3. Space Groups

Space lattices

Lattice points are all equivalent by translational symmetry. We start with a *primitive* lattice, having points at $\mathbf{r}_{uvw} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$, where $(u, v, w) \in \not\subset$. So lattice points exist at (0,0,0) and all equivalent positions. If we have a lattice point at (x, y, z), then we also have a lattice point at $(x + u, y + v, z + w)$.

Suppose two lattice points exist at (x_1, y_1, z_1) and (x_2, y_2, z_2). If (x, y, z) is a lattice point, then $(x, y, z) + (x_2 - x_1, y_2 - y_1, z_2 - z_1)$ is also a lattice point. But this does not imply that for all (x, y, z) representing lattice points, the values of (x, y, z) are integers. In particular, it is often useful to represent some of them by half integers.

A primitive cell has lattice points at $(0,0,0)$. Centered cells have additional lattice points.

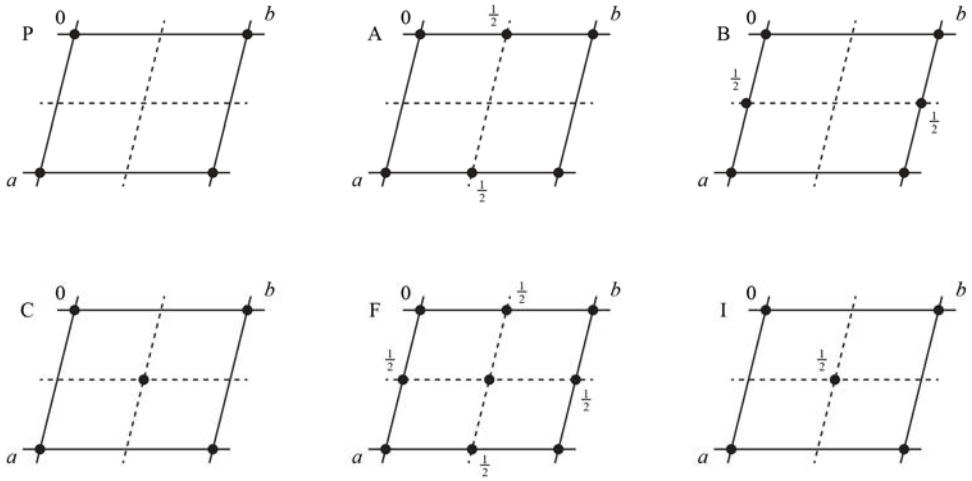
An A-centered cell also has points at $(0, \frac{1}{2}, \frac{1}{2})$. (Center of the A face.)

A B-centered cell also has points at $(\frac{1}{2}, 0, \frac{1}{2})$. (Center of the B face.)

A C-centered cell also has points at $(\frac{1}{2}, \frac{1}{2}, 0)$. (Center of the C face.)

An F (face)-centered cell also has points at $(0, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, 0, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, 0)$. (Centers of all three faces.)

An I (body)-centered cell also has points at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. (Center point of the unit cell.)



Observations

I. Suppose a cell is both A- and B-centered. The lattice points exist at

$P_1 : (0,0,0)$, $P_2 : (0, \frac{1}{2}, \frac{1}{2})$, and $P_3 : (\frac{1}{2}, 0, \frac{1}{2})$

and equivalent positions. P_1 and P_2 form a *lattice row*. P_3 must lie on a parallel lattice row. So we must also have a point at

$$P_4 = P_3 + (P_2 - P_1) = (\tfrac{1}{2}, \tfrac{1}{2}, 1) \rightarrow (\tfrac{1}{2}, \tfrac{1}{2}, 0)$$

[We can always translate back to the the range $(0 \le x < 1, 0 \le y < 1, 0 \le z < 1)$.] P_4 is a C-centered lattice point, so the lattice is F-centered. In general, a lattice may be either A-, B-, C-, or F-centered, but it cannot more than one of these types of centering simultaneously.

II. Suppose a cell is both I- and F-centered. Lattice points exist at

$$P_1 : (0,0,0),\ P_2 : (\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}),\ P_3 : (0,\tfrac{1}{2},\tfrac{1}{2}),\ P_4 : (\tfrac{1}{2},0,\tfrac{1}{2}),\ P_5 : (\tfrac{1}{2},\tfrac{1}{2},0)$$

and equivalent positions. P_2 and P_3 form a lattice row. P_1 must lie on a parallel lattice row, so we also have a point at

$$P_6 = P_1 + (P_2 - P_3) = (\tfrac{1}{2},0,0)$$

Likewise, we have points at

$$P_7 = P_1 + (P_2 - P_4) = (0,\tfrac{1}{2},0) \text{ and } P_8 = P_1 + (P_2 - P_5) = (0,0,\tfrac{1}{2})$$

These points can be described by a smaller P lattice with lattice vectors

$$\mathbf{a}' = \mathbf{a}/2,\ \mathbf{b}' = \mathbf{b}/2,\ \mathbf{c}' = \mathbf{c}/2$$

So a lattice cannot be both F- and I- centered.

III. Suppose a cell is both I- and C-centered.

Lattice points exist at

$$P_1 : (0,0,0),\ P_2 : (\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}),\ P_3 : (\tfrac{1}{2},\tfrac{1}{2},0)$$

and equivalent positions. P_2 and P_3 form a lattice row. P_1 must lie on a parallel lattice row, so we also have a point at

$$P_4 = P_1 + (P_2 - P_3) = (0,0,\tfrac{1}{2})$$

These points can be described by a smaller C-centered lattice with vectors

$$\mathbf{a}' = \mathbf{a},\ \mathbf{b}' = \mathbf{b},\ \mathbf{c}' = \mathbf{c}/2$$

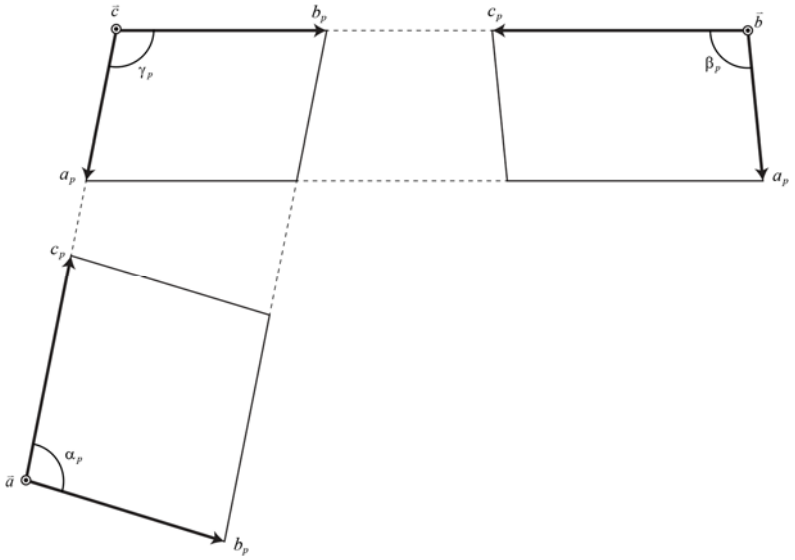
So a lattice cannot be both I- and C- centered.

Seven crystal systems

We can classify the unit-cell geometries by the point groups with which they are compatible.

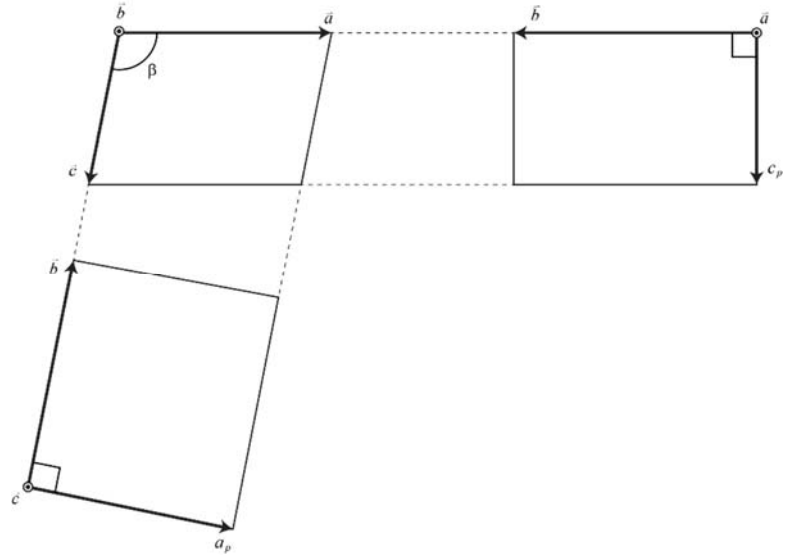
1. Triclinic

Compatible with point groups 1 and $\bar{1}$. The unit cell may have at most center of symmetry (inversion center). The lattice parameter ratios $a:b:c$ and angles α,β,γ are unrestricted.



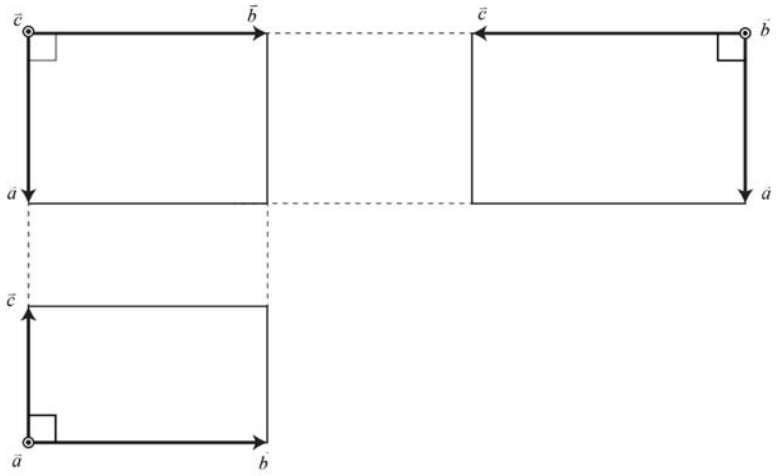
2. Monoclinic

Compatible with point groups 2, m, and $2/\mathrm{m}$. The lattice parameter ratios $a{:}b{:}c$ and β are unrestricted, with $\alpha = \gamma = 90°$.



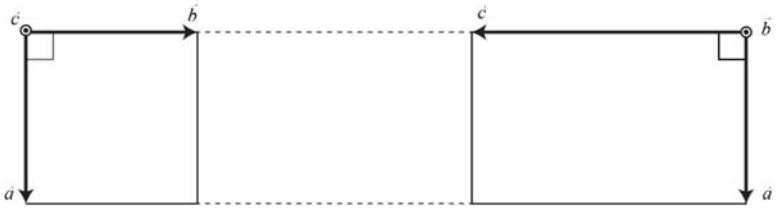
3. Orthorhombic

Compatible with point groups 222, mm2, and mmm. The lattice parameter ratios $a{:}b{:}c$ are unrestricted, with $\alpha = \beta = \gamma = 90°$.



4. Tetragonal

Compatible with point groups 4, $\bar{4}$, $4/\mathrm{m}$, 422, 4mm, $\bar{4}2\mathrm{m}$, and $4/\mathrm{mmm}$. The lattice parameters ratio $a{:}c$ is unrestricted, with $a = b$ and $\alpha = \beta = \gamma = 90°$.



5. Cubic

Compatible with point groups 23, $\mathrm{m}\bar{3}$, 432, $\bar{4}3\mathrm{m}$, and $\mathrm{m}\bar{3}\mathrm{m}$. The lattice parameters satisfy $a = b = c$, with $\alpha = \beta = \gamma = 90°$.

6. Hexagonal

Compatible with point groups 6, $\bar{6}$, $6/\mathrm{m}$, 622, 6mm, $\bar{6}2\mathrm{m}$, $6/\mathrm{mmm}$. The lattice parameters ratio $a{:}c$ is unrestricted, with $a = b$, $\alpha = \beta = 90°$, and $\gamma = 120°$. The 6 or $\bar{6}$ is along $\mathbf{c}$. We sometimes define a fourth in-plane axis $\mathbf{d} = -(\mathbf{a} + \mathbf{b})$, which is symmetric w.r.t. $\mathbf{a}$ and $\mathbf{b}$.

7. Trigonal

Compatible with point groups 3, $\bar{3}$, 32, 3m, and $\bar{3}\mathrm{m}$. The angle lattice parameters satisfy $a = b = c$, with $\alpha = \beta = \gamma \neq 90°$.

The trigonal unit cell is often referenced using an hexagonal lattice with

$\mathbf{a}' = \mathbf{a} - \mathbf{b}$, $\mathbf{b}' = \mathbf{b} - \mathbf{c}$, ($\mathbf{d}' = \mathbf{c} - \mathbf{a}$), and $\mathbf{c} = \mathbf{a} + \mathbf{b} + \mathbf{c}$

Bravais lattices

1. Triclinic

A triclinic lattice can always be described by a P cell. (There is no advantage to using a centered cell.)

2. Monoclinic

Suppose we have an C-centered monoclinic cell. This cannot be described by a P cell without changing the symmetry (e.g., $\mathbf{a}' = (\mathbf{a} + \mathbf{b})/2$, $\mathbf{b}' = (-\mathbf{a} + \mathbf{b})/2$). The assignments of $\mathbf{a}$ and $\mathbf{c}$ are arbitrary, so we have no need for both A- and C- centering. We will only use C-centered monoclinic here.

Suppose a monoclinic cell is B-centered. The lengths of a and c and the angle beta are arbitrary, so we can always pick a smaller, P cell (e.g., $\mathbf{a}' = \mathbf{a}$, $\mathbf{b}' = \mathbf{b}$, $\mathbf{c}' = (\mathbf{a} + \mathbf{c})/2$). Thus, there is no need to have a B-centered monoclinic cell.

Suppose a monoclinic cell is I-centered. We can choose the basis $\mathbf{a}' = (\mathbf{a} + \mathbf{c})/2$, $\mathbf{b}' = \mathbf{b}$, $\mathbf{c}' = \mathbf{c}$, which is C-centered. So an I monoclinic cell can always be represented by a C monoclinic cell. Thus we have no need for I-centered monoclinic.

Suppose a monoclinic cell is F-centered. We can always pick a smaller, C-centered cell (e.g., $\mathbf{a}' = \mathbf{a}$, $\mathbf{b}' = \mathbf{b}$, $\mathbf{c}' = (\mathbf{a} + \mathbf{c})/2$). Thus, there is no need to have a F-centered monoclinic cell.

The only types of monoclinic cells are P and C.

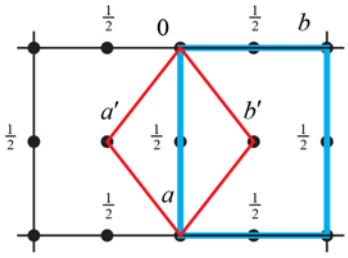
3. Orthorhombic

An I-centered orthorhombic cell is not interchangeable with a P orthorhombic cell.

An I-centered orthorhombic cell is not interchangeable with a C-centered orthorhombic cell.

An F-centered orthorhombic cell is not interchangeable with a P orthorhombic cell.

Suppose an orthorhombic cell is F-centered. A smaller, C-centered cell, defined by $\mathbf{a}' = (\mathbf{a} - \mathbf{b})/2$, $\mathbf{b}' = (\mathbf{a} + \mathbf{b})/2$, $\mathbf{c}' = \mathbf{c}$, is not orthorhombic. So we cannot change an F-centered orthorhombic cell to a C-centered orthorhombic cell.



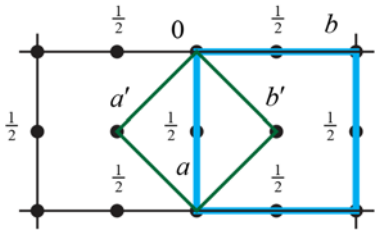
An orthorhombic cell can be P, C, F, or I.

4. Tetragonal

Because of the four-fold symmetry, an A-centered tetragonal cell must also be B-centered. Therefore, it must also be an F-centered cell.

Consider an F-centered tetragonal cell. The smaller cell $\mathbf{a}' = (\mathbf{a} - \mathbf{b})/2$, $\mathbf{b}' = (\mathbf{a} + \mathbf{b})/2$, $\mathbf{c}' = \mathbf{c}$ is I-centered tetragonal. So an F-centered tetragonal can be represented by an I-centered tetragonal.

An I-centered tetragonal cannot be transformed into a P tetragonal. So we have only P and I tetragonal cells.



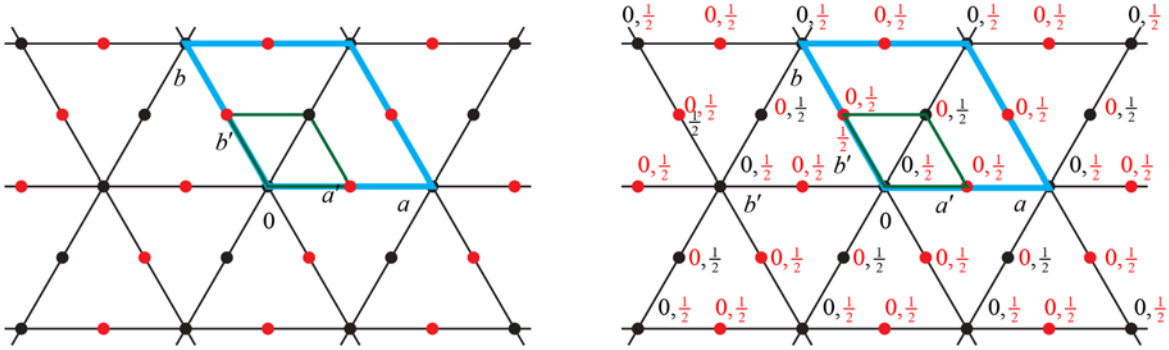
5. Cubic

The threefold symmetry along the diagonal of a cube ensures that the three adjacent faces of the cube are symmetry equivalent. So we cannot have A-, B-, or C-centering, but we can have F-centered cubic, which cannot be transformed to a P cubic cell. The I-centered cubic cell is also not interchangeable with a P cubic. So cubic P, F, and I cells represent unique Bravais lattice types.

6. Hexagonal

The only type of hexagonal Bravais lattice is P. Consider a C-centered hexagonal lattice. Additional lattice points are needed to preserve the six-fold symmetry about c. So we can define a P hexagonal cell with lattice vectors $\mathbf{a}' = \mathbf{a}/2$, $\mathbf{b}' = \mathbf{b}/2$, $\mathbf{c}' = \mathbf{c}$.

Likewise, an I-centered hexagonal lattice requires additional lattice points, which form a P hexagonal cell with lattice vectors $\mathbf{a}' = \mathbf{a}/2$, $\mathbf{b}' = \mathbf{b}/2$, $\mathbf{c}' = \mathbf{c}/2$. The same reasoning applies for an F-centered cell.



7. Trigonal

As for a cube, the threefold symmetry among the diagonal of a rhombohedron ensures that we cannot have A-, B-, or C-centering. If we try F-centering, we can define a P trigonal cell with basis vectors $\mathbf{a}' = (\mathbf{b} + \mathbf{c})/2$, $\mathbf{b}' = (\mathbf{a} + \mathbf{c})/2$, $\mathbf{c}' = (\mathbf{a} + \mathbf{b})/2$. For an I-centered trigonal cell, we can find a P trigonal cell with basis vectors $\mathbf{a}' = (-\mathbf{a} + \mathbf{b} + \mathbf{c})/2$, $\mathbf{b}' = (\mathbf{a} - \mathbf{b} + \mathbf{c})/2$, $\mathbf{c}' = (\mathbf{a} + \mathbf{b} - \mathbf{c})/2$. So trigonal only occurs as a P cell. Oddly, the trigonal P cell is referred to as an R cell.

How many Bravais lattices did we find?

Triclinic - P (1)

Monoclinic - P, C (2)

Orthorhombic - P, C, I , F (4)

Tetragonal - P, I (2)

Cubic - P, F, I (3)

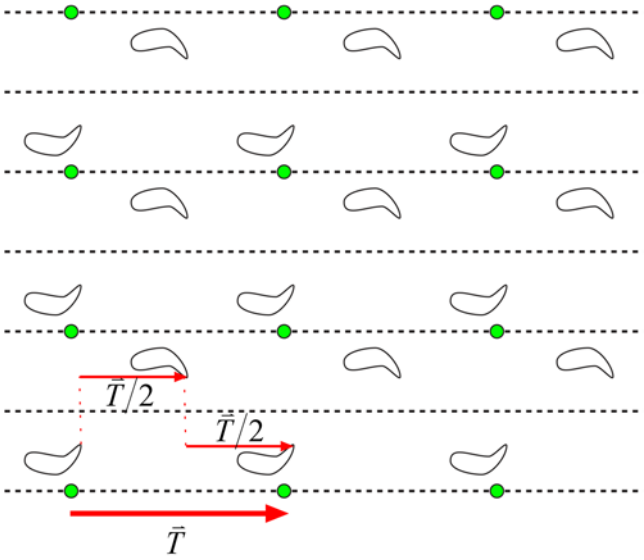
Hexagonal - P (1)

Trigonal - R (1)

Total: 14 Bravais lattices

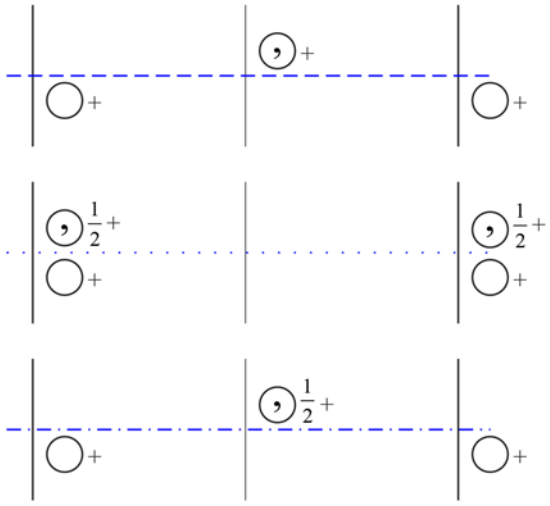
Glide planes

A glide plane exists when a reflection across the plane, combined with a translation parallel to the plane, leaves the crystal unchanged.

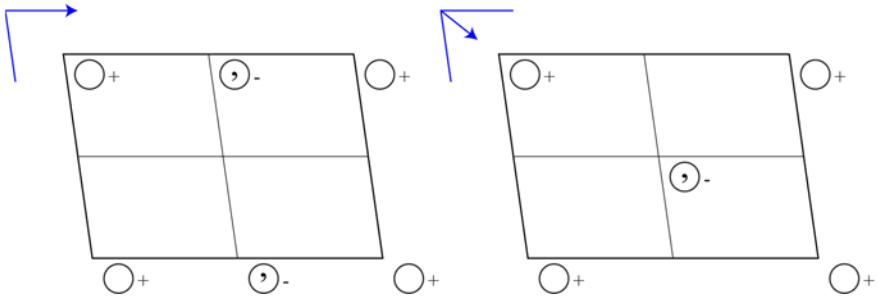


Say the translation vector associated with glide is $\mathbf{t}$. If we apply the glide operation twice, the total translation is $2\mathbf{t} = p\mathbf{T}$, where p is an integer and $\mathbf{T}$ is a translational symmetry lattice vector for the crystal. So $\mathbf{t} = (p/2)\cdot\mathbf{T}$, i.e., a half integer times $\mathbf{T}$. If $p = 0$, the operation is just a reflection, and the glide plane is really a mirror plane. If $p = 1$, we have a glide plane with translation vector $\mathbf{t} = \mathbf{T}/2$. If $p = 2$, we have $\mathbf{t} = \mathbf{T}$, which is the same as $\mathbf{t} = \mathbf{0}$, by translation symmetry. By that reasoning, $p = 3$ is the same as $p = 1$. So glide planes always involve translations by $\mathbf{T}/2$, where $\mathbf{T}$ is a translational symmetry vector perpendicular to the glide plane.

The existence of a glide plane is indicated in a manner similar to a mirror plane, but with additional variations to show the direction of glide. If the glide plane is perpendicular to the page, the translation may be either parallel, perpendicular, or oblique, that is along the diagonal of the unit cell.



A glide plane parallel to the page is indicated by a modified mirror symbol, with an arrowhead indicating the translation direction.

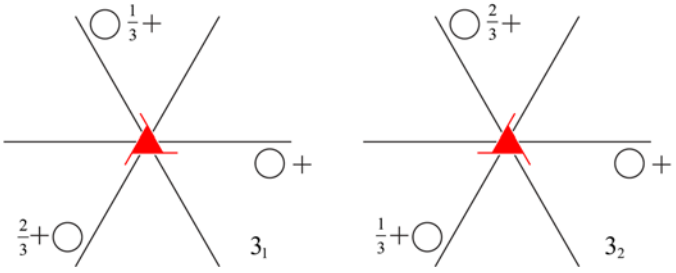


Screw axes

We saw that a 2-D "net" of lattice points can be compatible with *N*=2,3,4, or 6 rotational symmetry points. Likewise, a 3-D lattice can be compatible N=2,3,4, or 6 rotational symmetry axes *iff*: 1) N is perpendicular to a lattice net compatible with the rotational symmetry axes and 2) N is parallel to a lattice row. Let's say the lattice row parallel to the axes has period $\mathbf{T}$.

We know $N^N = 1$; that is *N* applications of the *N*-fold rotation returns the crystal to its original orientation. We define a rototranslation N_p as an *N* combined with a translation t. The rotation and translation must commute: $\mathbf{r}' = N \cdot \mathbf{r} + \mathbf{t} = N \cdot (\mathbf{r} + \mathbf{t})$. This implies that $N \cdot \mathbf{t} = \mathbf{t}$, so $\mathbf{t}$ is parallel to the N axis. If we apply N_p *N* times, we must have $N \cdot \mathbf{t} = p \cdot \mathbf{T}$, so $\mathbf{t} = (p/N) \cdot \mathbf{T}$. If $p = 0$, the transformation is just a rotation; Likewise for $p = N$. But *p*=1,…,*N*-1 describe N_p screw axes. Applying N_p m times is equivalent to a translation of $\mathbf{t} = (mp/N) \cdot \mathbf{T}$ and a rotation by N^m.

Consider an object with a 3_1 screw axis. $\mathbf{t} = (1/3) \cdot \mathbf{T}$. A rotation by 120° about the axis, combined with a translation by $(1/3) \cdot \mathbf{T}$ along the axis, leaves the object unchanged. The crystal is periodic, so a second application produces a net rotation of 240° and a net translation of $(2/3) \cdot \mathbf{T}$. A third application produces a full 360 deg rotation and a translation of T, which maps onto the original object. So there are always three copies of an object or molecule with the unit cell if the crystal contains a 3_1 screw axis.

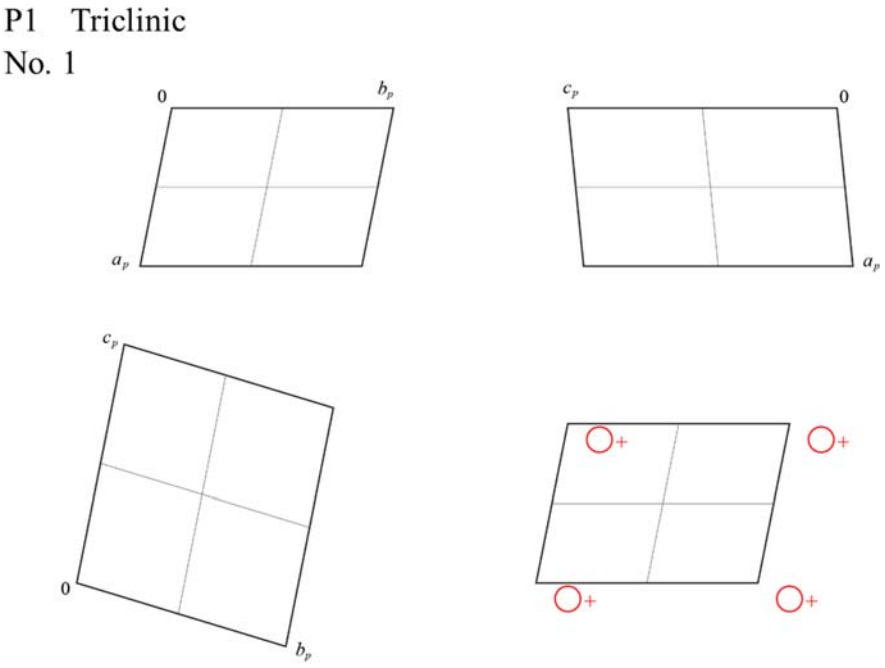


Space groups

A space group is generated by combining a point-group symmetry with a compatible Bravais lattice. We also allow replacements of 1) rotation axes by screw axes and 2) mirror planes by glide planes. Space groups without screw axes or glide planes are called *symmorphic*. The international tables show the symmetry elements and general positions for a unit cell in each space group.

Space group P1

The most simple - and least interesting - is the triclinic space group P1, which has been assigned number 1 (No. 1) in the list of 230 space groups. It has no symmetry elements and only one occurrence of a particular object (molecule) placed at an arbitrary position within the the unit cell. (The object itself must have no symmetry.) The symmetry elements (of which there are none) are shown in "elevations" of the unit cell viewed along the **a**, **b**, and **c** axes, respectively. For each elevation, the other two axes are oblique to the plane of the projection, so they are labeled as a_p, b_p, and c_p. The general-position diagram is usually shown in the lower right and divided into quadrants for reasons we will soon see.



All space groups have two types of symmetry, which we could label 0 and 1:

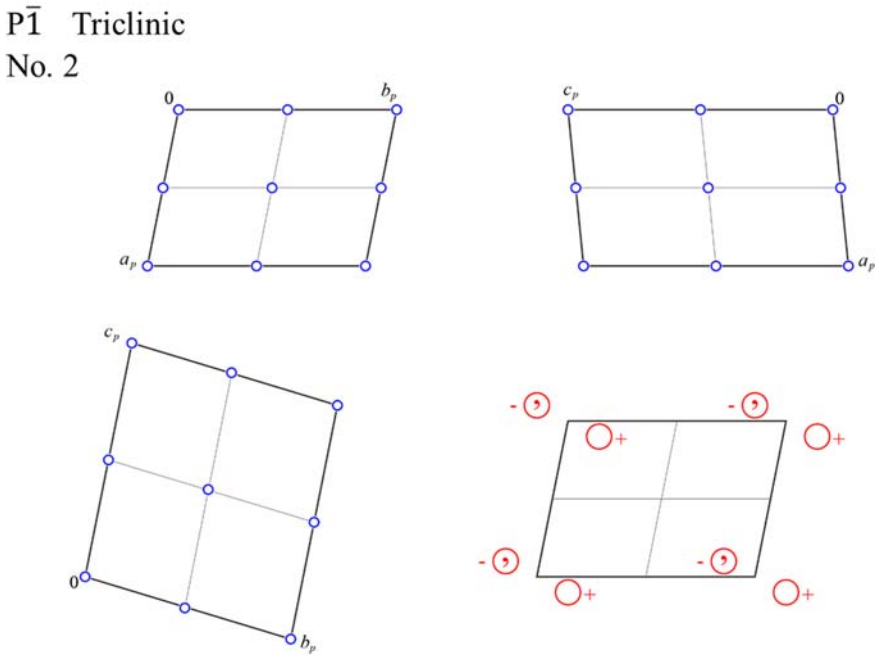
0: $\rho(\mathbf{r}) = \rho(\mathbf{r} + \mathbf{T})$ //translational symmetry, $\mathbf{T} = \mathbf{r}_{uvw}$

1: $\rho(\mathbf{r}) = \rho(1 \cdot \mathbf{r})$ //identity

These are useful for identifying the positions shown in the general-position diagram. In the case of P1, the three elements shown outside the unit-cell can be associated with transformation 0. The one inside the unit cell is associated with transformation 1.

Space group P$\bar{1}$

The only other triclinic space group, P$\bar{1}$, No. 2, has an inversion center, which we want to place at the origin whenever possible, for reasons that will be clear later.



The inversion center at (0,0,0) is reproduced at (1,0,0), (0,1,0), and (0,0,1) by translation symmetry. We can indicate this additional symmetry element algebraically by

$$2:\ \rho(\mathbf{r}) = \rho(-\mathbf{r})\ \ //\bar{1}\ @\ \mathbf{0}$$

There are now two molecules shown within the unit cell. The one just added must be the enantiomer of the first. Combining transformations 2 and 0:

$$\rho(\mathbf{r}) = \rho(-\mathbf{r}+\mathbf{T}) = \rho\{-[\mathbf{r}-(u\mathbf{a}+v\mathbf{b}+w\mathbf{c})/2]+(u\mathbf{a}+v\mathbf{b}+w\mathbf{c})/2\}\ \ //\bar{1}\ @\ (u\mathbf{a}+v\mathbf{b}+w\mathbf{c})/2$$

This implies the existence of seven additional inversion centers within the unit cell:

$$\rho(\mathbf{r}) = \rho[-(\mathbf{r}-\mathbf{a}/2)+\mathbf{a}/2]\ //\bar{1}\ @\ \mathbf{a}/2$$

$$\rho(\mathbf{r}) = \rho[-(\mathbf{r}-\mathbf{b}/2)+\mathbf{b}/2]\ //\bar{1}\ @\ \mathbf{b}/2$$

$$\rho(\mathbf{r}) = \rho[-(\mathbf{r}-\mathbf{c}/2)+\mathbf{c}/2]\ //\bar{1}\ @\ \mathbf{c}/2$$

$$\rho(\mathbf{r}) = \rho\{-[\mathbf{r}-(\mathbf{a}+\mathbf{b})/2]+(\mathbf{a}+\mathbf{b})/2\}\ //\bar{1}\ @\ (\mathbf{a}+\mathbf{b})/2$$

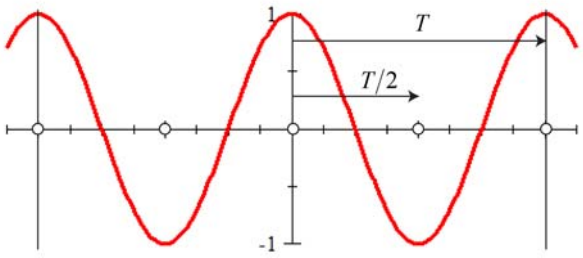
$$\rho(\mathbf{r}) = \rho\{-[\mathbf{r}-(\mathbf{b}+\mathbf{c})/2]+(\mathbf{b}+\mathbf{c})/2\}\ //\bar{1}\ @\ (\mathbf{b}+\mathbf{c})/2$$

$\rho(\mathbf{r}) = \rho\{-[\mathbf{r} - (\mathbf{a}+\mathbf{c})/2] + (\mathbf{a}+\mathbf{c})/2\} \;//\, \bar{1} \;@\; (\mathbf{a}+\mathbf{c})/2$, and

$\rho(\mathbf{r}) = \rho\{-[\mathbf{r} - (\mathbf{a}+\mathbf{b}+\mathbf{c})/2] - (\mathbf{a}+\mathbf{b}+\mathbf{c})/2\} \;//\, \bar{1} \;@\; (\mathbf{a}+\mathbf{b}+\mathbf{c})/2$

The space group has inversion centers at the origin and all ½ positions in the unit cell. Note that the some of the inversion centers relate the original molecule to enantiomers at various locations outside the unit cell. In fact, on the original molecule and the enantiomer generated by inversion through $(\mathbf{a}+\mathbf{b}+\mathbf{c})/2$ are centered within the unit cell boundary. Thus, only two general positions appear within the unit cell.

We can see why the additional inversion centers exist by examining a simple sinusoidal function, such as a cosine. The cosine is both even, meaning that $\cos(x) = \cos(-x)$, and periodic, such that $\cos(x) = \cos(x + 2\pi n)$, where $n \in \not\in$. So $\cos(x) = \cos(-x + 2\pi n) = \cos[-(x - \pi n) + \pi n]$. The last form describes inversion about any point $x = \pi n$ including those at half the period.



Space group P2

The monoclinic crystal system was identified as being compatible with a single binary axis, which we will generally consider to be the b axis. This can be a two-fold rotation or screw axis, the normal to a mirror or glide plane, or some combination. For clarity, the axis or plane should always coincide with the b axis, or the a-c plane, respectively.

If the only additional symmetry imposed is a 2-axis then, in addition to symmetries 0 and 1, we have

$2\text{:}\;\; \rho(\mathbf{r}) = \rho(2_b \cdot \mathbf{r}) \,//\, 2_b \;@\; \mathbf{0}$

We will develop the notation more later but, for the moment, suffice it to say that $\mathbf{b} = b\hat{\mathbf{z}}$, i.e., $2_b = 2_z$,

$$2_b = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

Therefore

$2_b \cdot \mathbf{a} = -\mathbf{a}$, $2_b \cdot \mathbf{b} = \mathbf{b}$, $2_b \cdot \mathbf{c} = -\mathbf{c}$

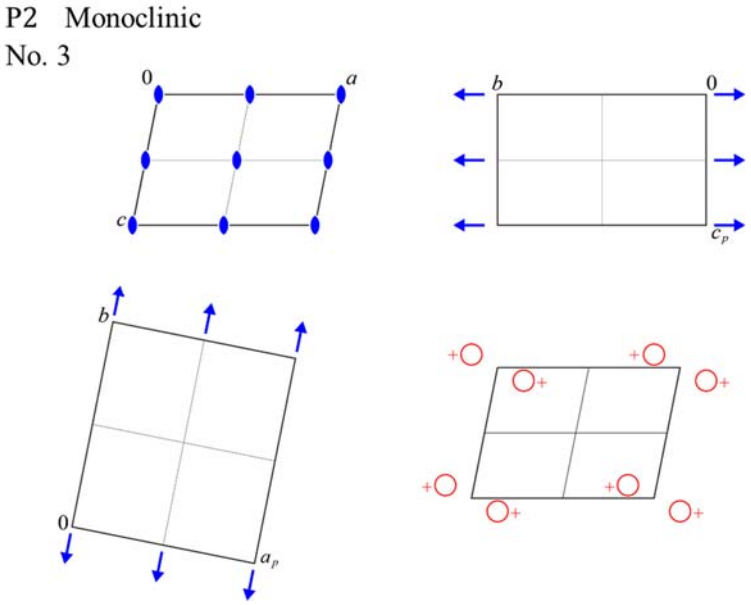
When we combine symmetries 0 and 2, using various translations $\mathbf{T}$, we find three additional symmetry elements within the unit cell

$\rho(\mathbf{r}) = \rho(2_b \cdot \mathbf{r} + \mathbf{a}) = \rho[2_b \cdot (\mathbf{r} - \mathbf{a}/2) + \mathbf{a}/2] \,//\, 2_b \;@\; \mathbf{a}/2$

$\rho(\mathbf{r}) = \rho(2_b \cdot \mathbf{r} + \mathbf{c}) = \rho[2_b \cdot (\mathbf{r} - \mathbf{c}/2) + \mathbf{c}/2] \,//\, 2_b \;@\; \mathbf{c}/2$

$$\rho(\mathbf{r}) = \rho[2_b \cdot \mathbf{r} + (\mathbf{a}+\mathbf{c})] = \rho\{2_b \cdot [\mathbf{r} - (\mathbf{a}+\mathbf{c})/2] + (\mathbf{a}+\mathbf{c})/2\} \,//\, 2_b \;@\; (\mathbf{a}+\mathbf{c})/2$$

We have described the symmetry of the space group P2.



Space group Pm

Instead of a twofold-rotation axis 2_b, we can have a twofold-rotoinversion axis $\bar{2}_b = m_b$, which passes through the origin.

$$2:\ \rho(\mathbf{r}) = \rho(m_b \cdot \mathbf{r}) \,//\, m_b \;@\; \mathbf{0}$$

Using $m_b = m_z$, we have

$$m_b = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

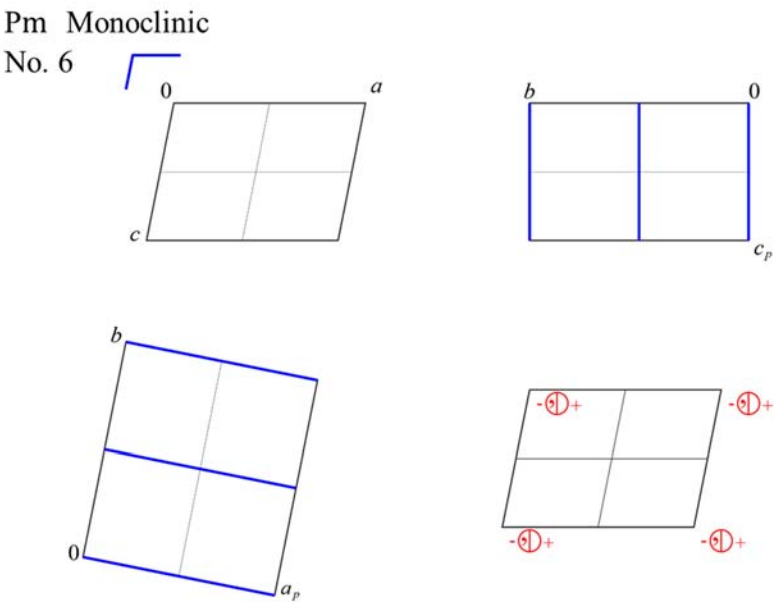
In this case,

$$m_b \cdot \mathbf{a} = \mathbf{a},\ m_b \cdot \mathbf{b} = -\mathbf{b},\ m_b \cdot \mathbf{c} = \mathbf{c}$$

Again combining 0 and 2 gives

$$\rho(\mathbf{r}) = \rho(m_b \cdot \mathbf{r} + \mathbf{b}) = \rho[m_b \cdot (\mathbf{r} - \mathbf{b}/2) + \mathbf{b}/2] \,//\, m_b \;@\; \mathbf{b}/2$$

The mirror plane at $\mathbf{b}/2$ relates the original molecule and its enantiomer within the unit cell.



Orthogonal, binary, proper axes (I): Space group P222

The identifying characteristic of orthorhombic crystals is the presence of binary axes parallel to each of the three orthogonal basis vectors. If any two are proper symmetry axes, that is, either a 2 or a 2_1, the third must also be a proper symmetry axis. There are four distinct combinations of 2s and 2_1 s that can coexist, though we can permute these among the three lattice vectors in several ways.

First, assume we have two intersecting 2s, one parallel to **a** and the other parallel to **b**. We will pick the point of intersection to be the origin.

1: $\rho(\mathbf{r}) = \rho(1 \cdot \mathbf{r})$ // identity

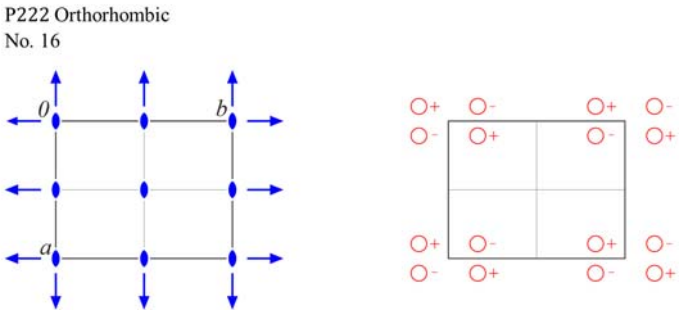
2: $\rho(\mathbf{r}) = \rho(2_a \cdot \mathbf{r})$ // 2_a @ **0**

3: $\rho(\mathbf{r}) = \rho(2_b \cdot \mathbf{r})$ // 2_b @ **0**

Combining 2 and 3:

4: $\rho(\mathbf{r}) = \rho[2_a \cdot (2_b \cdot \mathbf{r})] = \rho(2_c \cdot \mathbf{r})$ // 2_c @ **0**

A third, orthogonal 2 must intersect both axes at the origin. This gives rise to the space group P222.



Orthogonal, binary, proper axes (II): Space group $P222_1$

Let's instead assume the 2s do not intersect. In that case, we can have one pass through the origin and the other should be displaced by $1/4$ of a basis vector from the origin.

1: $\rho(\mathbf{r}) = \rho(1 \cdot \mathbf{r})$ // identity

2: $\rho(\mathbf{r}) = \rho(2_a \cdot \mathbf{r})$ $//2_a$ @ $\mathbf{0}$

3: $\rho(\mathbf{r}) = \rho[2_b \cdot (\mathbf{r} - \mathbf{c}/4) + \mathbf{c}/4]$ $//2_b$ @ $\mathbf{c}/4$

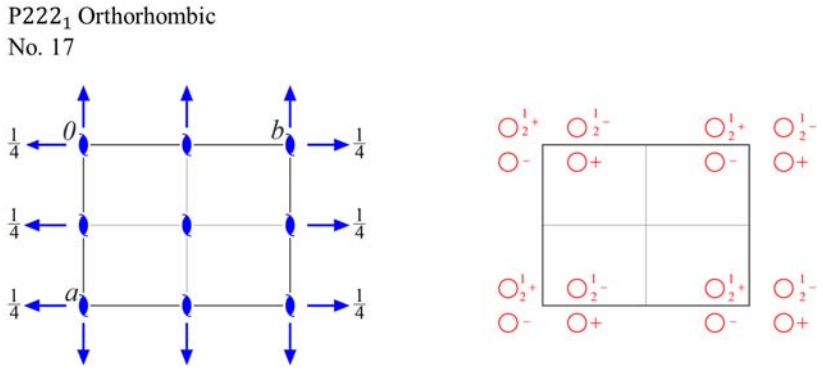
Having identified 3, we can expand the expression to obtain the general form

$$\rho(\mathbf{r}) = \rho(2_b \cdot \mathbf{r} + \mathbf{c}/2)$$

Combining with 2:

4: $\rho(\mathbf{r}) = \rho[2_b \cdot (2_a \cdot \mathbf{r}) + \mathbf{c}/2] = \rho(2_c \cdot \mathbf{r} + \mathbf{c}/2)$ $//2_{1c}$ @ $\mathbf{0}$

The third axis has a 2_1 passing through the origin. This 2_1 both of the non-intersecting, orthogonal 2s. This is the basis for the space group $P222_1$.



Orthogonal binary, proper axes (III): Space group $P2_12_12$

Now consider intersecting 2_1 s. We will pick for them to both be offset from the origin.

1: $\rho(\mathbf{r}) = \rho(1 \cdot \mathbf{r})$ // identity

2: $\rho(\mathbf{r}) = \rho[2_a \cdot (\mathbf{r} - \mathbf{b}/4) + \mathbf{b}/4 + \mathbf{a}/2]$ $//2_{1a}$ @ $\mathbf{b}/4$

3: $\rho(\mathbf{r}) = \rho[2_b \cdot (\mathbf{r} - \mathbf{a}/4) + \mathbf{a}/4 + \mathbf{b}/2]$ $//2_{1b}$ @ $\mathbf{a}/4$

In the general forms, 2 and 3 become

$$\rho(\mathbf{r}) = \rho[2_a \cdot \mathbf{r} + (\mathbf{a} + \mathbf{b})/2]$$

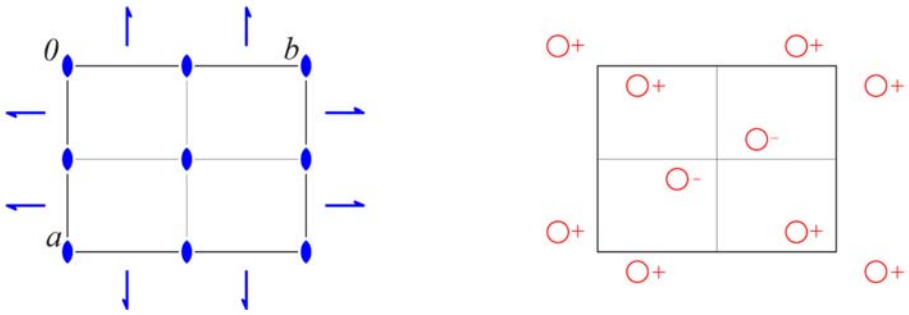
$$\rho(\mathbf{r}) = \rho[2_b \cdot \mathbf{r} + (\mathbf{a} + \mathbf{b})/2]$$

Combining:

$$\rho(\mathbf{r}) = \rho\{2_b \cdot [2_a \cdot \mathbf{r} + (\mathbf{a} + \mathbf{b})/2] + (\mathbf{a} + \mathbf{b})/2\}$$

4: $\rho(\mathbf{r}) = \rho(2_c \cdot \mathbf{r}) \;//2_c \;@\mathbf{0}$

$P2_12_12$ Orthorhombic
No. 18



We don't expect a 2_{1c}, because neither 2 nor 3 contains any translation along $\mathbf{c}$.

Orthogonal binary, proper axes (IV): Space group $P2_12_12_1$
The only other unique combination involves non-intersecting 2_1 s:

1: $\rho(\mathbf{r}) = \rho(1 \cdot \mathbf{r})$ // identity

2: $\rho(\mathbf{r}) = \rho[2_a \cdot (\mathbf{r} - \mathbf{b}/4) + \mathbf{b}/4 + \mathbf{a}/2] \;//2_{1a} \;@\mathbf{b}/4$

3: $\rho(\mathbf{r}) = \rho[2_b \cdot (\mathbf{r} - \mathbf{c}/4) + \mathbf{c}/4 + \mathbf{b}/2] \;//2_{1b} \;@\mathbf{c}/4$

The general forms of 2 and 3 are

$$\rho(\mathbf{r}) = \rho[2_a \cdot \mathbf{r} + (\mathbf{a} + \mathbf{b})/2]$$

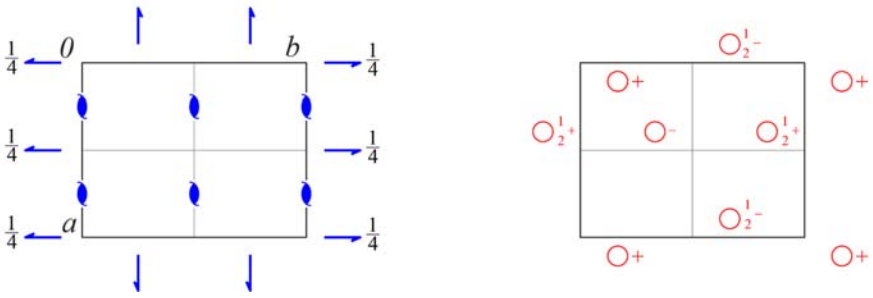
$$\rho(\mathbf{r}) = \rho[2_b \cdot \mathbf{r} + (\mathbf{b} + \mathbf{c})/2]$$

Combining 2 and 3:

$$\begin{aligned}\rho(\mathbf{r}) &= \rho\{2_b \cdot [2_a \cdot \mathbf{r} + (\mathbf{a} + \mathbf{b})/2] + (\mathbf{b} + \mathbf{c})/2\} \\ &= \rho(2_c \cdot \mathbf{r} - \mathbf{a}/2 + \mathbf{c}/2) = \rho[2_c \cdot \mathbf{r} + (\mathbf{a} + \mathbf{c})/2]\end{aligned}$$

4: $\rho(\mathbf{r}) = \rho[2_c \cdot (\mathbf{r} - \mathbf{a}/4) + \mathbf{a}/4 + \mathbf{c}/2] \;//2_{1c} \;@\mathbf{a}/4$

$P2_12_12_1$ Orthorhombic
No. 19



The various combinations can be summarized in a table. Examples of each of the four distinct pairs are highlighted.

	$2_b\,@\,\mathbf{0}$	$2_{1b}\,@\,\mathbf{a}/4$	$2_{1b}\,@\,\mathbf{c}/4$
$2_a\,@\,\mathbf{0}$	$2_c\,@\,\mathbf{0}$	$2_c\,@\,\mathbf{a}/4$	$2_{1c}\,@\,\mathbf{b}/4$
$2_a\,@\,\mathbf{c}/4$	$2_{1c}\,@\,\mathbf{0}$	$2_{1c}\,@\,(\mathbf{a}+\mathbf{b})/4$	$2_c\,@\,\mathbf{b}/4$
$2_{1a}\,@\,\mathbf{b}/4$	$2_c\,@\,(\mathbf{a}+\mathbf{b})/4$	$2_c\,@\,\mathbf{0}$	$2_{1c}\,@\,\mathbf{a}/4$

Orthogonal, binary, improper axes (I): Space group Pmm2

We can make 2 rotation axes into $\bar{2}$ rotoinversion axes, which correspond to *m*s passing perpendicular to the axes and passing through the inversion point. Starting with the groups having three proper axes, if we make one of the axes improper, then another axis must also be improper. For example, we can change the 2_a into an m_a and the 2_b into an m_b.

1: $\rho(\mathbf{r}) = \rho(1\cdot\mathbf{r})$ // identity

2: $\rho(\mathbf{r}) = \rho(m_a\cdot\mathbf{r})$ // m_a @ $\mathbf{0}$

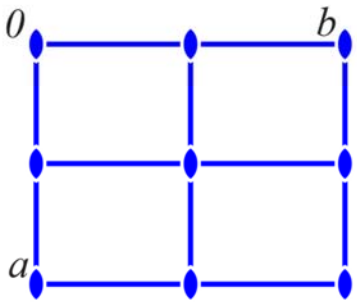
3: $\rho(\mathbf{r}) = \rho(m_b\cdot\mathbf{r})$ // m_b @ $\mathbf{0}$

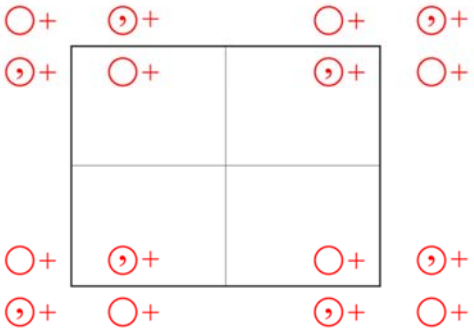
We know that reflections across intersecting planes correspond to a rotation of twice the angle between the planes about the axis of intersection.

$\rho(\mathbf{r}) = \rho[m_a\cdot(m_b\cdot\mathbf{r})]$

4: $\rho(\mathbf{r}) = \rho(2_c\cdot\mathbf{r})$ // 2_c @ $\mathbf{0}$

Pmm2 Orthorhombic
No. 25





Orthogonal, binary, improper axes (II): Space group Pma2

Any of the mirror planes could instead be a glide plane. There are three possible translation vectors for each glide plane in this system. For example, a glide plane normal to $\mathbf{a}$ could involve translation of $\mathbf{b}/2$, $\mathbf{c}/2$, or $(\mathbf{b}+\mathbf{c})/2$, We refer to these as b_a, c_a, and n_a, respectively.

Consider the substitution of m_b in the preceding case with a_b. We will judiciously place the m_a at $\mathbf{a}/4$.

1: $\rho(\mathbf{r}) = \rho(1 \cdot \mathbf{r})$ // identity

2: $\rho(\mathbf{r}) = \rho[m_a \cdot (\mathbf{r} - \mathbf{a}/4) + \mathbf{a}/4]$ // m_a @ $\mathbf{a}/4$

3: $\rho(\mathbf{r}) = \rho(m_b \cdot \mathbf{r} + \mathbf{a}/2)$ // a_b @ $\mathbf{0}$

In its general form, 2 becomes

$$\rho(\mathbf{r}) = \rho(m_a \cdot \mathbf{r} + \mathbf{a}/2)$$

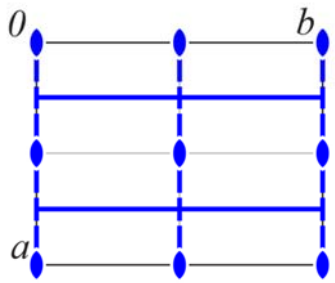
Combining

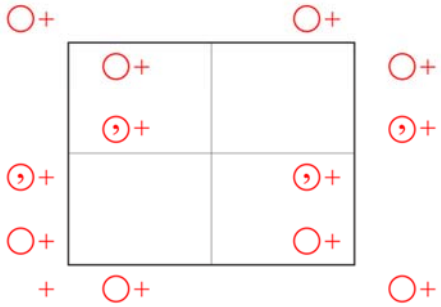
$$\rho(\mathbf{r}) = \rho[m_b \cdot (m_a \cdot \mathbf{r} + \mathbf{a}/2) + \mathbf{a}/2]$$

This becomes

4: $\rho(\mathbf{r}) = \rho(2_c \cdot \mathbf{r})$ // 2_c @ $\mathbf{0}$

Pma2 Orthorhombic
No. 28





Orthogonal, binary, improper axes (III): Space group $Pmc2_1$

Now let's use a c_b, instead of an a_b, and place the m_a at the origin.

1: $\rho(\mathbf{r}) = \rho(1 \cdot \mathbf{r})$ // identity

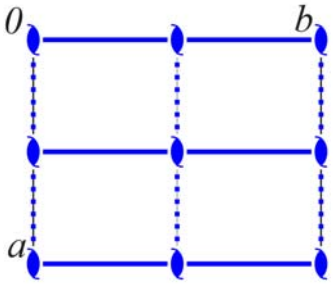
2: $\rho(\mathbf{r}) = \rho(m_a \cdot \mathbf{r})$ // m_a @ $\mathbf{0}$

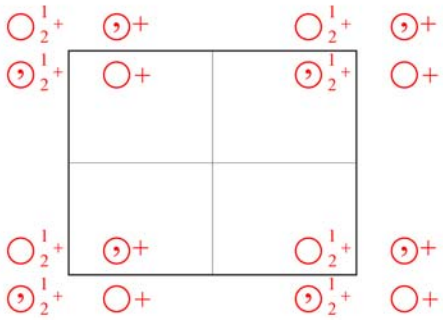
3: $\rho(\mathbf{r}) = \rho(m_b \cdot \mathbf{r} + \mathbf{c}/2)$ // c_b @ $\mathbf{0}$

Combining

$$\rho(\mathbf{r}) = \rho[m_b \cdot (m_a \cdot \mathbf{r}) + \mathbf{c}/2]$$

4: $\rho(\mathbf{r}) = \rho(2_c \cdot \mathbf{r} + \mathbf{c}/2)$ // 2_{1c} @ $\mathbf{0}$





Orthogonal, binary, improper axes (III): Space group $Pmn2_1$

Next we will use a diagonal glide plane n_b, with m_a at the origin.

1: $\rho(\mathbf{r}) = \rho(1 \cdot \mathbf{r})$ // identity

2: $\rho(\mathbf{r}) = \rho(m_a \cdot \mathbf{r})$ // m_a @ $\mathbf{0}$

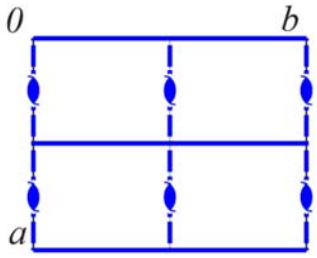
3: $\rho(\mathbf{r}) = \rho[m_b \cdot \mathbf{r} + (\mathbf{a} + \mathbf{c})/2]$ // n_b @ $\mathbf{0}$

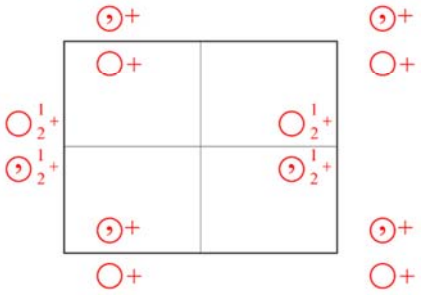
Combining

$$\rho(\mathbf{r}) = \rho[m_b \cdot (m_a \cdot \mathbf{r}) + (\mathbf{a} + \mathbf{c})/2] = \rho[2_c \cdot \mathbf{r} + (\mathbf{a} + \mathbf{c})/2]$$

4: $\rho(\mathbf{r}) = \rho[2_c \cdot (\mathbf{r} - \mathbf{a}/4) + \mathbf{a}/4 + \mathbf{c}/2]$ // 2_{1c} @ $\mathbf{a}/4$

$Pmn2_1$ Orthorhombic
No. 31





Double glide planes

Centered lattices are compatible with configurations of glide planes that were not discussed previously. For example, consider a C-centered lattice, which will have the following symmetry operations

1: $\rho(\mathbf{r}) = \rho(1 \cdot \mathbf{r})$ // identity

2: $\rho(\mathbf{r}) = \rho[\mathbf{r} + (\mathbf{a} + \mathbf{b})/2]$ //C centering

If the c-axis is compatible with binary symmetry elements, we can include an a_c glide plane at $\mathbf{c}/4$, i.e.,

3: $\rho(\mathbf{r}) = \rho[m_c \cdot (\mathbf{r} - \mathbf{c}/4) + \mathbf{c}/4 + \mathbf{a}/2]$ // a_c @ $\mathbf{c}/4$

$$\rho(\mathbf{r}) = \rho[m_c \cdot \mathbf{r} + (\mathbf{a} + \mathbf{c})/2]$$

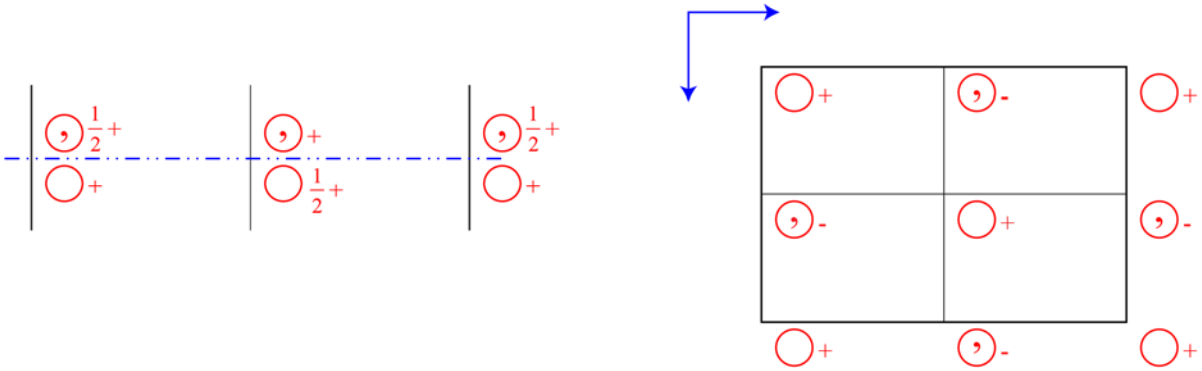
Combining 2 and 3 gives

$$\rho(\mathbf{r}) = \rho[m_c \cdot \mathbf{r} + (\mathbf{b} + \mathbf{c})/2]$$

which becomes

4: $\rho(\mathbf{r}) = \rho[m_c \cdot (\mathbf{r} - \mathbf{c}/4) + \mathbf{c}/4 + \mathbf{b}/2] \;//\, b_c \;@\, \mathbf{a}/4$

Therefore, the plane at $\mathbf{c}/4$ is both a a_c and a b_c ,which is called a *double* glide plane. It can be referred to as an $e_c \;@\, \mathbf{c}/4$, although there is not much benefit to this notation. When viewed parallel to the glide plane, double glide is indicated by alternating dashes and multiple dots. Viewed normal to the plane, it is indicated by a mirror symbol with arrowheads on both ends. Note that space groups containing double glide planes will have additional symmetry elements that are not shown here.



Double glide arises when the glide plane is parallel to a centered net of lattice points, when the glide translation does not correspond to the translation for centering. This occurs in some F- or C-centered orthorhombic, I-centered tetragonal, and F- and I-centered cubic lattices.

Diamond glide planes

Let's again start with a C-centered lattice

1: $\rho(\mathbf{r}) = \rho(1 \cdot \mathbf{r})$ // identity

2: $\rho(\mathbf{r}) = \rho[\mathbf{r} + (\mathbf{a} + \mathbf{b})/2]$ //C centering

If the a axis is compatible with binary symmetry elements, we can consider a new type of glide plane in with translation in the diagonal direction, but with a translation vector of $(\mathbf{b} + \mathbf{c})/4$, which has only half the length of the conventional diagonal glide plane. Let's assume the glide plane is positioned at $\mathbf{a}/8$, and refer to it by the notation d_{a+} , for reasons that will be clear shortly.

3: $\rho(\mathbf{r}) = \rho[m_a \cdot (\mathbf{r} - \mathbf{a}/8) + \mathbf{a}/8 + (\mathbf{b} + \mathbf{c})/4] \;//\, d_{a+}^{(+)} \;@\, \mathbf{a}/8$

which reduces to

$$\rho(\mathbf{r}) = \rho[m_a \cdot \mathbf{r} + (\mathbf{a} + \mathbf{b} + \mathbf{c})/4]$$

Combining 2 and 3 gives

$$\rho(\mathbf{r}) = \rho[m_a \cdot \mathbf{r} + (3\mathbf{a} + 3\mathbf{b} + \mathbf{c})/4]$$

which corresponds to

4: $\rho(\mathbf{r}) = \rho[m_a \cdot (\mathbf{r} - 3\mathbf{a}/8) + 3\mathbf{a}/8 + (-\mathbf{b} + \mathbf{c})/4]$ // $d_{a-}^{(+)}$ @ $3\mathbf{a}/8$

We have labeled these as $d_{a+}^{(+)}$ and $d_{a-}^{(+)}$ to indicate that we are not done yet. Combining 3 and 4 gives

5: $\rho(\mathbf{r}) = \rho[\mathbf{r} + (\mathbf{a} + \mathbf{c})/2]$ //A centering

The lattice must also be B centered. Combining 2 and 5 gives

6: $\rho(\mathbf{r}) = \rho[\mathbf{r} + (\mathbf{b} + \mathbf{c})/2]$ //B centering

So we have an F-centered lattice. Combining 3 and 6 gives

$$\rho(\mathbf{r}) = \rho[m_a \cdot \mathbf{r} + (\mathbf{a} + 3\mathbf{b} + 3\mathbf{c})/4]$$

7: $\rho(\mathbf{r}) = \rho[m_a \cdot (\mathbf{r} - \mathbf{a}/8) + \mathbf{a}/8 - (\mathbf{b} + \mathbf{c})/4]$ // $d_{a+}^{(-)}$ @ $\mathbf{a}/8$

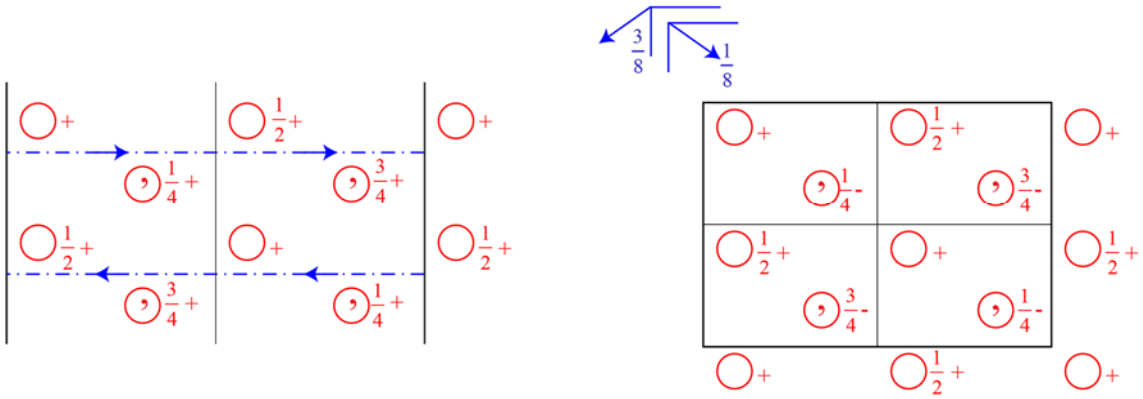
Next, 3 and 5 give

$$\rho(\mathbf{r}) = \rho[m_a \cdot \mathbf{r} + (3\mathbf{a} + \mathbf{b} + 3\mathbf{c})/4]$$

8: $\rho(\mathbf{r}) = \rho[m_a \cdot (\mathbf{r} - 3\mathbf{a}/8) + 3\mathbf{a}/8 - (-\mathbf{b} + \mathbf{c})/4]$ // $d_{a-}^{(-)}$ @ $3\mathbf{a}/8$

Each of these *diamond* glide planes represents two opposite glide translation components within the same plane, i.e., $d_{a+}^{(+)}$ and $d_{a+}^{(-)}$. They are each accompanied by another diamond glide plane displaced by one-quarter of the unit cell that has translation along the other available diagonal direction.

When viewed parallel to the plane, diamond glide planes are indicated by alternating dots/dashes with an arrowhead superimposed on the line. In a normal projection, a double mirror symbol is used in which each right angle has an attached diagonal arrow showing the translation direction. Note that space groups with diamond glide planes will necessarily contain additional symmetry elements not shown here.



Basis matrix

We previously wrote a vector in terms of its components in cartesian coordinates as

$$\mathbf{r} = A^T \cdot X = x\hat{\mathbf{x}} + y\hat{\mathbf{y}} + z\hat{\mathbf{z}}$$

where the basis matrix and the column vector are

$$\mathrm{A}^T = (\hat{\mathbf{x}} \quad \hat{\mathbf{y}} \quad \hat{\mathbf{z}}) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = I \,, \; \mathbf{r} = X = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

The notation indicates that the columns of A^T contain the basis vectors, which in this case are unit vectors along the cartesian axes, as measured with respect to the cartesian axes, themselves. This means that rows 1, 2, and 3 of A^T contain the dot products of each of the basis vectors with $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\hat{\mathbf{z}}$, respectively. We can instead pick basis vectors that correspond to the unit cell of the crystal under consideration, which may also be measured with respect to the cartesian axes.

$$\mathrm{A}^T = (\mathbf{a} \quad \mathbf{b} \quad \mathbf{c}) = \begin{pmatrix} a_x & b_x & c_x \\ a_y & b_y & c_y \\ a_z & b_z & c_z \end{pmatrix}$$

The determinant of A is

$$\det(\mathrm{A}) = a_x \cdot (b_y \cdot c_z - b_z \cdot c_y) - a_y \cdot (b_x \cdot c_z - b_z \cdot c_y) + a_z \cdot (b_x \cdot c_y - b_y \cdot c_x)$$

Consider the cross-product $\mathbf{b} \times \mathbf{c}$:

$$\mathbf{b} \times \mathbf{c} = \begin{vmatrix} \hat{\mathbf{x}} & \hat{\mathbf{y}} & \hat{\mathbf{z}} \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{vmatrix} = (b_y \cdot c_z - b_z \cdot c_y) \cdot \hat{\mathbf{x}} - a_y \cdot (b_x \cdot c_z - b_z \cdot c_y) \cdot \hat{\mathbf{y}} + a_z \cdot (b_x \cdot c_y - b_y \cdot c_x) \cdot \hat{\mathbf{z}}$$

We can see that $\det(\mathrm{A}) = \mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}) = V$.

Reciprocal basis

The inverse of A satisfies $\mathrm{A}^{-1} \cdot \mathrm{A} = \mathrm{A} \cdot \mathrm{A}^{-1} = \mathrm{I}$. Let's write $\mathrm{A}^{-1} = \begin{pmatrix} \mathbf{a}^* & \mathbf{b}^* & \mathbf{c}^* \end{pmatrix}$, where $\mathbf{a}^*$, $\mathbf{b}^*$, and $\mathbf{c}^*$ are vectors that will need to be identified. We can think of the product as

$$\mathrm{A} \cdot \mathrm{A}^{-1} = \begin{pmatrix} \mathbf{a}^T \\ \mathbf{b}^T \\ \mathbf{c}^T \end{pmatrix} \cdot \begin{pmatrix} \mathbf{a}^* & \mathbf{b}^* & \mathbf{c}^* \end{pmatrix} = \begin{pmatrix} \mathbf{a} \cdot \mathbf{a}^* & \mathbf{a} \cdot \mathbf{b}^* & \mathbf{a} \cdot \mathbf{c}^* \\ \mathbf{b} \cdot \mathbf{a}^* & \mathbf{b} \cdot \mathbf{b}^* & \mathbf{b} \cdot \mathbf{c}^* \\ \mathbf{c} \cdot \mathbf{a}^* & \mathbf{c} \cdot \mathbf{b}^* & \mathbf{c} \cdot \mathbf{c}^* \end{pmatrix}$$

Clearly $\mathbf{a} \cdot \mathbf{a}^* = \mathbf{b} \cdot \mathbf{b}^* = \mathbf{c} \cdot \mathbf{c}^* = 1$ and $\mathbf{a} \cdot \mathbf{b}^* = \mathbf{a} \cdot \mathbf{c}^* = \mathbf{b} \cdot \mathbf{a}^* = \mathbf{b} \cdot \mathbf{c}^* = \mathbf{c} \cdot \mathbf{a}^* = \mathbf{c} \cdot \mathbf{b}^* = 0$. To keep on the same footing as the direct basis A, we will identify a reciprocal basis $\mathrm{A}^* = (\mathrm{A}^{-1})^T$. If we combine any two of the three modifications to A – inverse (A^{-1}), transpose (A^T), or reciprocal (A^*) – we will get the third:

$$(\mathrm{A}^*)^{-1} = \mathrm{A}^T \,, \; (\mathrm{A}^{-1})^T = \mathrm{A}^* \,, \; (\mathrm{A}^*)^T = \mathrm{A}^{-1}$$

Reciprocal-lattice basis vectors

We showed that $\det(\mathrm{A}) = V$. In general, $\det(\mathrm{A}) = \det(\mathrm{A}^T)$. Notice that

$$\det\left((\mathrm{A}^*)^T \cdot \mathrm{A}\right) = \det\left((\mathrm{A}^*)^T \cdot \mathrm{A}\right) = \det\left((\mathrm{A}^*)^T\right) \cdot \det(\mathrm{A}) = V \cdot \det\left((\mathrm{A}^*)^T\right) = \det(\mathrm{A}^{-1} \cdot \mathrm{A}) = \det(I) = 1$$

So

$$\det\left((\mathrm{A}^*)^T\right) = \det(\mathrm{A}^*) = 1/V = V^*$$

We know a bit about the orientations of $\mathbf{a}^*$, $\mathbf{b}^*$, and $\mathbf{c}^*$. For example, $\mathbf{a}^*$ is perpendicular to both $\mathbf{b}$ and $\mathbf{c}$, so $\mathbf{a}^* = p\cdot(\mathbf{b}\times\mathbf{c})$, where p is an unknown coefficient. But $\mathbf{a}\cdot\mathbf{a}^* = p\cdot[\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c})] = p\cdot V = 1$, so $p = 1/V$

$$\mathbf{a}^* = \frac{\mathbf{b}\times\mathbf{c}}{V} \quad \mathbf{b}^* = \frac{\mathbf{c}\times\mathbf{a}}{V} \qquad \mathbf{c}^* = \frac{\mathbf{a}\times\mathbf{b}}{V}$$