^{i(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{R}} = N \, \delta_{\boldsymbol{k},\boldsymbol{k}'} \qquad , \qquad \sum_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot(\boldsymbol{R}-\boldsymbol{R}')} = N \, \delta_{\boldsymbol{R},\boldsymbol{R}'} \quad . \tag{2.68}$$

In the limit $N \to \infty$, these equations become

$$\sum_{\boldsymbol{R}} e^{i(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{R}} = \hat{\Omega} \sum_{\boldsymbol{K}} \delta(\boldsymbol{k}' - \boldsymbol{k} - \boldsymbol{K}) \qquad , \qquad \Omega \int_{\hat{\Omega}} \frac{d^d k}{(2\pi)^d}\, e^{i\boldsymbol{k}\cdot(\boldsymbol{R}-\boldsymbol{R}')} = \delta_{\boldsymbol{R},\boldsymbol{R}'} \quad . \tag{2.69}$$

The first of these is the generalized Poisson summation formula from Eqn. 2.7. In the second, the integral is over the first Brillouin zone, $\hat{\Omega}$. Recall $\hat{\Omega} = (2\pi)^d/\Omega$ is the volume of $\hat{\Omega}$.

2.3.6 Space group representations

We follow Lax §8.6 and §8.7. When solving for electronic or vibrational states of a crystal, the first order of business is to classify eigenstates by wavevector, *i.e.* to diagonalize the operations $\{\, E \,|\, \boldsymbol{R} \,\}$ in the space group $\mathcal{S}$. For states of crystal momentum $\boldsymbol{k}$, we have $\{\, E \,|\, \boldsymbol{R} \,\}\,|\, \boldsymbol{k}, \lambda \,\rangle = e^{i\boldsymbol{k}\cdot\boldsymbol{R}}\,|\, \boldsymbol{k}, \lambda \,\rangle$, where λ denotes other quantum numbers not related to crystal momentum.

Acting on Bloch states, a general space group operation has the following action:

$$\begin{aligned} \{\, g \,|\, \boldsymbol{t} \,\}\, \overbrace{e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\, u(\boldsymbol{r})}^{\psi_{\boldsymbol{k}}(\boldsymbol{r})} &= \exp\Big[i\boldsymbol{k} \cdot \{\, g \,|\, \boldsymbol{t} \,\}^{-1} \boldsymbol{r} \Big]\, u\big(\{\, g \,|\, \boldsymbol{t} \,\}^{-1} \boldsymbol{r}\big) \\ &= e^{ig\boldsymbol{k}\boldsymbol{r}}\, u\big(g^{-1}(\boldsymbol{r} - \boldsymbol{t})\big) \equiv e^{ig\boldsymbol{k}\cdot\boldsymbol{r}}\, e^{-ig\boldsymbol{k}\cdot\boldsymbol{t}}\, \widetilde{u}(\boldsymbol{r}) = \widetilde{\psi}_{g\boldsymbol{k}}(\boldsymbol{r}) \quad , \end{aligned} \tag{2.70}$$

where if $u(\boldsymbol{r}) = \sum_{\boldsymbol{K}} C_{\boldsymbol{K}}\, e^{i\boldsymbol{K}\cdot\boldsymbol{r}}$ is the original cell function, then

$$\widetilde{u}(\boldsymbol{r}) = \sum_{\boldsymbol{K}} C_{g^{-1}\boldsymbol{K}}\, e^{-i\boldsymbol{K}\cdot\boldsymbol{t}}\, e^{i\boldsymbol{K}\cdot\boldsymbol{r}} \equiv \sum_{\boldsymbol{K}} \widetilde{C}_{\boldsymbol{K}}\, e^{i\boldsymbol{K}\cdot\boldsymbol{r}} \tag{2.71}$$

is a new cell function, *i.e.* it satisfies $\widetilde{u}(\boldsymbol{r} + \boldsymbol{R}) = \widetilde{u}(\boldsymbol{r})$ for all direct lattice vectors $\boldsymbol{R}$. Thus, application of $\{\, g \,|\, \boldsymbol{t} \,\} \in \mathcal{S}$ to a Bloch function $\psi_{\boldsymbol{k}}(\boldsymbol{r})$ generates a new Bloch function $\widetilde{\psi}_{g\boldsymbol{k}}(\boldsymbol{r})$ at wavevector $g\boldsymbol{k}$.[25]

Group and star of the wavevector $\boldsymbol{k}$

If $g\boldsymbol{k} = \boldsymbol{k} + \boldsymbol{K}$, then $\{\, g \,|\, \boldsymbol{t} \,\}$ does not change the wavevector of the Bloch function. We define the *point group* $\mathcal{P}_{\boldsymbol{k}}$ *of the wavevector* $\boldsymbol{k}$ to be those point group operations $g \in \mathcal{P}$ which leave $\boldsymbol{k}$ unchanged up to a reciprocal lattice vector[26]. The space group of the wavevector $\mathcal{S}_{\boldsymbol{k}}$ is then all $\{\, g \,|\, \boldsymbol{t} \,\} \in \mathcal{S}$ for which $g \in \mathcal{P}_{\boldsymbol{k}}$. The *star of the wavevector* $\boldsymbol{k}$ is defined to be the set of points including $\boldsymbol{k}$ and all its images $g\boldsymbol{k}$, where $g \in \mathcal{P} \setminus \mathcal{P}_{\boldsymbol{k}}$.[27]

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[25] The phase $e^{-ig\boldsymbol{k}\cdot\boldsymbol{t}}$ amounts to a gauge transformation.

[26] $\mathcal{P}_{\boldsymbol{k}}$ is also known as the *little group* of $\boldsymbol{k}$.

[27] We use the notation $A \setminus B$ to denote set subtraction, with $B \subseteq A$. *I.e.* $A \setminus B = A - B$, which is to say the set of elements in A that are not in B.

Algebra and representation of the space group

Recall the results of Eqns. 2.62 and 2.63. From

$$\{\, g \,|\, \boldsymbol{\tau}_g \,\}\,\{\, h \,|\, \boldsymbol{\tau}_h \,\} = \{\, E \,|\, \boldsymbol{R}_{g,h} \,\}\,\{\, gh \,|\, \boldsymbol{\tau}_{gh} \,\} = \{\, gh \,|\, \boldsymbol{\tau}_{gh} \,\}\,\{\, E \,|\, (gh)^{-1}\boldsymbol{R}_{g,h} \,\} \quad , \tag{2.72}$$

we see that, acting on a Bloch state,

$$\{\, g \,|\, \boldsymbol{\tau}_g \,\}\,\{\, h \,|\, \boldsymbol{\tau}_h \,\}\,\psi_{\boldsymbol{k}}(\boldsymbol{r}) = e^{-igh\boldsymbol{k}\cdot\boldsymbol{R}_{g,h}}\,\{\, gh \,|\, \boldsymbol{\tau}_{gh} \,\}\,\psi_{\boldsymbol{k}}(\boldsymbol{r}) \quad , \tag{2.73}$$

and so if g and h are both elements of $\mathcal{P}_{\boldsymbol{k}}$, then

$$\{\, g \,|\, \boldsymbol{\tau}_g \,\}\,\{\, h \,|\, \boldsymbol{\tau}_h \,\} = e^{-i\boldsymbol{k}\cdot\boldsymbol{R}_{g,h}}\,\{\, gh \,|\, \boldsymbol{\tau}_{gh} \,\} \tag{2.74}$$

when acting on Bloch states of crystal momentum $\boldsymbol{k}$, where $\boldsymbol{R}_{g,h} = \boldsymbol{\tau}_g + g\boldsymbol{\tau}_h - \boldsymbol{\tau}_{gh}$ is a direct lattice vector. The above equation establishes a projective representation for $\mathcal{S}_{\boldsymbol{k}}$. Alternatively, one may define the operators

$$\Lambda_{\boldsymbol{k}}(g) \equiv \{\, g \,|\, \boldsymbol{\tau}_g \,\}\, e^{i\boldsymbol{k}\cdot\boldsymbol{\tau}_g} = \{\, g \,|\, \boldsymbol{R} + \boldsymbol{\tau}_g \,\}\, e^{i\boldsymbol{k}\cdot(\boldsymbol{R}+\boldsymbol{\tau}_g)} \quad , \tag{2.75}$$

which act on states of crystal momentum $\boldsymbol{k}$, and which satisfy the projective algebra

$$\begin{aligned} \Lambda_{\boldsymbol{k}}(g)\,\Lambda_{\boldsymbol{k}}(h) &= \omega_{\boldsymbol{k}}(g,h)\,\Lambda(gh) \\ \omega_{\boldsymbol{k}}(g,h) &= e^{i\boldsymbol{k}\cdot(\boldsymbol{\tau}_h - g\boldsymbol{\tau}_h)} = e^{i\boldsymbol{K}_g\cdot\boldsymbol{\tau}_h} \end{aligned} \tag{2.76}$$

because $\boldsymbol{k}\cdot g\boldsymbol{\tau}_h = g^{-1}\boldsymbol{k}\cdot\boldsymbol{\tau}_h \equiv (\boldsymbol{k}-\boldsymbol{K}_g)\cdot\boldsymbol{\tau}_h$, with $\boldsymbol{K}_g = \boldsymbol{k} - g^{-1}\boldsymbol{k} = \boldsymbol{k} - \boldsymbol{k}g$.

Representations of symmorphic space groups

When $\mathcal{S}$ is symmorphic, $\boldsymbol{\tau}_g = 0$ for all $g \in \mathcal{P}$, hence $\omega_{\boldsymbol{k}}(g,h) = 1$ for all $\boldsymbol{k}$. We don't have to worry about projective representations of the little groups, and therefore

$$\begin{aligned} D^{\Gamma\,;\,\mathcal{S}_{\boldsymbol{k}}}\big(\{\, g \,|\, \boldsymbol{0} \,\}\big) &= D^{\Gamma\,;\,\mathcal{P}_{\boldsymbol{k}}}(g) \\ \chi^{\Gamma\,;\,\mathcal{S}_{\boldsymbol{k}}}\big(\{\, g \,|\, \boldsymbol{0} \,\}\big) &= \chi^{\Gamma\,;\,\mathcal{P}_{\boldsymbol{k}}}(g) \quad , \end{aligned} \tag{2.77}$$

i.e. we can use the ordinary point group representation matrices.

Representations of nonsymmorphic space groups

If $\boldsymbol{k} \notin \partial\hat{\Omega}$ lies in the interior of the Brillouin zone and not on its boundary, then both $\boldsymbol{k}$ and $g^{-1}\boldsymbol{k}$ lie inside $\hat{\Omega}$, which means $\boldsymbol{k}_g = 0$ and the cocycle is unity: $\omega_{\boldsymbol{k}}(g,h) = 1$. Thus we have

$$\begin{aligned} D^{\Gamma\,;\,\mathcal{S}_{\boldsymbol{k}}}\big(\{\, g \,|\, \boldsymbol{\tau}_g \,\}\big) &= e^{-i\boldsymbol{k}\cdot\boldsymbol{\tau}_g}\, D^{\Gamma\,;\,\mathcal{P}_{\boldsymbol{k}}}(g) \\ \chi^{\Gamma\,;\,\mathcal{S}_{\boldsymbol{k}}}\big(\{\, g \,|\, \boldsymbol{\tau}_g \,\}\big) &= e^{-i\boldsymbol{k}\cdot\boldsymbol{\tau}_g}\, \chi^{\Gamma\,;\,\mathcal{P}_{\boldsymbol{k}}}(g) \quad , \end{aligned} \tag{2.78}$$

where Γ can only be the trivial representation if $\boldsymbol{k} \neq \boldsymbol{0}$. Again, we only need the ordinary point group representation matrices.

If $\boldsymbol{k} \in \partial\hat{\Omega}$, then $\mathcal{P}_{\boldsymbol{k}}$ may be nontrivial. In this case there are two possibilities:

(i) If there is a one-dimensional IRREP of $\mathcal{S}_{\boldsymbol{k}}$, $d_{\boldsymbol{k}}(g)$, with $d_{\boldsymbol{k}}(g)\, d_{\boldsymbol{k}}(h) = \omega_{\boldsymbol{k}}(g,h)\, d_{\boldsymbol{k}}(gh)$, define the ratio $\widetilde{\Lambda}_{\boldsymbol{k}}(g) \equiv \Lambda_{\boldsymbol{k}}(g)/d_{\boldsymbol{k}}(g)$. The operators $\widetilde{\Lambda}_{\boldsymbol{k}}(g)$ then satisfy $\widetilde{\Lambda}_{\boldsymbol{k}}(g)\, \widetilde{\Lambda}_{\boldsymbol{k}}(h) = \widetilde{\Lambda}_{\boldsymbol{k}}(gh)$, *i.e.* the point group multiplication table. Thus,

$$\begin{aligned} D^{\Gamma\,;\,\mathcal{S}_{\boldsymbol{k}}}\big(\{\, g \,|\, \boldsymbol{\tau}_g \,\}\big) &= e^{-i\boldsymbol{k}\cdot\boldsymbol{\tau}_g}\, d_{\boldsymbol{k}}(g)\, D^{\Gamma\,;\,\mathcal{P}_{\boldsymbol{k}}}(g) \\ \chi^{\Gamma\,;\,\mathcal{S}_{\boldsymbol{k}}}\big(\{\, g \,|\, \boldsymbol{\tau}_g \,\}\big) &= e^{-i\boldsymbol{k}\cdot\boldsymbol{\tau}_g}\, d_{\boldsymbol{k}}(g)\, \chi^{\Gamma\,;\,\mathcal{P}_{\boldsymbol{k}}}(g) \quad . \end{aligned} \tag{2.79}$$

and again we can use the ordinary point group representations.

(ii) If there is no one-dimensional IRREP of $\mathcal{S}_{\boldsymbol{k}}$, if one wishes to avoid needless work, one can consult tables, *e.g.* in appendix F of Lax, or appendix C of Dresselhaus, Dresselhaus, and Jorio.

2.4 Fourier Space Crystallography

Thus far our understanding of crystallography has been based on real space structures and their transformation properties under point and space group operations. An equivalent approach, originally due to Bienenstock and Ewald (1962), and formalized and further developed by Mermin and collaborators in the 1990s, focuses on the Fourier modes $\hat{\rho}(\boldsymbol{K})$ of the density $\rho(\boldsymbol{r})$. This is known in the literature as *Fourier space crystallography*[28]. Writing $\rho(\boldsymbol{r})$ as a Fourier sum,

$$\rho(\boldsymbol{r}) = \sum_{\boldsymbol{K}} \hat{\rho}(\boldsymbol{K})\, e^{i\boldsymbol{K}\cdot\boldsymbol{r}} \quad , \tag{2.80}$$

where each $\boldsymbol{K} \in \hat{\mathcal{L}}$. Since $\rho(\boldsymbol{r}) \in \mathbb{R}$ is real, we have $\hat{\rho}(-\boldsymbol{K}) = \hat{\rho}^*(\boldsymbol{K})$ for all $\boldsymbol{K} \in \hat{\mathcal{L}}$. The inverse of the above relation is

$$\hat{\rho}(\boldsymbol{K}) = \int\! d^d\!r\; \rho(\boldsymbol{r})\, e^{-i\boldsymbol{K}\cdot\boldsymbol{r}} \quad . \tag{2.81}$$

Note that if $\rho'(\boldsymbol{r}) = \rho(\boldsymbol{r} + \boldsymbol{d})$ then $\hat{\rho}'(\boldsymbol{K}) = \hat{\rho}(\boldsymbol{K})\, e^{i\chi(\boldsymbol{K})}$ where $\chi(\boldsymbol{K}) = \boldsymbol{K}\cdot\boldsymbol{d}$ is a linear function on $\hat{\mathcal{L}}$.

2.4.1 Space group symmetries

We now ask how the $\hat{\rho}(\boldsymbol{K})$ transform under space group operations of the crystal. The general space group operation may be written as $\{\, g \,|\, \boldsymbol{R} + \boldsymbol{\tau}_g \,\}$. We have already accounted for the symmetries under Bravais lattice translations, which says that $\rho(\boldsymbol{r})$ is given as the above Fourier sum. So now restrict our attention to operations of the form $\{\, g \,|\, \boldsymbol{\tau}_g \,\}$. If $\rho(\boldsymbol{r})$ is invariant under all space group operations, we must have

$$\rho(\boldsymbol{r}) = \{\, g \,|\, \boldsymbol{\tau}_g \,\}\, \rho(\boldsymbol{r}) = \rho\big(\{\, g \,|\, \boldsymbol{\tau}_g \,\}^{-1} \boldsymbol{r}\big) = \rho\big(g^{-1}(\boldsymbol{r} - \boldsymbol{\tau}_g)\big) \quad . \tag{2.82}$$

Taking the Fourier transform, we have

$$\hat{\rho}(\boldsymbol{K}) = \int\! d^d\!r\; \rho\big(g^{-1}(\boldsymbol{r} - \boldsymbol{\tau}_g)\big)\, e^{-i\boldsymbol{K}\cdot\boldsymbol{r}} = \hat{\rho}(\boldsymbol{K}g)\, e^{-i\boldsymbol{K}\cdot\boldsymbol{\tau}_g} \quad , \tag{2.83}$$

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[28] Here we follow the pedagogical treatment in A. König and N. D. Mermin, *Am. J. Phys.* **68**, 525 (2000), with some minor notational differences.

which is easily established by changing the integration variables[29] from $\boldsymbol{r}$ to $\boldsymbol{r}' = g^{-1}(\boldsymbol{r} - \boldsymbol{\tau}_g)$. Note that g denotes both an abstract element of the point group $\mathcal{P}$ as well as its 3×3 matrix representation, and that by $\boldsymbol{K}g$ we treat $\boldsymbol{K}$ as a row vector and multiply by the matrix of g on the right. We therefore have

$$\hat{\rho}(\boldsymbol{K}g) = \hat{\rho}(\boldsymbol{K})\, e^{i\phi_g(\boldsymbol{K})} \quad , \tag{2.84}$$

where $\phi_g(\boldsymbol{K}) = \boldsymbol{K} \cdot \boldsymbol{\tau}_g$ acts linearly on $\hat{\mathcal{L}}$, with $\phi_g(\boldsymbol{0}) \cong 0$ for all $g \in \mathcal{P}$ and $\phi_E(\boldsymbol{K}) \cong 0$ for all $\boldsymbol{K} \in \hat{\mathcal{L}}$. Here the symbol $\cong$ denotes equality modulo 2π. We call $\phi_g(\boldsymbol{K})$ a *phase function* on the reciprocal lattice.

We then have

$$\begin{aligned} \hat{\rho}(\boldsymbol{K}gh) &= \hat{\rho}(\boldsymbol{K}g)\, e^{i\phi_h(\boldsymbol{K}g)} = \hat{\rho}(\boldsymbol{K})\, e^{i\phi_g(\boldsymbol{K})}\, e^{i\phi_h(\boldsymbol{K}g)} \\ &= \hat{\rho}(\boldsymbol{K})\, e^{i\phi_{gh}(\boldsymbol{K})} \quad , \end{aligned} \tag{2.85}$$

and therefore the *group compatibility condition* for the phase functions is

$$\phi_{gh}(\boldsymbol{K}) \cong \phi_h(\boldsymbol{K}g) + \phi_g(\boldsymbol{K}) \quad , \tag{2.86}$$

which is the same condition as that in eqn. 2.63.

Suppose $\rho'(\boldsymbol{r})$ and $\rho(\boldsymbol{r})$ differ by a translation. Then $\hat{\rho}'(\boldsymbol{K}) = \hat{\rho}(\boldsymbol{K})\, e^{i\chi(\boldsymbol{K})}$, hence

$$\begin{aligned} \hat{\rho}'(\boldsymbol{K}g) &= \hat{\rho}'(\boldsymbol{K})\, e^{i\phi'_g(\boldsymbol{K})} = \hat{\rho}(\boldsymbol{K})\, e^{i\chi(\boldsymbol{K})}\, e^{i\phi'_g(\boldsymbol{K})} \\ &= \hat{\rho}(\boldsymbol{K}g)\, e^{i\chi(\boldsymbol{K}g)} = \hat{\rho}(\boldsymbol{K})\, e^{i\phi_g(\boldsymbol{K})}\, e^{i\chi(\boldsymbol{K}g)} \quad , \end{aligned} \tag{2.87}$$

and therefore

$$\phi'_{\boldsymbol{g}}(\boldsymbol{K}) \cong \phi_g(\boldsymbol{K}) + \overbrace{\chi(\boldsymbol{K}g) - \chi(\boldsymbol{K})}^{\chi(\boldsymbol{K}g - \boldsymbol{K})} \quad . \tag{2.88}$$

We say that the the above equation constitutes a *gauge transformation* and thus that the functions $\phi'_g(\boldsymbol{K})$ and $\phi_g(\boldsymbol{K})$ are *gauge equivalent*. We then have the following:

◇ *A space group $\mathcal{S}$ is symmorphic iff there exists a gauge in which $\phi_g(\boldsymbol{K}) \cong 0$ for all $g \in \mathcal{P}$ and all $\boldsymbol{K} \in \hat{\mathcal{L}}$.*

2.4.2 Extinctions

In §2.1.5 we noted how in certain crystals, the amplitude of Bravais lattice Bragg peaks observed in a diffraction experiment can be reduced or even extinguished due to the crystal structure. Bragg peak extinction is thus a physical manifestation of the crystallographic point group symmetry, and as such must be encoded in the gauge-invariant content of the phase functions. Suppose that $\boldsymbol{K}g = \boldsymbol{K}$. Then

$$\hat{\rho}(\boldsymbol{K}) = \hat{\rho}(\boldsymbol{K}g) = \hat{\rho}(\boldsymbol{K})\, e^{i\phi_g(\boldsymbol{K})} \quad , \tag{2.89}$$

and thus if $\phi_g(\boldsymbol{K}) \ncong 0$, we necessarily have $\hat{\rho}(\boldsymbol{K}) = 0$, *i.e.* the Bragg peak at $\boldsymbol{K}$ is extinguished. $\boldsymbol{K}g = g^{\mathsf{T}}\boldsymbol{K} = \boldsymbol{K}$ means that $\boldsymbol{K}$ lies within the invariant subspace of g (and that of $g^{\mathsf{T}} = g^{-1}$ as well, of

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[29] Since $g \in \mathsf{O}(n)$, we have that the Jacobian of the transformation is $|\det g| = 1$.

course). Now the only nontrivial ($g \neq E$) point group operations (in three dimensions) with invariant subspaces are (i) proper rotations r, and (ii) mirror reflections m. Every proper rotation has an invariant axis, and every mirror reflection has an invariant plane. We now consider the consequences of each for extinctions.

- *Mirrors* : If m is a mirror, then $m^2 = E$. Consider a reciprocal lattice vector $\boldsymbol{K} = \boldsymbol{K}m$ lying in the invariant plane of m. Then

  $$0 \cong \phi_E(\boldsymbol{K}) \cong \phi_{m^2}(\boldsymbol{K}) \cong \phi_m(\boldsymbol{K}m) + \phi_m(\boldsymbol{K}) \cong 2\phi_m(\boldsymbol{K}) \quad . \tag{2.90}$$

  Thus, $2\phi_m(\boldsymbol{K}) \cong 0$ which means either $\phi_m(\boldsymbol{K}) \cong 0$ or $\phi_m(\boldsymbol{K}) \cong \pi$. *Unless* $\phi_m(\boldsymbol{K}) = 0$ *for all* $\boldsymbol{K} = \boldsymbol{K}m$ *in the mirror plane, we say that* m *is a glide mirror.* Let $\boldsymbol{\beta}_1$ and $\boldsymbol{\beta}_2$ be basis vectors for the two-dimensional sublattice of $\hat{\mathcal{L}}$ in the invariant plane of m. Linearity of the phase functions says

  $$\phi_m(n_1\,\boldsymbol{\beta}_1 + n_2\,\boldsymbol{\beta}_2) = n_1\,\phi_m(\boldsymbol{\beta}_1) + n_2\,\phi_m(\boldsymbol{\beta}_2) \quad . \tag{2.91}$$

  Suppose now that $\phi_m(\boldsymbol{\beta}_1) \cong \phi_m(\boldsymbol{\beta}_2) \cong 0$. In this case, the mirror is ordinary and we have not a glide, *i.e.* there are no extinctions due to m. Next suppose $\phi_m(\boldsymbol{\beta}_1) \cong \pi$ and $\phi_m(\boldsymbol{\beta}_2) \cong 0$. In this case, we have extinctions for all $\boldsymbol{K} = n_1\,\boldsymbol{\beta}_1 + n_2\,\boldsymbol{\beta}_2$ with n_1 odd, for all n_2. A corresponding result holds for the case $\phi_m(\boldsymbol{\beta}_1) \cong 0$ and $\phi_m(\boldsymbol{\beta}_2) \cong \pi$. Finally, suppose $\phi_m(\boldsymbol{\beta}_1) \cong \phi_m(\boldsymbol{\beta}_2) \cong \pi$. Then $\boldsymbol{K}$ is extinguished whenever $n_1 + n_2$ is odd.

- *Proper rotations* : In this case, $r^n = E$ with $n =$ 2, 3, 4, or 6. Suppose $\boldsymbol{K} = \boldsymbol{K}r$ lies along the invariant axis of r. Then

  $$0 \cong \phi_E(\boldsymbol{K}) \cong \phi_{r^n}(\boldsymbol{K}) \cong n\,\phi_r(\boldsymbol{K}) \quad , \tag{2.92}$$

  which says $\phi_r(\boldsymbol{K}) = 2\pi j/n$. If $\phi_r(\boldsymbol{K}) = 0$ for all $\boldsymbol{K} = \boldsymbol{K}r$, the rotation is ordinary. *If* $\phi_r(\boldsymbol{K}) \ncong 0$ *for any* $\boldsymbol{K} = \boldsymbol{K}r$ *along the invariant axis, we say that* r *is a screw.* Let $\boldsymbol{\beta}_1$ be the basis vector for $\boldsymbol{K}$ points along the invariant axis. Then $\phi_r(\boldsymbol{\beta}_1) \cong 2\pi j/n$, with $j \in \{0, \ldots, n-1\}$. The case $j = 0$ corresponds to an ordinary rotation. For $\boldsymbol{K} = l\,\boldsymbol{\beta}_1$, we have $\phi_r(\boldsymbol{K}) \cong 2\pi jl/n$, and Bragg vectors with $jl \neq 0$ modulo n are extinguished.

- *Special circumstances* : Suppose an n-fold proper rotation r lies within the invariant plane of a mirror m. Then $rmr = m$, *i.e.* $mrm = r^{-1}$. This is the case, for example, for the groups C_{nv}, D_{nd}, and D_{nh}. Let $\boldsymbol{K} = \boldsymbol{K}r = \boldsymbol{K}m$. Then

  $$\begin{aligned} \phi_m(\boldsymbol{K}) = \phi_{rmr}(\boldsymbol{K}) &\cong \phi_{mr}(\boldsymbol{K}r) + \phi_r(\boldsymbol{K}) \\ &\cong \phi_r(\boldsymbol{K}rm) + \phi_m(\boldsymbol{K}r) + \phi_r(\boldsymbol{K}) \cong 2\phi_r(\boldsymbol{K}) + \phi_m(\boldsymbol{K}) \quad . \end{aligned} \tag{2.93}$$

  We then have $2\phi_r(\boldsymbol{K}) \cong 0$, and so the screw symmetry is restricted to two possible cases: either $\phi_r(\boldsymbol{K}) \cong 0$ or $\phi_r(\boldsymbol{K}) \cong \pi$. Such a screw requires n even and $j = \frac{1}{2}n$.

  Suppose next that the n-fold rotation axis is perpendicular to a mirror plane, as in the groups C_{nh} and D_{nh}. In this case $mr = rm$, and we have

  $$\begin{aligned} \phi_{mr}(\boldsymbol{K}) &= \phi_r(\boldsymbol{K}m) + \phi_m(\boldsymbol{K}) \\ \phi_{rm}(\boldsymbol{K}) &= \phi_m(\boldsymbol{K}r) + \phi_r(\boldsymbol{K}) \quad . \end{aligned} \tag{2.94}$$

There are two interesting possibilities. First, if $\boldsymbol{K} = \boldsymbol{K}r$ is along the invariant axis of r, then $\boldsymbol{K}m = -\boldsymbol{K}$, and we have $\phi_r(\boldsymbol{K}) \cong \phi_r(-\boldsymbol{K}) \cong -\phi_r(\boldsymbol{K})$, hence $2\phi_r(\boldsymbol{K}) \cong 0$, which entails the same restrictions as in the case where $rmr = m$ analyzed above. Second, if $\boldsymbol{K}m = \boldsymbol{K}$, then we obtain $\phi_m(\boldsymbol{K}r) = \phi_m(\boldsymbol{K})$, which says that the diffraction pattern in the invariant plane, including any extinctions, is symmetric under the r operation.

2.4.3 Sticky bands

Consider now the Schrödinger equation $\hat{H}\psi = E\psi$, where[30]

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{r}) \quad , \tag{2.95}$$

where $V(\boldsymbol{r})$ is invariant under space group operations. Typically $V(\boldsymbol{r})$ is purely due to (screened) Coulomb interactions between a given electron and the combined electron-ion charge density $\rho(\boldsymbol{r})$, in which case

$$V(\boldsymbol{r}) = \int d^d\!r'\, v(\boldsymbol{r} - \boldsymbol{r}')\, \rho(\boldsymbol{r}') \quad , \tag{2.96}$$

where $v(\boldsymbol{r}) = v(r)$ is the screened potential at separation $\boldsymbol{r}$. According to Bloch's theorem, eigenfunctions $\psi_{n\boldsymbol{k}}(\boldsymbol{r})$ of H are labeled by crystal momentum $\boldsymbol{k} \in \hat{\Omega}$ as well as by a *band index* n, and may be written as

$$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \sum_{\boldsymbol{K}} C_{n\boldsymbol{k}}(\boldsymbol{K})\, e^{i(\boldsymbol{K}+\boldsymbol{k})\cdot\boldsymbol{r}} \quad . \tag{2.97}$$

The Schrödinger equation for band n can then be written as

$$E\, C_{n\boldsymbol{k}}(\boldsymbol{K}) = \sum_{\boldsymbol{K}'} \overbrace{\left[\frac{\hbar^2(\boldsymbol{K}+\boldsymbol{k})^2}{2m}\, \delta_{\boldsymbol{K},\boldsymbol{K}'} + \hat{V}(\boldsymbol{K}-\boldsymbol{K}')\right]}^{\langle\, \boldsymbol{K} \,|\, \hat{H}(\boldsymbol{k}) \,|\, \boldsymbol{K}' \,\rangle} C_{n\boldsymbol{k}}(\boldsymbol{K}') \quad , \tag{2.98}$$

where $\hat{V}(\boldsymbol{K}) = \hat{v}(\boldsymbol{K})\, \hat{\rho}(\boldsymbol{K})$, since the Fourier transform of a convolution is the product of the Fourier transforms. Since $v(\boldsymbol{r})$ is isotropic, we have $\hat{v}(\boldsymbol{q}\, g) = \hat{v}(\boldsymbol{q})$ for all $\boldsymbol{q}$, and therefore $\hat{V}(\boldsymbol{K}g) = \hat{V}(\boldsymbol{K})\, e^{i\phi_g(\boldsymbol{K})}$. Let us define $\hat{\omega}(\boldsymbol{q}) \equiv \hbar^2\boldsymbol{q}^2/2m$, which is the isotropic free particle dispersion. Note that

$$\hat{\omega}(\boldsymbol{K}g + \boldsymbol{k}) = \hat{\omega}\big((\boldsymbol{K}+\boldsymbol{k})\, g + (\boldsymbol{k} - \boldsymbol{k}\, g)\big) \quad . \tag{2.99}$$

We now (re-)introduce the notion of the *little group* of a wavevector:

> DEFINITION : Given a wavevector $\boldsymbol{k} \in \hat{\Omega}$, the set of all $g \in \mathcal{P}$ for which $\boldsymbol{K}_g \equiv \boldsymbol{k} - \boldsymbol{k}g$ is in $\hat{\mathcal{L}}$ is called the *little group* of $\boldsymbol{k}$, and notated $\mathcal{P}_{\boldsymbol{k}}$.

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[30] In this section, we will use hats to denote operators as well as Fourier transformed quantities, so keep on your toes to recognize the meaning of the hat symbol in context.

Since $\boldsymbol{k}g$ must also lie within $\hat{\Omega}$, we have that $\mathcal{P}_{\boldsymbol{k}} = \{E\}$ if $\boldsymbol{k}$ lies in the interior of the first Brillouin zone. For wavevectors $\boldsymbol{k} \in \partial\hat{\Omega}$ lying on the boundary of $\hat{\Omega}$, the little group $\mathcal{P}_{\boldsymbol{k}}$ can contain other elements. Consider for example the case of a square lattice, for which $\hat{\Omega}$ is itself a square, and let $\boldsymbol{k} = \frac{1}{2}\boldsymbol{b}_1$, which lies at the center of one of the edges. Let $\mathcal{P} = C_{4v}$, which is generated by r (90° rotation) and σ (x-axis reflection). Then E and σ are in $P_{\boldsymbol{k}}$ because they leave $\boldsymbol{k}$ fixed and hence $\boldsymbol{K}_g = \boldsymbol{0}$, but so are r^2 and σr^2, which send $\boldsymbol{k} \to -\boldsymbol{k}$, in which case $\boldsymbol{K}_g = \boldsymbol{b}_1 \in \hat{\mathcal{L}}$. It should be clear that $\mathcal{P}_{\boldsymbol{k}} \subset \mathcal{P}$ is a subgroup of the crystallographic point group, containing those operations $g \in \mathcal{P}$ which leave $\boldsymbol{k}$ invariant or changed by a reciprocal lattice vector. Note that if $g, h \in \mathcal{P}_{\boldsymbol{k}}$, then

$$\boldsymbol{K}_{gh} = \boldsymbol{k} - \boldsymbol{k}gh = (\boldsymbol{k} - \boldsymbol{k}h) + (\boldsymbol{k}h - \boldsymbol{k}gh) = \boldsymbol{K}_h + \boldsymbol{K}_g\, h \quad . \tag{2.100}$$

For each element g of the little group $\mathcal{P}_{\boldsymbol{k}}$, define the unitary operator $\hat{U}(g)$ such that

$$\hat{U}^\dagger(g)\,\big|\,\boldsymbol{K}\,\big\rangle = e^{i\phi_g(\boldsymbol{K})}\big|\,\boldsymbol{K}g - \boldsymbol{K}_g\,\big\rangle \quad . \tag{2.101}$$

We then have

$$\begin{aligned} \big\langle\,\boldsymbol{K}\,\big|\,\hat{U}(g)\,\hat{H}(\boldsymbol{k})\,\hat{U}^\dagger(g)\,\big|\,\boldsymbol{K}'\,\big\rangle &= \big\langle\,\boldsymbol{K}g - \boldsymbol{K}_g\,\big|\,\hat{H}(\boldsymbol{k})\,\big|\,\boldsymbol{K}'g - \boldsymbol{K}_g\,\big\rangle\, e^{i\phi_g(\boldsymbol{K}'-\boldsymbol{K})} \\ &= \hat{\omega}\big(\boldsymbol{K}g - \boldsymbol{K}_g + \boldsymbol{K}\big)\,\delta_{\boldsymbol{K},\boldsymbol{K}'} + \hat{V}(\boldsymbol{K} - \boldsymbol{K}') \\ &= \hat{\omega}\big((\boldsymbol{K} + \boldsymbol{k})\,g\big)\,\delta_{\boldsymbol{K},\boldsymbol{K}'} + \hat{V}(\boldsymbol{K} - \boldsymbol{K}') = \big\langle\,\boldsymbol{K}\,\big|\,\hat{H}(\boldsymbol{k})\,\big|\,\boldsymbol{K}'\,\big\rangle \end{aligned} \tag{2.102}$$

for all $\boldsymbol{k}$, $\boldsymbol{K}$, and $\boldsymbol{K}'$. This tells us that $\big[\hat{H}(\boldsymbol{k}), \hat{U}(g)\big] = 0$ for all $\boldsymbol{k} \in \hat{\mathcal{L}}$ and $g \in \mathcal{P}_{\boldsymbol{k}}$. Next, we have

$$\begin{aligned} \hat{U}^\dagger(h)\,\hat{U}^\dagger(g)\,\big|\,\boldsymbol{K}\,\big\rangle &= e^{i\phi_g(\boldsymbol{K})}\,e^{i\phi_h(\boldsymbol{K}g-\boldsymbol{K}_g)}\,\big|\,\boldsymbol{K}gh - \boldsymbol{K}_g\,h - \boldsymbol{K}_h\,\big\rangle \\ \hat{U}^\dagger(gh)\,\big|\,\boldsymbol{K}\,\big\rangle &= e^{i\phi_{gh}(\boldsymbol{K})}\,\big|\,\boldsymbol{K}gh - \boldsymbol{K}_{gh}\,\big\rangle \quad . \end{aligned} \tag{2.103}$$

Invoking Eqn. 2.100, we see that the ket vectors on the RHS of the above two equations are identical. Appealing to the compatibility condition Eqn. 2.86, we conclude $\hat{U}^\dagger(h)\,\hat{U}^\dagger(g) = \hat{U}^\dagger(gh)\,e^{-i\phi_h(\boldsymbol{K}_g)}$, *i.e.*

$$\hat{U}(g)\,\hat{U}(h) = \hat{U}(gh)\,e^{i\phi_h(\boldsymbol{K}_g)} \quad , \tag{2.104}$$

which is to say a projective representation of the little group.

Suppose $\hat{H}(\boldsymbol{k})\,|\,\psi_{\boldsymbol{k}}\,\rangle = E(\boldsymbol{k})\,|\,\psi_{\boldsymbol{k}}\,\rangle$, where we have dropped the band index n. Since $\big[\hat{H}(\boldsymbol{k}), \hat{U}(g)\big] = 0$, the state $\hat{U}(g)\,|\,\psi_{\boldsymbol{k}}\,\rangle$ is also an eigenstate of $\hat{H}(\boldsymbol{k})$ with eigenvalue $E(\boldsymbol{k})$. If $|\,\psi_{\boldsymbol{k}}\,\rangle$ is nondegenerate, then we must have $\hat{U}(g)\,|\,\psi_{\boldsymbol{k}}\,\rangle = \lambda_g(\boldsymbol{k})\,|\,\psi_{\boldsymbol{k}}\,\rangle$ for all $g \in \mathcal{P}_{\boldsymbol{k}}$. But then $\big[\hat{U}(g), \hat{U}(h)\big]\,|\,\psi_{\boldsymbol{k}}\,\rangle = 0$, and we must have

$$e^{i\phi_h(\boldsymbol{K}_g)}\,\hat{U}(gh)\,\big|\,\psi_{\boldsymbol{k}}\,\big\rangle = e^{i\phi_g(\boldsymbol{K}_h)}\,\hat{U}(hg)\,\big|\,\psi_{\boldsymbol{k}}\,\big\rangle \quad . \tag{2.105}$$

Thus, if $gh = hg$, we must have either (i) $\phi_h(\boldsymbol{K}_g) = \phi_g(\boldsymbol{K}_h)$ or else (ii) $|\,\psi_{\boldsymbol{k}}\,\rangle = 0$, *i.e.* there is no such nondegenerate eigenstate at wavevector $\boldsymbol{k}$. Therefore,

⋆ *If $gh = hg$ and $\phi_h(\boldsymbol{K}_g) \neq \phi_g(\boldsymbol{K}_h)$, all the eigenstates of $\hat{H}(\boldsymbol{k})$ appear in degenerate multiplets.*

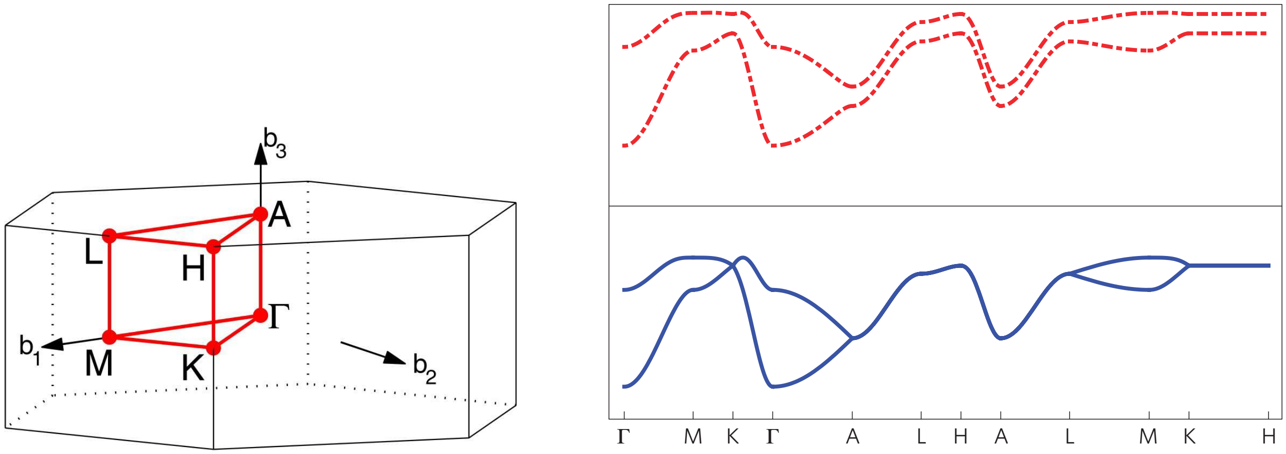
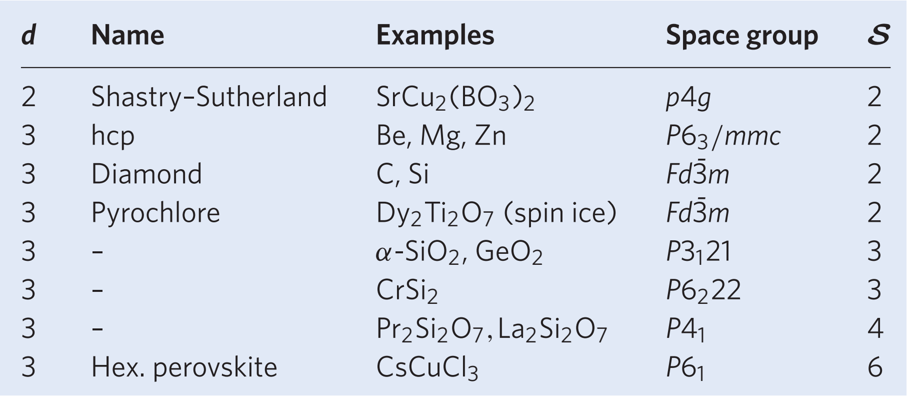


Figure 2.22: Stickiness of tight binding energy bands $\varepsilon_n(\boldsymbol{q})$ in an hcp crystal. Left: First Brillouin zone of the hexagonal Bravais lattice, with high symmetry points identified. Right: Tight binding energy levels for the hcp structure are shown in blue. Note the degeneracies at $\boldsymbol{q} = \mathrm{K}$, $\boldsymbol{q} = \mathrm{H}$, and all along the $\mathrm{A} - \mathrm{H} - \mathrm{L} - \mathrm{A}$ triangle on the top face and along the $\mathrm{K} - \mathrm{H}$ edge. When an alternating site energy on the two sublattices is present (dashed red curves), the screw symmetry is broken, and the space group is reduced from $P6_3/mmc$ to $P\overline{6}m2$.



d	Name	Examples	Space group	$\mathcal{S}$
2	Shastry-Sutherland	$SrCu_2(BO_3)_2$	$p4g$	2
3	hcp	Be, Mg, Zn	$P6_3/mmc$	2
3	Diamond	C, Si	$Fd\bar{3}m$	2
3	Pyrochlore	$Dy_2Ti_2O_7$ (spin ice)	$Fd\bar{3}m$	2
3	-	α-SiO_2, GeO_2	$P3_121$	3
3	-	$CrSi_2$	$P6_222$	3
3	-	$Pr_2Si_2O_7, La_2Si_2O_7$	$P4_1$	4
3	Hex. perovskite	$CsCuCl_3$	$P6_1$	6

Figure 2.23: Examples of space groups and their nonsymmorphic ranks.

That is, two or more bands become ”stuck” together at these special $\boldsymbol{k}$ points. Note that the sticking conditions cannot be satisfied in a symmorphic space group, because the phase functions can all be set to zero by a choice of gauge (*i.e.* by a choice of origin for the point group operations). Note also that under a gauge transformation, the change in $\phi_h(\boldsymbol{K}_g) - \phi_g(\boldsymbol{K}_h)$ is

$$\Delta\big(\phi_h(\boldsymbol{K}_g) - \phi_g(\boldsymbol{K}_h)\big) = \chi(\boldsymbol{K}_g\, h - \boldsymbol{K}_g) - \chi(\boldsymbol{K}_h\, g - \boldsymbol{K}_h) = \chi(\boldsymbol{k}\, gh - \boldsymbol{k}\, hg) \quad , \tag{2.106}$$

which vanishes when $gh = hg$.

Since $\phi_g(\boldsymbol{0}) = 0$ for all g, the sticking conditions require that either $\boldsymbol{K}_g$ or $\boldsymbol{K}_h$ be nonzero. This is possible only when $\boldsymbol{k} \in \partial\hat{\Omega}$ lies on the boundary of the first Brillouin zone, for otherwise the vectors $\boldsymbol{K}_g$ and $\boldsymbol{K}_h$

are too short to be reciprocal lattice vectors[31]. Thus, in nonsymmorphic crystals, band sticking occurs only along the boundary. Consider, for example, the case of diamond, with nonsymmorphic space group $F\frac{4_1}{d}\bar{3}\frac{2}{m}$ ($Fd\bar{3}m$ in the short notation). The diamond structure consists of two interpenetrating fcc Bravais lattices, and exhibits a 4_1 screw axis and a diamond (d) glide[32]. Let $\boldsymbol{k} = \frac{1}{2}\boldsymbol{K}$, where $\boldsymbol{K}$ is the shortest reciprocal lattice vector along the screw axis. Then $\boldsymbol{K}_r = \boldsymbol{k} - \boldsymbol{k}r = 0$ because $\boldsymbol{k}$ is along the invariant axis of the fourfold rotation r, hence r is in the little group. Diamond is centrosymmetric, meaning that its point group contains the inversion operator I, which commutes with all other point group elements. Clearly $\boldsymbol{K}_I = \boldsymbol{k} - I\boldsymbol{k} = 2\boldsymbol{k} = \boldsymbol{K}$, so I is in the little group as well. The sticking conditions then require $\phi_r(\boldsymbol{K}) \neq 0$, which is the condition we found for r to be a screw in the first place. So we have band sticking at $\boldsymbol{k} = \frac{1}{2}\boldsymbol{K}$. This is a special case of the following general rule: in nonsymmorphic centrosymmetric crystals, there is band sticking at every $\boldsymbol{k} = \frac{1}{2}\boldsymbol{K}$ where $\boldsymbol{K}$ is an extinguished reciprocal lattice (Bragg) vector.

Band sticking can also occur along *continuous lines* along the zone boundary. This is possible when the point group contains perpendicular mirrors, such as in the case D_{3h}. Let $\boldsymbol{k}$ lie along the line where the horizontal Brillouin zone surface intersects the vertical mirror plane. The vertical component of $\boldsymbol{k}$ is thus $\frac{1}{2}\boldsymbol{K}$, where $\boldsymbol{K}$ is the shortest vertical reciprocal lattice vector, but otherwise $\boldsymbol{k}$ can lie anywhere along this line. Then $\boldsymbol{K}_{m_h} = \boldsymbol{K}$ and $\boldsymbol{K}_{m_v} = 0$, for all $\boldsymbol{k}$ along the line, where $m_{h,v}$ are the horizontal and vertical mirror operations, respectively. The sticking condition is $\phi_{m_v}(\boldsymbol{K}) \neq 0$, which says that m_v is a glide mirror and $\boldsymbol{K}$ is extinguished. Introducing a perturbation which breaks the nonsymmorphic symmetries unsticks the bands and revives the extinguished Bragg vectors. An example is the hcp structure, shown in Fig. 2.22.

A more detailed result was derived by Michel and Zak[33]. In nonsymmorphic crystals, energy bands stick together in groups of $\mathcal{S}$, where $\mathcal{S} = 2, 3, 4$, or 6 is the *nonsymmorphic rank* of the space group. In such cases, groups of $\mathcal{S}$ bands are stuck at high symmetry points or along high symmetry lines in the Brillouin zone, and one must fill an integer multiple of $\mathcal{S}$ bands of spinless electrons in order to construct a band insulating state.

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[31] My childhood dreams of becoming a reciprocal lattice vector were dashed for the same reason.

[32] Diamond has a diamond (d) glide. The d is for "duh".

[33] L. Michel and J. Zak, *Phys. Rev. B* **59**, 5998 (1999).