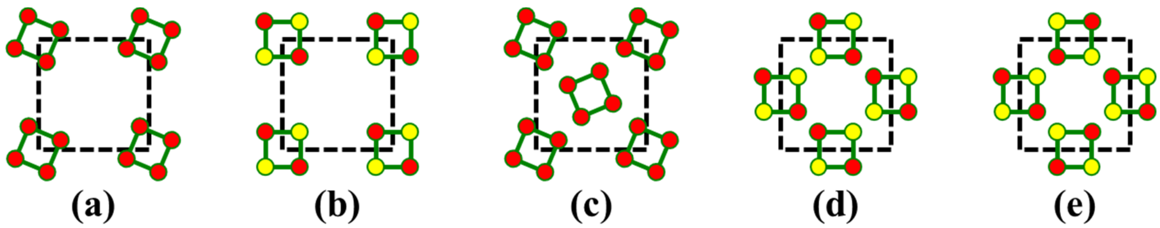
SPACE GROUPS

(25) *Space groups* identify the possible ways to describe the rotational and translational symmetry of crystalline structures in real space. As we have seen, these aspects of 3-d crystalline symmetry are separately described by 32 crystallographic point groups and 14 Bravais lattices. For any space group, these two types of symmetry must be compatible with each other. For example, consider a 2-d tetragonal lattice, which demands a unit cell with $a = b$ and $\gamma = 90°$, decorated with different arrangements of 4-atom molecules (A = red circles; B = yellow circles).



If the atomic arrangement has four-fold symmetry at each lattice point, then the crystalline symmetry will retain tetragonal characteristics, i.e., four-fold rotational symmetry at the corners and center of each unit cell. Among these five structures, (a), (c), and (e) are tetragonal. Cases (a) and (c) are constructed of square molecules A_4, whereas case (e) involves a specific packing of A_2B_2 molecules that creates four-fold symmetry between four distinct molecules. Combining the 32 crystallographic point groups and 14 Bravais lattices for 3-d real space in all compatible ways generates 230 space groups. For 2-d space, there are 17 *plane groups* generated from 10 point groups and 5 Bravais lattices.

Rotation-Translation Operations: Every member of a space group is a *rotation-translation* operation, which can be represented by augmented matrices and symbolized by the *Seitz notation*, which facilitates evaluating combinations of these operations. Accordingly, every rotation-translation operation is symbolized by $(R|\boldsymbol{\tau})$, such that R is a proper or improper rotation and $\boldsymbol{\tau}$ is a displacement. The effect of this operation on a position vector $\boldsymbol{r}$ is

$$(R|\boldsymbol{\tau})\,\boldsymbol{r} = R\boldsymbol{r} + \boldsymbol{\tau} = \begin{pmatrix} R_{11} & R_{12} & R_{13} \\ R_{21} & R_{22} & R_{23} \\ R_{31} & R_{32} & R_{33} \end{pmatrix}\boldsymbol{r} + \begin{pmatrix} \tau_1 \\ \tau_2 \\ \tau_3 \end{pmatrix} = \begin{pmatrix} R_{11} & R_{12} & R_{13} & \tau_1 \\ R_{21} & R_{22} & R_{23} & \tau_2 \\ R_{31} & R_{32} & R_{33} & \tau_3 \\ 0 & 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \\ 1 \end{pmatrix}.$$

If $\boldsymbol{\tau}$ is a lattice translation $\boldsymbol{T}$, then $(E|\boldsymbol{T}) = (1|\boldsymbol{T})$ symbolizes a lattice translation:

$$(1|\boldsymbol{T})\,\boldsymbol{r} = \boldsymbol{r} + \boldsymbol{T}.$$

Also, the sequential product of two operations is:

$$(R_2|\boldsymbol{\tau}_2)(R_1|\boldsymbol{\tau}_1)\,\boldsymbol{r} = (R_2|\boldsymbol{\tau}_2)[R_1\boldsymbol{r} + \boldsymbol{\tau}_1] = R_2[R_1\boldsymbol{r} + \boldsymbol{\tau}_1] + \boldsymbol{\tau}_2 = R_2R_1\boldsymbol{r} + (R_2\boldsymbol{\tau}_1 + \boldsymbol{\tau}_2).$$

Note that the sequence in the product proceeds right-to-left. Therefore,

$$(R_2|\boldsymbol{\tau}_2)(R_1|\boldsymbol{\tau}_1) = (R_2R_1|R_2\boldsymbol{\tau}_1 + \boldsymbol{\tau}_2)$$

defines the product of two rotation-translation operations. Let $\mathcal{G} = \{(R_1|\boldsymbol{\tau}_1), (R_2|\boldsymbol{\tau}_2), \ldots\}$ a set of these operations. For $\mathcal{G}$ to be a space group, this set must satisfy the definitions of a group:

(a) Closure under multiplication: $(R_2|\boldsymbol{\tau}_2)(R_1|\boldsymbol{\tau}_1) = (R_2R_1|R_2\boldsymbol{\tau}_1 + \boldsymbol{\tau}_2)$ must also be a member of $\mathcal{G}$. The product of two rotations R_2R_1 is another rotation (Euler's theorem) and the vector $R_2\boldsymbol{\tau}_1 + \boldsymbol{\tau}_2$ is a displacement, so the new operation is another rotation-translation operation. There may be certain constraints placed on the allowed displacements depending on the nature of the rotational symmetry. We will examine these constraints shortly.

(b) Existence of an identity operation: $(E|\mathbf{0}) = (1|\mathbf{0})$ is a member of $\mathcal{G}$ such that

$$(E|\mathbf{0})\,\boldsymbol{r} = E\boldsymbol{r} + \mathbf{0} = \boldsymbol{r}.$$

(c) Multiplication is associative: $(R_3|\boldsymbol{\tau}_3)[(R_2|\boldsymbol{\tau}_2)(R_1|\boldsymbol{\tau}_1)] = [(R_3|\boldsymbol{\tau}_3)(R_2|\boldsymbol{\tau}_2)](R_1|\boldsymbol{\tau}_1)$. We show this by considering the two different products of the three sequential operations:

$$(R_3|\boldsymbol{\tau}_3)[(R_2|\boldsymbol{\tau}_2)(R_1|\boldsymbol{\tau}_1)] = (R_3|\boldsymbol{\tau}_3)(R_2R_1|R_2\boldsymbol{\tau}_1 + \boldsymbol{\tau}_2) = (R_3R_2R_1|R_3R_2\boldsymbol{\tau}_1 + R_3\boldsymbol{\tau}_2 + \boldsymbol{\tau}_3)$$
$$[(R_3|\boldsymbol{\tau}_3)(R_2|\boldsymbol{\tau}_2)](R_1|\boldsymbol{\tau}_1) = (R_3R_2|R_3\boldsymbol{\tau}_2 + \boldsymbol{\tau}_3)(R_1|\boldsymbol{\tau}_1) = (R_3R_2R_1|R_3R_2\boldsymbol{\tau}_1 + R_3\boldsymbol{\tau}_2 + \boldsymbol{\tau}_3).$$

To verify this assertion, it is very important to maintain the correct order of operations.

(d) Existence of an inverse for every operation: Let $(R_1|\boldsymbol{\tau}_1) = (R|\boldsymbol{\tau})^{-1}$. Then

$$(R|\boldsymbol{\tau})^{-1}(R|\boldsymbol{\tau}) = (R_1|\boldsymbol{\tau}_1)(R|\boldsymbol{\tau}) = (R_1R|R_1\boldsymbol{\tau} + \boldsymbol{\tau}_1) = (E|\mathbf{0}).$$

As a result, $R_1 = R^{-1}$ and $\boldsymbol{\tau}_1 = -R^{-1}\boldsymbol{\tau}$. Therefore, $(R|\boldsymbol{\tau})^{-1} = (R^{-1}|-R^{-1}\boldsymbol{\tau})$.

(26) What specific rotations R and displacements $\boldsymbol{\tau}$ are possible for any general rotation-translation operation $(R|\boldsymbol{\tau})$ of a space group $\mathcal{G}$?

ALLOWED ROTATIONS (R): The set of Bravais lattice vectors describes the translational periodicity of the space group. Each Bravais lattice vector corresponds to an operation $(1|\boldsymbol{T})$ in $\mathcal{G}$. Therefore, if $(R|\boldsymbol{\tau})$ is a member of space group $\mathcal{G}$, then so is the similarity transformation

$$(R|\boldsymbol{\tau})(1|\boldsymbol{T})(R|\boldsymbol{\tau})^{-1} = (R|\boldsymbol{\tau})(R^{-1}|\boldsymbol{T} - R^{-1}\boldsymbol{\tau}) = (RR^{-1}|R\boldsymbol{T} - RR^{-1}\boldsymbol{\tau} + \boldsymbol{\tau}) = (1|R\boldsymbol{T}).$$

As a result, $R\boldsymbol{T}$ is a Bravais lattice vector, so that R must be among the allowed rotations of 3-d lattices, i.e., proper rotations $1, 2, 3, 4, 6$ and improper rotations $\bar{1}, \bar{2} = m, \bar{3}, \bar{4}, \bar{6}$.

This result also points out that the Bravais lattice operations $(1|R\boldsymbol{T})$ form collections of operations that make up complete classes of the space group $\mathcal{G}$. A subset of group operations that form complete classes and is a subgroup is called an *invariant subgroup*, a result that has profound impacts on the irreducible representations of the group. As an example, consider any centrosymmetric point group. Then, the subgroup $C_i = \{E, i\}$ is an invariant subgroup because both the identity E and inversion i commute with every rotation operation. As a result, $\{E, i\}$ is formed by two complete classes for every centrosymmetric point group. To see the impact on irreducible representations (ir's), the ir's of every centrosymmetric point group are labeled as either symmetric (*gerade*) or antisymmetric (*ungerade*) with respect to inversion i.

ALLOWED TRANSLATIONS ($\boldsymbol{\tau}$): For every rotation $R = n$ or $\bar{n}$, there is an integer N such that $R^N =$ identity. For the proper rotation n, $N = n$; for the improper rotation $\bar{n}$, $N = n$ (for n even) and $N = 2n$ (for n odd). By closure, $(R|\boldsymbol{\tau})^N$ is also a member of $\mathcal{G}$. Expanding this expression

$$(R|\boldsymbol{\tau})^N = (R|\boldsymbol{\tau})(R|\boldsymbol{\tau})\cdots(R|\boldsymbol{\tau}) = (R\cdot R\cdots R|\boldsymbol{\tau} + R\boldsymbol{\tau} + \cdots + R^{N-1}\boldsymbol{\tau}) = (R^N|\boldsymbol{\tau} + R\boldsymbol{\tau} + \cdots + R^{N-1}\boldsymbol{\tau})$$
$$= \left(1\middle|\textstyle\sum_{j=1}^{N} R^{j-1}\boldsymbol{\tau}\right).$$

Therefore, allowed translations $\boldsymbol{\tau}$ must satisfy the condition that $\sum_{j=1}^{N} R^{j-1}\boldsymbol{\tau}$ is a Bravais lattice vector. If R is the identity, then $\boldsymbol{\tau}$ must be a Bravais lattice vector. Also, if $\boldsymbol{\tau}$ is already a Bravais lattice vector, then this condition is satisfied. So, are there *any other vectors* $\boldsymbol{\tau}$ for an allowed rotation R that satisfy this equation? Because R is a linear operator, we can rewrite $\sum_{j=1}^{N} R^{j-1}\boldsymbol{\tau}$ as $\left(\sum_{j=1}^{N} R^{j-1}\right)\boldsymbol{\tau}$. The orientation of the rotation R is specified by the direction of its axis. To evaluate the operation in parentheses and without loss of generality, consider the rotation axis to be parallel to the $\boldsymbol{c}$-axis of the unit cell and let $\boldsymbol{\tau} = \tau_1\boldsymbol{a} + \tau_2\boldsymbol{b} + \tau_3\boldsymbol{c}$, such that vectors $\boldsymbol{a}$ and $\boldsymbol{b}$ are perpendicular to $\boldsymbol{c}$. Now, evaluate this condition systematically for each allowed rotation:

For proper rotations n (matrices are written using the lattice vectors as the basis):

$$2_{\boldsymbol{c}} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}: \quad \left(\sum_{j=1}^{2} 2_{\boldsymbol{c}}^{j-1}\right)\boldsymbol{\tau} = (1 + 2_{\boldsymbol{c}})\boldsymbol{\tau} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 2 \end{pmatrix}\begin{pmatrix} \tau_1 \\ \tau_2 \\ \tau_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 2\tau_3 \end{pmatrix} = p\boldsymbol{c} = (2\tau_3)\boldsymbol{c}$$

Distinct solutions: $\tau_3 = 0, ½$ (all other solutions are related by the lattice vector $\boldsymbol{c}$);

$$3_{\boldsymbol{c}} = \begin{pmatrix} 0 & -1 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}: \quad \left(\sum_{j=1}^{3} 3_{\boldsymbol{c}}^{j-1}\right)\boldsymbol{\tau} = (1 + 3_{\boldsymbol{c}} + 3_{\boldsymbol{c}}^2)\boldsymbol{\tau} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 3 \end{pmatrix}\begin{pmatrix} \tau_1 \\ \tau_2 \\ \tau_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 3\tau_3 \end{pmatrix} = p\boldsymbol{c} = (3\tau_3)\boldsymbol{c}$$

Distinct solutions: $\tau_3 = 0, ⅓, ⅔$;

$$4_{\boldsymbol{c}} = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}: \quad \left(\sum_{j=1}^{4} 4_{\boldsymbol{c}}^{j-1}\right)\boldsymbol{\tau} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 4 \end{pmatrix}\begin{pmatrix} \tau_1 \\ \tau_2 \\ \tau_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 4\tau_3 \end{pmatrix} = p\boldsymbol{c} = (4\tau_3)\boldsymbol{c}$$

Distinct solutions: $\tau_3 = 0, ¼, ½, ¾$;

$$6_{\boldsymbol{c}} = \begin{pmatrix} 1 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}: \quad \left(\sum_{j=1}^{6} 6_{\boldsymbol{c}}^{j-1}\right)\boldsymbol{\tau} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 6 \end{pmatrix}\begin{pmatrix} \tau_1 \\ \tau_2 \\ \tau_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 6\tau_3 \end{pmatrix} = p\boldsymbol{c} = (6\tau_3)\boldsymbol{c}$$

Distinct solutions: $\tau_3 = 0, ⅙, ⅓, ½, ⅔, ⅚$.

Therefore, for a proper rotation n, the allowed translations that are not lattice vectors are all rational fractions j/n $(j = 1, \ldots, n-1)$ of the smallest lattice vector parallel to the rotation axis. These operations are called *screw rotations*. Translations perpendicular to the rotation axis simply set the rotation away from the origin.

For improper rotations $\bar{n}$ (matrices written using the lattice vectors as the basis):

$$\bar{1} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}: \quad \left(\sum_{j=1}^{2} \bar{1}^{j-1}\right)\boldsymbol{\tau} = (1 + \bar{1})\boldsymbol{\tau} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} \tau_1 \\ \tau_2 \\ \tau_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} = \boldsymbol{0} \text{ (No solutions)}$$

$$\bar{2}_{\boldsymbol{c}} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}: \quad \left(\sum_{j=1}^{2} \bar{2}_{\boldsymbol{c}}^{j-1}\right)\boldsymbol{\tau} = \begin{pmatrix} 2 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} \tau_1 \\ \tau_2 \\ \tau_3 \end{pmatrix} = \begin{pmatrix} 2\tau_1 \\ 2\tau_2 \\ 0 \end{pmatrix} = m\boldsymbol{a} + n\boldsymbol{b} = (2\tau_1)\boldsymbol{a} + (2\tau_2)\boldsymbol{b}$$

Distinct solutions: $\tau_1 = 0, ½$ and $\tau_2 = 0, ½$.

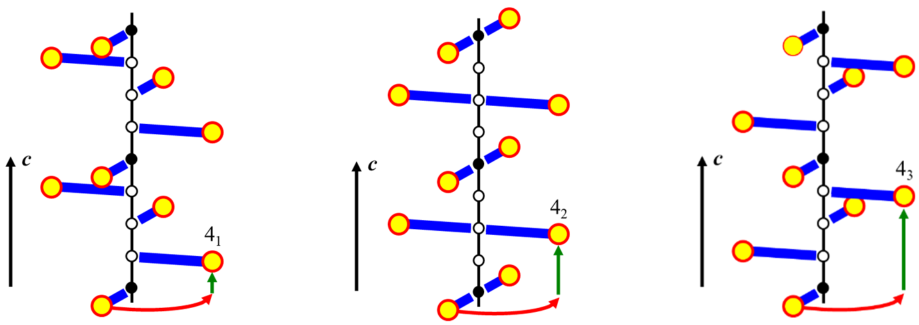
$$\bar{3}_{\boldsymbol{c}} = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}: \quad \left(\sum_{j=1}^{6} \bar{3}_{\boldsymbol{c}}^{j-1}\right)\boldsymbol{\tau} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} \tau_1 \\ \tau_2 \\ \tau_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} = \boldsymbol{0} \text{ (No solutions)}$$

$$\bar{4}_{\boldsymbol{c}} = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}: \quad \left(\sum_{j=1}^{4} \bar{4}_{\boldsymbol{c}}^{j-1}\right)\boldsymbol{\tau} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} \tau_1 \\ \tau_2 \\ \tau_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} = \boldsymbol{0} \text{ (No solutions)}$$

$$\bar{6}_{\boldsymbol{c}} = \begin{pmatrix} -1 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}: \quad \left(\sum_{j=1}^{6} \bar{6}_{\boldsymbol{c}}^{j-1}\right)\boldsymbol{\tau} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} \tau_1 \\ \tau_2 \\ \tau_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} = \boldsymbol{0} \text{ (No solutions)}$$

Only reflections $\bar{2} = m$ allow translations that are not lattice vectors. These displacements are parallel to the reflection plane, i.e., perpendicular to the improper $\bar{2}$ axis, and one-half the length of a lattice vector. These operations are called *glide reflections*. Translations perpendicular to the reflection plane set the reflection away from the origin. Since the other improper rotations occur with respect to a single point in space, any translation will set this point away from the origin.

(27) A <u>screw rotation</u>, symbolized by n_j $(j < n)$, is a proper $2\pi/n$ ccw rotation accompanied by the fractional displacement $\frac{j}{n}\boldsymbol{T}$ along the lattice vector $\boldsymbol{T}$, which is parallel to the rotation axis. The subscript j can be any one of the positive integers less than n. There are 11 possible screw rotations in crystalline structures: 2_1; $3_1, 3_2$; $4_1, 4_2, 4_3$; $6_1, 6_2, 6_3, 6_4, 6_5$. The Seitz notation for a screw rotation n_j when the rotation axis passes through the origin is $n_m = \left(n_{\boldsymbol{T}}\middle|\frac{j\boldsymbol{T}}{n}\right)$. As an example, consider the three possible four-fold screw rotations with their rotation axes along $\boldsymbol{c}$:



4_1: $\left(4_{\boldsymbol{c}}\middle|\frac{\boldsymbol{c}}{4}\right)$ 4_2: $\left(4_{\boldsymbol{c}}\middle|\frac{2\boldsymbol{c}}{4}\right) = \left(4_{\boldsymbol{c}}\middle|\frac{\boldsymbol{c}}{2}\right)$ 4_3: $\left(4_{\boldsymbol{c}}\middle|\frac{3\boldsymbol{c}}{4}\right)$

Each operation is a 90° ccw rotation along with one of the displacements $\frac{\boldsymbol{c}}{4}$, $\frac{2\boldsymbol{c}}{4} = \frac{\boldsymbol{c}}{2}$, or $\frac{3\boldsymbol{c}}{4}$. As the diagram points out, the actions of 4_1 and 4_3 screw rotations on an object create equivalent objects at steps of $\frac{\boldsymbol{c}}{4}$; whereas the action of 4_2 creates objects at steps of $\frac{\boldsymbol{c}}{2}$. To see how this occurs, evaluate the sequential products of two, three, and four operations.

$$4_1^{\,2}:\quad \left(4_{\boldsymbol{c}}\middle|\frac{\boldsymbol{c}}{4}\right)^2 = \left(4_{\boldsymbol{c}}^2\middle|4_{\boldsymbol{c}}\left(\frac{\boldsymbol{c}}{4}\right) + \frac{\boldsymbol{c}}{4}\right) = \left(2_{\boldsymbol{c}}\middle|\frac{2\boldsymbol{c}}{4}\right) = \left(2_{\boldsymbol{c}}\middle|\frac{\boldsymbol{c}}{2}\right);$$

$$4_2^{\,2}:\quad \left(4_{\boldsymbol{c}}\middle|\frac{2\boldsymbol{c}}{4}\right)^2 = \left(4_{\boldsymbol{c}}^2\middle|4_{\boldsymbol{c}}\left(\frac{\boldsymbol{c}}{2}\right) + \frac{\boldsymbol{c}}{2}\right) = (2_{\boldsymbol{c}}|\boldsymbol{c});$$

$$4_3^{\,2}:\quad \left(4_{\boldsymbol{c}}\middle|\frac{3\boldsymbol{c}}{4}\right)^2 = \left(4_{\boldsymbol{c}}^2\middle|4_{\boldsymbol{c}}\left(\frac{3\boldsymbol{c}}{4}\right) + \frac{3\boldsymbol{c}}{4}\right) = \left(2_{\boldsymbol{c}}\middle|\frac{6\boldsymbol{c}}{4}\right) = \left(2_{\boldsymbol{c}}\middle|\frac{3\boldsymbol{c}}{2}\right).$$

Each of two successive 4_j operations is a 180° rotation accompanied by different displacements parallel to $\boldsymbol{c}$. Notice that the four-fold rotation does not affect $\boldsymbol{c}$, i.e., $4_{\boldsymbol{c}}\boldsymbol{c} = \boldsymbol{c}$. Due to translational periodicity along the $\boldsymbol{c}$-axis, if $\left(n_{\boldsymbol{c}}^j\middle|\boldsymbol{c}\right)$ is an operation, then so is $\left(n_{\boldsymbol{c}}^j\middle|\boldsymbol{0}\right)$. Therefore, the 4_2 screw rotation includes a proper 2-fold rotation $(2_{\boldsymbol{c}}|\boldsymbol{0})$, which is shown in the middle diagram. Likewise, because two successive 4_3 screw rotations generate $\left(2_{\boldsymbol{c}}\middle|\frac{3\boldsymbol{c}}{2}\right)$, then so is $\left(2_{\boldsymbol{c}}\middle|\frac{\boldsymbol{c}}{2}\right)$, as seen in the right-hand diagram. Now, three successive 4_j operations yield

$$4_1^{\,3}:\quad \left(4_{\boldsymbol{c}}\middle|\frac{\boldsymbol{c}}{4}\right)^3 = \left(4_{\boldsymbol{c}}^3\middle|\frac{3\boldsymbol{c}}{4}\right);$$

$$4_2^{\,3}:\quad \left(4_{\boldsymbol{c}}\middle|\frac{2\boldsymbol{c}}{4}\right)^3 = \left(4_{\boldsymbol{c}}^3\middle|\frac{6\boldsymbol{c}}{4}\right) \rightarrow \left(4_{\boldsymbol{c}}^3\middle|\frac{2\boldsymbol{c}}{4}\right) = \left(4_{\boldsymbol{c}}^3\middle|\frac{\boldsymbol{c}}{2}\right);$$

$$4_3^{\,3}:\quad \left(4_{\boldsymbol{c}}\middle|\frac{3\boldsymbol{c}}{4}\right)^3 = \left(4_{\boldsymbol{c}}^3\middle|3\cdot\frac{3\boldsymbol{c}}{4}\right) \rightarrow \left(4_{\boldsymbol{c}}^3\middle|\frac{\boldsymbol{c}}{4}\right);$$

and four consecutive operations yield

$$4_1^{\,4}:\quad \left(4_{\boldsymbol{c}}\middle|\frac{\boldsymbol{c}}{4}\right)^4 = \left(4_{\boldsymbol{c}}^4\middle|\frac{4\boldsymbol{c}}{4}\right) = (1|\boldsymbol{c}) = \text{lattice translation by } \boldsymbol{c};$$

$4_2{}^4$: $\left(4_{\boldsymbol{c}}\middle|\frac{2\boldsymbol{c}}{4}\right)^4 = \left(4_{\boldsymbol{c}}^4\middle|\frac{4\boldsymbol{c}}{2}\right) = (1|2\boldsymbol{c})$ = lattice translation by $2\boldsymbol{c}$;

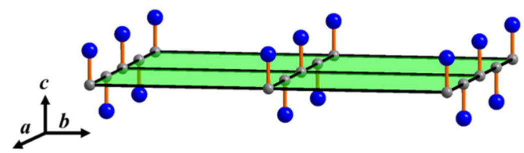
$4_3{}^4$: $\left(4_{\boldsymbol{c}}\middle|\frac{3\boldsymbol{c}}{4}\right)^4 = \left(4_{\boldsymbol{c}}^4\middle|4\cdot\frac{3\boldsymbol{c}}{4}\right) = (1|3\boldsymbol{c})$ = lattice translation by $3\boldsymbol{c}$;

which are some multiple of the lattice translation $\boldsymbol{c}$. According to this analysis and the diagrams, the 4_1 and 4_3 screw rotations are enantiomorphic because they are related by a mirror plane parallel to the rotation axes. If the 4_1 operation is described as a right-handed screw, then the 4_3 operation is a left-handed screw. In general, n_j and n_{n-j} screw rotations form an enantiomorphic pair.

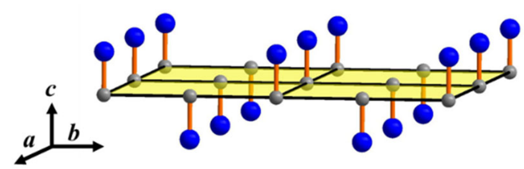
The general Seitz symbol for a screw rotation n_j is $\left(n_{\boldsymbol{T}}\middle|\frac{j\boldsymbol{T}}{n}+\boldsymbol{\tau}_{\perp\boldsymbol{T}}\right)$ in which $\boldsymbol{\tau}_{\perp\boldsymbol{T}}$ is a displacement perpendicular to the rotation axis and will set the axis relative to the origin.

(28) A glide reflection, symbolized by a letter other than m (see below), is a reflection $m = \bar{2}$ accompanied by a displacement that is one-half a lattice translation parallel to the plane of the reflection. The general Seitz symbol is $\left(m_{\boldsymbol{T}}\middle|\frac{\boldsymbol{T}'}{2}\right)$, in which $\boldsymbol{T}$ is the lattice direction perpendicular to the reflection plane and $\frac{\boldsymbol{T}'}{2}$ is one-half the lattice vector parallel to the plane. Therefore, $\boldsymbol{T}'$ is perpendicular to $\boldsymbol{T}$. There are three distinct types of glide reflections depending on the direction of the displacement with respect to the unit cell vectors:

(a) *Axial glides*, symbolized as $a, b,$ or c, have displacements parallel to the unit cell side specified by the letter. For example, an a-glide perpendicular to the $\boldsymbol{c}$-direction, which can be symbolized as $a_{\boldsymbol{c}} = \left(m_{\boldsymbol{c}}\middle|\frac{\boldsymbol{a}}{2}\right)$, is a reflection perpendicular to $\boldsymbol{c}$ along with displacement of $\frac{\boldsymbol{a}}{2}$, so the lattice vector $\boldsymbol{a}$ must be parallel to the mirror plane. Similarly, the b-glide perpendicular to $\boldsymbol{c}$ is $b_{\boldsymbol{c}} = \left(m_{\boldsymbol{c}}\middle|\frac{\boldsymbol{b}}{2}\right)$. These two axial glides are illustrated to the right. For the axial glides shown, reflection occurs with respect to the $\boldsymbol{ab}$-lattice plane through the origin. A second consecutive axial glide reflection results in a lattice translation:



$a_{\boldsymbol{c}} = \left(m_{\boldsymbol{c}}\middle|\frac{\boldsymbol{a}}{2}\right)$

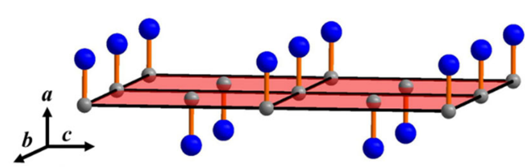


$b_{\boldsymbol{c}} = \left(m_{\boldsymbol{c}}\middle|\frac{\boldsymbol{b}}{2}\right)$

$a_{\boldsymbol{c}}{}^2$: $\left(m_{\boldsymbol{c}}\middle|\frac{\boldsymbol{a}}{2}\right)^2 = \left(m_{\boldsymbol{c}}^2\middle|m_{\boldsymbol{c}}\left(\frac{\boldsymbol{a}}{2}\right)+\frac{\boldsymbol{a}}{2}\right) = (1|\boldsymbol{a})$.

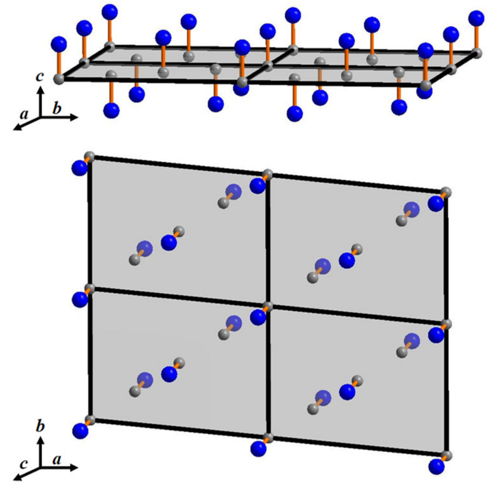
In space group symbols, there is also the symbol "e", which stands for a single plane showing axial glide displacements along two different directions. This type of axial glide occurs only for some centered, non-primitive lattices.

(b) *Diagonal glides*, symbolized as n, involve displacements along a face-diagonal direction of the unit cell, i.e., $\frac{\boldsymbol{a}+\boldsymbol{b}}{2}$, $\frac{\boldsymbol{a}+\boldsymbol{c}}{2}$, or $\frac{\boldsymbol{b}+\boldsymbol{c}}{2}$. As an example, the diagonal glide $n_{\boldsymbol{a}} = \left(m_{\boldsymbol{a}}\middle|\frac{\boldsymbol{b}+\boldsymbol{c}}{2}\right)$ is a reflection perpendicular to $\boldsymbol{a}$ accompanied by displacement along the diagonal of the $\boldsymbol{bc}$-face of the unit cell.



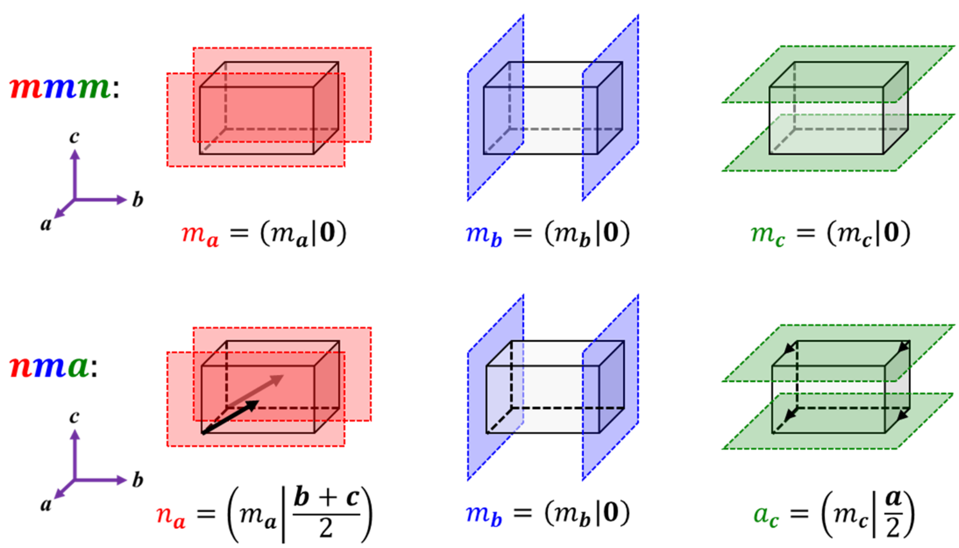
$n_{\boldsymbol{a}} = \left(m_{\boldsymbol{a}}\middle|\frac{\boldsymbol{b}+\boldsymbol{c}}{2}\right)$

(c) *Diamond glides*, denoted as *d*, resemble diagonal glides but occur only for face- (*F*) and body-centered (*I*) lattices. For example, consider a diamond glide reflection that is perpendicular to the $\boldsymbol{c}$-axis of a face-centered orthorhombic lattice. Vectors of this lattice will be integer combinations of $\frac{\boldsymbol{a}+\boldsymbol{b}}{2}$, $\frac{\boldsymbol{b}+\boldsymbol{c}}{2}$, and $\frac{\boldsymbol{a}+\boldsymbol{c}}{2}$. This diamond glide, which is illustrated to the right using two perspectives, is $d_{\boldsymbol{c}} = \left(m_{\boldsymbol{c}} \middle| \frac{\boldsymbol{a}+\boldsymbol{b}}{4}\right)$.



$d_c = \left(m_c \middle| \frac{\boldsymbol{a}+\boldsymbol{b}}{4}\right)$

The orientation of a reflection plane is given by the perpendicular vector to the plane and is determined by the symbol's position in the point group symbol. For example, the point group $\mathcal{D}_{2h}$ is mmm in the International notation. With respect to an orthorhombic unit cell, the reflection planes are oriented perpendicular to $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$, respectively, in the symbol. Then, if an orthorhombic crystal exhibits any glide reflections, then the symbol for the space group may show "nma". In this case, a diagonal glide is perpendicular to $\boldsymbol{a}$, $n_{\boldsymbol{a}} = \left(m_{\boldsymbol{a}} \middle| \frac{\boldsymbol{b}+\boldsymbol{c}}{2}\right)$, and an a-axial glide is perpendicular to $\boldsymbol{c}$, $a_{\boldsymbol{c}} = \left(m_{\boldsymbol{c}} \middle| \frac{\boldsymbol{a}}{2}\right)$.



The general Seitz symbol for a glide reflection is $\left(m_{\boldsymbol{T}} \middle| \frac{\boldsymbol{T}'_{\perp \boldsymbol{T}}}{2} + \boldsymbol{\tau}_{\parallel \boldsymbol{T}}\right)$ in which $\boldsymbol{T}'_{\perp \boldsymbol{T}}$ is a Bravais lattice vector parallel to the reflection plane (perpendicular to the axis of the plane) and $\boldsymbol{\tau}_{\parallel \boldsymbol{T}}$ is a displacement perpendicular to plane (parallel to the axis of the plane). The vector $\boldsymbol{\tau}_{\parallel \boldsymbol{T}}$ determines the position of the plane relative to the origin.

In summary, the types of rotation-translation operations allowed for 3-d space groups include:

(a) *Bravais lattice translations* $(1|\boldsymbol{T}_{mnp})$.

(b) *Proper rotations* $(2_{\boldsymbol{T}}|\boldsymbol{\tau}_{\perp T}), (3_{\boldsymbol{T}}|\boldsymbol{\tau}_{\perp T}), (4_{\boldsymbol{T}}|\boldsymbol{\tau}_{\perp T})$, and $(6_{\boldsymbol{T}}|\boldsymbol{\tau}_{\perp T})$, oriented by their axes $\boldsymbol{T}$ and located away from the origin if $\boldsymbol{\tau}_{\perp T} \neq \mathbf{0}$.

(c) *Improper rotations* $(\bar{1}|\boldsymbol{\tau})$, $(m_{\boldsymbol{T}}|\boldsymbol{\tau}_{||T})$, $(\bar{3}_{\boldsymbol{T}}|\boldsymbol{\tau})$, $(\bar{4}_{\boldsymbol{T}}|\boldsymbol{\tau})$, and $(\bar{6}_{\boldsymbol{T}}|\boldsymbol{\tau})$. Higher order improper rotations are oriented by their axes $\boldsymbol{T}$; reflection planes are oriented by the direction perpendicular to the plane. If $\boldsymbol{\tau} \neq \mathbf{0}$, then the operation is shifted away from the origin.

(c) *Screw rotations* $2_1, 3_1, 3_2, 4_1, 4_2, 4_3, 6_1, 6_2, 6_3, 6_4, 6_5$.

(d) *Glide reflections* a, b, or c (axial; also e), n (diagonal), and d (diamond).

PRACTICE EXERCISE 1: Determine the Seitz symbol for the following operations:

(a) a 4_1 screw rotation along $\boldsymbol{a}$ and its axis intersecting the $\boldsymbol{bc}$-plane at (0, ¼, 0) in a cubic cell;

(b) a b-glide reflection perpendicular to $\boldsymbol{a}$ and intersecting (½, 0, 0) in an orthorhombic cell;

(c) a $\bar{4}$ improper rotation with respect to $\boldsymbol{c}$ and the point (¼, ¼, ¼) in a tetragonal cell;

(d) a 3-fold proper rotation with respect to $\boldsymbol{c}$ and located at (⅔, ⅓, 0) in a trigonal cell.

The general strategy follows the procedure discussed in slide **(18)** for considering an operation when its symmetry element (point, line, or plane) does not intersect the origin. That is,

$$(R|\boldsymbol{\tau}) = (1|\boldsymbol{t})(R|\boldsymbol{\tau}_R)(1|-\boldsymbol{t}),$$

in which $\boldsymbol{t}$ is the displacement specified by the invariant point in space for the symmetry element. If the operation is a proper or improper rotation, then $\boldsymbol{\tau}_R = \mathbf{0}$; if it is a screw rotation or glide reflection, then $\boldsymbol{\tau}_R \neq \mathbf{0}$ and depends on the type of operation it is as discussed in **(27)** and **(28)**.

(a) 4_1 screw rotation along $\boldsymbol{a}$ through the origin is $\left(4_{\boldsymbol{a}}\middle|\frac{\boldsymbol{a}}{4}\right)$ and $\boldsymbol{t} = \frac{\boldsymbol{b}}{4}$:

$$(R|\boldsymbol{\tau}) = \left(1\middle|\frac{\boldsymbol{b}}{4}\right)\left(4_{\boldsymbol{a}}\middle|\frac{\boldsymbol{a}}{4}\right)\left(1\middle|\frac{-\boldsymbol{b}}{4}\right) = \left(1\middle|\frac{\boldsymbol{b}}{4}\right)\left(4_{\boldsymbol{a}}\middle|\frac{\boldsymbol{a}-\boldsymbol{c}}{4}\right) = \left(4_{\boldsymbol{a}}\middle|\frac{\boldsymbol{a}+\boldsymbol{b}-\boldsymbol{c}}{4}\right).$$

NOTE: $4_{\boldsymbol{a}}(-\boldsymbol{b}) = (-\boldsymbol{c})$.

(b) b-glide reflection perpendicular to $\boldsymbol{a}$ through the origin is $\left(m_{\boldsymbol{a}}\middle|\frac{\boldsymbol{b}}{2}\right)$ and $\boldsymbol{t} = \frac{\boldsymbol{a}}{2}$:

$$(R|\boldsymbol{\tau}) = \left(1\middle|\frac{\boldsymbol{a}}{2}\right)\left(m_{\boldsymbol{a}}\middle|\frac{\boldsymbol{b}}{2}\right)\left(1\middle|\frac{-\boldsymbol{a}}{2}\right) = \left(1\middle|\frac{\boldsymbol{a}}{2}\right)\left(m_{\boldsymbol{a}}\middle|\frac{\boldsymbol{a}+\boldsymbol{b}}{2}\right) = \left(m_{\boldsymbol{a}}\middle|\boldsymbol{a}+\frac{\boldsymbol{b}}{2}\right).$$

(c) $\bar{4}$ improper rotation with respect to $\boldsymbol{c}$ at the origin is $(\bar{4}_{\boldsymbol{c}}|\mathbf{0})$ and $\boldsymbol{t} = \frac{\boldsymbol{a}+\boldsymbol{b}+\boldsymbol{c}}{4}$:

$$(R|\boldsymbol{\tau}) = \left(1\middle|\frac{\boldsymbol{a}+\boldsymbol{b}+\boldsymbol{c}}{4}\right)(\bar{4}_{\boldsymbol{c}}|\mathbf{0})\left(1\middle|\frac{-\boldsymbol{a}-\boldsymbol{b}-\boldsymbol{c}}{4}\right) = \left(1\middle|\frac{\boldsymbol{a}+\boldsymbol{b}+\boldsymbol{c}}{4}\right)\left(\bar{4}_{\boldsymbol{c}}\middle|\frac{\boldsymbol{b}-\boldsymbol{a}+\boldsymbol{c}}{4}\right) = \left(\bar{4}_{\boldsymbol{c}}\middle|\frac{\boldsymbol{b}+\boldsymbol{c}}{2}\right).$$

NOTE: $\bar{4}_{\boldsymbol{c}}(-\boldsymbol{a}) = (+\boldsymbol{b})$, $\bar{4}_{\boldsymbol{c}}(-\boldsymbol{b}) = (-\boldsymbol{a})$, and $\bar{4}_{\boldsymbol{c}}(-\boldsymbol{c}) = (+\boldsymbol{c})$.

(d) 3-fold proper rotation with respect to $\boldsymbol{c}$ through the origin is $(3_{\boldsymbol{c}}|\mathbf{0})$ and $\boldsymbol{t} = \frac{2\boldsymbol{a}+\boldsymbol{b}}{3}$:

$$(R|\boldsymbol{\tau}) = \left(1\middle|\frac{2\boldsymbol{a}+\boldsymbol{b}}{3}\right)(3_{\boldsymbol{c}}|\mathbf{0})\left(1\middle|\frac{-2\boldsymbol{a}-\boldsymbol{b}}{3}\right) = \left(1\middle|\frac{2\boldsymbol{a}+\boldsymbol{b}}{3}\right)\left(3_{\boldsymbol{c}}\middle|\frac{-2\boldsymbol{b}+\boldsymbol{a}+\boldsymbol{b}}{3}\right) = (3_{\boldsymbol{c}}|\boldsymbol{a}).$$

NOTE: $3_{\boldsymbol{c}}(-2\boldsymbol{a}) = (-2\boldsymbol{b})$ and $3_{\boldsymbol{c}}(-\boldsymbol{b}) = (\boldsymbol{a}+\boldsymbol{b})$.

PRACTICE EXERCISE 2: Describe the following operations for a cubic cell from the Seitz symbol:

(a) $\left(4_{\boldsymbol{c}}\middle|\boldsymbol{a}+\frac{\boldsymbol{c}}{2}\right)$ (b) $\left(m_{\boldsymbol{b}}\middle|\frac{\boldsymbol{a}}{2}+\frac{\boldsymbol{b}}{2}+\frac{\boldsymbol{c}}{2}\right)$ (c) $(\bar{1}|\boldsymbol{a}+\boldsymbol{b})$ (d) $\left(2_{\boldsymbol{a}}\middle|\frac{\boldsymbol{a}}{2}+\frac{\boldsymbol{b}}{2}+\frac{\boldsymbol{c}}{2}\right)$

Again, the general strategy follows the procedure discussed in slide **(18)** for considering an operation when its symmetry element (point, line, or plane) does not intersect the origin:

$$(R|\boldsymbol{\tau}) = (1|\boldsymbol{t})(R|\boldsymbol{\tau}_R)(1|-\boldsymbol{t}).$$

For this exercise, we need to identify $\boldsymbol{t}$, i.e., the location of the invariant point for the symmetry element of the operation, and $\boldsymbol{\tau}_R$.

(a) $\left(4_{\boldsymbol{c}}\middle|\boldsymbol{a}+\frac{\boldsymbol{c}}{2}\right)$: R is 4-fold proper rotation about $\boldsymbol{c}$; $\boldsymbol{\tau}$ is lattice translation by $\boldsymbol{a}$ and shift by $\frac{\boldsymbol{c}}{2}$, which is parallel to the rotation axis. This operation is a 4_2 screw rotation along $\boldsymbol{c}$. Now, where is the axis located?

$$\left(4_{\boldsymbol{c}}\middle|\boldsymbol{a}+\frac{\boldsymbol{c}}{2}\right) = (1|\boldsymbol{t})\left(4_{\boldsymbol{c}}\middle|\frac{\boldsymbol{c}}{2}\right)(1|-\boldsymbol{t}) = \left(4_{\boldsymbol{c}}\middle|\frac{\boldsymbol{c}}{2}+\boldsymbol{t}-4_{\boldsymbol{c}}\boldsymbol{t}\right).$$

Therefore, $\boldsymbol{a} = \begin{pmatrix}1\\0\\0\end{pmatrix} = (\boldsymbol{t}-4_{\boldsymbol{c}}\boldsymbol{t}) = \begin{pmatrix}t_x\\t_y\\t_z\end{pmatrix} - \begin{pmatrix}0&-1&0\\1&0&0\\0&0&1\end{pmatrix}\begin{pmatrix}t_x\\t_y\\t_z\end{pmatrix} = \begin{pmatrix}t_x+t_y\\-t_x+t_y\\0\end{pmatrix} \rightarrow \boldsymbol{t} = \frac{\boldsymbol{a}+\boldsymbol{b}}{2}.$

$\left(4_{\boldsymbol{c}}\middle|\boldsymbol{a}+\frac{\boldsymbol{c}}{2}\right)$ = 4_2 screw rotation along $\boldsymbol{c}$ with its axis intersecting the ***ab***-plane at (½, ½, 0).

(b) $\left(m_{\boldsymbol{b}}\middle|\frac{\boldsymbol{a}}{2}+\frac{\boldsymbol{b}}{2}+\frac{\boldsymbol{c}}{2}\right)$: R is reflection perpendicular to $\boldsymbol{b}$; $\boldsymbol{\tau}$ is glide by $\frac{\boldsymbol{a}}{2}+\frac{\boldsymbol{c}}{2}$ and shift by $\frac{\boldsymbol{b}}{2}$. This operation is a diagonal glide reflection. Now, where is the plane located?

$$\left(m_{\boldsymbol{b}}\middle|\frac{\boldsymbol{a}}{2}+\frac{\boldsymbol{b}}{2}+\frac{\boldsymbol{c}}{2}\right) = (1|\boldsymbol{t})\left(m_{\boldsymbol{b}}\middle|\frac{\boldsymbol{a}}{2}+\frac{\boldsymbol{c}}{2}\right)(1|-\boldsymbol{t}) = \left(m_{\boldsymbol{b}}\middle|\frac{\boldsymbol{a}}{2}+\frac{\boldsymbol{c}}{2}+\boldsymbol{t}-m_{\boldsymbol{b}}\boldsymbol{t}\right).$$

Therefore, $\frac{\boldsymbol{b}}{2} = \begin{pmatrix}0\\½\\0\end{pmatrix} = (\boldsymbol{t}-m_{\boldsymbol{b}}\boldsymbol{t}) = \begin{pmatrix}t_x\\t_y\\t_z\end{pmatrix} - \begin{pmatrix}1&0&0\\0&-1&0\\0&0&1\end{pmatrix}\begin{pmatrix}t_x\\t_y\\t_z\end{pmatrix} = \begin{pmatrix}0\\2t_y\\0\end{pmatrix} \rightarrow \boldsymbol{t} = \frac{\boldsymbol{b}}{4}.$

$\left(m_{\boldsymbol{b}}\middle|\frac{\boldsymbol{a}}{2}+\frac{\boldsymbol{b}}{2}+\frac{\boldsymbol{c}}{2}\right)$ = n-glide reflection perpendicular to $\boldsymbol{b}$ and intersecting (0, ¼, 0).

(c) $(\bar{1}|\boldsymbol{a}+\boldsymbol{b})$: R is inversion; $\boldsymbol{\tau}$ is lattice translation by $\boldsymbol{a}+\boldsymbol{b}$. This operation is inversion located away from the origin:

$(\bar{1}|\boldsymbol{a}+\boldsymbol{b}) = (1|\boldsymbol{t})(\bar{1}|\boldsymbol{0})(1|-\boldsymbol{t}) = (\bar{1}|\boldsymbol{t}-\bar{1}\boldsymbol{t}) = (\bar{1}|2\boldsymbol{t})$. Therefore, $\boldsymbol{t} = \frac{\boldsymbol{a}+\boldsymbol{b}}{2}$.

$(\bar{1}|\boldsymbol{a}+\boldsymbol{b})$ = an inversion center located at (½, ½, 0).

(d) $\left(2_{\boldsymbol{a}}\middle|\frac{\boldsymbol{a}}{2}+\frac{\boldsymbol{b}}{2}+\frac{\boldsymbol{c}}{2}\right)$: R is 2-fold proper rotation about $\boldsymbol{a}$; $\boldsymbol{\tau}$ is shift by $\frac{\boldsymbol{a}}{2}$, which is parallel to the rotation axis, as well as a shift by $\frac{\boldsymbol{b}}{2}+\frac{\boldsymbol{c}}{2}$. This operation is a 2_1 screw rotation along $\boldsymbol{a}$. Now, where is the axis located?

$$\left(2_{\boldsymbol{a}}\middle|\frac{\boldsymbol{a}}{2}+\frac{\boldsymbol{b}}{2}+\frac{\boldsymbol{c}}{2}\right) = (1|\boldsymbol{t})\left(2_{\boldsymbol{a}}\middle|\frac{\boldsymbol{a}}{2}\right)(1|-\boldsymbol{t}) = \left(2_{\boldsymbol{a}}\middle|\frac{\boldsymbol{a}}{2}+\boldsymbol{t}-2_{\boldsymbol{a}}\boldsymbol{t}\right).$$

Therefore, $\frac{\boldsymbol{b}}{2}+\frac{\boldsymbol{c}}{2} = \begin{pmatrix}0\\½\\½\end{pmatrix} = (\boldsymbol{t}-2_{\boldsymbol{a}}\boldsymbol{t}) = \begin{pmatrix}t_x\\t_y\\t_z\end{pmatrix} - \begin{pmatrix}1&0&0\\0&-1&0\\0&0&-1\end{pmatrix}\begin{pmatrix}t_x\\t_y\\t_z\end{pmatrix} = \begin{pmatrix}0\\2t_y\\2t_z\end{pmatrix} \rightarrow \boldsymbol{t} = \frac{\boldsymbol{b}+\boldsymbol{c}}{4}.$

$\left(2_{\boldsymbol{a}}\middle|\frac{\boldsymbol{a}}{2}+\frac{\boldsymbol{b}}{2}+\frac{\boldsymbol{c}}{2}\right)$ = 2_1 screw rotation along $\boldsymbol{a}$ with its axis intersecting the ***bc***-plane at (0, ¼, ¼).

(29) Every space group $\mathcal{G}$ is the *semi-direct product* of two sets, $\mathcal{R} \otimes \mathcal{L}$:

$\mathcal{L} = \{(1|\boldsymbol{T}_{mnp})\}$, the set of *N* Bravais lattice vectors that is an invariant subgroup of $\mathcal{G}$. The order of $\mathcal{L}$ is determined by setting periodic boundary conditions for the crystalline lattice. Since these conditions generally involve many unit cells, *N* is a very large value.

$\mathcal{R} = \{(R_i|\boldsymbol{\tau}_i): i = 1, \ldots, h\}$, a set of *h* rotation-displacement operations called *essential symmetry operations* that is not an invariant subgroup. $\mathcal{R}$ contains the identity operation $(1|\boldsymbol{0}) = (R_1|\boldsymbol{\tau}_1)$, and any nonzero displacement $\boldsymbol{\tau}_i$ are not lattice vectors. Therefore, $\mathcal{R}$ can include proper or improper rotations, screw rotations, and glide reflections. The related set $\mathcal{R}_0 = \{R_i: i = 1, \ldots, h\}$, consisting of the *h* rotations, is one of the 32 crystallographic point groups.

As a result, the order of the space group $\mathcal{G}$ is *hN*, and every member has the form

$$(R_i|R_i\boldsymbol{T}_{mnp} + \boldsymbol{\tau}_i) = (R_i|\boldsymbol{\tau}_i)(1|\boldsymbol{T}_{mnp}),$$

which emphasizes the compatibility between the Bravais lattice and rotational symmetry because $R_i\boldsymbol{T}_{mnp}$ must be a lattice vector. By expanding the product of sets,

$$\begin{aligned}\mathcal{G} &= \mathcal{R} \otimes \mathcal{L}\\ &= \{(1|\boldsymbol{0}), (R_2|\boldsymbol{\tau}_2), \ldots, (R_h|\boldsymbol{\tau}_h)\} \otimes \{(1|\boldsymbol{T}_{mnp})\}\\ &= (1|\boldsymbol{0}) \times \{(1|\boldsymbol{T}_{mnp})\} \oplus (R_2|\boldsymbol{\tau}_2) \times \{(1|\boldsymbol{T}_{mnp})\} \oplus \cdots \oplus (R_h|\boldsymbol{\tau}_h) \times \{(1|\boldsymbol{T}_{mnp})\}\\ &= \{(1|\boldsymbol{T}_{mnp})\} \oplus \{(R_2|R_2\boldsymbol{T}_{mnp} + \boldsymbol{\tau}_2)\} \oplus \cdots \oplus \{(R_h|R_h\boldsymbol{T}_{mnp} + \boldsymbol{\tau}_h)\},\end{aligned}$$

the space group $\mathcal{G}$ is also the *sum* of *h cosets* of $\mathcal{G}$ with respect to the invariant subgroup $\mathcal{L}$. These *h* cosets form the *factor group* "$\mathcal{G}/\mathcal{L}$" of the space group $\mathcal{G}$ with respect to the Bravais lattice $\mathcal{L}$:

$$\mathcal{G}/\mathcal{L} = \Big\{\{(1|\boldsymbol{T}_{mnp})\}, \{(R_2|R_2\boldsymbol{T}_{mnp} + \boldsymbol{\tau}_2)\}, \ldots, \{(R_h|R_h\boldsymbol{T}_{mnp} + \boldsymbol{\tau}_h)\}\Big\}.$$

This factor group has order *h* and is isomorphic (i.e., follows the same multiplication table) with the crystallographic point group $\mathcal{R}_0$. The identity member is the subgroup $\mathcal{L} = \{(1|\boldsymbol{T}_{mnp})\}$.

FACTOR GROUPS: To form a factor group of any group $\mathcal{G}$, $\mathcal{G}$ must have an invariant subgroup, which is a subset of members that form complete classes of $\mathcal{G}$. To illustrate important features of factor groups applied to space groups, consider the point group $\mathcal{C}_{4v} = \{1, 4_z, 2_z, 4_z^3, m_x, m_y, m_{x+y}, m_{x-y}\}$, which consists of 8 members and 5 classes: $\mathcal{K}_1 = \{1\}$; $\mathcal{K}_2 = \{4_z, 4_z^3\}$; $\mathcal{K}_3 = \{2_z\}$; $\mathcal{K}_4 = \{m_x, m_y\}$; and $\mathcal{K}_5 = \{m_{x+y}, m_{x-y}\}$.

$\mathcal{C}_4 = \{1, 4_z, 2_z, 4_z^3\} = \mathcal{K}_1 \oplus \mathcal{K}_2 \oplus \mathcal{K}_3$ is an invariant subgroup (order 4) of $\mathcal{C}_{4v}$ because it consists of three complete classes. By considering how the members of $\mathcal{C}_{4v}$ multiply with each other, then $\mathcal{C}_4$ can be factored out of $\mathcal{C}_{4v}$ as follows:

$$\begin{aligned}\mathcal{C}_{4v} &= \{1, 4_z, 2_z, 4_z^3\} \oplus \{m_x, m_{x+y}, m_y, m_{x-y}\} = \{1, 4_z, 2_z, 4_z^3\} \oplus \{m_x \times \{1, 4_z, 2_z, 4_z^3\}\}\\ &= \{1, m_x\} \otimes \{1, 4_z, 2_z, 4_z^3\} = \mathcal{C}_s \otimes \mathcal{C}_4.\end{aligned}$$

So, according to the first line, $\mathcal{C}_{4v}$ is the *sum* of 2 (= 8/4) cosets with respect to the subgroup $\mathcal{C}_4$. We selected m_x as the coset representative in the factoring, but any one of $m_x, m_y, m_{x+y}, m_{x-y}$ would serve that purpose. Therefore, the second line shows that $\mathcal{C}_{4v}$ is also the *product* of two subgroups $\mathcal{C}_s$ and $\mathcal{C}_4$. However, $\mathcal{C}_s$ is not an invariant subgroup of $\mathcal{C}_{4v}$ because m_x is not the only member of class $\mathcal{K}_4$. Accordingly, the factor group of $\mathcal{C}_{4v}$ with respect to $\mathcal{C}_4$ is

$$\mathcal{C}_{4v}/\mathcal{C}_4 = \Big\{\{1, 4_z, 2_z, 4_z^3\}, \{m_x, m_y, m_{x+y}, m_{x-y}\}\Big\},$$

which contains 2 members. The member $\{1, 4_z, 2_z, 4_z^3\} = \mathcal{C}_4$ is the identity, and this 2-member factor group is isomorphic with $\mathcal{C}_s$.

Another invariant subgroup of $\mathcal{C}_{4v}$ is $\mathcal{C}_{2v} = \{1, 2_z, m_x, m_y\} = \mathcal{K}_1 \oplus \mathcal{K}_3 \oplus \mathcal{K}_4$. In this case

$$\mathcal{C}_{4v} = \{1, 2_z, m_x, m_y\} \oplus \{4_z, 4_z^3, m_{x+y}, m_{x-y}\} = \{1, 2_z, m_x, m_y\} \oplus \{4_z \times \{1, 2_z, m_x, m_y\}\}$$
$$= \{1, 4_z\} \otimes \{1, 2_z, m_x, m_y\} = \{1, 4_z\} \otimes \mathcal{C}_{2v}.$$

As above, $\mathcal{C}_{4v}$ is the *sum* of 2 (= 8/4) cosets. However, by choosing 4_z as a coset representative, $\mathcal{C}_{4v}$ is the *product* of the set $\{1, 4_z\}$, which is not a group, and the invariant subgroup $\mathcal{C}_{2v}$. The factor group of $\mathcal{C}_{4v}$ with respect to $\mathcal{C}_{2v}$ is

$$\mathcal{C}_{4v}/\mathcal{C}_{2v} = \{\{1, 2_z, m_x, m_y\}, \{4_z, 4_z^3, m_{x+y}, m_{x-y}\}\},$$

and contains 2 members. The member $\{1, 2_z, m_x, m_y\} = \mathcal{C}_{2v}$ is the identity. This 2-member factor group is also isomorphic with the group $\mathcal{C}_s$.

This example summarizes important features of factor groups that are relevant for space groups:

For a space group $\mathcal{G}$ (order *hN*) with the lattice group $\mathcal{L}$ (order *N*) as an invariant subgroup, then

(a) The factor group $\mathcal{G}/\mathcal{L}$ is the set of the *h* (= *hN*/*N*) different cosets of $\mathcal{G}$ with respect to $\mathcal{L}$;
(b) The identity member of the factor group $\mathcal{G}/\mathcal{L}$ is the set $\mathcal{L}$;
(c) The subset $\mathcal{R}$ of $\mathcal{G}$, such that $\mathcal{G} = \mathcal{R} \otimes \mathcal{L}$, consists of *h* coset representatives of $\mathcal{G}$ with respect to $\mathcal{L}$;
(d) The subset $\mathcal{R}$ of $\mathcal{G}$ may or may not be a group, but it always contains the identity $(1|\mathbf{0})$.

As mentioned above, the factor group $\mathcal{G}/\mathcal{L}$ of space group $\mathcal{G}$ is *isomorphic* with one of the crystallographic point groups $\mathcal{R}_0$ because they have the same abstract group multiplication table. Therefore, $\mathcal{R}_0$ is called *the point group of the space group* $\mathcal{G}$ and it describes the spatial characteristics of all vector or tensor properties of a crystal with space group $\mathcal{G}$. Examples of such properties include crystalline shapes, electrical resistivities, and magnetic susceptibilities.

Also, characteristics of the set $\mathcal{R}$ are important when considering irreducible representations of a space group. If $\mathcal{R}$ is a group, then $\boldsymbol{\tau}_i = \mathbf{0}$ for every member $(R_i|\boldsymbol{\tau}_i)$ of $\mathcal{R}$, i.e., $\mathcal{R} = \{(1|\mathbf{0}), (R_2|\mathbf{0}), \dots, (R_h|\mathbf{0})\}$. Therefore, $\mathcal{R}$ is one of the 32 crystallographic point groups, and the corresponding space group is called *symmorphic*. On the other hand, if $\mathcal{R}$ is not a group, then the displacement component $\boldsymbol{\tau}_i \neq \mathbf{0}$ for some $(R_i|\boldsymbol{\tau}_i)$. Such space groups are called *nonsymmorphic*. Of the 230 3-d space groups, 73 are symmorphic and 157 are nonsymmorphic. Among the 17 2-d space groups, also called *plane groups*, 13 are symmorphic and 4 are nonsymmorphic.

SPACE GROUP NOTATION: The International symbolism is preferred over the Schönflies notation because it conveys information about how symmetry operations are oriented with respect to the unit cell axes. Every space group symbol is based on the product $\mathcal{R} \otimes \mathcal{L}$ because it consists of two parts: (1) a lattice designator; and (2) a point group or point group-like symbol that indicates the essential symmetry operations. For 3-d space groups, the lattice designators include primitive (*P*), base-centered (*A*, *B*, or *C*), body-centered (*I*), face-centered (*F*), or rhombohedral (*R*), and the point group or point group-like symbol is derived from one of the 32 crystallographic point groups. For symmorphic groups, such as $C2/m$, $I4/mmm$, and $Fm\bar{3}m$, the symbols show only proper rotations, improper rotations, or reflections. For nonsymmorphic groups, such as $P2_1/c$, $P6_3/mmc$, and $Fd\bar{3}m$, the symbol explicitly includes screw rotations and/or glide planes. From every space group symbol, three important characteristics are evident:

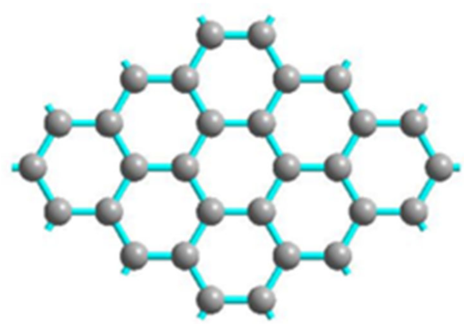
(a) Point Group of the Space Group: For a symmorphic space group, it is the symbol for $\mathcal{R}$; for a nonsymmorphic space group, it is the symbol arising by converting all screw rotations n_j to rotations n and all glide reflection $(a, b, c, n,$ or $d)$ to reflections m in the symbol for $\mathcal{R}$.
(b) Crystal Class: Determined by the point group of the space group.
(c) Lattice Type: Given by the lattice designator.

PLANE GROUPS (Space Groups in 2-d): There are five possible rotational symmetries: 1-, 2-, 3-, 4-, and 6-fold with their axes perpendicular to the plane, but there are no screw rotations and no improper rotations $\bar{n}$, because inversion is the 2-fold rotation. There can also be vertical reflection planes (lines) m and a single type of glide reflection, designated by g (there are no diagonal glides in 2-d). Translational periodicity is specified by either primitive *p* or centered rectangular *c* lattices. Combining the 11 possible 2-d point symmetries with these lattices generates five crystal classes and the following 17 plane groups:

Crystal Class	Space Group (Comments)	
Oblique:	*p*1	Asymmetric
	*p*2	2-fold rotation is also the inversion in 2-d (holohedral)
Rectangular:	*pm*	No inversion center but reflection symmetry
	pg	Nonsymmorphic; no inversion center, but glide reflections
	*p*2*mm*	Full lattice symmetry (holohedral)
	*p*2*mg*	Nonsymmorphic; reflections do not intersect 2-fold axis; equivalent to *p*2*gm*
	*p*2*gg*	Nonsymmorphic; glide reflections do not intersect 2-fold axis
	cm	Equivalent to "*cg*" because *c*-centering generates glide reflections
	*c*2*mm*	Equivalent to "*c*2*mg*" and "*c*2*gg*"
Trigonal:	*p*3	3-fold rotation; no inversion center
	*p*3*m*1	Reflections perpendicular to ***a***-, ***b***-, ***a***+***b***-axes
	*p*31*m*	Reflections perpendicular to 2***a***+***b***-, ***a***+2***b***-, ***a***–***b***-directions
Tetragonal:	*p*4	4-fold rotation
	*p*4*mm*	Full lattice symmetry (holohedral)
	*p*4*gm*	Nonsymmorphic; glide reflections perpendicular to ***a***-, ***b***-axes
Hexagonal:	*p*6	6-fold rotation
	*p*6*mm*	Full lattice symmetry (holohedral

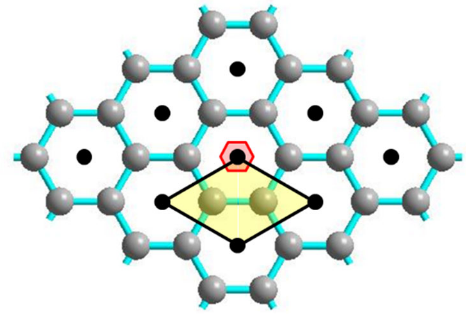
Plane groups *p*2*mg* and *p*2*gm* are equivalent because the assignment of ***a***- and ***b***-axes in the rectangular system is arbitrary from the perspective of abstract mathematical groups.

EXAMPLE: Determine the 2-d space group symbol for ***graphene***, which consists of regular hexagons of three-connected carbon atoms fused along every edge to create a honeycomb network (shown to the right).

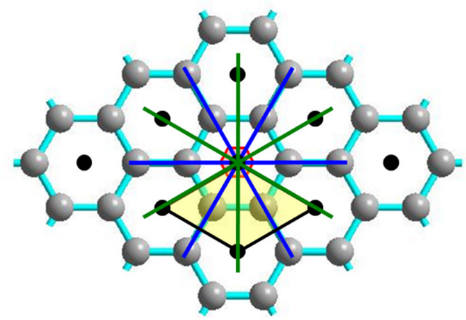


The rotational and translational symmetries of a crystal are closely related. For 2-d crystals, it is often easiest to identify the crystal system first, then the lattice, and then the set of essential symmetry operations.

Crystal System and **Lattice**: Because 6-fold rotational symmetry occurs at the centers of each hexagon, the system is ***hexagonal***. As a result, the unit cell is the rhombus with $a = b$, $\gamma = 120°$, highlighted in yellow.



Essential Symmetry Operations: The 6-fold axis intersects each lattice point, so this operation is $(6|\mathbf{0})$. As a result, five additional operations are: $(6|\mathbf{0})^2 = (3|\mathbf{0})$, $(6|\mathbf{0})^3 = (2|\mathbf{0})$, $(6|\mathbf{0})^4 = (3^2|\mathbf{0})$, $(6|\mathbf{0})^5 = (6^5|\mathbf{0})$, and $(6|\mathbf{0})^6 = (1|\mathbf{0})$. There is also reflection symmetry and these vertical planes (lines) intersect lattice points. There are 3 reflections perpendicular to ***a***-, ***b***-, and ***a***+***b***-directions (blue; parallel to C–C bonds): $(m_{\boldsymbol{a}}|\mathbf{0})$, $(m_{\boldsymbol{b}}|\mathbf{0})$, $(m_{\boldsymbol{a}+\boldsymbol{b}}|\mathbf{0})$; and 3 reflections perpendicular to 2***a***+***b***-, ***a***+2***b***-, and ***a***–***b***-directions (green; bisecting C–C bonds): $(m_{2\boldsymbol{a}+\boldsymbol{b}}|\mathbf{0})$, $(m_{\boldsymbol{a}+2\boldsymbol{b}}|\mathbf{0})$, $(m_{\boldsymbol{a}-\boldsymbol{b}}|\mathbf{0})$.



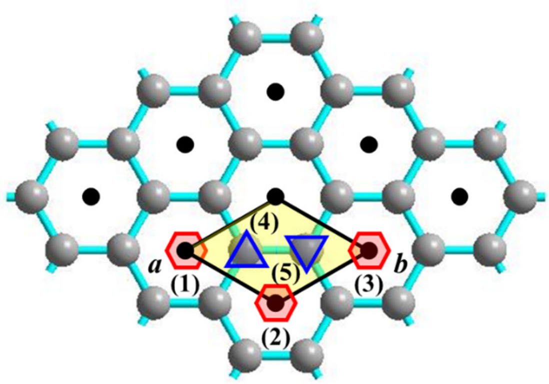
Therefore, the set of *essential symmetry operations* contains 12 operations

$$\mathcal{R} = \begin{Bmatrix} (1|\mathbf{0}), (6|\mathbf{0}), (3|\mathbf{0}), (2|\mathbf{0}), (3^2|\mathbf{0}), (6^5|\mathbf{0}), \\ (m_{\boldsymbol{a}}|\mathbf{0}), (m_{\boldsymbol{b}}|\mathbf{0}), (m_{\boldsymbol{a}+\boldsymbol{b}}|\mathbf{0}), (m_{2\boldsymbol{a}+\boldsymbol{b}}|\mathbf{0}), (m_{\boldsymbol{a}+2\boldsymbol{b}}|\mathbf{0}), (m_{\boldsymbol{a}-\boldsymbol{b}}|\mathbf{0}) \end{Bmatrix},$$

and is the point group $6mm = \mathcal{C}_{6v}$. The *Bravais lattice* set is:

$$\mathcal{L} = \{(1|n_1\boldsymbol{a} + n_2\boldsymbol{b}): n_1, n_2 = \text{integers}; a = b, \gamma = 120°\},$$

which is a *primitive* (*p*) lattice. The space group is $\mathcal{G} = \mathcal{R} \otimes \mathcal{L} = \boldsymbol{p6mm}$ and is symmorphic. To verify that space group $p6mm$ is the product of the point group $6mm = \mathcal{R}$ and the lattice $\mathcal{L}$, determine the rotation-translation operations for positions (1)-(5) in graphene. These sites are not at the origin point, so we must apply the approach $(R|\boldsymbol{\tau}) = (1|\boldsymbol{t})(R|\boldsymbol{\tau}_R)(1|-\boldsymbol{t})$:



(1) $(6|\boldsymbol{\tau}_1) = (1|\boldsymbol{a})(6|\mathbf{0})(1|-\boldsymbol{a}) = (1|\boldsymbol{a})(6|-\boldsymbol{a}-\boldsymbol{b})$
$= (6|-\boldsymbol{b}) = (1|-\boldsymbol{b})(6|\mathbf{0})$

(2) $(6|\boldsymbol{\tau}_2) = (1|\boldsymbol{a}+\boldsymbol{b})(6|\mathbf{0})(1|-\boldsymbol{a}-\boldsymbol{b})$
$= (1|\boldsymbol{a}+\boldsymbol{b})(6|-\boldsymbol{b}) = (6|\boldsymbol{a}) = (1|\boldsymbol{a})(6|\mathbf{0})$

(3) $(6|\boldsymbol{\tau}_3) = (1|\boldsymbol{b})(6|\mathbf{0})(1|-\boldsymbol{b}) = (1|\boldsymbol{b})(6|\boldsymbol{a})$
$= (6|\boldsymbol{a}+\boldsymbol{b}) = (1|\boldsymbol{a}+\boldsymbol{b})(6|\mathbf{0})$

(4) $(3|\boldsymbol{\tau}_4) = (1|\tfrac{2}{3}\boldsymbol{a} + \tfrac{1}{3}\boldsymbol{b})(3|\mathbf{0})(1|-\tfrac{2}{3}\boldsymbol{a} - \tfrac{1}{3}\boldsymbol{b})$
$= (3|\boldsymbol{a}) = (1|\boldsymbol{a})(3|\mathbf{0})$

(5) $(3|\boldsymbol{\tau}_5) = (1|\tfrac{1}{3}\boldsymbol{a} + \tfrac{2}{3}\boldsymbol{b})(3|\mathbf{0})(1|-\tfrac{1}{3}\boldsymbol{a} - \tfrac{2}{3}\boldsymbol{b})$
$= (3|\boldsymbol{a}+\boldsymbol{b}) = (1|\boldsymbol{a}+\boldsymbol{b})(3|\mathbf{0})$

Each of these operations is the product of a Bravais lattice vector $(1|n_1\boldsymbol{a} + n_2\boldsymbol{b})$ and an essential symmetry operation $(R|\mathbf{0})$.

(30) Notation - Symmorphic 3-d Space Groups: ***Pmm*2**

Three significant characteristics of the space group are determined from its symbol.

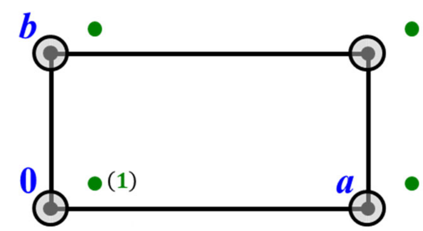
Point Group of the Space Group: $mm2 = C_{2v}$, which comes directly from the symbol for the essential symmetry operations.

Crystal Class: *Orthorhombic*, which is determined from the point group of the space group and identifies the necessary rotational symmetry of the lattice. The unit cell involves three different and mutually perpendicular sides, so it is sufficient to specify just the lengths of each unit cell side.

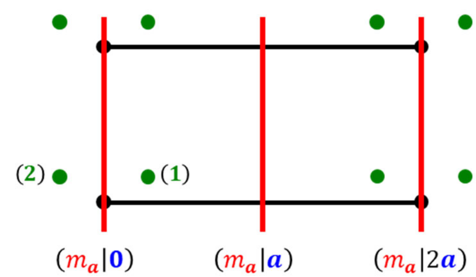
Lattice Type: *Primitive*, based upon the lattice designator, so that the unit cell contains one lattice point, which is typically located at cell corner(s), and, therefore, one repeating unit throughout the crystal.

Now we examine each part of the symbol $Pmm2$ and its implication(s) for a general position, designated by the coordinates $(x, y, z) = (\mathbf{1})$:

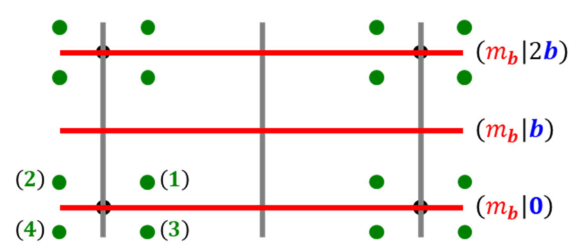
***Pmm*2:** Primitive unit cell projected down $\boldsymbol{c}$ using a right-handed perspective with lattice points at the corners. The general point in the unit cell $(\mathbf{1}) = (x, y, z)$ corresponds to the identity operation $(1|\mathbf{0})$. Translational symmetry generates equivalent positions (**green**) associated with each lattice point.



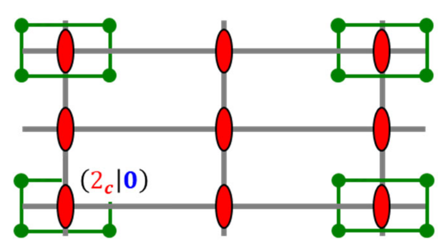
***Pmm*2:** Reflection planes (**red**) perpendicular to $\boldsymbol{a}$. The essential operation is $(m_a|\mathbf{0})$, which intersects the origin and generates point $(\mathbf{2}) = (m_a|\mathbf{0})(\mathbf{1}) = (\bar{x}, y, z)$. All other parallel m_a planes are generated by lattice translations along $\boldsymbol{a}$: $(m_a|n_1\boldsymbol{a}) = (1|n_1\boldsymbol{a})(m_a|\mathbf{0})$.



***Pmm*2:** Reflection planes (**red**) perpendicular to $\boldsymbol{b}$. The essential operation is $(m_b|\mathbf{0})$, which intersects the origin and generates points $(\mathbf{3}) = (m_b|\mathbf{0})(\mathbf{1}) = (x, \bar{y}, z)$ and $(\mathbf{4}) = (m_b|\mathbf{0})(\mathbf{2}) = (\bar{x}, \bar{y}, z)$. All other parallel m_b planes are generated by lattice translations along $\boldsymbol{b}$: $(m_b|n_2\boldsymbol{b}) = (1|n_2\boldsymbol{b})(m_b|\mathbf{0})$.



***Pmm*2:** 2-fold rotation axes (**red**) parallel to $\boldsymbol{c}$. The essential operation is $(2_c|\mathbf{0})$, which intersects the origin and is generated by the two orthogonal reflections: $(2_c|\mathbf{0}) = (m_b|\mathbf{0})(m_a|\mathbf{0})$. As a result, no additional general points occur in the unit cell. All other parallel 2_c axes are generated by lattice translations $(1|n_1\boldsymbol{a} + n_2\boldsymbol{b})$.



As a result of this analysis, the two sets that build up the space group $Pmm2$ are

$\mathcal{L} = \{(1|n_1\boldsymbol{a} + n_2\boldsymbol{b} + n_3\boldsymbol{c}): n_1, n_2, n_3 = \text{integers}; a \neq b \neq c, \alpha = \beta = \gamma = 90°\} = P(\text{ortho})$, and

$\mathcal{R} = \{(1|\mathbf{0}), (m_a|\mathbf{0}), (m_b|\mathbf{0}), (2_c|\mathbf{0})\} = mm2 = C_{2v}$.

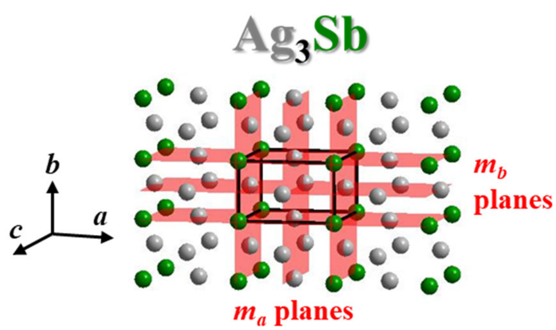
"$mm2$"	$(1\|\mathbf{0})$	$(m_a\|\mathbf{0})$	$(m_b\|\mathbf{0})$	$(2_c\|\mathbf{0})$
$(1\|\mathbf{0})$	$(1\|\mathbf{0})$	$(m_a\|\mathbf{0})$	$(m_b\|\mathbf{0})$	$(2_c\|\mathbf{0})$
$(m_a\|\mathbf{0})$	$(m_a\|\mathbf{0})$	$(1\|\mathbf{0})$	$(2_c\|\mathbf{0})$	$(m_b\|\mathbf{0})$
$(m_b\|\mathbf{0})$	$(m_b\|\mathbf{0})$	$(2_c\|\mathbf{0})$	$(1\|\mathbf{0})$	$(m_a\|\mathbf{0})$
$(2_c\|\mathbf{0})$	$(2_c\|\mathbf{0})$	$(m_b\|\mathbf{0})$	$(m_a\|\mathbf{0})$	$(1\|\mathbf{0})$

According to its multiplication table, the set $\mathcal{R}$ is a group. The operation $(2_c|\mathbf{0})$ is generated from the product of the two perpendicular mirror planes in either order:

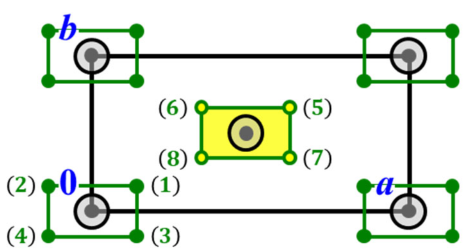
$$(2_c|\mathbf{0}) = (m_a|\mathbf{0})(m_b|\mathbf{0}) = (m_b|\mathbf{0})(m_a|\mathbf{0}).$$

Since lattice points occur along lines where m_a and m_b intersect, these intersections coincide with the 2-fold rotation axes. Therefore, the point symmetry at each lattice point is $mm2 = C_{2v}$. Furthermore, this is the highest point symmetry anywhere in 3-d space for this space group. As the final diagram above illustrates, besides lattice points, which include $(0,0,z)$, this point symmetry occurs at $(½, 0, z)$, $(0, ½, z)$, and $(½, ½, z)$.

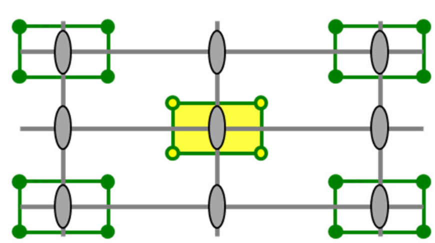
Ag_3Sb[8] forms a crystalline structure in the space group $Pmm2$. The accompanying figure includes the outline of a unit cell with Ag atoms in gray, Sb atoms in light green, and two sets of perpendicular reflection planes highlighted in red. The lattice constants are $a = 4.890$ Å, $b = 3.022$ Å, $c = 5.276$ Å. Planes through lattice points contain equal numbers of Ag and Sb atoms; planes bisecting the unit cell contain only Ag atoms.



***Imm*2:** Symmorphic space groups involving centered lattices contain screw rotations and glide reflections, although they are not included in the space group symbol. Like $Pmm2$, the point group of this space group is $mm2 = C_{2v}$, the crystal class is *orthorhombic*, but the lattice type is *body-centered*, which means there are 2 lattice points per unit cell.



***Imm*2:** Body-centering takes the image around (0,0,0) and reproduces it around (½, ½, ½). For example, $\left(1\middle|\frac{\boldsymbol{a}+\boldsymbol{b}+\boldsymbol{c}}{2}\right)(\mathbf{1}) = (x + ½, y + ½, z + ½) = (\mathbf{5})$. As a result, each unit cell contains 8 sites generated from the general position.



***Imm*2:** The point symmetry $mm2$ is repeated around every lattice point.

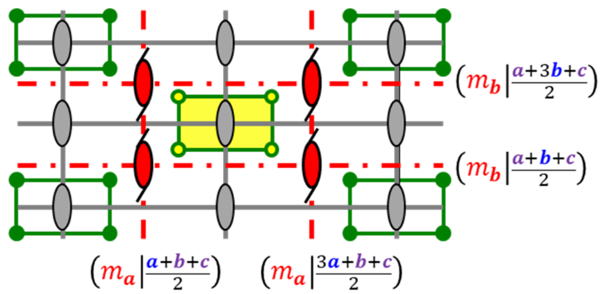
[8] J.-L. Mi, et al., *Chem. Mater*. **2017**, *29*, 6378-6388.

Therefore, the two sets that build up the space group $Imm2$ are

$$\mathcal{L} = \left\{\left(1\middle|\frac{n_1}{2}\boldsymbol{a} + \frac{n_2}{2}\boldsymbol{b} + \frac{n_3}{2}\boldsymbol{c}\right): n_1, n_2, n_3 = \text{all even or odd integers}; a \neq b \neq c, \alpha = \beta = \gamma = 90°\right\}$$
$$= I(\text{ortho}), \text{ and}$$

$$\mathcal{R} = \{(1|\mathbf{0}), (m_{\boldsymbol{a}}|\mathbf{0}), (m_{\boldsymbol{b}}|\mathbf{0}), (2_{\boldsymbol{c}}|\mathbf{0})\} = mm2 = C_{2v}, \text{ which is a group.}$$

The body-centering lattice translations, when multiplied with the essential reflections and rotations, generate additional symmetry operations noted in red:



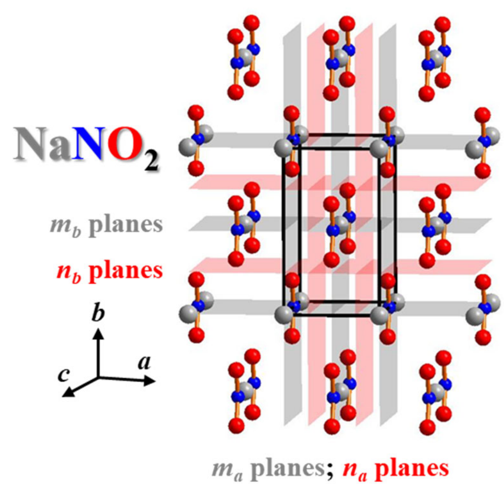
$\left(1\middle|\frac{\boldsymbol{a}+\boldsymbol{b}+\boldsymbol{c}}{2}\right)(m_{\boldsymbol{a}}|\mathbf{0}) = \left(m_{\boldsymbol{a}}\middle|\frac{\boldsymbol{a}+\boldsymbol{b}+\boldsymbol{c}}{2}\right) = \left(1\middle|\frac{\boldsymbol{a}}{4}\right)\left(m_{\boldsymbol{a}}\middle|\frac{\boldsymbol{b}+\boldsymbol{c}}{2}\right)\left(1\middle|\frac{-\boldsymbol{a}}{4}\right)$ = a *diagonal glide plane* $n_{\boldsymbol{a}}$ oriented perpendicular to $\boldsymbol{a}$ and intersecting the point (¼, 0,0).

$\left(1\middle|\frac{\boldsymbol{a}+\boldsymbol{b}+\boldsymbol{c}}{2}\right)(m_{\boldsymbol{b}}|\mathbf{0}) = \left(m_{\boldsymbol{b}}\middle|\frac{\boldsymbol{a}+\boldsymbol{b}+\boldsymbol{c}}{2}\right) = \left(1\middle|\frac{\boldsymbol{b}}{4}\right)\left(m_{\boldsymbol{b}}\middle|\frac{\boldsymbol{a}+\boldsymbol{c}}{2}\right)\left(1\middle|\frac{-\boldsymbol{b}}{4}\right)$ = a *diagonal glide plane* $n_{\boldsymbol{b}}$ oriented perpendicular to $\boldsymbol{b}$ and intersecting the point (0, ¼, 0).

$\left(1\middle|\frac{\boldsymbol{a}+\boldsymbol{b}+\boldsymbol{c}}{2}\right)(2_{\boldsymbol{c}}|\mathbf{0}) = \left(2_{\boldsymbol{c}}\middle|\frac{\boldsymbol{a}+\boldsymbol{b}+\boldsymbol{c}}{2}\right) = \left(1\middle|\frac{\boldsymbol{a}+\boldsymbol{b}}{4}\right)\left(2_{\boldsymbol{c}}\middle|\frac{\boldsymbol{c}}{2}\right)\left(1\middle|\frac{-(\boldsymbol{a}+\boldsymbol{b})}{4}\right)$ = a *two-fold screw axis* 2_1 parallel to $\boldsymbol{c}$ and intersecting the point (¼, ¼, 0).

Therefore, lattice centering generates glide reflections and screw rotations to symmorphic space groups. In $Imm2$, there are diagonal glide reflections perpendicular to $\boldsymbol{a}$ and $\boldsymbol{b}$, as well as two-fold screw axes along $\boldsymbol{c}$. Therefore, another possible symbol for this space group could be $Inn2_1$. However, there is a hierarchy of symbolism for the International notation: straightforward rotations and reflections take precedent over any screw rotations and glide reflections, respectively.

$NaNO_2$[9] forms a crystalline structure in the space group $Imm2$. The accompanying figure shows the outline of a unit cell with Na atoms in gray, N atoms in blue, O atoms in red, two sets of perpendicular reflections highlighted in gray, and two sets of perpendicular diagonal glide planes highlighted in red. The lattice constants are $a = 3.512$ Å, $b = 6.148$ Å, $c = 5.17$ Å. All atoms lie on $m_{\boldsymbol{a}}$ reflection planes as Na^+ cations and NO_2^- anions.



[9] G.B. Carpenter, *Acta Crystallogr.* **1952**, *5*, 132-135.

(31) Notation - Symmorphic 3-d Space Groups: $\boldsymbol{Pma2}$

Three characteristics of this space group are:

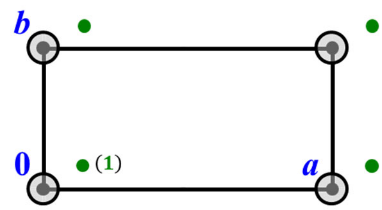
Point Group of the Space Group: $mm2 = C_{2v}$, which comes from the symbol "$ma2$" by replacing the glide reflection "a" with a normal reflection "m". The highest point symmetry in the unit cell is a proper subgroup of $mm2$, while the physical properties of any crystal exhibits $mm2$ symmetry.

Crystal Class: *Orthorhombic*, which is determined from the point group of the space group. The unit cell involves three different and mutually perpendicular sides.

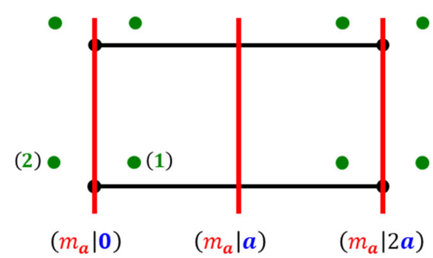
Lattice Type: *Primitive*, based upon the lattice designator, so that the unit cell contains one lattice point and, therefore, one repeating unit throughout the crystal.

Now, we examine each part of the symbol $Pma2$ and its implication(s) for a general position, designated by the coordinates $(x, y, z) = (\mathbf{1})$. As for $Pmm2$, we set lattice points at the intersections of the two sets of perpendicular planes.

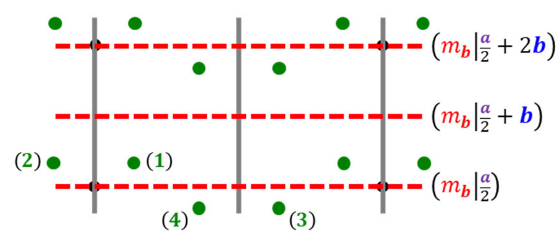
$\boldsymbol{Pma2}$: Primitive unit cell projected down $\boldsymbol{c}$ using a right-handed perspective with lattice points at the corners. The general point in the unit cell $(\mathbf{1}) = (x, y, z)$ corresponds to the identity operation $(1|\mathbf{0})$. Translational symmetry generates equivalent positions (**green**) associated with each lattice point.



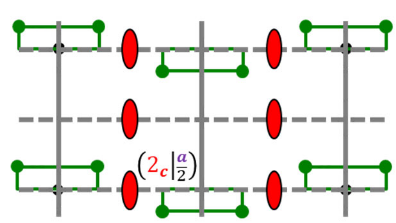
$\boldsymbol{Pma2}$: Reflection planes (**red**) perpendicular to $\boldsymbol{a}$. The essential operation is $(m_a|\mathbf{0})$, which intersects (0,0,0) and generates point $(\mathbf{2}) = (m_a|\mathbf{0})(\mathbf{1}) = (\bar{x}, y, z)$. All other parallel m_a planes are generated by lattice translations along $\boldsymbol{a}$: $(m_a|n_1\boldsymbol{a}) = (1|n_1\boldsymbol{a})(m_a|\mathbf{0})$.



$\boldsymbol{Pma2}$: Axial glide reflection planes (dashed **red**) perpendicular to $\boldsymbol{b}$. The essential operation is $\left(m_b\middle|\frac{a}{2}\right)$, which intersects (0,0,0) and generates points $(\mathbf{3}) = \left(m_b\middle|\frac{a}{2}\right)(\mathbf{1}) = (x + ½, \bar{y}, z)$ and $(\mathbf{4}) = \left(m_b\middle|\frac{a}{2}\right)(\mathbf{2}) = (½ - x, \bar{y}, z)$. All other parallel glides planes are generated by lattice translations along $\boldsymbol{b}$.



$\boldsymbol{Pma2}$: 2-fold rotation axes (**red**) parallel to $\boldsymbol{c}$. The essential operation is $\left(2_c\middle|\frac{a}{2}\right)$, which intersects the point (¼, 0,0) and is generated by the two reflections: $\left(2_c\middle|\frac{a}{2}\right) = \left(m_b\middle|\frac{a}{2}\right)(m_a|\mathbf{0})$. All other parallel 2_c axes are generated by lattice translations $(1|n_1\boldsymbol{a} + n_2\boldsymbol{b})$.



The two sets that build up the space group $Pma2$ are

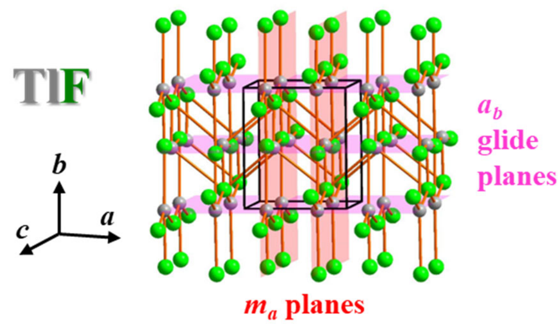
$$\mathcal{L} = \{(1|n_1\boldsymbol{a} + n_2\boldsymbol{b} + n_3\boldsymbol{c}): n_1, n_2, n_3 = \text{integer}; a \neq b \neq c, \alpha = \beta = \gamma = 90°\} = P(\text{ortho}).$$

$$\mathcal{R} = \left\{(1|\mathbf{0}), (m_{\boldsymbol{a}}|\mathbf{0}), \left(m_{\boldsymbol{b}}\middle|\frac{\boldsymbol{a}}{2}\right), \left(2_{\boldsymbol{c}}\middle|\frac{\boldsymbol{a}}{2}\right)\right\}.$$

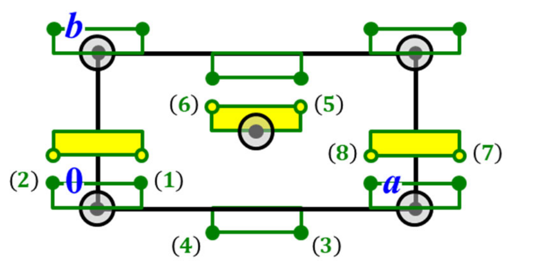
"***ma*2**"	$(1\|\mathbf{0})$	$(m_{\boldsymbol{a}}\|\mathbf{0})$	$\left(m_{\boldsymbol{b}}\middle\|\frac{\boldsymbol{a}}{2}\right)$	$\left(2_{\boldsymbol{c}}\middle\|\frac{\boldsymbol{a}}{2}\right)$
$(1\|\mathbf{0})$	$(1\|\mathbf{0})$	$(m_{\boldsymbol{a}}\|\mathbf{0})$	$\left(m_{\boldsymbol{b}}\middle\|\frac{\boldsymbol{a}}{2}\right)$	$\left(2_{\boldsymbol{c}}\middle\|\frac{\boldsymbol{a}}{2}\right)$
$(m_{\boldsymbol{a}}\|\mathbf{0})$	$(m_{\boldsymbol{a}}\|\mathbf{0})$	$(1\|\mathbf{0})$	$\left(2_{\boldsymbol{c}}\middle\|-\frac{\boldsymbol{a}}{2}\right)$	$\left(m_{\boldsymbol{b}}\middle\|-\frac{\boldsymbol{a}}{2}\right)$
$\left(m_{\boldsymbol{b}}\middle\|\frac{\boldsymbol{a}}{2}\right)$	$\left(m_{\boldsymbol{b}}\middle\|\frac{\boldsymbol{a}}{2}\right)$	$\left(2_{\boldsymbol{c}}\middle\|\frac{\boldsymbol{a}}{2}\right)$	$(1\|\boldsymbol{a})$	$(m_{\boldsymbol{a}}\|\boldsymbol{a})$
$\left(2_{\boldsymbol{c}}\middle\|\frac{\boldsymbol{a}}{2}\right)$	$\left(2_{\boldsymbol{c}}\middle\|\frac{\boldsymbol{a}}{2}\right)$	$\left(m_{\boldsymbol{b}}\middle\|\frac{\boldsymbol{a}}{2}\right)$	$(m_{\boldsymbol{a}}\|\mathbf{0})$	$(1\|\mathbf{0})$

According to the multiplication table, the set $\mathcal{R}$ is not a group because the products highlighted in light green are not members of $\mathcal{R}$. Nevertheless, they are members of the space group $\mathcal{R} \otimes \mathcal{L}$. Also, the perpendicular reflection planes intersect at lattice points, but the resulting 2-fold axes do not. Therefore, the point symmetry at each lattice point is $m = C_s$. Points coincident with the 2-fold axes have point symmetry $2 = C_2$. Because both of these groups are proper subgroups of $mm2$ with 2, the origin point (lattice points) could be assigned to either one of these settings.

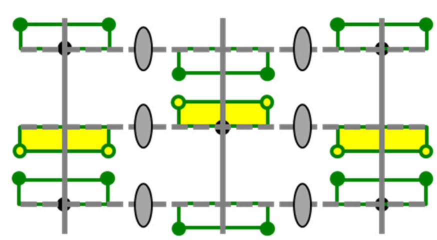
TlF[10] forms a crystalline structure in the space group $Pma2$. The accompanying figure shows the outline of a unit cell with Tl atoms in gray, F atoms in light green. Normal mirror planes perpendicular to the $\boldsymbol{a}$ are highlighted in red; a axial glide planes perpendicular to $\boldsymbol{b}$ are shown in magenta. These two sets of planes do not intersect at lattice points, which occur along the intersections of 2_c axes and a_b glide planes. The lattice constants are $a = 5.175$ Å, $b = 6.092$ Å, $c = 5.488$ Å. All atoms lie on the $m_{\boldsymbol{a}}$ reflection planes.



***Ima*2:** Let's examine how lattice centering affects nonsymmorphic space groups. The point group of this space group is $mm2 = C_{2v}$, the crystal class is *orthorhombic*, and the lattice type is *body-centered*, so that there are 2 lattice points per unit cell.



***Ima*2:** Body-centering takes the image associated with (0,0,0) and reproduces it around (½, ½, ½). As a result, each unit cell contains 8 sites generated from the general position.



***Ima*2:** The point symmetry $mm2$ is repeated around every lattice point.

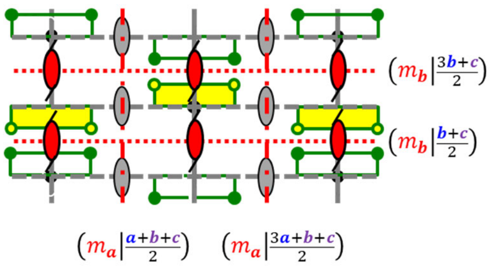
[10] N.W. Alcock, *Acta Crystallogr. Sect. A* **1969**, *A25*, S101-S101.

Therefore, the two sets that build up the space group $Ima2$ are

$$\mathcal{L} = \left\{\left(1\middle|\frac{n_1}{2}\boldsymbol{a} + \frac{n_2}{2}\boldsymbol{b} + \frac{n_3}{2}\boldsymbol{c}\right): n_1, n_2, n_3 = \text{all even or odd integers}; a \neq b \neq c, \alpha = \beta = \gamma = 90°\right\} = I(\text{ortho}), \text{ and}$$

$$\mathcal{R} = \left\{(1|\boldsymbol{0}), (m_{\boldsymbol{a}}|\boldsymbol{0}), \left(m_{\boldsymbol{b}}\middle|\frac{\boldsymbol{a}}{2}\right), \left(2_{\boldsymbol{c}}\middle|\frac{\boldsymbol{a}}{2}\right)\right\}, \text{ which is not a group.}$$

The body-centering lattice translations, when multiplied with the essential reflections and rotations, generate additional symmetry operations:



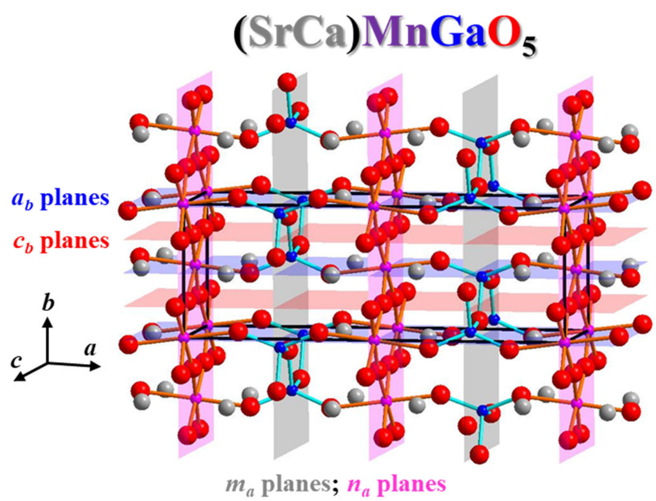
$\left(1\middle|\frac{\boldsymbol{a}+\boldsymbol{b}+\boldsymbol{c}}{2}\right)(m_{\boldsymbol{a}}|\boldsymbol{0}) = \left(m_{\boldsymbol{a}}\middle|\frac{\boldsymbol{a}+\boldsymbol{b}+\boldsymbol{c}}{2}\right) = \left(1\middle|\frac{\boldsymbol{a}}{4}\right)\left(m_{\boldsymbol{a}}\middle|\frac{\boldsymbol{b}+\boldsymbol{c}}{2}\right)\left(1\middle|\frac{-\boldsymbol{a}}{4}\right)$ = a *diagonal glide plane* $n_{\boldsymbol{a}}$ oriented perpendicular to $\boldsymbol{a}$ and intersecting the point $(¼, 0, 0)$.

$\left(1\middle|\frac{-\boldsymbol{a}+\boldsymbol{b}+\boldsymbol{c}}{2}\right)\left(m_{\boldsymbol{b}}\middle|\frac{\boldsymbol{a}}{2}\right) = \left(m_{\boldsymbol{b}}\middle|\frac{\boldsymbol{b}+\boldsymbol{c}}{2}\right) = \left(1\middle|\frac{\boldsymbol{b}}{4}\right)\left(m_{\boldsymbol{b}}\middle|\frac{\boldsymbol{c}}{2}\right)\left(1\middle|\frac{-\boldsymbol{b}}{4}\right)$ = an *axial glide plane* $c_{\boldsymbol{b}}$ along $\boldsymbol{c}$ oriented perpendicular to $\boldsymbol{b}$ and intersecting the point $(0, ¼, 0)$.

$\left(1\middle|\frac{-\boldsymbol{a}+\boldsymbol{b}+\boldsymbol{c}}{2}\right)\left(2_{\boldsymbol{c}}\middle|\frac{\boldsymbol{a}}{2}\right) = \left(2_{\boldsymbol{c}}\middle|\frac{\boldsymbol{b}+\boldsymbol{c}}{2}\right) = \left(1\middle|\frac{\boldsymbol{b}}{4}\right)\left(2_{\boldsymbol{c}}\middle|\frac{\boldsymbol{c}}{2}\right)\left(1\middle|\frac{-\boldsymbol{b}}{4}\right)$ = a *two-fold screw axis* 2_1 parallel to $\boldsymbol{c}$ and intersecting the point $(0, ¼, 0)$.

In $Ima2$, there are diagonal glide reflections perpendicular to $\boldsymbol{a}$, axial glide reflections along $\boldsymbol{c}$ and perpendicular to $\boldsymbol{b}$, as well as two-fold screw axes along $\boldsymbol{c}$. Therefore, another possible symbol for this space group could be $Inc2_1$.

(SrCa)$MnGaO_5$[11] forms a crystalline structure in the space group $Ima2$. The accompanying figure shows the structure with Sr/Ca atoms in gray, Mn atoms in purple, Ga atoms in blue, and O atoms in red. Perpendicular to $\boldsymbol{a}$ are the mirrors (gray) and diagonal glide (magenta) reflections; perpendicular to $\boldsymbol{b}$ are the axial a-glide (blue) and axial c-glide (red) reflections. Lattice points occur along lines where the diagonal n_a planes and axial a_b planes intersect – these lines correspond to the 2-fold rotation axes so that the point symmetry at each lattice point is $2 = C_2$. Ga atoms sit only on $m_{\boldsymbol{a}}$ planes; Mn atoms sit at the intersections of $n_{\boldsymbol{a}}$ and $a_{\boldsymbol{b}}$ glide planes.



[11] P.D. Battle, et al. *J. Solid State Chem.* **2002**, *167*, 188-195.

(32) PRACTICE QUESTION 1: Extracting information from the space groups symbol. Fill in the blanks for each of the following space group symbols.

$\boldsymbol{C2/m}$: Point Group = ________ Crystal Class = ________
Lattice Type = ________ Highest Point Symmetry = ________

$\boldsymbol{I4/mmm}$: Point Group = ________ Crystal Class = ________
Lattice Type = ________ Highest Point Symmetry = ________

$\boldsymbol{Fm\bar{3}m}$: Point Group = ________ Crystal Class = ________
Lattice Type = ________ Highest Point Symmetry = ________

$\boldsymbol{P2_1/c}$: Point Group = ________ Crystal Class = ________
Lattice Type = ________ Highest Point Symmetry = ________

$\boldsymbol{P6_3/mmc}$: Point Group = ________ Crystal Class = ________
Lattice Type = ________ Highest Point Symmetry = ________

$\boldsymbol{Fd\bar{3}m}$: Point Group = ________ Crystal Class = ________
Lattice Type = ________ Highest Point Symmetry = ________

ANSWERS:

$\boldsymbol{C2/m}$: Point Group = $\boldsymbol{2/m\ (\mathcal{C}_{2h})}$ Crystal Class = ***Monoclinic***
Lattice Type = ***Base-centered*** Highest Point Symmetry = $\boldsymbol{2/m\ (\mathcal{C}_{2h})}$

$\boldsymbol{I4/mmm}$: Point Group = $\boldsymbol{4/mmm\ (\mathcal{D}_{4h})}$ Crystal Class = ***Tetragonal***
Lattice Type = ***Body-centered*** Highest Point Symmetry = $\boldsymbol{4/mmm\ (\mathcal{D}_{4h})}$

$\boldsymbol{Fm\bar{3}m}$: Point Group = $\boldsymbol{m\bar{3}m\ (\mathcal{O}_h)}$ Crystal Class = ***Cubic***
Lattice Type = ***Face-centered*** Highest Point Symmetry = $\boldsymbol{m\bar{3}m\ (\mathcal{O}_h)}$

(Adopted by FCC metals such as Cu, Al, and Pb)

$\boldsymbol{P2_1/c}$: Point Group = $\boldsymbol{2/m\ (\mathcal{C}_{2h})}$ Crystal Class = ***Monoclinic***
Lattice Type = ***Primitive*** Highest Point Symmetry = $\boldsymbol{\bar{1}\ (\mathcal{C}_i)}$

(Most common space group, along with $P\bar{1}$)

$\boldsymbol{P6_3/mmc}$: Point Group = $\boldsymbol{6/mmm\ (\mathcal{D}_{6h})}$ Crystal Class = ***Hexagonal***
Lattice Type = ***Primitive*** Highest Point Symmetry = $\boldsymbol{\bar{3}m\ (\mathcal{D}_{3d})}$
= $\boldsymbol{\bar{6}m2\ (\mathcal{D}_{3h})}$

(Adopted by HCP metals such as Mg, Ti, and Gd)

$\boldsymbol{Fd\bar{3}m}$: Point Group = $\boldsymbol{m\bar{3}m\ (\mathcal{O}_h)}$ Crystal Class = ***Cubic***
Lattice Type = ***Face-centered*** Highest Point Symmetry = $\boldsymbol{\bar{4}3m\ (\mathcal{T}_d)}$
= $\boldsymbol{\bar{3}m\ (\mathcal{D}_{3d})}$

(Space group of diamond-type structures such as C, Si, and Ge)

There are two settings for the origin because the site of highest point symmetry does not coincide with an inversion center.

(33) PRACTICE QUESTION 2: The nickel-carbon plane in $CeNiC_2$ consists of Ni atoms and C_2-dimers that form [NiC_2] triangles and 7-membered rings of atoms (see right).

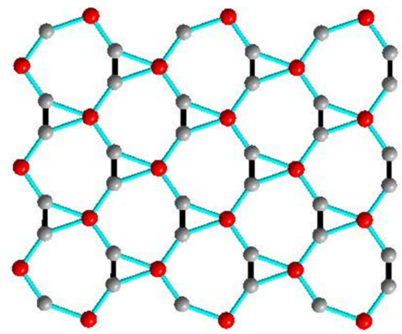
Determine the space group symbol for this 2-d structure by

(a) identifying rotational symmetry points or reflection lines, if they exist;

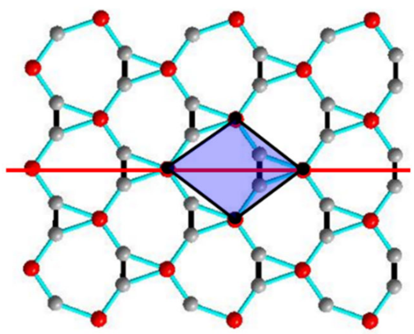
(b) identifying a unit cell and lattice type, placing lattice points at centers of inversion, if they occur;

(c) determining the set of essential symmetry operations and writing their Seitz symbols;

(d) assigning the space group.

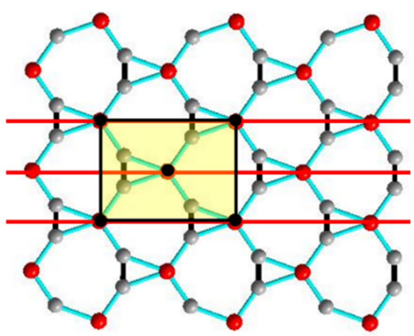


Nickel-Carbon Plane in $CeNiC_2$. C atoms in gray; Ni atoms in red.



Rotational Symmetry: There are no C_n rotation axes but there are reflection planes (**red**), which bisect the C_2-dimers.

Unit Cell: Lattice points can be selected arbitrarily because there are no C_n axes, so we choose the Ni sites. The smallest unit cell is a rhombus with no symmetry restrictions on the angle: $a = b$, $\gamma \neq 90°$ or $120°$.



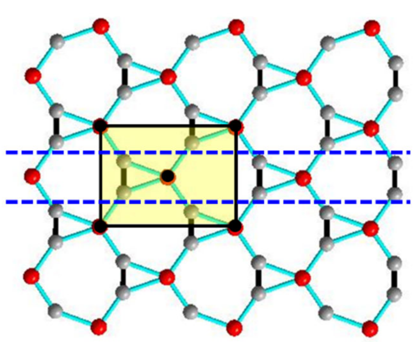
Lattice Type: The primitive unit cell describes the centered-rectangular lattice (c), so a revised unit cell with two lattice points can be identified with a rectangular shape: $a \neq b$, $\gamma = 90°$.

Centered-rectangular:

$$\mathcal{L} = c = \left\{\frac{n_1}{2}\boldsymbol{a} + \frac{n_2}{2}\boldsymbol{b};\ n_1, n_2 = \text{both even or both odd integers}\right\}$$

Essential Symmetry Operations: Reflection planes intersect lattice points, and they are oriented (arbitrarily) perpendicular to $\boldsymbol{a}$ of the rectangular unit cell.

$\mathcal{R} = \{(1|\mathbf{0}), (m_{\boldsymbol{a}}|\mathbf{0})\}$. This set is a group $m = C_s$.



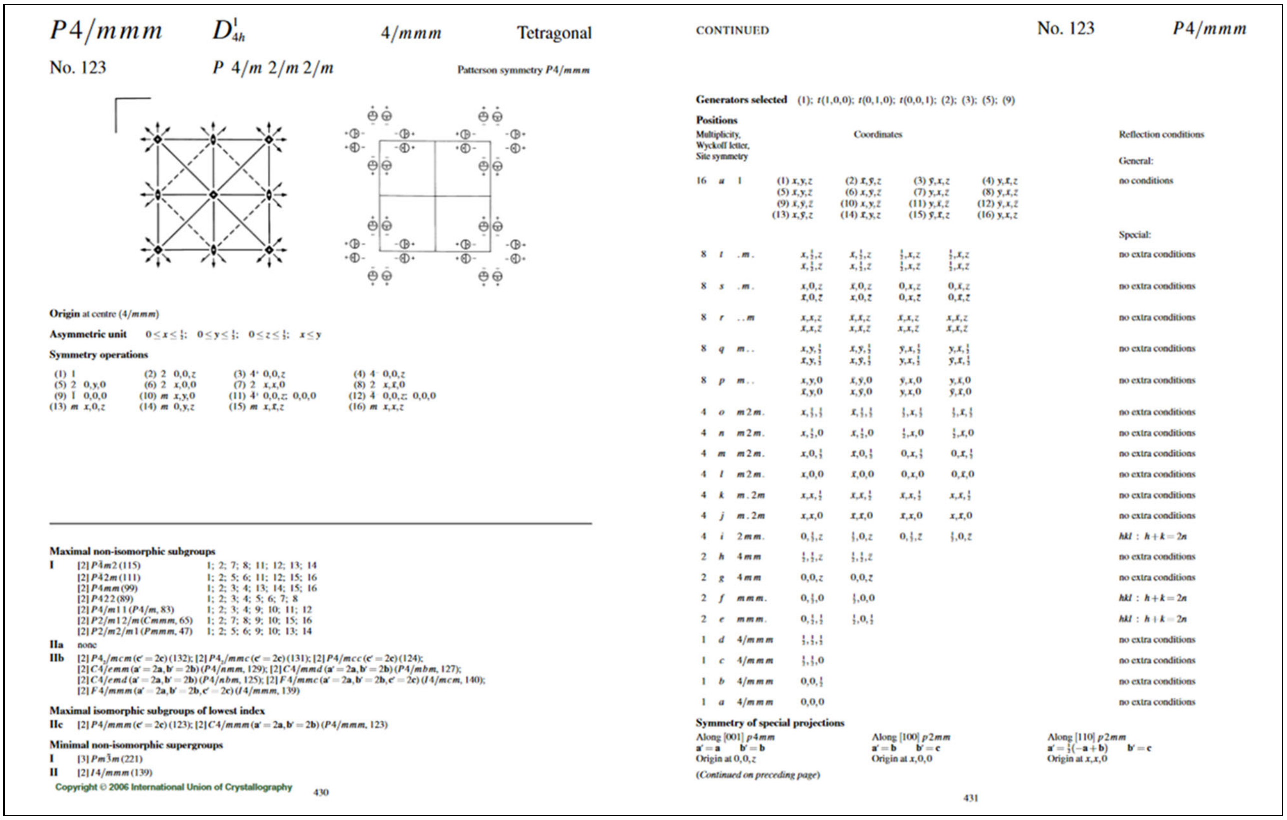
Space Group: ***cm*** $= \mathcal{R} \otimes \mathcal{L}$

Base-centering with reflections generates glide planes:

$$\left(1\middle|\tfrac{a+b}{2}\right)(m_{\boldsymbol{a}}|\mathbf{0}) = \left(m_{\boldsymbol{a}}\middle|\tfrac{a+b}{2}\right) = \left(1\middle|\tfrac{a}{4}\right)\left(m_{\boldsymbol{a}}\middle|\tfrac{b}{2}\right)\left(1\middle|\tfrac{-a}{4}\right)$$

which shows a b-glide intersecting the point (¼, 0). Lattice vectors along $\boldsymbol{a}$ generate other b-glide reflections.

(34) Volume A of the International Tables of Crystallography comprehensively summarizes all structural and diffraction information about space groups that is useful for structure determination and analysis. Each 3-d space group gets at least 2 pages, such as shown for $P4/mmm$:



The first (left) page includes:

(i) the space group symbol in both International and Schönflies notations;
(ii) the point group of the space group;
(iii) the crystal system;
(iv) a graphical display of symmetry operations using different projections of the unit cell;
(v) a listing of essential symmetry operations and lattice origin.

The second (right) page includes:

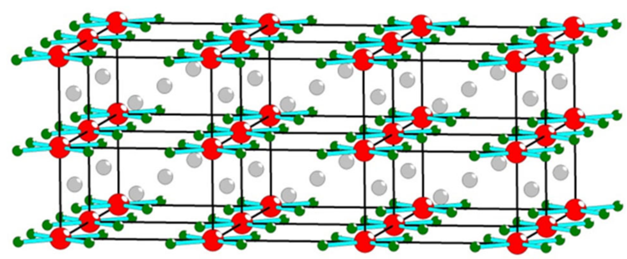
(vi) a list of *generators*, which are the fewest symmetry operations that create the entire space group when combined. This list includes three primitive lattice vectors;
(vii) a list of *Wyckoff sites*, which are sets of equivalent positions in one unit cell. Each Wyckoff site is designated by its *multiplicity* (the number of different positions in one unit cell) and a *letter*, listed in reverse alphabetical order from top-to-bottom (see discussion below);
(viii) conditions for observable intensities in diffraction experiments;
(ix) the symmetry of certain 2-d projections (2-d plane groups).

One of these pages also contains a listing of maximal subgroups and minimal supergroups. For $P4/mmm$, this listing occurs at the bottom of the first (left) page.

The information for the various Wyckoff sites is the most important aspect of this table concerning crystalline structure and stoichiometry. *General positions* (x, y, z) are listed first.

There are no restrictions by symmetry among the coordinates and no symmetry elements intersect these sites. Therefore, general positions have the highest multiplicity, which equals the order of the point group of the space group times the number of lattice points in one unit cell. The remaining sites, called *special positions*, occur with decreasing multiplicity because they fall on certain symmetry elements, i.e., rotation axes or reflection planes. At the bottom of this list is the Wyckoff "a" site, which typically has the highest point symmetry of any site in the crystal. Since $P4/mmm$ is symmorphic, the Wyckoff site $1a$ has point symmetry $4/mmm = \mathcal{D}_{4h}$. However, for some centrosymmetric nonsymmorphic space groups, the sites with highest point symmetry may not coincide with the inversion centers. These particular groups are listed using two settings for the characteristic at the origin $(0,0,0)$: either highest overall point symmetry or highest centrosymmetric point symmetry. One example is $Fd\bar{3}m$, the space group of diamond structures. Setting #1 puts lattice points at locations with $\bar{4}3m = \mathcal{T}_d$ point symmetry (order 24, no inversion, Wyckoff site 8*a*); setting #2 puts lattice points at locations with $\bar{3}m = \mathcal{D}_{3d}$ point symmetry (order 16, inversion, Wyckoff site 16*c*).

As an example of how to use the International Tables, consider K_2PtCl_4. The information listed below the figure provides all the information that is needed to generate the complete crystal structure. The crystal structure is tetragonal with overall point group symmetry $4/mmm$ $(\mathcal{D}_{4h})$, and the unit cell shape is $a = b \neq c$ with angles $\alpha = \beta = \gamma = 90°$. The *asymmetric unit*, which is listed below the lattice parameters, includes each inequivalent atom with its Wyckoff site designation and the fractional coordinates of one site. When every space group operation is applied to the asymmetric unit, the entire crystal structure is generated. For K_2PtCl_4, all atoms occupy special positions: all coordinates for the Pt and K atoms are fixed, but the $4j$ Cl sites "$(x, x, 0)$" allow one free parameter "x", which has an experimental uncertainty. One unit cell of K_2PtCl_4 contains 1 Pt atom at $(0,0,0)$, 2 K atoms at $(0, ½, ½)$ and $(½, 0, ½)$, and 4 Cl atoms at $(0.2324, 0.2324, 0)$, $(-0.2324, -0.2324, 0)$, $(-0.2324, 0.2324, 0)$, and $(0.2324, -0.2324, 0)$, a content that is also the empirical formula. The point symmetries of each site are $4/mmm$ $(\mathcal{D}_{4h})$ for Pt, mmm $(\mathcal{D}_{2h})$ for K, and $m.2m$ $(\mathcal{C}_{2v})$ for Cl. *Why does the point group symbol for the 4j sites contain the dot*? The symmetry elements that intersect the specific site $(x, x, 0)$ are m_c, m_{a-b}, and 2_{a+b}, none of which have axes parallel $\boldsymbol{a}$ or $\boldsymbol{b}$. In the space group symbol $P4/mmm$, the first part "$4/m..$" has its axis along $\boldsymbol{c}$, the second part "$.m.$" has its axes along $\boldsymbol{a}$ and $\boldsymbol{b}$, and the third part "$..m$" has its axes along $(\boldsymbol{a}+\boldsymbol{b})$ and $(\boldsymbol{a}-\boldsymbol{b})$. Therefore, the dot signifies that no symmetry elements with axes parallel to $\boldsymbol{a}$ or $\boldsymbol{b}$ intersect these equivalent sites. Now, to obtain the complete crystal structure, the unit cell parameters provide the length scales and angles so that local structures can be determined. In K_2PtCl_4, each Pt atom is square planar coordinated by 4 Cl atoms at Pt–Cl distances of 2.310(1) Å. Each K atom is surrounded by 8 Cl atoms in a square prism (distorted cube) with a K–Cl distance of 3.240(1) Å.



K_2PtCl_4: $P4/mmm$; a = 7.024 Å, c = 4.147 Å

Pt (red):	1*a* (0, 0, 0)
K (gray):	2*e* (0, ½, ½)
Cl (green):	4*j* (0.2323(1), 0.2323(1), 0)

(35) In 3-d, there are 230 space groups, which are best categorized according to the 7 crystal classes and the 32 crystallographic point groups. In the following, space groups are first listed according to their lattice types, and then symmorphic groups precede nonsymmorphic groups.

Triclinic System (2 space groups)

1 ($\mathcal{C}_1$)	$P1$
$\bar{1}$ ($\mathcal{C}_i$)	$P\bar{1}$

- No special symmetry other than possible inversion centers.
- $P\bar{1}$ is among the most populous space groups for crystals that have been characterized.

Monoclinic System (13 space groups)

2 ($\mathcal{C}_2$)	$P2$	$P2_1$	$C2$			
m ($\mathcal{C}_s$)	Pm	Pc	Cm	Cc		
$2/m$ ($\mathcal{C}_{2h}$)	$P2/m$	$P2_1/m$	$P2/c$	$P2_1/c$	$C2/m$	$C2/c$

- Standard convention assigns the ***b***-axis parallel to the 2-fold axis.
- $P2_1/c$ is among the most populous space groups for crystals that have been studied because it describes the pattern for effective packing of ellipsoids, which roughly model many molecular structures.

Orthorhombic System (59 space groups)

222 ($\mathcal{D}_2$)	$P222$	$P222_1$	$P2_12_12$	$P2_12_12_1$	$C222$	$C222_1$	$F222$
	$I222$	$I2_12_12_1$					
$mm2$ ($\mathcal{C}_{2v}$)	$Pmm2$	$Pmc2_1$	$Pcc2$	$Pma2$	$Pca2_1$	$Pnc2$	$Pmn2_1$
	$Pba2$	$Pna2_1$	$Pnn2$	$Cmm2$	$Cmc2_1$	$Ccc2$	$Amm2$
	$Aem2$	$Ama2$	$Aea2$	$Fmm2$	$Fdd2$	$Imm2$	$Iba2$
	$Ima2$						
mmm ($\mathcal{D}_{2h}$)	$Pmmm$	$Pnnn$	$Pccm$	$Pban$	$Pmma$	$Pnna$	$Pmna$
	$Pcca$	$Pbam$	$Pccn$	$Pbcm$	$Pnnm$	$Pmmn$	$Pbcn$
	$Pbca$	$Pnma$	$Cmmm$	$Cmcm$	$Cmce$	$Cccm$	$Cmme$
	$Ccce$	$Fmmm$	$Fddd$	$Immm$	$Ibam$	$Ibca$	$Imma$

- Assignments of ***a***-, ***b***-, and ***c***-axes can be arbitrary, which leads to other equivalent space group symbols, e.g., $Pm2m$ and $P2mm$ for $Pmm2$.
- A standard orientation of axes is right-handed, so that the direction of ***a*** × ***b*** matches the ***c***-direction; a left-handed orientation would have the direction of ***a*** × ***b*** along the –***c***-direction.
- The symbol "e" in some space groups stands for axial glide reflections along two different directions, e.g., $Ccce$ means that a-glides and b-glides occur with respect to the ***c***-axis.

Tetragonal System (68 space groups)

4 ($\mathcal{C}_4$)	$P4$	$P4_1$	$P4_2$	$P4_3$	$I4$	$I4_1$	
$\bar{4}$ ($\mathcal{S}_4$)	$P\bar{4}$	$I\bar{4}$					
$4/m$ ($\mathcal{C}_{4h}$)	$P4/m$	$P4_2/m$	$P4/n$	$P4_2/n$	$I4/m$	$I4_1/a$	
422 ($\mathcal{D}_4$)	$P422$	$P42_12$	$P4_122$	$P4_12_12$	$P4_222$	$P4_22_12$	$P4_322$
	$P4_32_12$	$I422$	$I4_122$				
$4mm$ ($\mathcal{C}_{4v}$)	$P4mm$	$P4bm$	$P4_2cm$	$P4_2nm$	$P4cc$	$P4nc$	$P4_2mc$
	$P4_2bc$	$I4mm$	$I4cm$	$I4_1md$	$I4_1cd$		
$\bar{4}2m$ ($\mathcal{D}_{2d}$)	$P\bar{4}2m$	$P\bar{4}2c$	$P\bar{4}2_1m$	$P\bar{4}2_1c$	$P\bar{4}m2$	$P\bar{4}c2$	$P\bar{4}b2$
	$P\bar{4}n2$	$I\bar{4}2m$	$I\bar{4}2d$	$I\bar{4}m2$	$I\bar{4}c2$		
$4/mmm$ ($\mathcal{D}_{4h}$)	$P4/mmm$	$P4/mcc$	$P4/nbm$	$P4/nnc$	$P4/mbm$	$P4/mnc$	$P4/nmm$
	$P4/ncc$	$P4_2/mmc$	$P4_2/mcm$	$P4_2/nbc$	$P4_2/nnm$	$P4_2/mbc$	$P4_2/mnm$
	$P4_2/nmc$	$P4_2/ncm$	$I4/mmm$	$I4/mcm$	$I4_1/amd$	$I4_1/acd$	

- The ***c***-axis as parallel to the 4- or $\bar{4}$-axis.
- Space groups with the point group $\mathcal{D}_{2d}$ have two distinct settings according to the orientations of the 2-fold axes and vertical mirror planes with respect to lattice vectors in the ***ab***-plane.

Trigonal System (25 space groups)

3 ($\mathcal{C}_3$)	$P3$	$P3_1$	$P3_2$	$R3$			
$\bar{3}$ ($\mathcal{S}_6$)	$P\bar{3}$	$R\bar{3}$					
32 ($\mathcal{D}_3$)	$P321$	$P3_121$	$P3_221$	$P312$	$P3_112$	$P3_212$	$R32$
$3m$ ($\mathcal{C}_{3v}$)	$P3m1$	$P3c1$	$P31m$	$P31c$	$R3m$	$R3c$	
$\bar{3}m$ ($\mathcal{D}_{3d}$)	$P\bar{3}m1$	$P\bar{3}c1$	$P\bar{3}1m$	$P\bar{3}1c$	$R\bar{3}m$	$R\bar{3}c$	

- The ***c***-axis as parallel to the 3- or $\bar{3}$-axis.
- Space groups with the point groups $\mathcal{D}_{3d}$ and $\mathcal{C}_{3v}$ have two distinct settings according to the orientations of the vertical mirror planes with respect to lattice vectors in the ***ab***-plane.

Hexagonal System (27 space groups)

6 ($\mathcal{C}_6$)	$P6$	$P6_1$	$P6_2$	$P6_3$	$P6_4$	$P6_5$
$\bar{6}$ ($\mathcal{C}_{3h}$)	$P\bar{6}$					
$6/m$ ($\mathcal{C}_{6h}$)	$P6/m$	$P6_3/m$				
622 ($\mathcal{D}_6$)	$P622$	$P6_122$	$P6_222$	$P6_322$	$P6_422$	$P6_522$
$\bar{6}m2$ ($\mathcal{D}_{3h}$)	$P\bar{6}m2$	$P\bar{6}c2$	$P\bar{6}2m$	$P\bar{6}2c$		
$6/mmm$ ($\mathcal{D}_{6h}$)	$P6/mmm$	$P6/mcc$	$P6_3/mcm$	$P6_3/mmc$		

- The ***c***-axis as parallel to the 6- or $\bar{6}$-axis.
- Space groups with the point group $\mathcal{D}_{3h}$ have two distinct settings according to the orientations of the 2-fold axes and the vertical mirror planes with respect to lattice vectors in the ***ab***-plane.
- Hexagonally closed packed (*hcp*) metals adopt the space group $P6_3/mmc$.

Cubic System (36 space groups)

23 ($\mathcal{T}$)	$P23$	$P2_13$	$F23$	$I23$	$I2_13$		
$m\bar{3}$ ($\mathcal{T}_h$)	$Pm\bar{3}$	$Pn\bar{3}$	$Pa\bar{3}$	$Fm\bar{3}$	$Fd\bar{3}$	$Im\bar{3}$	$Ia\bar{3}$
$\bar{4}3m$ ($\mathcal{T}_d$)	$P\bar{4}3m$	$P\bar{4}3n$	$F\bar{4}3m$	$F\bar{4}3c$	$I\bar{4}3m$	$I\bar{4}3d$	
432 ($\mathcal{O}$)	$P432$	$P4_132$	$P4_232$	$P4_332$	$F432$	$F4_132$	$I432$
	$I4_132$						
$m\bar{3}m$ ($\mathcal{O}_h$)	$Pm\bar{3}m$	$Pn\bar{3}n$	$Pm\bar{3}n$	$Pn\bar{3}m$	$Fm\bar{3}m$	$Fm\bar{3}c$	$Fd\bar{3}m$
	$Fd\bar{3}c$	$Im\bar{3}m$	$Ia\bar{3}d$				

- Cubic closed packed (*ccp*) metals adopt the space group $Fm\bar{3}m$.
- Body-centered cubic (*bcc*) metals adopt the space group $Im\bar{3}m$.
- The diamond structure (C, Si, Ge, and Sn) adopts the space group $Fd\bar{3}m$.

The characteristics of the crystallographic point groups influence the characteristics of the corresponding space groups. Among the 230 3-d space groups, 92 are centrosymmetric and 138 are noncentrosymmetric. Among the 138 noncentrosymmetric space groups, there are 65 chiral groups (no improper rotations) and 68 polar groups (no fixed origin). These symmetry characteristics influence the properties of crystals, e.g., chiral crystals can rotate plane polarized light and polar crystals can exhibit spontaneous electrical polarization (ferroelectricity).

<u>Deriving the 230 3-d Space Groups</u>: Space groups are derived systematically from the 32 crystallographic point groups and the corresponding Bravais lattices for each crystal system. The derivations can be accomplished either geometrically, by examining the spatial relationships among symmetry operations, or arithmetically, by considering the allowed combinations of symmetry operations using appropriate lattice algebra. This section illustrates the algebraic approach to obtain the 13 monoclinic space groups.

The general derivation procedure involves determining the rotation-displacement operations of the set of essential symmetry operations for each crystallographic point group that are compatible with translational periodicity of the lattice. The distinct solutions to this problem identify the allowed space groups for each crystallographic point group. This approach can yield redundant solutions arising from specific characteristics of each crystal class. The specific procedure is:

(1) Listing the generators $(R|\alpha\boldsymbol{a} + \beta\boldsymbol{b} + \gamma\boldsymbol{c}) \equiv (R|\alpha\ \beta\ \gamma)$ of the group. The short-hand expression is meant to be spatially efficient. The displacement parameters are set by addition *modulo* 1, which means that $0 \le \alpha, \beta, \gamma < 1$. For example, all primitive lattice vectors are $(1|0\ 0\ 0)$; *C*-centered lattices have lattice vectors $(1|0\ 0\ 0)$ and $(1|½\ ½\ 0)$; and a two-fold screw axis along $\boldsymbol{b}$ and intersecting the origin is $(2_{010}|0\ ½\ 0)$.

(2) Identifying the point group presentation from the generators. This step is equivalent to obtaining the multiplication table for the point group of the space group. Each expression involves a product of operations that provide arithmetical constraints on the displacement parameters $\alpha\ \beta\ \gamma$, whose solutions become the basis for determining the space groups.

(3) Applying the presentation equations to each of the allowed lattice types within the crystal class. The solutions of these equations give the allowed values of the displacement parameters $\alpha\ \beta\ \gamma$ in the generators.

(4) Constructing a table that lists all possible solutions. In some crystal classes, every possible solution does not necessarily lead to a distinct space group, especially for lower symmetry crystal classes for which there are equivalent ways of assigning the unit cell parameters.

(5) Summarizing the distinct space groups for each crystallographic point group.

The monoclinic crystal class is uniaxial and is generated by 2-fold proper or improper rotations with axes along $\boldsymbol{b}$. These space groups are determined from 3 point groups and 2 lattice types, primitive and base-centered. For the direction of the 2-fold axes, allowed base-centered lattices are *A*- and *C*-types; *C*-centering is the standard setting. Furthermore, there are 4 equivalent ways to assign the unit cell vectors that maintain a right-handed coordinate system: $\boldsymbol{abc}$, $\bar{\boldsymbol{c}}\boldsymbol{ba}$, $(\boldsymbol{a}+\boldsymbol{c})\boldsymbol{bc}$, and $\bar{\boldsymbol{c}}\boldsymbol{b}(\boldsymbol{a}+\boldsymbol{c})$.

Point Group $\boldsymbol{C_2} = \mathbf{2}$: This group has order 2, containing a 2-fold rotation axis.

Generator: $(2_{010}|0\ \beta\ 0)$: set the 2_{010} axes to intersect lattice points.
Presentation: $(2_{010}|0\ \beta\ 0)^2 = (1|0\ 2\beta\ 0)$ = lattice translation: sets allowed values for β.

Solutions: Determine possible values of one parameter: β.

P-lattice: $(1|0\ 2\beta\ 0) = (1|0\ 0\ 0)$. $\beta = 0, ½$.
C-lattice: $(1|0\ 2\beta\ 0) = (1|0\ 0\ 0)$. $\beta = 0, ½$.

Each lattice type has two possible solutions:

β	Lattice Type	Operations		Space Group
0	Primitive	$(2_{010}|0\ 0\ 0)$	2-fold $(0\ y\ 0)$	$P2$
	C-centered	$(2_{010}|0\ 0\ 0)$ $(2_{010}|½\ ½\ 0)$	2-fold $(0\ y\ 0)$ 2_1-screw $(¼\ y\ 0)$	$C2$
½	Primitive	$(2_{010}|0\ ½\ 0)$	2_1-screw $(0\ y\ 0)$	$P2_1$
	C-centered	$(2_{010}|0\ ½\ 0)$ $(2_{010}|½\ 0\ 0)$	2_1-screw $(0\ y\ 0)$ 2-fold $(¼\ y\ 0)$	$C2_1 = C2$

C-centering generates 2_1-screw axes from 2-fold rotation axes along $\boldsymbol{b}$ and vice versa. Therefore, the two possible solutions for the *C*-centered monoclinic lattice give the same space groups and differ only by the positions of the two types of rotation axes.

There are 3 distinct space groups: $P2, P2_1$, and $C2$.

Point Group $\boldsymbol{C_s} = \boldsymbol{m}$: This group has order 2, containing a reflection plane.

Generator: $(m_{010}|\alpha\ 0\ \gamma)$: set the m_{010} planes to intersect lattice points.
Presentation: $(m_{010}|\alpha\ 0\ \gamma)^2 = (1|2\alpha\ 0\ 2\gamma)$ = lattice translation: sets allowed values for α, γ.

Solutions: Determine possible values of two parameters: α and γ.

P-lattice: $(1|2\alpha\ 0\ 2\gamma) = (1|0\ 0\ 0)$. $\alpha = 0, ½;\ \gamma = 0, ½$.
C-lattice: $(1|2\alpha\ 0\ 2\gamma) = (1|0\ 0\ 0)$. $\alpha = 0, ½;\ \gamma = 0, ½$.

Each lattice type has four possible solutions because there is no relationship between α and γ.

α γ	**Lattice Type**	**Operations**		**Space Group**
0 0	Primitive	$(m_{010}\|0\ 0\ 0)$	mirror ($y = 0$)	Pm
	C-centered	$(m_{010}\|0\ 0\ 0)$ $(m_{010}\|½\ ½\ 0)$	mirror ($y = 0$) a-glide ($y = ¼$)	Cm
0 ½	Primitive	$(m_{010}\|0\ 0\ ½)$	c-glide ($y = 0$)	Pc
	C-centered	$(m_{010}\|0\ 0\ ½)$ $(m_{010}\|½\ ½\ ½)$	c-glide ($y = 0$) n-glide ($y = ¼$)	Cc
½ 0	Primitive	$(m_{010}\|½\ 0\ 0)$	a-glide ($y = 0$)	$Pa = Pc$ (lattice vectors: $\boldsymbol{c\bar{b}a}$)
	C-centered	$(m_{010}\|½\ 0\ 0)$ $(m_{010}\|0\ ½\ 0)$	a-glide ($y = 0$) mirror ($y = ¼$)	$Ca = Cm$
½ ½	Primitive	$(m_{010}\|½\ 0\ ½)$	n-glide ($y = 0$)	$Pn = Pc$ (lattice vectors: $\boldsymbol{c\bar{b}}(\boldsymbol{a} + \boldsymbol{c})$)
	C-centered	$(m_{010}\|½\ 0\ ½)$ $(m_{010}\|0\ ½\ ½)$	n-glide ($y = 0$) c-glide ($y = ¼$)	$Cn = Cc$

For primitive lattices, two of four possible solutions are redundant arising from the different equivalent assignments of unit cell settings (lattice vectors).

C-centering generates a-glides and n-glides, respectively, from mirrors and c-glides, and vice versa. Therefore, two of the four possible solutions are redundant and differ only by the positions of the two types of reflection planes.

There are 4 distinct space groups: Pm, Pc, Cm and Cc.

Point Group $\boldsymbol{C_{2h} = 2/m}$: The holohedral and centrosymmetric group has order 4 with 2-fold rotation axes and orthogonal reflection planes.

<u>Generators</u>: $(2_{010}|0\ \beta_1\ 0)$: set the 2_{010} axes to intersect lattice points;
$(m_{010}|\alpha_2\ 0\ \gamma_2)$: set the m_{010} planes to intersect lattice points.

<u>Presentation</u>: $(2_{010}|0\ \beta_1\ 0)^2 = (1|0\ 2\beta_1\ 0)$ = lattice translation: sets allowed values for β_1.
$(m_{010}|\alpha_2\ 0\ \gamma_2)^2 = (1|2\alpha_2\ 0\ 2\gamma_2)$ = lattice translation: sets allowed values for α_2, γ_2.
$\left((m_{010}|\alpha_2\ 0\ \gamma_2)(2_{010}|0\ \beta_1\ 0)\right)^2 = (\bar{1}|\alpha_2\ (-\beta_1)\ \gamma_2)^2 = (1|0\ 0\ 0)$: no other constraints.

<u>Solutions</u>: Determine possible values of three parameters: β_1, α_2, γ_2.

P-lattice: $(1|0\ 2\beta_1\ 0) = (1|0\ 0\ 0)$; β_1 = 0, ½;
$(1|2\alpha_2\ 0\ 2\gamma_2) = (1|0\ 0\ 0)$. α_2 = 0, ½; γ_2 = 0, ½.

C-lattice: $(1|0\ 2\beta_1\ 0) = (1|0\ 0\ 0)$; β_1 = 0, ½;
$(1|2\alpha_2\ 0\ 2\gamma_2) = (1|0\ 0\ 0)$. α_2 = 0, ½; γ_2 = 0, ½.

Each lattice type has eight possible solutions.

$\beta_1\ \alpha_2\ \gamma_2$	Lattice Type	Operations	Space Group
0 0 0	Primitive	$(2_{010}|0\ 0\ 0)$ 2-fold $(0\ y\ 0)$ $(m_{010}|0\ 0\ 0)$ mirror $(y = 0)$	$P2/m$
	C-centered	$(2_{010}|0\ 0\ 0)$ 2-fold $(0\ y\ 0)$ $(2_{010}|½\ ½\ 0)$ 2_1-screw $(¼\ y\ 0)$ $(m_{010}|0\ 0\ 0)$ mirror $(y = 0)$ $(m_{010}|½\ ½\ 0)$ a-glide $(y = ¼)$	$C2/m$
½ 0 0	Primitive	$(2_{010}|0\ ½\ 0)$ 2_1-screw $(0\ y\ 0)$ $(m_{010}|0\ 0\ 0)$ mirror $(y = 0)$	$P2_1/m$
	C-centered	$(2_{010}|0\ ½\ 0)$ 2_1-screw $(0\ y\ 0)$ $(2_{010}|½\ 0\ 0)$ 2-fold $(¼\ y\ 0)$ $(m_{010}|0\ 0\ 0)$ mirror $(y = 0)$ $(m_{010}|½\ ½\ 0)$ a-glide $(y = ¼)$	$C2_1/m = C2/m$
0 0 ½	Primitive	$(2_{010}|0\ 0\ 0)$ 2-fold $(0\ y\ 0)$ $(m_{010}|0\ 0\ ½)$ c-glide $(y = 0)$	$P2/c$
	C-centered	$(2_{010}|0\ 0\ 0)$ 2-fold $(0\ y\ 0)$ $(2_{010}|½\ ½\ 0)$ 2_1-screw $(¼\ y\ 0)$ $(m_{010}|0\ 0\ ½)$ c-glide $(y = 0)$ $(m_{010}|½\ ½\ ½)$ n-glide $(y = ¼)$	$C2/c$
½ 0 ½	Primitive	$(2_{010}|0\ ½\ 0)$ 2_1-screw $(0\ y\ 0)$ $(m_{010}|0\ 0\ ½)$ c-glide $(y = 0)$	$P2_1/c$
	C-centered	$(2_{010}|0\ ½\ 0)$ 2_1-screw $(0\ y\ 0)$ $(2_{010}|½\ 0\ 0)$ 2-fold $(¼\ y\ 0)$ $(m_{010}|0\ 0\ ½)$ c-glide $(y = 0)$ $(m_{010}|½\ ½\ ½)$ n-glide $(y = ¼)$	$C2_1/c = C2/c$
0 ½ 0	Primitive	$(2_{010}|0\ 0\ 0)$ 2-fold $(0\ y\ 0)$ $(m_{010}|½\ 0\ 0)$ a-glide $(y = 0)$	$P2/a = P2/c$ (lattice vectors: $\boldsymbol{c\bar{b}a}$)
	C-centered	$(2_{010}|0\ 0\ 0)$ 2-fold $(0\ y\ 0)$ $(2_{010}|½\ ½\ 0)$ 2_1-screw $(¼\ y\ 0)$ $(m_{010}|½\ 0\ 0)$ a-glide $(y = 0)$ $(m_{010}|0\ ½\ 0)$ mirror $(y = ¼)$	$C2/a = C2/m$

$\beta_1\ \alpha_2\ \gamma_2$	Lattice Type	Operations		Space Group
½ ½ 0	Primitive	$(2_{010}\|0\ ½\ 0)$ $(m_{010}\|½\ 0\ 0)$	2_1-screw $(0\ y\ 0)$ a-glide $(y = 0)$	$P2_1/a = P2_1/c$ (lattice vectors: $\boldsymbol{c\bar{b}a}$)
	C-centered	$(2_{010}\|0\ ½\ 0)$ $(2_{010}\|½\ 0\ 0)$ $(m_{010}\|½\ 0\ 0)$ $(m_{010}\|0\ ½\ 0)$	2_1-screw $(0\ y\ 0)$ 2-fold $(¼\ y\ 0)$ a-glide $(y = 0)$ mirror $(y = ¼)$	$C2_1/a = C2/m$
0 ½ ½	Primitive	$(2_{010}\|0\ 0\ 0)$ $(m_{010}\|½\ 0\ ½)$	2-fold $(0\ y\ 0)$ n-glide $(y = 0)$	$P2/n = P2/c$ (lattice vectors: $\boldsymbol{c\bar{b}}(\boldsymbol{a}+\boldsymbol{c})$)
	C-centered	$(2_{010}\|0\ 0\ 0)$ $(2_{010}\|½\ ½\ 0)$ $(m_{010}\|½\ 0\ ½)$ $(m_{010}\|0\ ½\ ½)$	2-fold $(0\ y\ 0)$ 2_1-screw $(¼\ y\ 0)$ n-glide $(y = 0)$ c-glide $(y = ¼)$	$C2/n = C2/c$
½ ½ ½	Primitive	$(2_{010}\|0\ ½\ 0)$ $(m_{010}\|½\ 0\ ½)$	2_1-screw $(0\ y\ 0)$ n-glide $(y = 0)$	$P2_1/n = P2_1/c$ (lattice vectors: $\boldsymbol{c\bar{b}}(\boldsymbol{a}+\boldsymbol{c})$)
	C-centered	$(2_{010}\|0\ ½\ 0)$ $(2_{010}\|½\ 0\ 0)$ $(m_{010}\|½\ 0\ ½)$ $(m_{010}\|0\ ½\ ½)$	2_1-screw $(0\ y\ 0)$ 2-fold $(¼\ y\ 0)$ n-glide $(y = 0)$ c-glide $(y = ¼)$	$C2_1/n = C2/c$

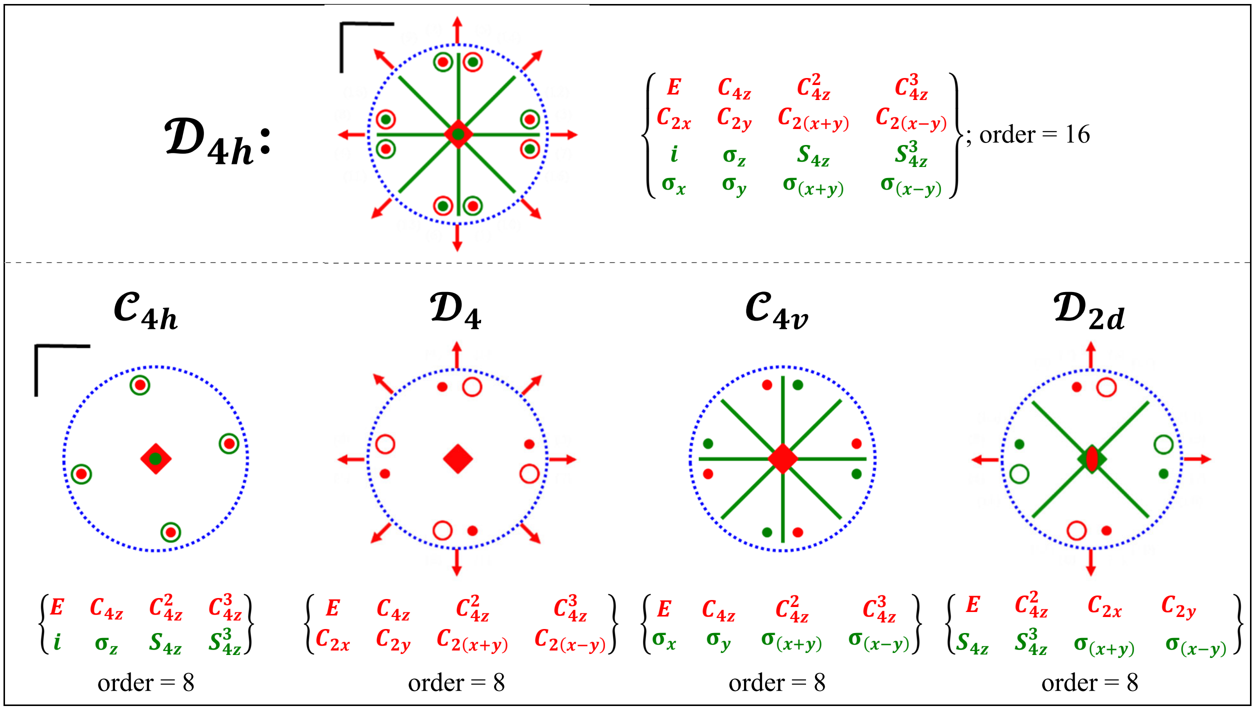
For primitive lattices, four of the eight possible space groups are redundant solutions arising from the different equivalent assignments of unit cell settings (lattice vectors).

C-centering generates a-glides and n-glides, respectively, from mirrors and c-glides, and vice versa. Therefore, two of the eight possible solutions are redundant and differ only by the positions of the two types of reflection planes.

There are 6 distinct space groups: $P2/m, P2_1/m, P2/c, P2_1/c, C2/m$ and $C2/c$.

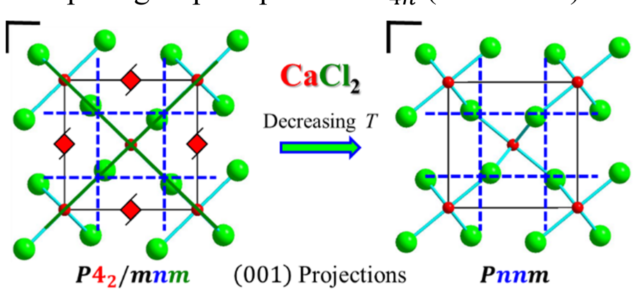
Summary: There are 13 monoclinic space groups. The arithmetic solution strategy generates other equivalent solutions. For primitive lattices, these other solutions arise because of the different equivalent ways to assign lattice vectors while retaining a right-handed perspective. For C-centered lattices, equivalence arises from the types of rotation-translation operations generated by C-centering.

(36-37) Group-Subgroup Relationships: A useful section for each space group in the International Tables lists certain subgroups and supergroups, which can be helpful for studying solid-solid phase transitions. A set $\mathcal{S}$ is a subgroup of $\mathcal{G}$ if all members of $\mathcal{S}$ are contained in $\mathcal{G}$. $\mathcal{S}$ is a *proper subgroup* if $\mathcal{G}$ contains members that are not in $\mathcal{S}$. $\mathcal{S}$ is a *maximal subgroup* of $\mathcal{G}$ if there are no other subgroups of $\mathcal{G}$ for which $\mathcal{S}$ is also a proper subgroup. This often occurs by removing inversion, a reflection, or a C_2 rotation from $\mathcal{G}$ so that most maximal subgroups $\mathcal{S}$ have one-half the number of operations of the original group $\mathcal{G}$. Among point groups, consider $\mathcal{D}_{4h}$ with order 16 consisting of 8 proper and 8 improper rotations. Each of the 4 groups in the second row has order 8 and is a maximal subgroup of $\mathcal{D}_{4h}$. Are there any other maximal subgroups of $\mathcal{D}_{4h}$?



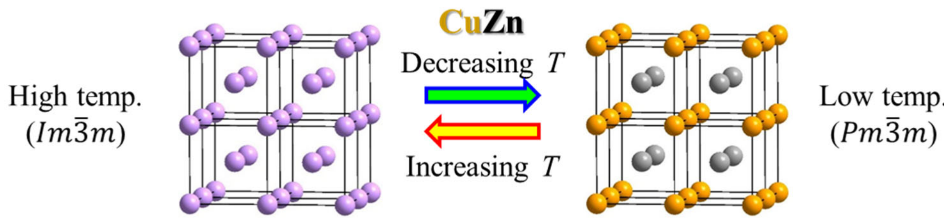
Subgroups of space groups arise by losing translations or rotations, leading to two major types of maximal subgroups:

Type I: ***Translation equivalent*** ("*Translationengleiche*") subgroups retain all translations, but they lose some rotational symmetry. Changing the point group may or may not retain the crystal system. One example is $CaCl_2$, which adopts a high-temperature form with space group $P4_2/mnm$ and a low-temperature form with space group $Pnnm$. In the low-temperature form, the 4_2-screw and reflections $..m$ are lost, but the glide planes $.n.$ and reflections $/m$ perpendicular to the original 4_2-axis are retained. As a result, the point group of the space group drops from $\mathcal{D}_{4h}$ (order = 16) to $\mathcal{D}_{2h}$ (order = 8).

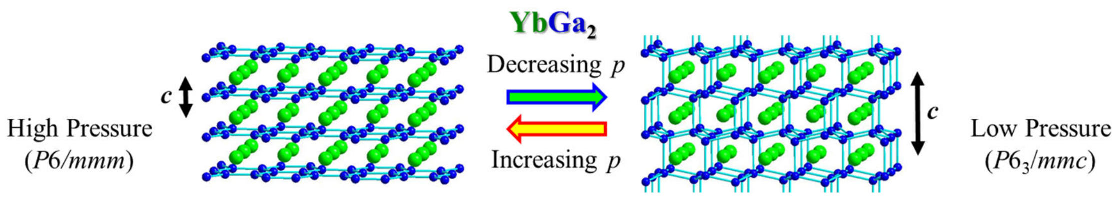


<u>Type II</u>: ***Class equivalent*** ("*klassengleiche*") subgroups preserve the point group of the space group, but they lose certain lattice translations. There are three subdivisions of this type:

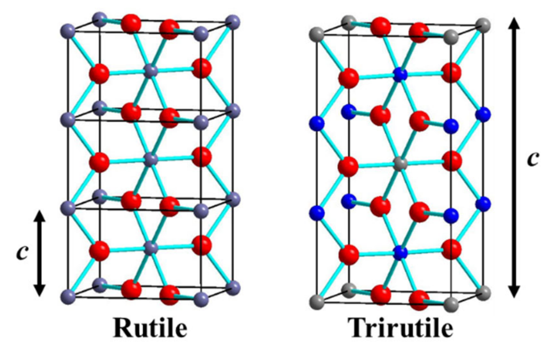
(IIa) If a space group involves a centered lattice, then this subgroup arises by removing all lattice centering translations. One example occurs during the order-disorder transition of β-CuZn. The high-temperature form is completely disordered Cu and Zn in a BCC-packing, space group $Im\bar{3}m$, whereas the low-temperature form exhibits ordering of Cu and Zn atoms, observed by neutron diffraction, space group $Pm\bar{3}m$.



(IIb) This subgroup differs from the original space group and the number of atoms in the unit cell of the subgroup is an integral multiple of those in the unit cell of the original space group. For example, $YbGa_2$ at ambient pressure is hexagonal $P6_3/mmc$. On increasing pressure, it transforms to a structure in which the ***c***-axis has approximately halved, space group $P6/mmm$. Both space groups have the same point group $\mathcal{D}_{6h} = 6/mmm$, but the high-pressure form has twice as many lattice translations as the ambient-pressure form.



(IIc) The space group and its subgroup are the same group, but some translations of the original group have been lost. The space group $P4_2/mnm$ has only Type IIc klassengleiche subgroups, an example of which is the trirutile structure of WV_2O_6 in which only threefold multiples of ***c*** of the rutile structure are retained. Ordering of W and V atoms create the subgroup.



Solid-solid phase transitions often involve both translation equivalent and class equivalent components simultaneously. These kinds of phase transitions may follow different possible pathways and belong to *first-order* phase transitions. On the other hand, continuous symmetry-breaking phase transitions, often called *second-order*, may be analyzed using Landau theory and belong to a single irreducible representation of the space group. Such transitions occur according to a single pathway, by either losing translations (class equivalent) or rotations (translation equivalent).