Introduction to crystallographic calculations

Didactic material for the MaThCryst schools

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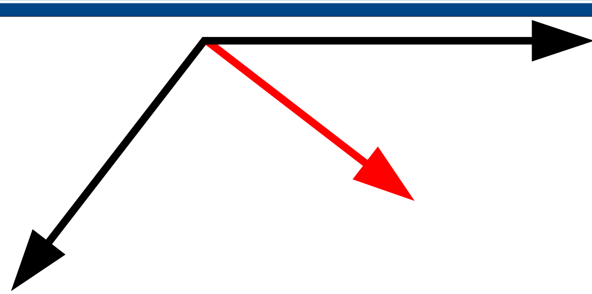
Covariant and contravariant quantities



Rotation of the red vector by 20º counterclockwise

Covariant quantities change like the basis and are written as row matrices

$$(\mathbf{abc}) \qquad (hkl)$$

Contravariant quantities change like the vector and are written as column matrices

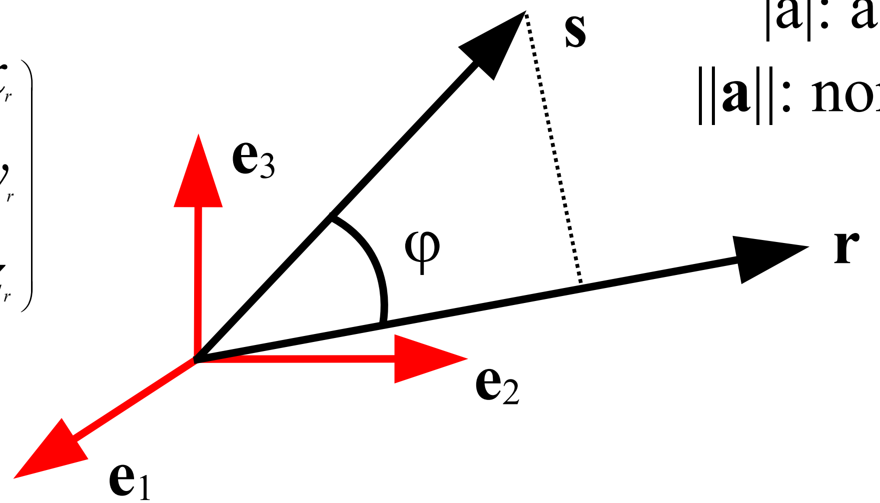
$$\begin{pmatrix}\mathbf{a}^*\\ \mathbf{b}^*\\ \mathbf{c}^*\end{pmatrix} \qquad \begin{pmatrix}x\\ y\\ z\end{pmatrix} \qquad \begin{pmatrix}u\\ v\\ w\end{pmatrix}$$

Scalar product in a Cartesian (orthonormal) basis

$\mathbf{r}\cdot\mathbf{s} = \|\mathbf{r}\|\cdot\|\mathbf{s}\|\cos\varphi$

|a|: absolute value of a

||**a**||: norm of the vector **a**



$$\mathbf{r} = x_r\mathbf{e}_1 + y_r\mathbf{e}_2 + z_r\mathbf{e}_3 = \begin{pmatrix}\mathbf{e}_1 & \mathbf{e}_2 & \mathbf{e}_3\end{pmatrix}\begin{pmatrix}x_r\\ y_r\\ z_r\end{pmatrix}$$

$$\mathbf{s} = x_s\mathbf{e}_1 + y_s\mathbf{e}_2 + z_s\mathbf{e}_3 = \begin{pmatrix}\mathbf{e}_1 & \mathbf{e}_2 & \mathbf{e}_3\end{pmatrix}\begin{pmatrix}x_s\\ y_s\\ z_s\end{pmatrix}$$

$$\mathbf{r}\cdot\mathbf{s} = x_r x_s + y_r y_s + z_r z_s = \begin{pmatrix}x_r & y_r & z_r\end{pmatrix}\begin{pmatrix}x_s\\ y_s\\ z_s\end{pmatrix} = \begin{pmatrix}x_r & y_r & z_r\end{pmatrix}\begin{pmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{pmatrix}\begin{pmatrix}x_s\\ y_s\\ z_s\end{pmatrix} = \begin{pmatrix}x_r & y_r & z_r\end{pmatrix}\begin{pmatrix}\mathbf{e}_1\\ \mathbf{e}_2\\ \mathbf{e}_3\end{pmatrix}\begin{pmatrix}\mathbf{e}_1 & \mathbf{e}_2 & \mathbf{e}_3\end{pmatrix}\begin{pmatrix}x_s\\ y_s\\ z_s\end{pmatrix}$$

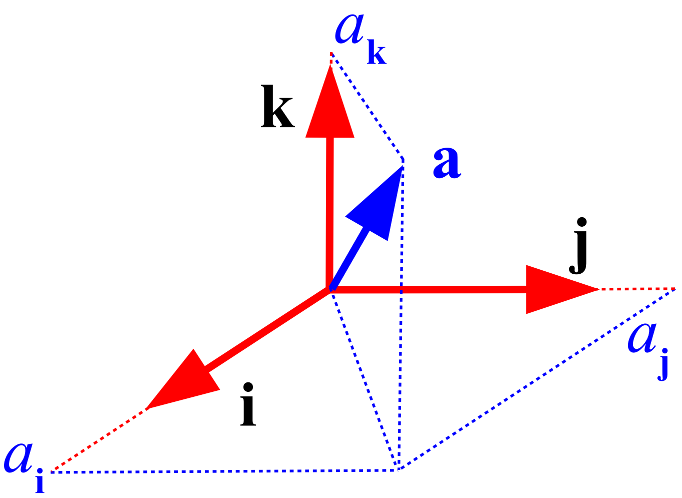
$\mathbf{r}_1^{\mathrm{T}}$ $\mathbf{r}_2$

Transposed vector! $\mathbf{r}_1^{\mathrm{T}}\cdot\mathbf{r}_2$

The scalar product being commutative, it can also be written as $\mathbf{r}_2^{\mathrm{T}}\cdot\mathbf{r}_1$.

Scalar product in a general basis

$$(\mathbf{abc}) = (\mathbf{e}_1\mathbf{e}_2\mathbf{e}_3)\begin{pmatrix} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \\ a_3 & b_3 & c_3 \end{pmatrix} = (\mathbf{e}_1\mathbf{e}_2\mathbf{e}_3)\mathbf{B}$$



Coordinates are contravariant

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix}_{\mathbf{abc}} = \begin{pmatrix} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \\ a_3 & b_3 & c_3 \end{pmatrix}^{-1} \begin{pmatrix} x \\ y \\ z \end{pmatrix}_{\mathbf{e}} = \mathbf{B}^{-1}\begin{pmatrix} x \\ y \\ z \end{pmatrix}_{\mathbf{e}}$$

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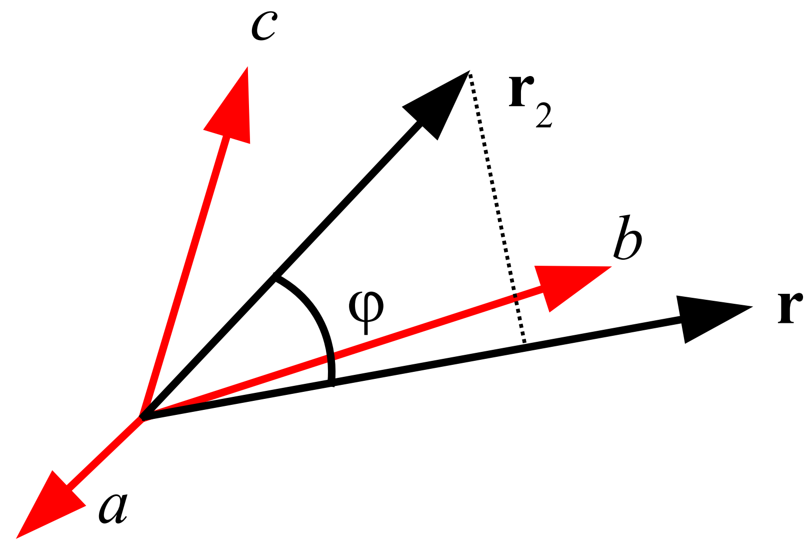
Scalar product in a general basis

$$\mathbf{r}\cdot\mathbf{s} = \|\mathbf{r}\|\cdot\|\mathbf{s}\|\cos\varphi$$

$$\mathbf{r} = x_r\mathbf{a}+y_r\mathbf{b}+z_r\mathbf{c}=(\mathbf{abc})\begin{pmatrix} x_r \\ y_r \\ z_r \end{pmatrix}$$

$$\mathbf{r}^{\mathrm{T}}\cdot\mathbf{s} = (x_r \;\; y_r \;\; z_r)\begin{pmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{pmatrix}(\mathbf{abc})\begin{pmatrix} x_s \\ y_s \\ z_s \end{pmatrix}$$



$$=\begin{pmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{pmatrix}(\mathbf{abc})=\begin{pmatrix} a_i & a_j & a_k \\ b_i & b_j & b_k \\ c_i & c_j & c_k \end{pmatrix}\begin{pmatrix} \mathbf{e}_1 \\ \mathbf{e}_2 \\ \mathbf{e}_3 \end{pmatrix}(\mathbf{e}_1\mathbf{e}_2\mathbf{e}_3)\begin{pmatrix} a_i & b_i & c_i \\ a_j & b_j & c_j \\ a_k & b_k & c_k \end{pmatrix}=\begin{pmatrix} \sum_m a_m^2 & \sum_m a_m b_m & \sum_m a_m c_m \\ \sum_m b_m a_m & \sum_m b_m^2 & \sum_m b_m c_m \\ \sum_m c_m a_m & \sum_m c_m b_m & \sum_m c_m^2 \end{pmatrix}$$

$\Sigma_i a_i b_i = \Sigma_i b_i a_i = \Sigma_i b_i(\mathbf{a}\cdot\mathbf{e}_i) = \Sigma_i \mathbf{a}\cdot(b_i\mathbf{e}_i) = \mathbf{a}\cdot\Sigma_i(b_i\mathbf{e}_i) = \mathbf{a}\cdot\mathbf{b}$, etc

Scalar product in a general basis

$$=\begin{pmatrix}\mathbf{a}\\\mathbf{b}\\\mathbf{c}\end{pmatrix}(\mathbf{abc})=\begin{pmatrix}\mathbf{a\cdot a} & \mathbf{a\cdot b} & \mathbf{a\cdot c}\\\mathbf{b\cdot a} & \mathbf{b\cdot b} & \mathbf{b\cdot c}\\\mathbf{c\cdot a} & \mathbf{c\cdot b} & \mathbf{c\cdot c}\end{pmatrix}= \quad =\begin{pmatrix}a^2 & ab\cos\gamma & ac\cos\beta\\ab\cos\gamma & b^2 & bc\cos\alpha\\ac\cos\beta & bc\cos\alpha & c^2\end{pmatrix}$$

Metric tensor

$$\mathbf{r}^{\mathrm{T}}\cdot\mathbf{s}=\begin{pmatrix}x_r & y_r & z_r\end{pmatrix}\begin{pmatrix}\mathbf{a}\\\mathbf{b}\\\mathbf{c}\end{pmatrix}(\mathbf{abc})\begin{pmatrix}x_s\\y_s\\z_s\end{pmatrix}=\begin{pmatrix}x_r & y_r & z_r\end{pmatrix}\begin{pmatrix}a^2 & ab\cos\gamma & ac\cos\beta\\ab\cos\gamma & b^2 & bc\cos\alpha\\ac\cos\beta & bc\cos\alpha & c^2\end{pmatrix}\begin{pmatrix}x_s\\y_s\\z_s\end{pmatrix}$$

$$=\begin{pmatrix}x_r & y_r & z_r\end{pmatrix}\mathbf{G}\begin{pmatrix}x_s\\y_s\\z_s\end{pmatrix}$$

The scalar product is commutative, the metric tensor is symmetric.

Calculation of the norm of a vector and of the angle between two vectors

$$\mathbf{r}\cdot\mathbf{s} = ||\mathbf{r}||\cdot||\mathbf{s}||\cos\varphi \qquad \mathbf{r}\cdot\mathbf{r} = ||\mathbf{r}||\cdot||\mathbf{r}||\cos 0^{o} = ||\mathbf{r}||^2$$

$$||\mathbf{r}|| = (\mathbf{r}\cdot\mathbf{r})^{1/2} = \sqrt{(x \;\; y \;\; z)\mathbf{G}\begin{pmatrix} x \\ y \\ z \end{pmatrix}}$$

Angle between two vectors

$$\mathbf{r}\cdot\mathbf{s} = ||\mathbf{r}||\cdot||\mathbf{rs}||\cos\varphi$$

$$\cos\varphi = \mathbf{r}\cdot\mathbf{s}\,/||\mathbf{r}||\cdot||\mathbf{s}|| = \frac{(x_r \;\; y_r \;\; z_r)\mathbf{G}\begin{pmatrix} x_s \\ y_s \\ z_s \end{pmatrix}}{\sqrt{(x_r \;\; y_r \;\; z_r)\mathbf{G}\begin{pmatrix} x_r \\ y_r \\ z_r \end{pmatrix}}\sqrt{(x_s \;\; y_s \;\; z_s)\mathbf{G}\begin{pmatrix} x_s \\ y_s \\ z_s \end{pmatrix}}}$$

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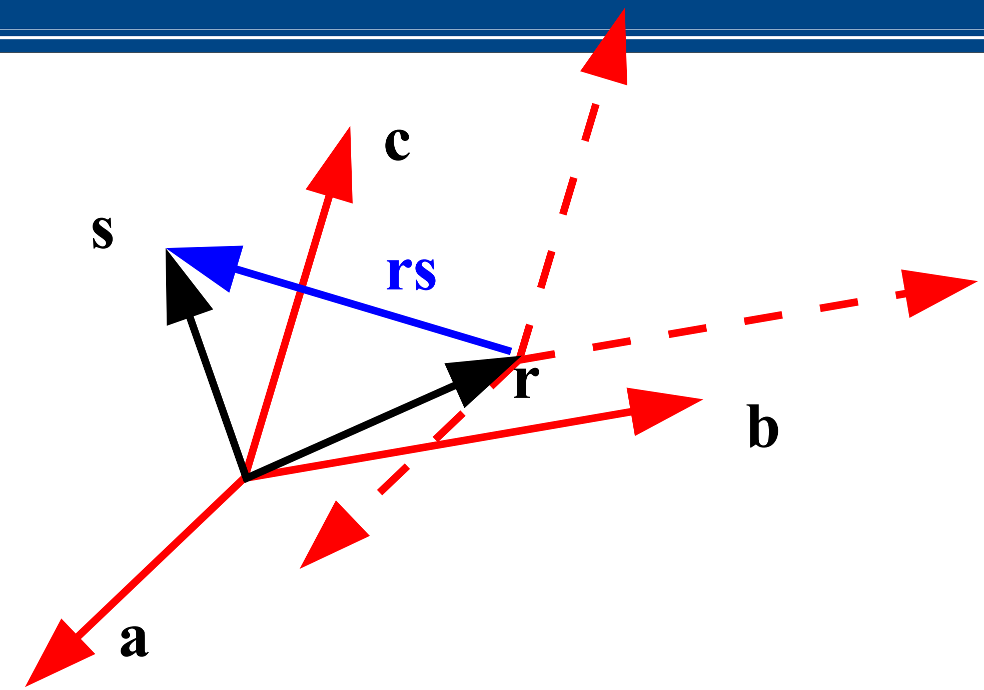
Calculation of the interatomic distances

The distance between atoms **r** and **s** is the norm of the vector **rs** = **s**-**r**.



$$\|\mathbf{rs}\| = (\mathbf{rs}\cdot\mathbf{rs})^{1/2} = \sqrt{\begin{pmatrix} x_s - x_r & y_s - y_r & z_s - z_r \end{pmatrix} \mathbf{G} \begin{pmatrix} x_s - x_r \\ y_s - y_r \\ z_s - z_r \end{pmatrix}} = \sqrt{\begin{pmatrix} \Delta x & \Delta y & \Delta z \end{pmatrix} \mathbf{G} \begin{pmatrix} \Delta x \\ \Delta y \\ \Delta z \end{pmatrix}}$$

To take the difference of coordinates is equivalent to use a local reference translated onto atom **r**. The result is the same if one uses **rs** because the dot product is commutative.

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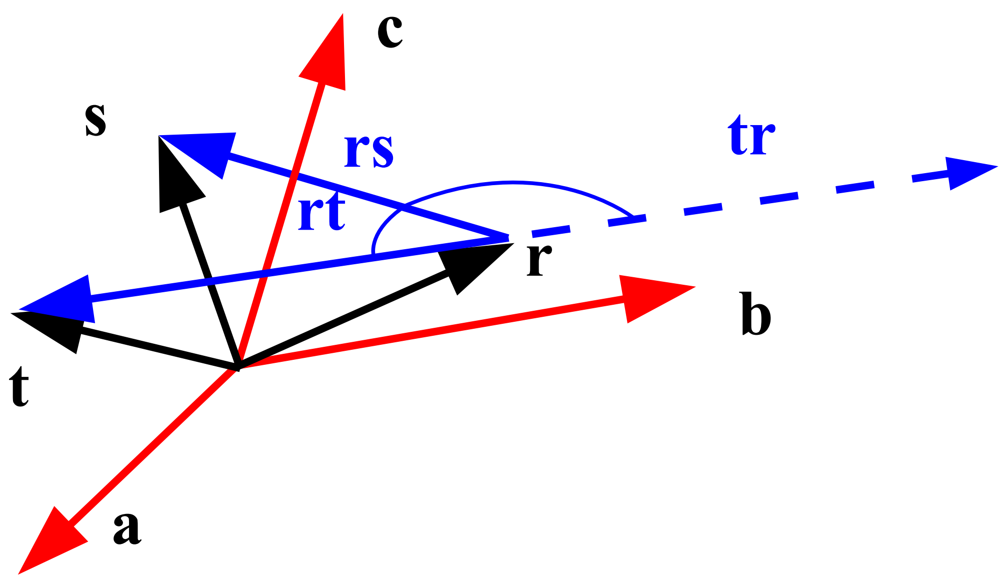
Calculation of the interatomic angles

The angle s-r-t is the angle between the vectors **rs** and **rt**.



To take the difference of coordinates is equivalent to use a local reference translated onto atom No. 1.

$$\mathbf{rs}\cdot\mathbf{rt} = \|\mathbf{rs}\|\cdot\|\mathbf{rt}\|\cos\varphi$$

$$\cos\varphi = \mathbf{rs}\cdot\mathbf{rt} / \|\mathbf{rs}\|\cdot\|\mathbf{rt}\| = \frac{\begin{pmatrix}\Delta x_{rs} & \Delta y_{rs} & \Delta z_{rs}\end{pmatrix}\mathbf{G}\begin{pmatrix}\Delta x_{rt}\\ \Delta y_{rt}\\ \Delta z_{rt}\end{pmatrix}}{\sqrt{\begin{pmatrix}\Delta x_{rs} & \Delta y_{rs} & \Delta z_{rs}\end{pmatrix}\mathbf{G}\begin{pmatrix}\Delta x_{rs}\\ \Delta y_{rs}\\ \Delta z_{rs}\end{pmatrix}}\sqrt{\begin{pmatrix}\Delta x_{rt} & \Delta y_{rt} & \Delta z_{rt}\end{pmatrix}\mathbf{G}\begin{pmatrix}\Delta x_{rt}\\ \Delta y_{rt}\\ \Delta z_{rt}\end{pmatrix}}}$$

Warning! Exchanging the sense of one of the two vectors results in the supplementary angle.

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Example - $P2_1/c$

a = 9.691 Å, b = 8.993 Å, c = 5.231 Å, β = 108.61°

$$\mathbf{G} = \begin{pmatrix} 9.691^2 & 0 & 9.691\cdot 5.231\cdot\cos 108.61 \\ 0 & 8.993^2 & 0 \\ 9.691\cdot 5.231\cdot\cos 108.61 & 0 & 5.231^2 \end{pmatrix} = \begin{pmatrix} 93.915 & 0 & -16.178 \\ 0 & 80.874 & 0 \\ -16.178 & 0 & 27.363 \end{pmatrix}$$

Distance Fe-O: Fe(0.7431 0.5154 0.2770), O(0.6313 0.5162 -0.1178)

Δ = 0.6313-0.7431, 0.5162-0.5154, -0.1178-0.2770= -0.1118, 0.0008, -0.3948

$$d = \|\mathbf{r}_{12}\|^{1/2} = \sqrt{\begin{pmatrix} -0.1118 & 0.0008 & -0.3948 \end{pmatrix} \begin{pmatrix} 93.915 & 0 & -16.178 \\ 0 & 80.874 & 0 \\ -16.178 & 0 & 27.363 \end{pmatrix} \begin{pmatrix} -0.1118 \\ 0.0008 \\ -0.3948 \end{pmatrix}}$$

$$= \sqrt{\begin{pmatrix} -4.1126 & 0.06470 & -8.9942 \end{pmatrix} \begin{pmatrix} -0.1118 \\ 0.0008 \\ -0.3948 \end{pmatrix}} = \sqrt{4.011} = 2.003 \text{ Å}$$

Example - $P2_1/c$

a = 9,691 Å, b = 8,993 Å, c = 5,231 Å, β = 108,61°

$$\mathbf{G} = \begin{pmatrix} 9.691^2 & 0 & 9.691\cdot 5.231\cdot\cos 108.61 \\ 0 & 8.993^2 & 0 \\ 9.691\cdot 5.231\cdot\cos 108.61 & 0 & 5.231^2 \end{pmatrix} = \begin{pmatrix} 93.915 & 0 & -16.178 \\ 0 & 80.874 & 0 \\ -16.178 & 0 & 27.363 \end{pmatrix}$$

Distance Fe-O: Fe(0.7431 0.5154 0.2770), O(0.8679 0.3378 0.1812)

Δ = 0.8679-0.7431, 0.3378-0.5154, 0.1812-0.2770 = 0.1248, -0.1776, -0.0958

$$\mathrm{d} = \|\mathbf{r}_{13}\|^{1/2} = \sqrt{\begin{pmatrix} 0.1258 & -0.1776 & -0.0958 \end{pmatrix} \begin{pmatrix} 93.915 & 0 & -16.178 \\ 0 & 80.874 & 0 \\ -16.178 & 0 & 27.363 \end{pmatrix} \begin{pmatrix} 0.1248 \\ -0.1776 \\ -0.0958 \end{pmatrix}}$$

$$= \sqrt{\begin{pmatrix} 13.136 & -14.363 & -4.657 \end{pmatrix} \begin{pmatrix} 0.1248 \\ -0.1776 \\ -0.0958 \end{pmatrix}} = \sqrt{4.636} = 2.153 \text{ Å}$$

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Example - $P2_1/c$

$$a = 9{,}691\ \text{Å},\ b = 8{,}993\ \text{Å},\ c = 5{,}231\ \text{Å},\ \beta = 108{,}61^{\circ}$$

$$\mathbf{G} = \begin{pmatrix} 9.691^2 & 0 & 9.691\cdot 5.231\cdot\cos 108.61 \\ 0 & 8.993^2 & 0 \\ 9.691\cdot 5.231\cdot\cos 108.61 & 0 & 5.231^2 \end{pmatrix} = \begin{pmatrix} 93.915 & 0 & -16.178 \\ 0 & 80.874 & 0 \\ -16.178 & 0 & 27.363 \end{pmatrix}$$

$$\cos\varphi = \mathbf{r}_{12}\cdot\mathbf{r}_{13} \,/\, \|\mathbf{r}_{12}\|\cdot\|\mathbf{r}_{13}\| = \frac{\begin{pmatrix} -0.1118 & 0.0008 & -0.3948 \end{pmatrix}\begin{pmatrix} 93.915 & 0 & -16.178 \\ 0 & 80.874 & 0 \\ -16.178 & 0 & 27.363 \end{pmatrix}\begin{pmatrix} 0.1248 \\ -0.1776 \\ -0.0958 \end{pmatrix}}{2.003\cdot 2.153}$$

$$= \frac{\begin{pmatrix} -4.1126 & 0.06470 & -8.9942 \end{pmatrix}\begin{pmatrix} 0.1248 \\ -0.1776 \\ -0.0958 \end{pmatrix}}{4.313} = \frac{0.3369}{4.313} = 0.0781 \qquad \varphi = 85.52^{\circ}$$

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Volume of the unit cell

$$V = \mathbf{a}\cdot\mathbf{b}\times\mathbf{c} = abc(1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma+2\cos\alpha\cos\beta\cos\gamma)^{½}$$

$$\det(\mathbf{G}) = \det\begin{pmatrix} a^2 & ab\cos\gamma & ac\cos\beta \\ ab\cos\gamma & b^2 & bc\cos\alpha \\ ac\cos\beta & bc\cos\alpha & c^2 \end{pmatrix} = a^2b^2c^2 + ac\cos\beta\, ab\cos\gamma\, bc\cos\alpha + ac\cos\beta\, ab\cos\gamma\, bc\cos\alpha - b^2(ac\cos\beta)^2 - a^2(bc\cos\alpha)^2 - c^2(ab\cos\gamma)^2$$

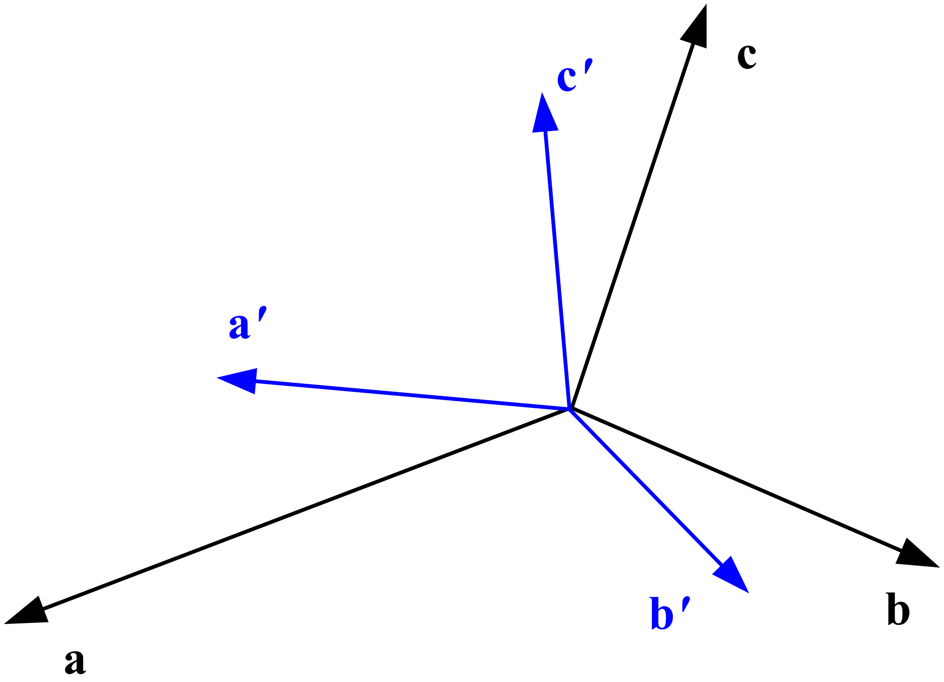
$$= a^2b^2c^2\,(1 - \cos^2\alpha - \cos^2\gamma - \cos^2\beta + 2\cos\beta\cos\gamma\cos\alpha)$$

$$\mathbf{V = \det(G)^{½}}$$

Question : why do we use a right-handed reference?

The determinant of the metric tensor being positive, the **volume** of the unit cell is **real**. If one uses a left-handed reference, the determinant of the metric tensor is negative and the volume of the unit cell becomes **imaginary**.

Unit cell transformation



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Change of basis

$$(\mathbf{abc})\mathbf{P} = (\mathbf{a'b'c'}) \qquad (\mathbf{abc}) = (\mathbf{ijk})\mathbf{B} \qquad (\mathbf{ijk}) = (\mathbf{abc})\mathbf{B}^{-1}$$

$$(\mathbf{a'b'c'}) = (\mathbf{ijk})\mathbf{B'} = (\mathbf{abc})\mathbf{B}^{-1}\mathbf{B'} \rightarrow \mathbf{P} = \mathbf{B}^{-1}\mathbf{B'} \rightarrow \mathbf{BP} = \mathbf{B'}$$

$$\mathbf{G} = \mathbf{B}^{\mathrm{T}}\mathbf{B} \qquad \mathbf{G'} = \mathbf{B'}^{\mathrm{T}}\mathbf{B'}$$

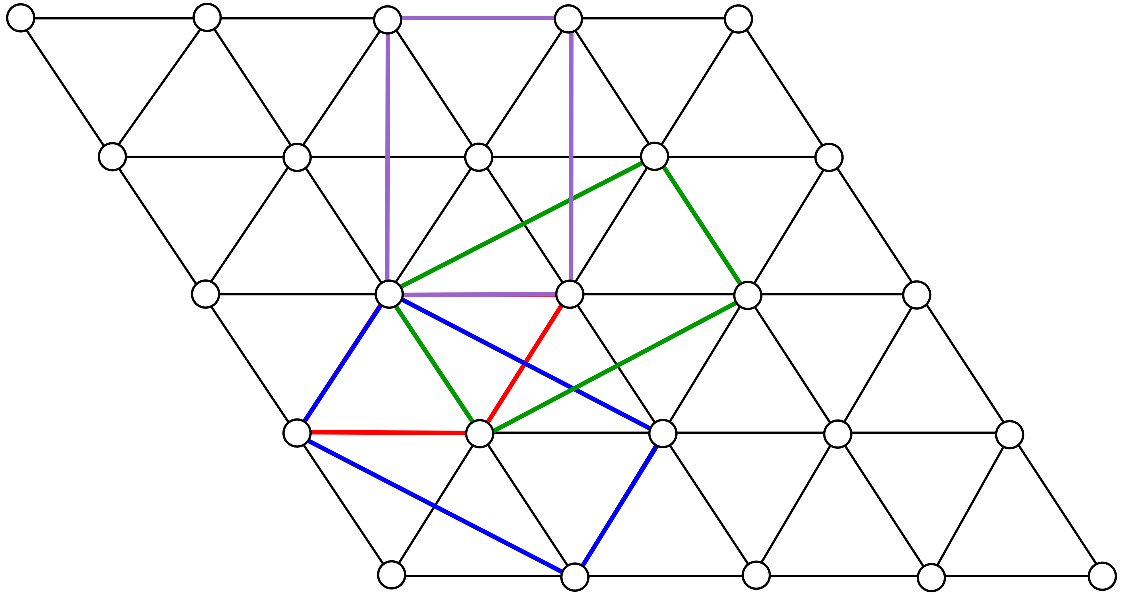
$$\mathbf{G'} = (\mathbf{BP})^{\mathrm{T}}(\mathbf{BP}) = \mathbf{P}^{\mathrm{T}}\mathbf{B}^{\mathrm{T}}\mathbf{BP} = \mathbf{P}^{\mathrm{T}}(\mathbf{B}^{\mathrm{T}}\mathbf{B})\mathbf{P} = \mathbf{P}^{\mathrm{T}}\mathbf{GP}$$

$$\mathbf{P} = \begin{array}{c} \\ \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{array} \begin{array}{c} \begin{array}{ccc} \mathbf{a'} & \mathbf{b'} & \mathbf{c'} \end{array} \\ \begin{bmatrix} a'_a & b'_a & c'_a \\ a'_b & b'_b & c'_b \\ a'_c & b'_c & c'_c \end{bmatrix} \end{array}$$

Check the determinant!

Orthohexagonal description of a hexagonal lattice

$A_1 = 5$ Å; $C = 7$ Å



$a, b, c = ?$

$$C_1 \quad \begin{bmatrix} 1 & 1 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$C_2 \quad \begin{bmatrix} 1 & \bar{1} & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$C_3 \quad \begin{bmatrix} 0 & \bar{2} & 0 \\ 1 & \bar{1} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

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Orthohexagonal description of a hexagonal lattice

$A_1 = 5$ Å; $C = 7$ Å

$$\mathbf{G} = \begin{bmatrix} 25 & -12.5 & 0 \\ -12.5 & 25 & 0 \\ 0 & 0 & 49 \end{bmatrix}$$

Det(**G**) = 22968.75

$$\mathbf{P} = \begin{bmatrix} 1 & \bar{1} & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Det(P) = 2 > 0

$$\mathbf{G'} = \mathbf{P}^t\mathbf{G}\mathbf{P} = \begin{bmatrix} 1 & 1 & 0 \\ \bar{1} & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 25 & -12.5 & 0 \\ -12.5 & 25 & 0 \\ 0 & 0 & 49 \end{bmatrix} \begin{bmatrix} 1 & \bar{1} & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$= \begin{bmatrix} 12.5 & 12.5 & 0 \\ -37.5 & 37.5 & 0 \\ 0 & 0 & 49 \end{bmatrix} \begin{bmatrix} 1 & \bar{1} & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 25 & 0 & 0 \\ 0 & 75 & 0 \\ 0 & 0 & 49 \end{bmatrix}$$

Det(**G'**) = 91875 = 4·Det(**G**)

$a = 5$ Å, $b = 8.6603$ Å; $c = 7$ Å $\alpha = \beta = \gamma = 90$ º $b = a\sqrt{3}$

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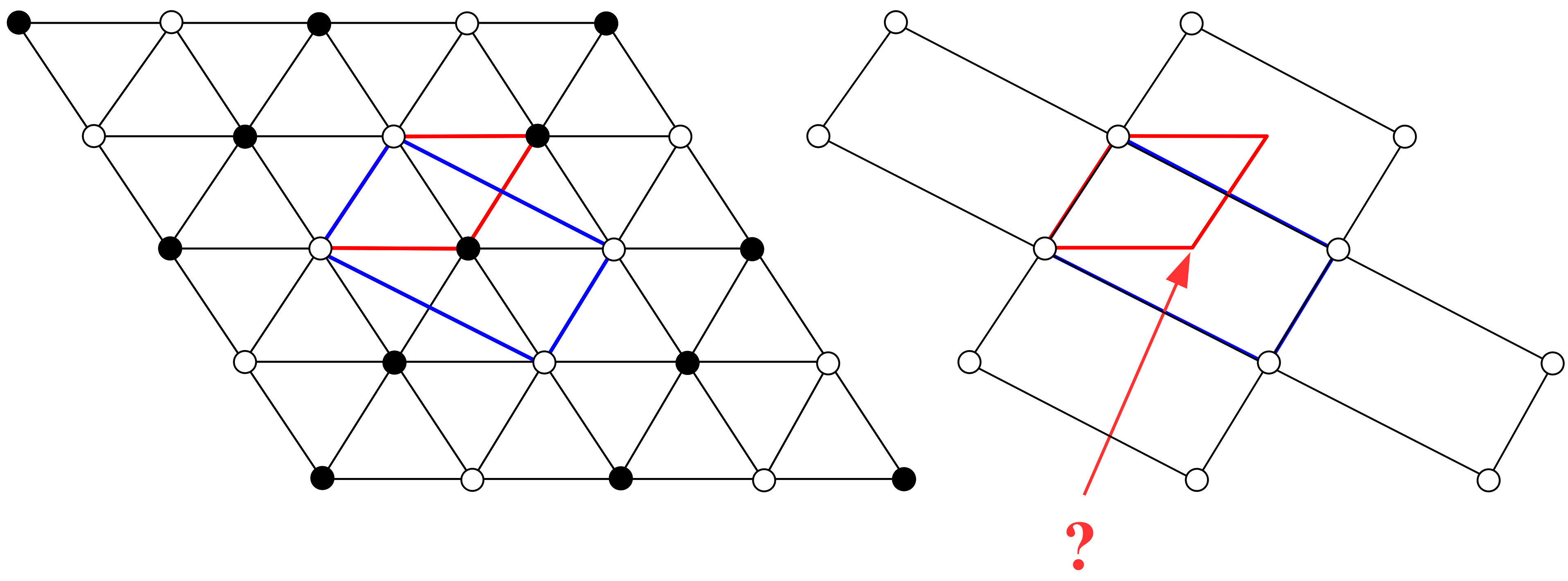
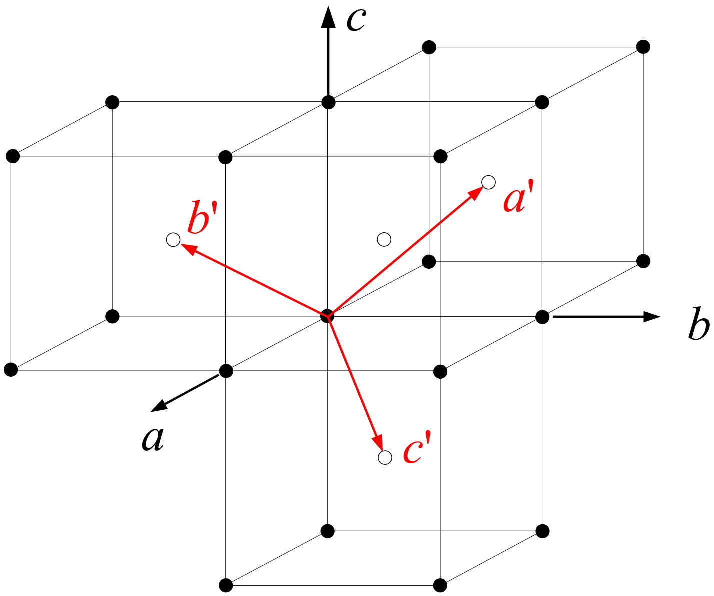
Orthohexagonal description of a hexagonal lattice

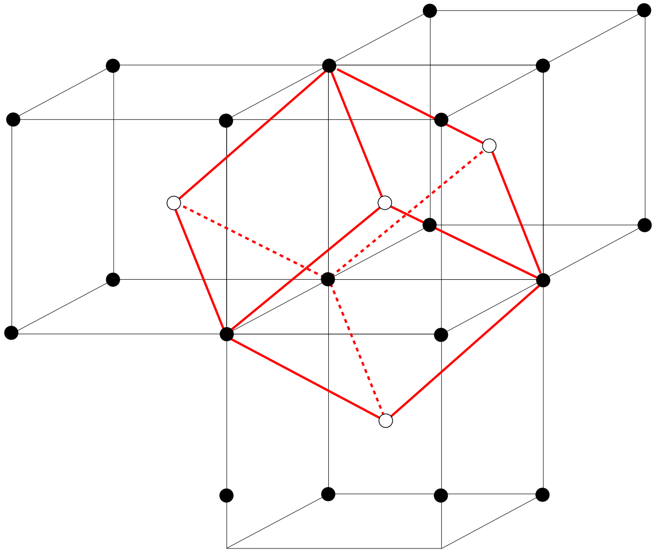
$$b \simeq a\sqrt{3}$$

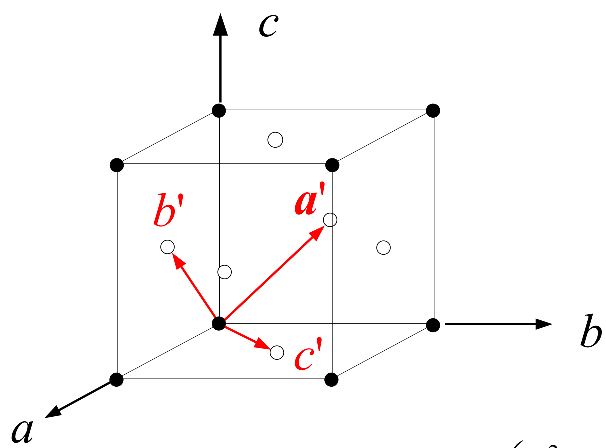
One can speak of pseudo-hexagonality only if the unit cell is of type *oC*!

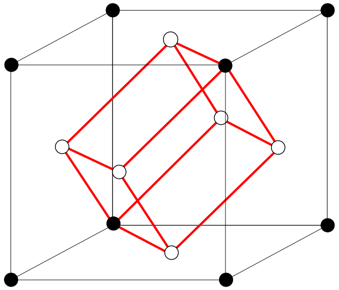


Exercise: the primitive cell of *cI* and *cF*









$\mathbf{G}_{\text{prim}} = \mathbf{P}^{t}\mathbf{G}_{\text{conv}}\mathbf{P}$

$\mathbf{G}_{\text{conv}} = \begin{pmatrix} a^2 & 0 & 0 \\ 0 & a^2 & 0 \\ 0 & 0 & a^2 \end{pmatrix} = a^2\mathbf{I}$

$\mathbf{G}_{\text{prim}} = a^2\mathbf{P}^{t}\mathbf{I}\mathbf{P} = a^2\mathbf{P}^{t}\mathbf{P}$

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Exercise: the primitive cell of *cI* and *cF*

cI

$$\mathbf{P} = \begin{pmatrix} \bar{1}/2 & 1/2 & 1/2 \\ 1/2 & \bar{1}/2 & 1/2 \\ 1/2 & 1/2 & \bar{1}/2 \end{pmatrix} \quad \mathbf{P}^t = \mathbf{P} \quad \mathrm{Det}(\mathbf{P}) = ½$$

$$\mathbf{G}_{\mathrm{prim}} = a^2\mathbf{P}^2 = \begin{pmatrix} \bar{1}/2 & 1/2 & 1/2 \\ 1/2 & \bar{1}/2 & 1/2 \\ 1/2 & 1/2 & \bar{1}/2 \end{pmatrix}^2$$

$$= a^2 \begin{pmatrix} 3/4 & -1/4 & -1/4 \\ -1/4 & 3/4 & -1/4 \\ -1/4 & -1/4 & 3/4 \end{pmatrix}$$

$$a' = b' = c' = a\sqrt{3/4} = a\sqrt{3}/2$$

$$\cos\alpha' = \cos\beta' = \cos\gamma' = \frac{-1/4}{3/4} = -\frac{1}{3}$$

→ $\alpha' = \beta' = \gamma' = \cos^{-1}(\bar{1}/3) = 109.47^{\circ}$

cF

$$\mathbf{P} = \begin{pmatrix} 0 & 1/2 & 1/2 \\ 1/2 & 0 & 1/2 \\ 1/2 & 1/2 & 0 \end{pmatrix} \quad \mathbf{P}^t = \mathbf{P} \quad \mathrm{Det}(\mathbf{P}) = ¼$$

$$\mathbf{G}_{\mathrm{prim}} = a^2\mathbf{P}^2 = \begin{pmatrix} 0 & 1/2 & 1/2 \\ 1/2 & 0 & 1/2 \\ 1/2 & 1/2 & 0 \end{pmatrix}^2$$

$$= a^2 \begin{pmatrix} 1/2 & 1/4 & 1/4 \\ 1/4 & 1/2 & 1/4 \\ 1/4 & 1/4 & 1/2 \end{pmatrix}$$

$$a' = b' = c' = a/\sqrt{2}$$

$$\cos\alpha' = \cos\beta' = \cos\gamma' = \frac{1/4}{1/2} = \frac{1}{2}$$

→ $\alpha' = \beta' = \gamma' = \cos^{-1}(1/2) = 60^{\circ}$

$a = b = c;\ \alpha = \beta = \gamma$ Rhombohedral unit cell

$\alpha = 90^{\circ}$: *cP* $\alpha = 109.47^{\circ}$: primitive of *cI* $\alpha = 60^{\circ}$: primitive of *cF*

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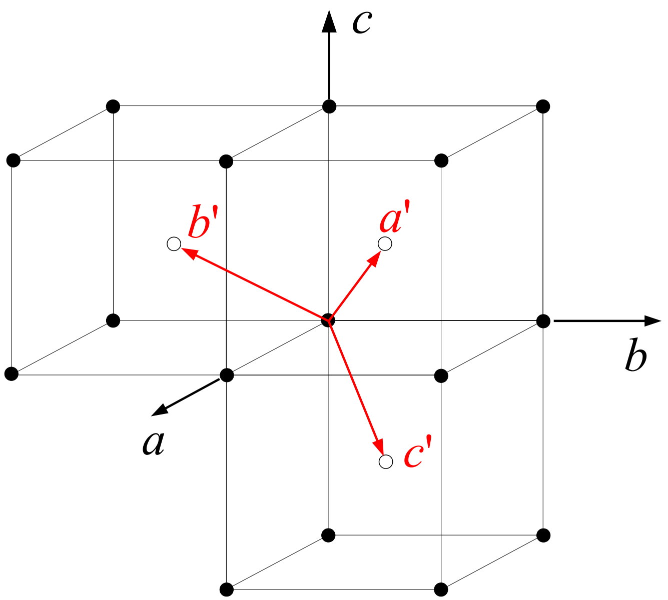
Exercise: the primitive cell of *cI* and *cF* (alternative reference)



$$\mathbf{P} = \begin{pmatrix} 1/2 & 1/2 & 1/2 \\ 1/2 & \bar{1}/2 & 1/2 \\ 1/2 & 1/2 & \bar{1}/2 \end{pmatrix} \qquad \mathbf{P}^t = \mathbf{P} \qquad \mathrm{Det}(\mathbf{P}) = ½$$

$$\mathbf{G}_{\mathrm{prim}} = a^2\mathbf{P}^2 = \begin{pmatrix} 1/2 & 1/2 & 1/2 \\ 1/2 & \bar{1}/2 & 1/2 \\ 1/2 & 1/2 & \bar{1}/2 \end{pmatrix}^2$$

$$= a^2 \begin{pmatrix} 3/4 & 1/4 & 1/4 \\ 1/4 & 3/4 & -1/4 \\ 1/4 & -1/4 & 3/4 \end{pmatrix}$$

$$a' = b' = c' = a\sqrt{3/4} = a\sqrt{3}/2$$

$$\cos\alpha' = \frac{-1/4}{3/4} = -\frac{1}{3}; \cos\beta' = \cos\gamma' = \frac{1/4}{3/4} = \frac{1}{3}$$

→ $\alpha' = \cos^{-1}(\bar{1}/3) = 109.47^{\circ}$; $\beta' = \gamma' = \cos^{-1}(1/3) = 70.53^{\circ}$

It looks less symmetric

But 70.53º is simply180-109.47º !