

Special Cases: Miller Indices For Hexagonal Crystals Planes and Directions in Cubic Crystals

- The justification for using four indices in the case of hexagonal crystals relates to the fact that equivalent planes are not directly apparent if only three indices are used (as is illustrated in the following example).
- | | | | |
|-----------------|--------|--------------------------|---------------------------------------|
| (0 1 0) | —————▶ | (0 1 <u>1</u> 0) | |
| (1 0 0) | —————▶ | (1 0 <u>1</u> 0) | |
| (1 1 0) | —————▶ | (1 1 <u>2</u> 0) | These two planes are equivalent |
| (<u>1</u> 2 0) | —————▶ | (<u>1</u> 2 <u>1</u> 0) | although it is not initially apparent |
- Only in the case of cubic crystals is a direction [hkl] always perpendicular to the plane (hkl) and the angle between two planes or directions is given by :

$$\cos(\theta) = \frac{h_1 h_2 + k_1 k_2 + l_1 l_2}{\sqrt{h_1^2 + k_1^2 + l_1^2} \sqrt{h_2^2 + k_2^2 + l_2^2}}$$

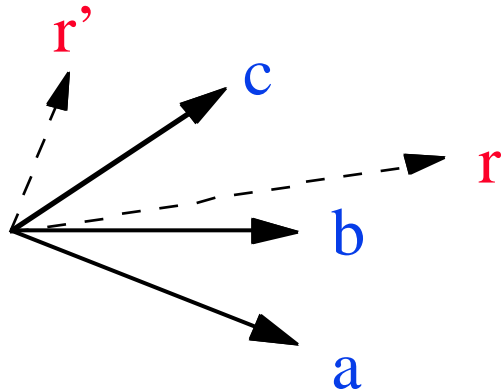
Mathematical Approach to Crystallography

- Lattice is defined by translational symmetry:

$$\vec{L} = n_1\vec{a} + n_2\vec{b} + n_3\vec{c}$$

where \mathbf{a} , \mathbf{b} and \mathbf{a} , \mathbf{c} and \mathbf{b} , \mathbf{c} are non-collinear and $\mathbf{a}, \mathbf{b}, \mathbf{c}$ are non-coplanar

- Rotations, Inversions, etc. (Not-translation Symmetry Operations)



$$\begin{matrix} X' & R_{11} & R_{12} & R_{13} & X \\ Y' & = & R_{21} & R_{22} & R_{23} & \cdot & Y \\ Z' & & R_{31} & R_{32} & R_{33} & & Z \end{matrix}$$

$$\vec{r}' = R\vec{r}$$

where R is a symmetry operator. If we move the space and leave the coordinate axes fixed, the symmetry operation is an **active** operation. If we leave the space fixed and move the coordinate axes, we have a **passive** symmetry operation.

- Identity Operation:

no change in position

Symbol: 1 (E Schoenflies Notation)

$$\begin{matrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{matrix}$$

- Rotation (proper) about c-axis by 180°

Symbol: 2 (C_2) or $2[hkl]$

$$\begin{matrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{matrix}$$

- Inversion through a point

Symbol: $\bar{1}$ (i)

Inversion through a point (center of symmetry) changes the chirality or the handedness. Objects before and after the operation are enantiomorphically related.

$$\begin{matrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{matrix}$$

- **Rotation by $2\pi/n$ around z- axis**

Symbol: n or $n [hkl]$ (C_n)

rotations do not change
the handedness of an object

$$\begin{matrix} \cos \frac{2\pi}{n} & -\sin \frac{2\pi}{n} & 0 \\ \sin \frac{2\pi}{n} & \cos \frac{2\pi}{n} & 0 \\ 0 & 0 & +1 \end{matrix}$$

- **Reflection**

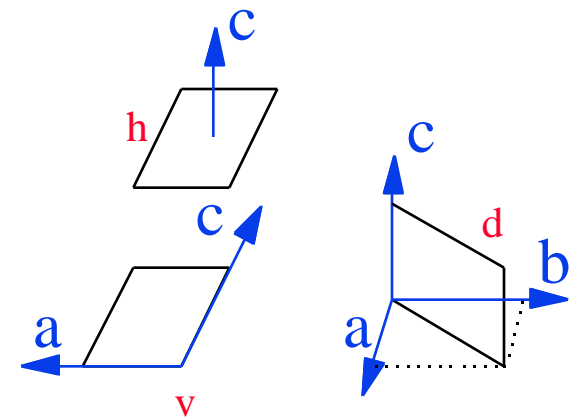
Symbol: m () or $m [hkl]$ (h, v, d)

reflection with respect to a mirror plane
which is perpendicular to the direction
given by $[hkl]$. For (x, y) mirror plane:

h is perpendicular to the principal axis
(**c**-axis). v contains the **c**- and **a**-axes.

d contains the **c**-axis but falls between
the **a** and **b** axis.

$$\begin{matrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{matrix}$$



- **Improper Rotations**

rotation followed by inversion (International)

rotation followed by reflection (Schoenflies)

Note that an improper rotation may be a symmetry operation for a given crystal, even if the two individual operations (rotation and inversion or reflection) are not.

Symbol: \underline{n} ($S_n = \sigma_h C_n$)

- The determinant of all symmetry operators are either +1 or -1:

+1: proper rotation and identity

-1: improper rotation, mirror and inversion

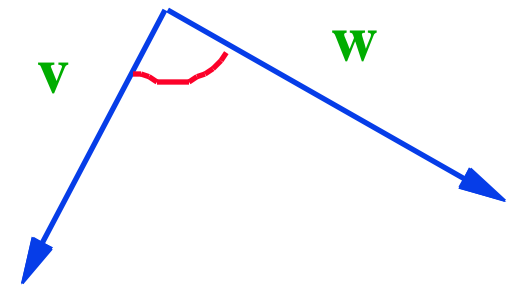
- Given a Lattice defined by : $\vec{L} = n_1\vec{a} + n_2\vec{b} + n_3\vec{c}$

the volume of the primitive cell is defined by: $V = \vec{a} \cdot (\vec{b} \times \vec{c})$

Given the basis of a lattice composed of vectors **a**, **b** and **c**, how does one calculate bond angles and bond length for atoms or groups of atoms in a crystal ? The bond length will be defined from the length of a vector connecting two points and the bond angle as the angle between two vectors.

If the vectors **a**, **b** and **c** define a basis for a rectangular coordinate system, then, the length of a vector **r** (x,y,z) is given by:

$$|\vec{r}| = \sqrt{x^2 + y^2 + z^2}$$



The angle between two vectors **v** (v_1, v_2, v_3) and **w** (w_1, w_2, w_3) is given by:

$$\vec{v} \cdot \vec{w} = |\vec{v}| |\vec{w}| \cos(\theta) = v_1 w_1 + v_2 w_2 + v_3 w_3$$

Then, since many lattices have a non-cartesian crystal lattice basis, how do we define bond length and angles in general ?

Generalized Equations for Bond Lengths and Bond Angles

$$\vec{v} \cdot \vec{w} = (v_1 \vec{a} + v_2 \vec{b} + v_3 \vec{c}) \cdot (w_1 \vec{a} + w_2 \vec{b} + w_3 \vec{c}) =$$

$$v_1 w_1 \vec{a} \cdot \vec{a} + v_2 w_1 \vec{b} \cdot \vec{a} + v_3 w_1 \vec{c} \cdot \vec{a} +$$

$$v_1 w_2 \vec{a} \cdot \vec{b} + v_2 w_2 \vec{b} \cdot \vec{b} + v_3 w_2 \vec{c} \cdot \vec{b} +$$

$$v_1 w_3 \vec{a} \cdot \vec{c} + v_2 w_3 \vec{b} \cdot \vec{c} + v_3 w_3 \vec{c} \cdot \vec{c}$$

$$= \begin{bmatrix} v_1 & v_2 & v_3 \end{bmatrix} \begin{bmatrix} \vec{a} \cdot \vec{a} & \vec{a} \cdot \vec{b} & \vec{a} \cdot \vec{c} \\ \vec{b} \cdot \vec{a} & \vec{b} \cdot \vec{b} & \vec{b} \cdot \vec{c} \\ \vec{c} \cdot \vec{a} & \vec{c} \cdot \vec{b} & \vec{c} \cdot \vec{c} \end{bmatrix} \begin{bmatrix} w_1 \\ w_2 \\ w_3 \end{bmatrix}$$

Metrical Matrix

$$\vec{v} \cdot \vec{w} = \vec{v}^T G \vec{w}$$

row matrix of components column matrix of components

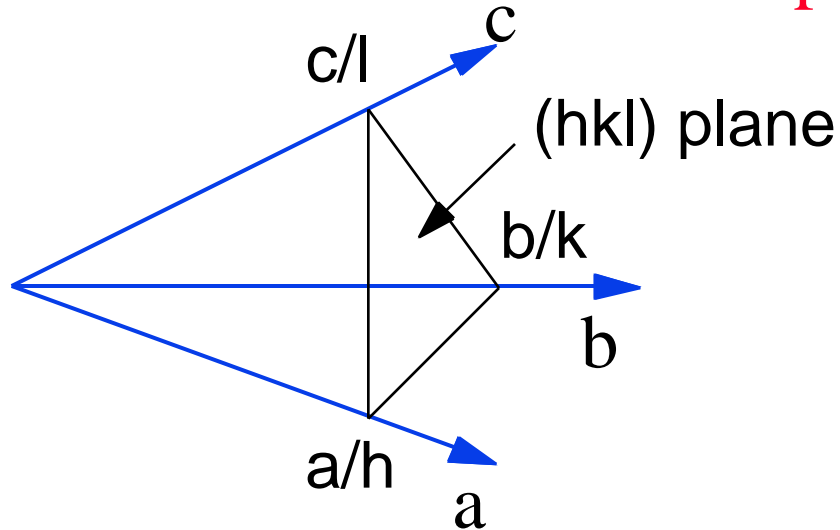
The G elements are the terms a^2 , $ab \cos(\theta)$, $ac \cos(\theta)$, etc,....which are easily obtained from the length of and the angles between the cell axes.

$$|\vec{v}| = \sqrt{\vec{v} \cdot \vec{v}} = \sqrt{\vec{v}^T G \vec{v}}$$

$$\cos(\theta) = \frac{\vec{v} \cdot \vec{w}}{|\vec{v}| |\vec{w}|} = \frac{\sqrt{\vec{v}^T G \vec{w}}}{\sqrt{\vec{v}^T G \vec{v}} \sqrt{\vec{w}^T G \vec{w}}}$$

Finally the bond length and the bond angle are obtained from:

Reciprocal Lattice



In diffraction experiments we will learn about distances between crystallographic planes of type (hkl). These **spacings** are measured along the normal between two adjacent planes having the same Miller indices.

The interplanar spacings are easily obtained by consideration of what is called the reciprocal lattice. Any lattice defined by a basis of three vectors, \mathbf{a} , \mathbf{b} , \mathbf{c} has an associated reciprocal lattice defined by a basis of three vectors \mathbf{a}^* , \mathbf{b}^* , \mathbf{c}^* which have the following properties:

1. The reciprocal lattice vector $\mathbf{g} = h \mathbf{a}^* + k \mathbf{b}^* + l \mathbf{c}^*$ is perpendicular to the direct lattice plane with Miller Indices (hkl).
2. The interplanar spacing d_{hkl} between successive (hkl) planes is:

$$d_{hkl} = \frac{1}{|\mathbf{g}|}$$

Determination of the Reciprocal Lattice Vectors

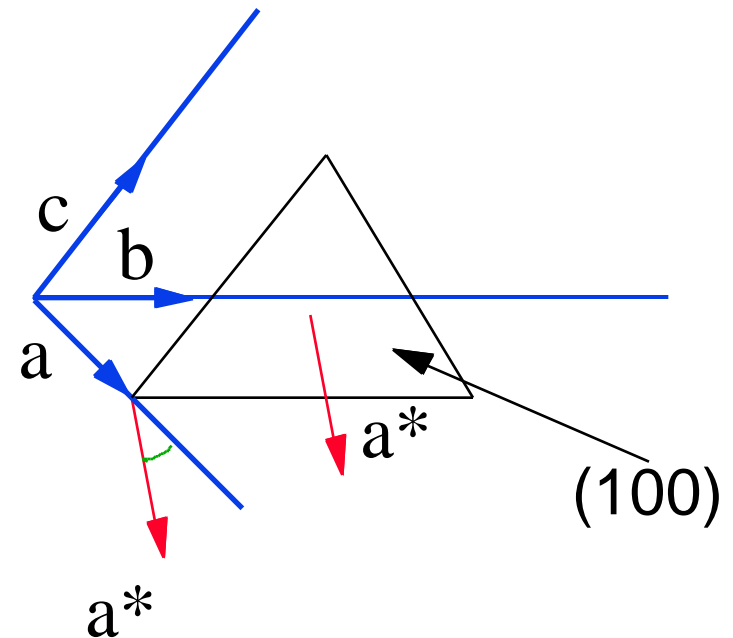
- \mathbf{a}^* , \mathbf{b}^* , \mathbf{c}^* must form a basis such that \mathbf{a}^* is perpendicular to \mathbf{b} & \mathbf{c} , \mathbf{b}^* is perpendicular to \mathbf{a} & \mathbf{c} and \mathbf{c}^* is perpendicular to \mathbf{a} & \mathbf{b} . That this must be so can be understood from the fact that the reciprocal space vector $\mathbf{g} = 1.\mathbf{a}^* + 0.\mathbf{b}^* + 0.\mathbf{c}^*$ ($\mathbf{g} = \mathbf{a}^*$) is normal to the (100) plane. Therefore \mathbf{a}^* must be parallel to the vector $\mathbf{b} \times \mathbf{c}$ which is perpendicular to both \mathbf{b} and \mathbf{c} .

$$\mathbf{a}^* = \text{const} (\mathbf{b} \times \mathbf{c}) \text{ and } |\vec{a}^*| = \frac{1}{d_{100}}$$

$$d_{100} = |\vec{a}| \cos(\theta) \quad |\vec{a}^*| = \frac{1}{|\vec{a}| \cos(\theta)}$$

$$|\vec{a}^*| |\vec{a}| \cos(\theta) = 1 \quad \vec{a}^* \cdot \vec{a} = 1$$

$$\text{const} = \frac{1}{\vec{a} \cdot (\vec{b} \times \vec{c})} \quad \rightarrow \text{Unit Cell Volume}$$



Therefore the reciprocal lattice vector \mathbf{a}^* is given by :

$$\vec{a}^* = \frac{\vec{b} \times \vec{c}}{\vec{a} \cdot (\vec{b} \times \vec{c})}$$

Following the same arguments, we can calculate \mathbf{b}^* and \mathbf{c}^*

$$\vec{b}^* = \frac{\vec{c} \times \vec{a}}{\vec{a} \cdot (\vec{b} \times \vec{c})} \quad \text{and} \quad \vec{c}^* = \frac{\vec{a} \times \vec{b}}{\vec{a} \cdot (\vec{b} \times \vec{c})}$$

Note that:

$$\vec{a} \cdot \vec{a}^* = \vec{b} \cdot \vec{b}^* = \vec{c} \cdot \vec{c}^* = 1$$

$$\vec{a} \cdot \vec{b}^* = \vec{b} \cdot \vec{a}^* = \vec{a} \cdot \vec{c}^* = \vec{c} \cdot \vec{a}^* = \vec{b} \cdot \vec{c}^* = \vec{c} \cdot \vec{b}^* = 0$$

If $\vec{g} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$

$$|\vec{g}|^2 = \frac{1}{d_{hkl}^2} = [h \quad k \quad l] G^{-1} \begin{matrix} h \\ k \\ l \end{matrix}$$

A given vector can be expressed in both the direct lattice and the reciprocal lattice. The coordinates of this vector in the two bases are related to each other through the Matrix H. **As a homework problem determine this matrix H.**

$$\vec{r}_{dir\ lat} = x\vec{a} + y\vec{b} + z\vec{c}$$

$$\vec{r}_{rec\ lat} = x'\vec{a}^* + y'\vec{b}^* + z'\vec{c}^*$$

$$\vec{r}_{rec\ lat} = H\vec{r}_{dir\ lat}$$

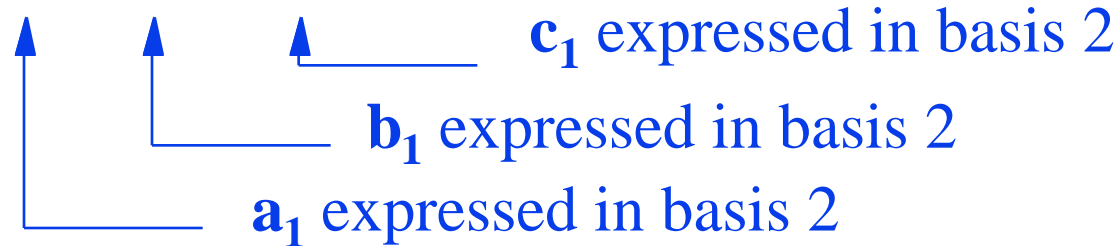
General coordinate transforms:

$$\vec{r}_{basis\ 2} = R\vec{r}_{basis\ 1}$$

basis 1: ($\mathbf{a}_1, \mathbf{b}_1, \mathbf{c}_1$)

basis 2: ($\mathbf{a}_2, \mathbf{b}_2, \mathbf{c}_2$)

$$where : R = \begin{pmatrix} a_1^X & b_1^X & c_1^X \\ a_1^Y & b_1^Y & c_1^Y \\ a_1^Z & b_1^Z & c_1^Z \end{pmatrix}$$



Physical Properties and Symmetry

- **Goal:** Use the crystal symmetry to determine the minimum symmetry of a physical property.

Neumann's Principle:

The symmetry elements of any physical property of a crystal must include at least the symmetry elements of the point group of the crystal. This implies the physical properties can have more symmetry elements than the point group.

- **Examples of physical properties:**

$$\vec{j} = \rho \vec{E} \quad \text{current density} = \text{conductivity} \times \text{electric field}$$

$$\vec{P} = \chi \vec{E} \quad \text{elect. polarization} = \text{elect. susceptibility} \times \text{elect. field}$$

$$\vec{q} = -k \vec{T} \quad \text{heat flux} = \text{thermal conductivity} \times \text{temperature gradient}$$

$$\varepsilon = S \sigma \quad \text{strain} = \text{elastic compliance} \times \text{stress}$$

- The property is a tensorial quantity as it generally depends on the choice of the coordinate system. Physical properties are described by **symmetric tensors**.
- Let us consider the example of the relationship between conductivity and electric field in the case of a cubic crystal and examine the effect of the crystal symmetry on the symmetry of the electric conductivity.

A cubic crystal has four 3-fold axes of symmetry along $\langle 111 \rangle$ axes. The electric conductivity must therefore have at least this degree of symmetry.

$$\vec{j} = \rho \vec{E}$$

$$(R\vec{j}) = \rho (R\vec{E})$$

$$\vec{j} = R^{-1} \rho R \vec{E}$$

$$\rho = R^{-1} \rho R$$

We rotate the space by 120° around the $[111]$ direction (R is the rotation matrix). Note that $R^{-1} R$ is a **similarity transformation** as we require the physical property (conductivity) to be unchanged by the rotation (symmetry element)

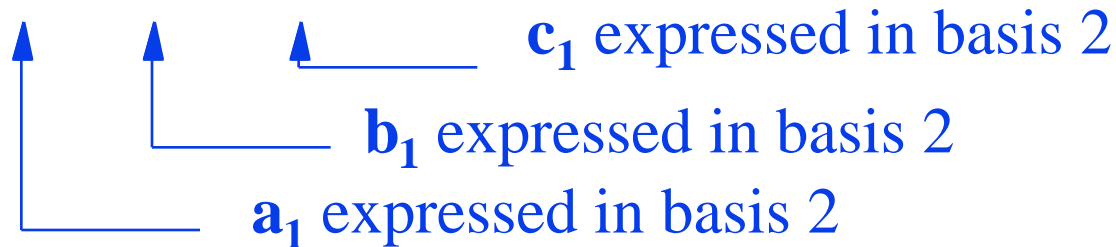
- Determination of R: R is the matrix associated with the rotation around the [111] axis, i.e. it is a coordinate axis transformation.

$$\vec{r}_{basis\ 2} = R\vec{r}_{basis\ 1}$$

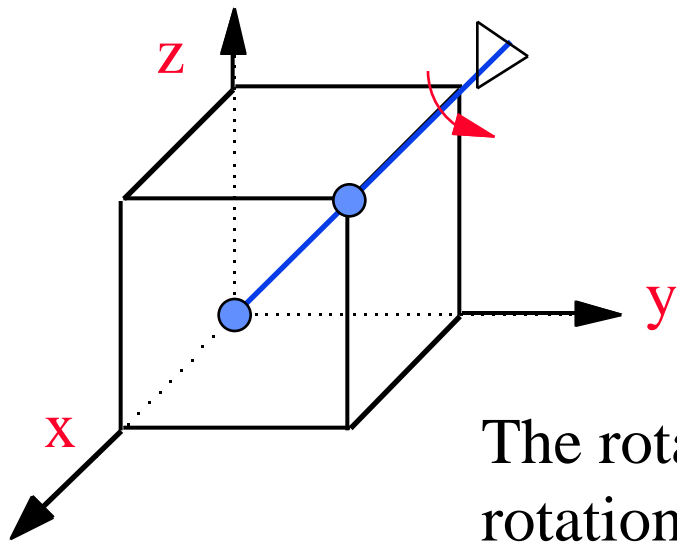
basis 1: ($\mathbf{a}_1, \mathbf{b}_1, \mathbf{c}_1$)

basis 2: ($\mathbf{a}_2, \mathbf{b}_2, \mathbf{c}_2$)

$$where : R = \begin{pmatrix} a_1^X & b_1^X & c_1^X \\ a_1^Y & b_1^Y & c_1^Y \\ a_1^Z & b_1^Z & c_1^Z \end{pmatrix}$$



For example: The first column of R corresponds to the coordinates of [100] in the new system.



old	new			
x	y'	$3 = C_3 = R =$	0	0
y	z'		1	0
z	x'		0	1

The rotation matrix R is orthogonal and the inverse rotation is equal to the transpose of the direct rotation.
 $R \cdot R^T = R^T \cdot R = 1$ or $R^T = R^{-1}$.

Therefore $R^{-1} = R^T$ R is equivalent to $R^T = R^{-1}$

$$\begin{array}{ccccccc}
 \rho_{11} & \rho_{12} & \rho_{13} & 0 & 1 & 0 & \rho_{11} & \rho_{12} & \rho_{13} & 0 & 0 & 1 \\
 \rho_{21} & \rho_{22} & \rho_{23} & = & 0 & 0 & 1 & \rho_{21} & \rho_{22} & \rho_{23} & 1 & 0 & 0 \\
 \rho_{31} & \rho_{32} & \rho_{33} & & 1 & 0 & 0 & \rho_{31} & \rho_{32} & \rho_{33} & 0 & 1 & 0 \\
 \\
 & \rho_{21} & \rho_{22} & \rho_{23} & 0 & 0 & 1 & & \rho_{22} & \rho_{23} & \rho_{21} & & \\
 = & \rho_{31} & \rho_{32} & \rho_{33} & 1 & 0 & 0 & = & \rho_{32} & \rho_{33} & \rho_{31} & & \\
 & \rho_{11} & \rho_{12} & \rho_{13} & 0 & 1 & 0 & & \rho_{12} & \rho_{13} & \rho_{11} & &
 \end{array}$$

The equality between matrices implies:

$$\rho_{11} = \rho_{22} = \rho_{33} \text{ and } \rho_{12} = \rho_{23} = \rho_{31} \text{ and } \rho_{13} = \rho_{21} = \rho_{32}$$

If we repeat these calculations for a rotation around another axis of the <111> family, we would find other constraints, such as

$$\rho_{12} = -\rho_{21} \text{ so that we can conclude } \rho_{ij} = -\rho_{ji} = 0$$

Therefore:

$$\rho = \begin{pmatrix} \rho_{11} & 0 & 0 \\ 0 & \rho_{11} & 0 \\ 0 & 0 & \rho_{11} \end{pmatrix} = \rho \cdot \underline{\underline{1}}$$

Note that to determine the inverse M^{-1} of any matrix, M , you should use the following approach:

$$M^{-1} = \text{Adjugate}(M) / \text{Determinant of } M$$

$$= \text{Transpose } (M(\text{cofactors})) / \text{Determinant of } M$$

where the cofactors of $M_{ij} = (-1)^{i+j}$ (Minor of M_{ij}) and the Minor of M_{ij} is obtained by calculating the determinant of the submatrix obtained by eliminating the i -th row and the j -th column.