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8-13 October 2017, Sofia, Bulgaria

European Crystallographic Association

MATRIX-CALCULUS APPLICATIONS

SIMPLE CRYSTALLOGRAPHIC CALCULATIONS

POINTS and THEIR COORDINATES

Affine 3D-space:

formed by the set of all columns of three real numbers
represents all points of the point space

Point space + Coordinate system

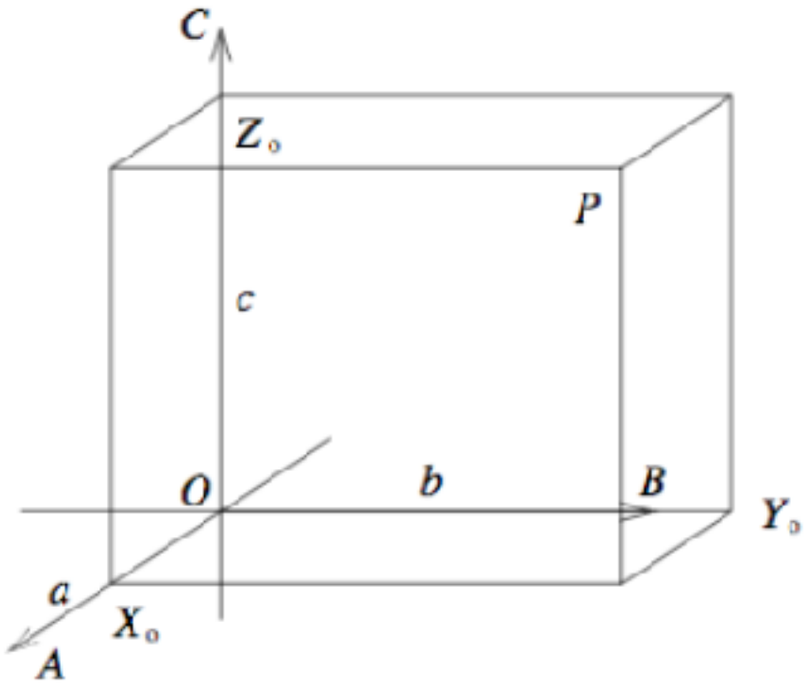


Fig. 1.1.1 Point P in a coordinate system $\{O, a, b, c\}$. The end points A, B and C of the arrows determine the different unit lengths on the lines a, b and c, respectively. The coordinate points are $X_\circ$, $Y_\circ$ and $Z_\circ$; the coordinates of P are
$x = (OX_\circ)/(OA)$,
$y = (OY_\circ)/(OB)$ and
$z = (OZ_\circ)/(OC)$.

$$P: \qquad \boldsymbol{x} = \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} \longleftrightarrow$$

to each point P
a triplet of coordinates

Vector coefficients

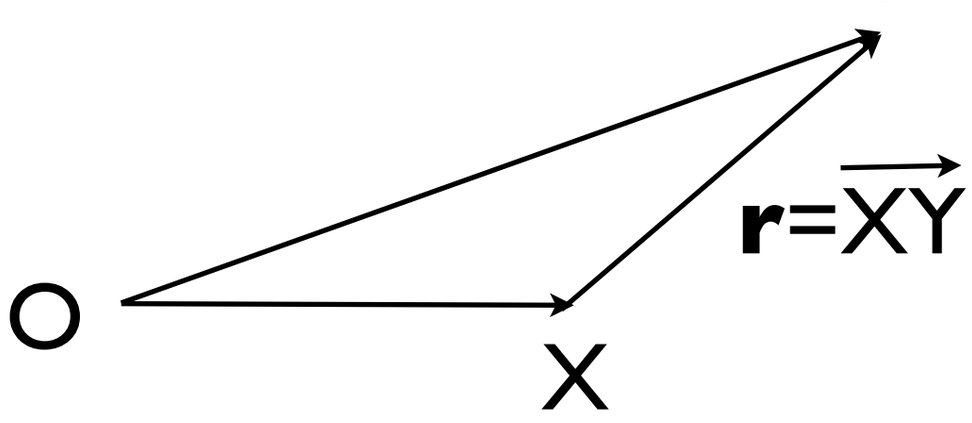
3D vector space V:

$\{\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3\}$: set of linearly independent vectors or *basis*

$\mathbf{r}=\lambda_1\mathbf{r}_1+ \lambda_2\mathbf{r}_2+\lambda_3\mathbf{r}_3$: $\forall \mathbf{r}\in V$, $\lambda_i\in\mathbb{R}$

λ_1
λ_2
λ_3

vector coefficients of $\mathbf{r}$ with respect to the basis $\{\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3\}$

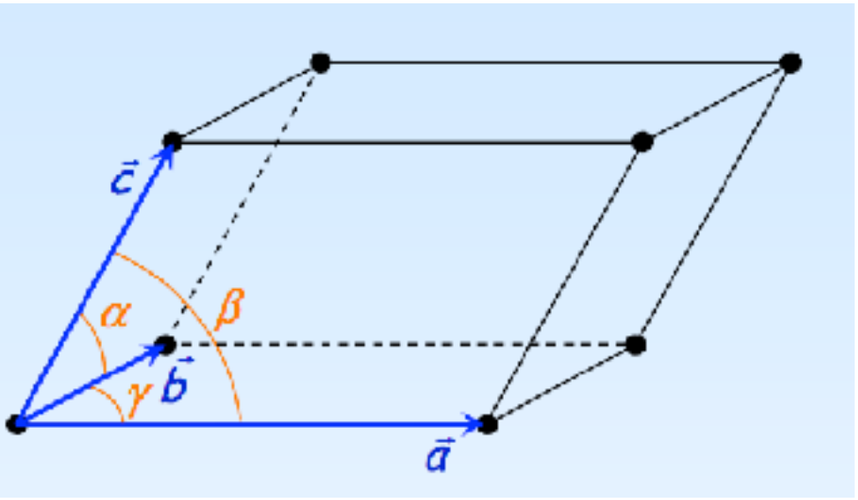


$$\boldsymbol{r} = \begin{pmatrix} y_1 - x_1 \\ y_2 - x_2 \\ y_3 - x_3 \end{pmatrix}, \text{ where } \boldsymbol{x} = \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} \text{ and } \boldsymbol{y} = \begin{pmatrix} y_1 \\ y_2 \\ y_3 \end{pmatrix}$$

METRIC TENSOR

BOND LENGTHS

BONDING ANGLES



Lattice parameters (3D)

basis vectors: $\{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3\}$
unit cell: parallelepiped defined by the basis vectors

Definition (D 1.5.3) The quantities

$$a_1 = |\mathbf{a}_1| = +\sqrt{(\mathbf{a}_1\,,\,\mathbf{a}_1)}, \qquad a_2 = |\mathbf{a}_2| = +\sqrt{(\mathbf{a}_2\,,\,\mathbf{a}_2)},$$

$$a_3 = |\mathbf{a}_3| = +\sqrt{(\mathbf{a}_3\,,\,\mathbf{a}_3)},$$

$$\alpha_1 = \arccos\left(|\mathbf{a}_2|^{-1}|\mathbf{a}_3|^{-1}(\mathbf{a}_2\,,\,\mathbf{a}_3)\right), \qquad \alpha_2 = \arccos\left(|\mathbf{a}_3|^{-1}|\mathbf{a}_1|^{-1}(\mathbf{a}_3\,,\,\mathbf{a}_1)\right),$$

$$\text{and} \quad \alpha_3 = \arccos\left(|\mathbf{a}_1|^{-1}|\mathbf{a}_2|^{-1}(\mathbf{a}_1\,,\,\mathbf{a}_2)\right)$$

are called the *lattice parameters* of the lattice.

Remark: the lengths of basis vectors are measured in

Å (1Å=10^{-10} m) *pm* (1*pm*=10^{-12} m) *nm* (1*nm*=10^{-9} m)

METRIC TENSOR (FUNDAMENTAL MATRIX)

Given a lattice **L** with a lattice basis: $\{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3\}$

Metric tensor ***G***

$$\boldsymbol{G} = \{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3\}^T . \{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3\} = \begin{bmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \\ \mathbf{a}_3 \end{bmatrix} . \{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3\} = \begin{bmatrix} G_{11} & G_{12} & G_{13} \\ G_{21} & G_{22} & G_{23} \\ G_{31} & G_{32} & G_{33} \end{bmatrix}$$

$$\boldsymbol{G}_{ik} = (\mathbf{a}_i, \mathbf{a}_k) = a_i a_k \cos\alpha_{ij},$$

Metric tensor ***G is symmetric:*** $G_{ik} = G_{ki}$

Metric tensor ***G*** in terms of lattice parameters

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

Crystallographic calculations: Volume of the unit cell

2.6.3 The volume of the unit cell

The volume V of the unit cell of a crystal structure, *i.e.* the body containing all points with coordinates $0 \leq x_1, x_2, x_3 < 1$, can be calculated by the formula

$$\det(\boldsymbol{G}) = V^2. \tag{2.6.5}$$

In the general case one obtains

$$V^2 = \begin{vmatrix} G_{11} & G_{12} & G_{13} \\ G_{21} & G_{22} & G_{23} \\ G_{31} & G_{32} & G_{33} \end{vmatrix} =$$

$$= a^2\, b^2\, c^2\, (1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma). \tag{2.6.6}$$

The formula (2.6.6) becomes simpler depending on the crystallographic symmetry, *i.e.* on the crystal system.

EXERCISE

Problem 2.1.6

Write down the metric tensors of the seven crystal systems in parametric form using the general expressions for their lattice parameters. For each of the cases, express the volume of the unit cell as a function of the lattice parameters.

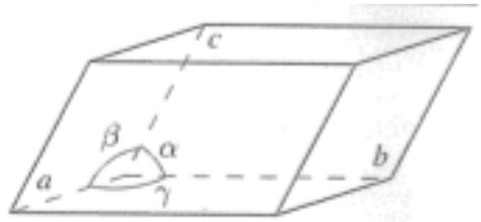
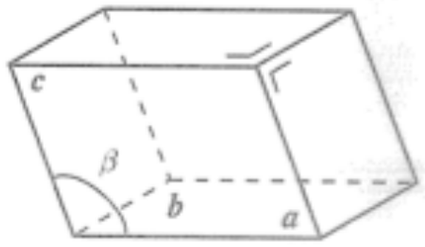
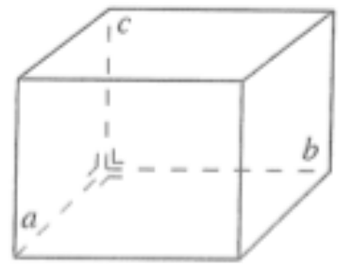
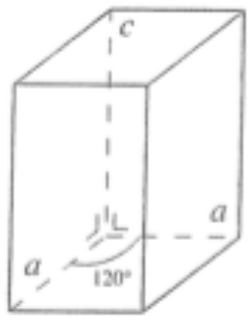
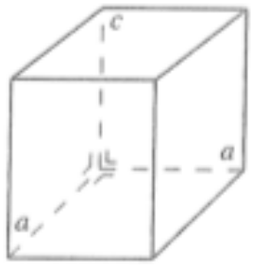
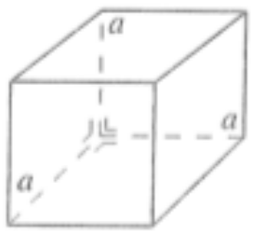
For example:

tetragonal crystal system: $a=b, c, \alpha=\beta=\gamma=90$

$$\boldsymbol{G} = \begin{pmatrix} a^2 & 0 & 0 \\ 0 & a^2 & 0 \\ 0 & 0 & c^2 \end{pmatrix}$$

V=?

The seven 3D-crystal systems

no conditions $\{a, b, c, \alpha, \beta, \gamma\}$	**TRICLINIC (ANORTHIC)**	
$\alpha = \gamma = 90°$† $\{a, b, c, 90, \beta, 90\}$	**MONOCLINIC**	
$\alpha = \beta = \gamma = 90°$ $\{a, b, c, 90, 90, 90\}$	**ORTHORHOMBIC**	
$a = b$, $\alpha = \beta = 90°$, $\gamma = 120°$ $\{a, a, c, 90, 90, 120\}$	**HEXAGONAL**	
$a = b$, $\alpha = \beta = \gamma = 90°$ $\{a, a, c, 90, 90, 90\}$	**TETRAGONAL**	
$a = b = c$, $\alpha = \beta = \gamma$ $\{a, a, a, \alpha, \alpha, \alpha\}$	**RHOMBOHEDRAL (TRIGONAL)**	
$a = b = c$, $\alpha = \beta = \gamma = 90°$ $\{a, a, a, 90, 90, 90\}$	**CUBIC**	

$$\boldsymbol{G} = \begin{pmatrix} a^2 & ab\cos\gamma & ac\cos\beta \\ ab\cos\gamma & b^2 & bc\cos\alpha \\ ac\cos\beta & bc\cos\alpha & c^2 \end{pmatrix}$$

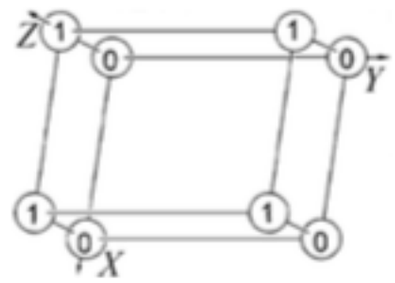
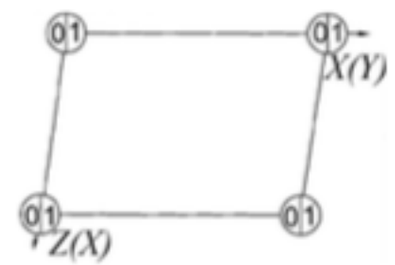
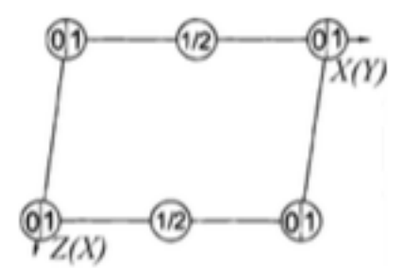
$V^2 = \det \boldsymbol{G} =$

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

Problem 2.4.5 (a)

SOLUTION

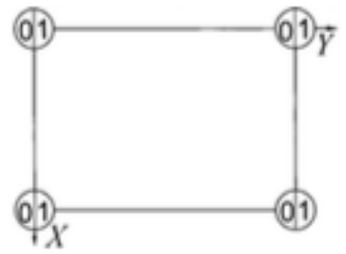
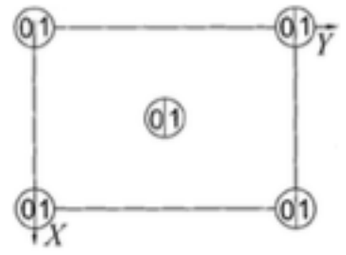
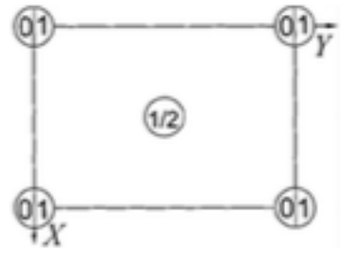
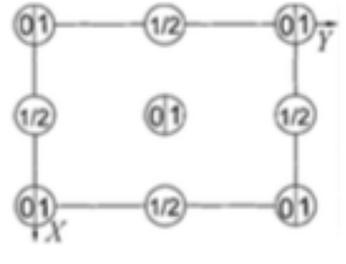
METRIC TENSORS

Bravais lattice*	Lattice parameters		Metric tensor			Projections
	Conventional	Primitive	Conventional	Primitive/transf.†	Relations of the components	
aP	a, b, c α, β, γ	a, b, c α, β, γ	$g_{11}\ g_{12}\ g_{13}$ $g_{22}\ g_{23}$ g_{33}	$g_{11}\ g_{12}\ g_{13}$ $g_{22}\ g_{23}$ g_{33}		
mP	a, b, c $\beta, \alpha = \gamma = 90°$	a, b, c $\beta, \alpha = \gamma = 90°$	$g_{11}\ 0\ g_{13}$ $g_{22}\ 0$ g_{33}	$g_{11}\ 0\ g_{13}$ $g_{22}\ 0$ g_{33}		
mC (*mS*)	a, b, c $\beta, \alpha = \gamma = 90°$	$a_1 = a_2, c$ $\gamma, \alpha = \beta$	$g_{11}\ 0\ g_{13}$ $g_{22}\ 0$ g_{33}	$\boldsymbol{P}(C)$ $g'_{11}\ g'_{12}\ g'_{13}$ $g'_{11}\ g'_{13}$ g_{33}	$g'_{11} = \frac{1}{4}(g_{11} + g_{22})$ $g'_{12} = \frac{1}{4}(g_{11} - g_{22})$ $g'_{13} = \frac{1}{2}g_{13}$ $g_{11} = 2(g'_{11} + g'_{12})$ $g_{22} = 2(g'_{11} - g'_{12})$ $g_{13} = 2g'_{13}$	

Problem 2.4.5 (a)

SOLUTION

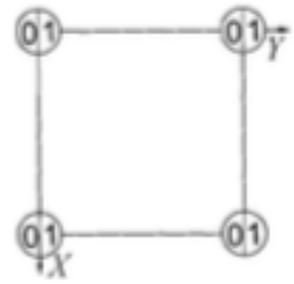
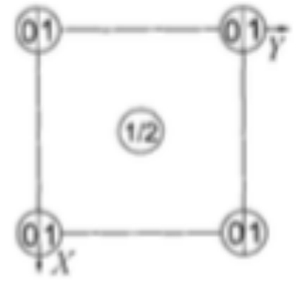
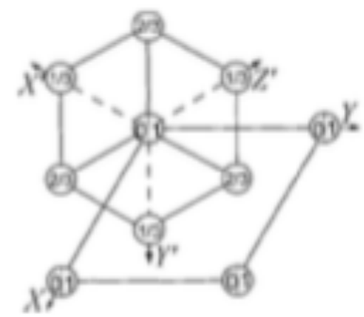
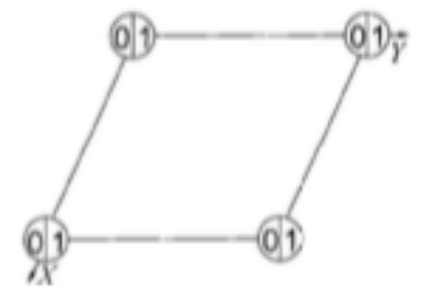
METRIC TENSORS

Bravais lattice*	Lattice parameters: Conventional	Lattice parameters: Primitive	Metric tensor: Conventional	Metric tensor: Primitive/transf.†	Metric tensor: Relations of the components	Projections
oP	a, b, c $\alpha = \beta = \gamma = 90°$	a, b, c $\alpha = \beta = \gamma = 90°$	$g_{11}\ 0\ 0$ $g_{22}\ 0$ g_{33}	$g_{11}\ 0\ 0$ $g_{22}\ 0$ g_{33}		
oC (*oS*)	a, b, c $\alpha = \beta = \gamma = 90°$	$a_1 = a_2, c$ $\gamma, \alpha = \beta = 90°$	$g_{11}\ 0\ 0$ $g_{22}\ 0$ g_{33}	***P***(*C*) $g'_{11}\ g'_{12}\ 0$ $g'_{11}\ 0$ g_{33}	$g'_{11} = \frac{1}{4}(g_{11} + g_{22})$ $g'_{12} = \frac{1}{4}(g_{11} - g_{22})$ $g_{11} = 2(g'_{11} + g'_{12})$ $g_{22} = 2(g'_{11} - g'_{12})$	
oI	a, b, c $\alpha = \beta = \gamma = 90°$	$a_1 = a_2 = a_3$ α, β, γ $\cos\alpha + \cos\beta + \cos\gamma = -1$	$g_{11}\ 0\ 0$ $g_{22}\ 0$ g_{33}	***P***(*I*) $-\tilde{g}\ g'_{12}\ g'_{13}$ $-\tilde{g}\ g'_{23}$ $-\tilde{g}$ $\tilde{g} = g'_{12} + g'_{13} + g'_{23}$	$g'_{12} = \frac{1}{4}(-g_{11} - g_{22} + g_{33})$ $g'_{13} = \frac{1}{4}(-g_{11} + g_{22} - g_{33})$ $g'_{23} = \frac{1}{4}(g_{11} - g_{22} - g_{33})$ $g_{11} = -2(g'_{12} + g'_{13})$ $g_{22} = -2(g'_{12} + g'_{23})$ $g_{33} = -2(g'_{13} + g'_{23})$	
oF	a, b, c $\alpha = \beta = \gamma = 90°$	a, b, c α, β, γ $\cos\alpha = \frac{-a^2 + b^2 + c^2}{2bc}$ $\cos\beta = \frac{a^2 + b^2 + c^2}{2ac}$ $\cos\gamma = \frac{a^2 + b^2 - c^2}{2ab}$	$g_{11}\ 0\ 0$ $g_{22}\ 0$ g_{33}	***P***(*F*) $\tilde{g}_1\ g'_{12}\ g'_{13}$ $\tilde{g}_2\ g'_{23}$ $\tilde{g}_3$ $\tilde{g}_1 = g'_{12} + g'_{13}$ $\tilde{g}_2 = g'_{12} + g'_{23}$ $\tilde{g}_3 = g'_{13} + g'_{23}$	$g'_{12} = \frac{1}{4} g_{33}$ $g'_{13} = \frac{1}{4} g_{22}$ $g'_{23} = \frac{1}{4} g_{11}$ $g_{11} = 4g'_{23}$ $g_{22} = 4g'_{13}$ $g_{33} = 4g'_{12}$	

Example

METRIC TENSORS

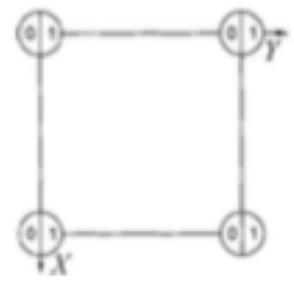
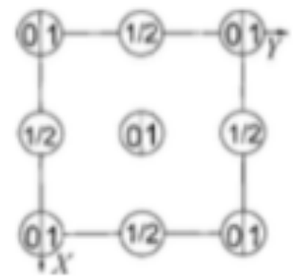
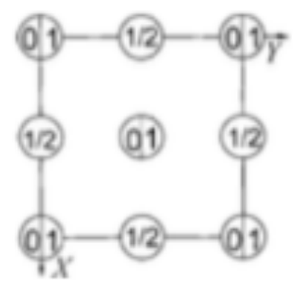
SOLUTION

Bravais lattice*	Lattice parameters: Conventional	Lattice parameters: Primitive	Metric tensor: Conventional	Metric tensor: Primitive/transf.†	Metric tensor: Relations of the components	Projections
tP	$a_1 = a_2, c$ $\alpha = \beta = \gamma = 90°$	$a_1 = a_2, c$ $\alpha = \beta = \gamma = 90°$	$\begin{matrix} g_{11} & 0 & 0 \\ & g_{11} & 0 \\ & & g_{33} \end{matrix}$	$\begin{matrix} g_{11} & 0 & 0 \\ & g_{11} & 0 \\ & & g_{33} \end{matrix}$		
tI		$a_1 = a_2 = a_3$ $\gamma, \alpha = \beta$ $2\cos\alpha + \cos\gamma = -1$		$\boldsymbol{P}(I)$ $\begin{matrix} \bar{g} & g'_{12} & g'_{13} \\ & \bar{g} & g'_{13} \\ & & \bar{g} \end{matrix}$ $\bar{g} = -(g'_{12} + 2g'_{13})$	$g'_{12} = \frac{1}{4}(-2g_{11} + g_{33})$ $g'_{13} = -\frac{1}{4}g_{33}$ $g_{11} = 2(g'_{12} + g'_{13})$ $g_{33} = -4g'_{13}$	
hR	$a_1 = a_2, c$ $\alpha = \beta = 90°$ $\gamma = 120°$	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma$	$\begin{matrix} g_{11} & -\frac{1}{2}g_{11} & 0 \\ & g_{11} & 0 \\ & & g_{33} \end{matrix}$	$\boldsymbol{P}(R)$ $\begin{matrix} g'_{11} & g'_{12} & g'_{12} \\ & g'_{11} & g'_{12} \\ & & g'_{11} \end{matrix}$	$g'_{11} = \frac{1}{9}(3g_{11} + g_{33})$ $g'_{12} = \frac{1}{9}(-\frac{3}{2}g_{11} + g_{33})$ $g_{11} = 2(g'_{11} - g'_{12})$ $g_{33} = 3(g'_{11} + 2g'_{12})$	
hP		$a_1 = a_2, c$ $\alpha = \beta = 90°$ $\gamma = 120°$		$\begin{matrix} g_{11} & -\frac{1}{2}g_{11} & 0 \\ & g_{11} & 0 \\ & & g_{33} \end{matrix}$		

Example

METRIC TENSORS

SOLUTION

Bravais lattice*	Lattice parameters		Metric tensor			Projections
	Conventional	Primitive	Conventional	Primitive/transf.†	Relations of the components	
cP	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma = 90°$	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma = 90°$	g_{11} 0 0 g_{11} 0 g_{11}	g_{11} 0 0 g_{11} 0 g_{11}		
cI		$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma = 109.5°$ $\cos\alpha = -\frac{1}{3}$		***P***(*I*) g'_{11} $-\frac{1}{3}g'_{11}$ $-\frac{1}{3}g'_{11}$ g'_{11} $-\frac{1}{3}g'_{11}$ g'_{11}	$g'_{11} = \frac{3}{4}g_{11}$ $g_{11} = \frac{4}{3}g'_{11}$	
cF		$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma = 60°$		***P***(*F*) g'_{11} $\frac{1}{2}g'_{11}$ $\frac{1}{2}g'_{11}$ g'_{11} $\frac{1}{2}g'_{11}$ g'_{11}	$g'_{11} = \frac{1}{2}g_{11}$ $g_{11} = 2g'_{11}$	

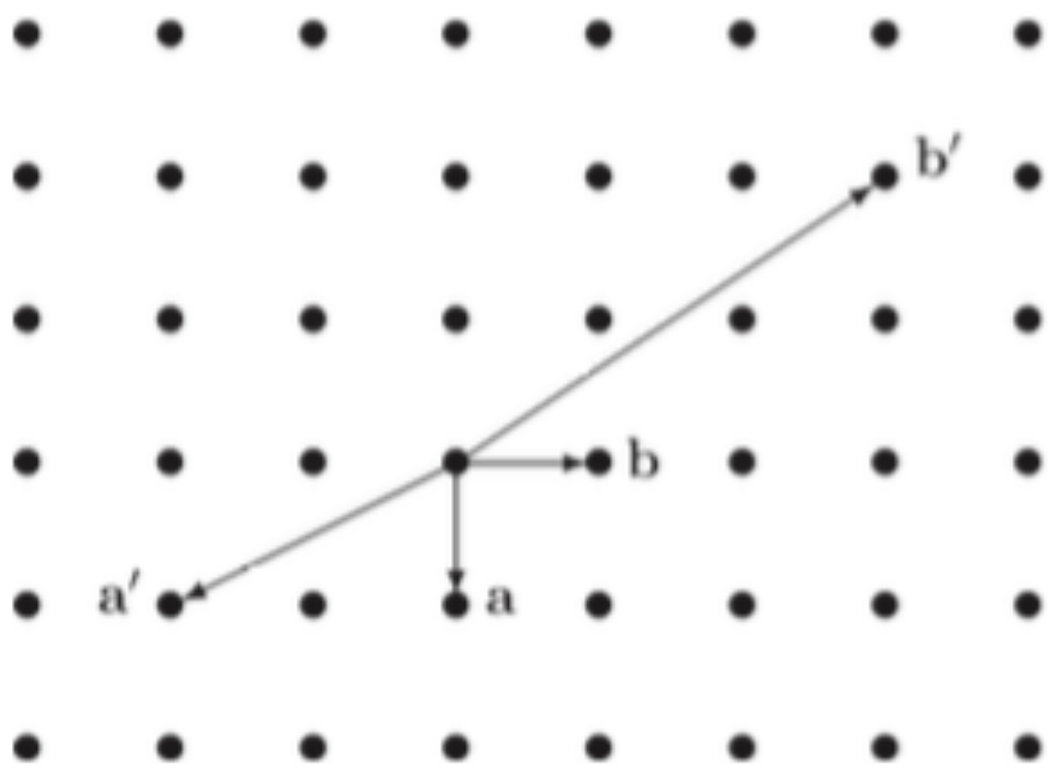
* See footnote to Table 9.1.7.1. Symbols in parentheses are standard symbols, see Table 2.1.2.1.
† $\boldsymbol{P}(C) = \frac{1}{2}(110/\bar{1}10/002), \boldsymbol{P}(I) = \frac{1}{2}(\bar{1}\bar{1}1/1\bar{1}1/11\bar{1}), \boldsymbol{P}(F) = \frac{1}{2}(011/101/110), \boldsymbol{P}(R) = \frac{1}{3}(\bar{1}2\bar{1}/\bar{2}11/111)$.

Basis transformation

Crystal Lattices

2D square lattice

$$\mathbf{L} = \mathbb{Z}^2 = \left\{ \begin{pmatrix} m \\ n \end{pmatrix} \mid m, n \in \mathbb{Z} \right\}$$



lattice bases and their relations

$$\mathbf{a} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \mathbf{b} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$\mathbf{a}' = \begin{pmatrix} 1 \\ -2 \end{pmatrix}, \quad \mathbf{b}' = \begin{pmatrix} -2 \\ 3 \end{pmatrix}$$

$$\mathbf{a} = -3\mathbf{a}' - 2\mathbf{b}' = \begin{pmatrix} -3 \\ 6 \end{pmatrix} + \begin{pmatrix} 4 \\ -6 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$\mathbf{b} = -2\mathbf{a}' - \mathbf{b}' = \begin{pmatrix} -2 \\ 4 \end{pmatrix} + \begin{pmatrix} 2 \\ -3 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

What is *P*? And *P*$^{-1}$

$$(\mathbf{a}', \mathbf{b}', \mathbf{c}') = (\mathbf{a}, \mathbf{b}, \mathbf{c})\boldsymbol{P}$$

$$(\mathbf{a}, \mathbf{b}, \mathbf{c}) = (\mathbf{a}', \mathbf{b}', \mathbf{c}')\boldsymbol{P}^{-1}$$

P, ***P***$^{-1}$: integral matrices

→ det ***P***=?

det ***P***$^{-1}$ = 1/ det ***P***

Transformation properties of ***G*** under basis transformation

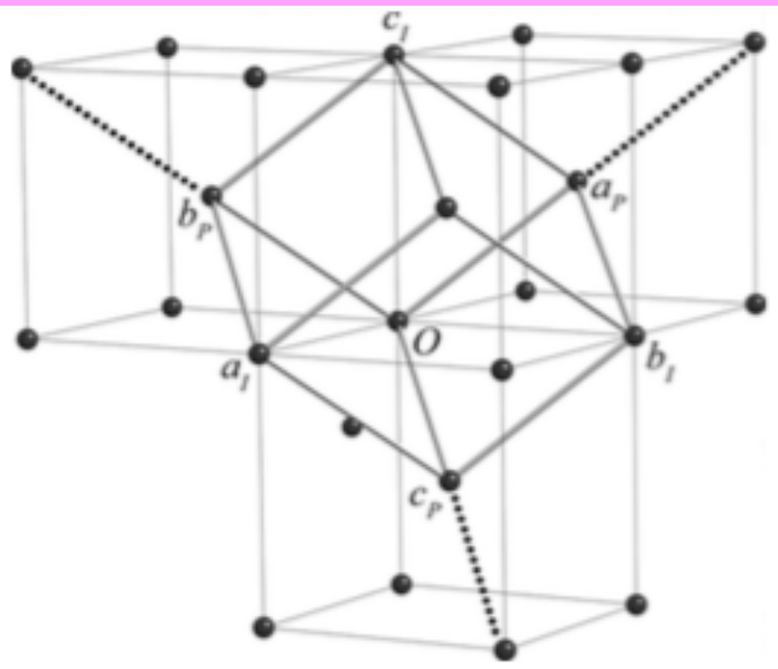
basis transformation:

$$\{\mathbf{a'}_1, \mathbf{a'}_2, \mathbf{a'}_3\} = \{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3\}\, \boldsymbol{P}$$

$$\boldsymbol{G'} = \{\mathbf{a'}_1, \mathbf{a'}_2, \mathbf{a'}_3\}^T . \{\mathbf{a'}_1, \mathbf{a'}_2, \mathbf{a'}_3\} = \boldsymbol{P}^T \{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3\}^T . \{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3\}\, \boldsymbol{P}$$

$$\boldsymbol{G'} = \boldsymbol{P}^T\, \boldsymbol{G}\, \boldsymbol{P}$$

Example



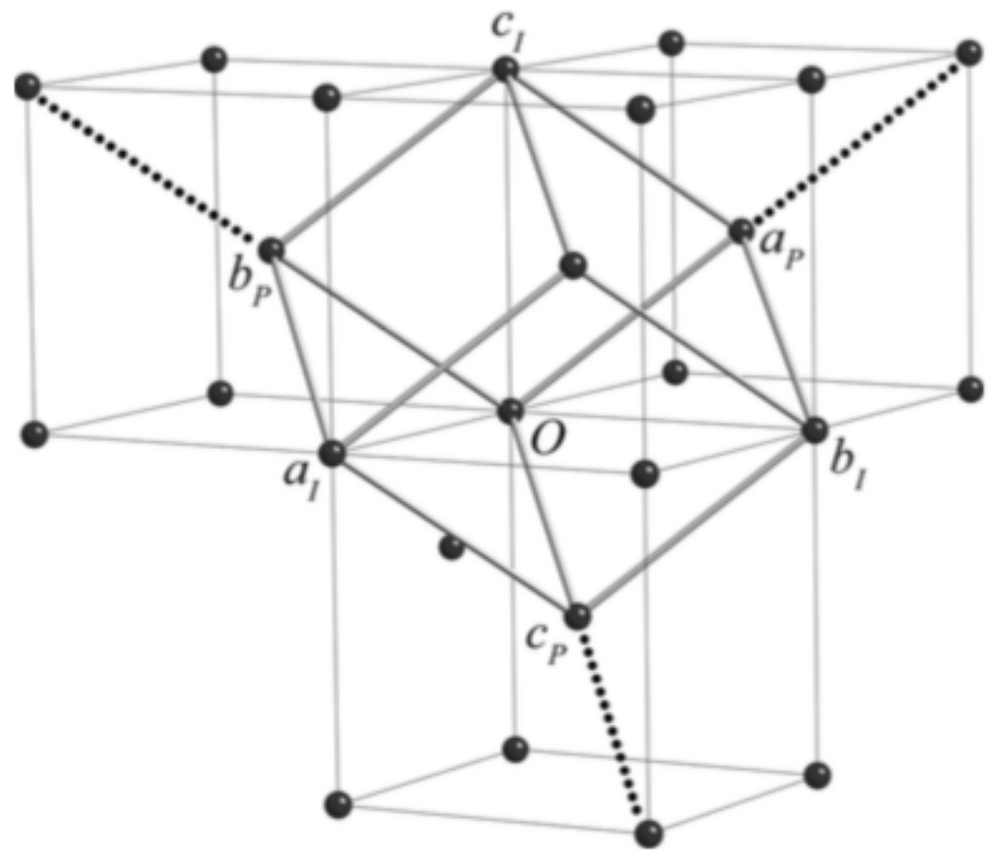
$$\boldsymbol{P} = 1/2 \begin{pmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{pmatrix}$$

$cI \longrightarrow cP$

$$\boldsymbol{G_I} = a^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \boldsymbol{G_P} = a^2/4 \begin{pmatrix} 3 & -1 & -1 \\ -1 & 3 & -1 \\ -1 & -1 & 3 \end{pmatrix}$$

EXERCISES

Problem 2.4.6



A body-centred cubic lattice (*cI*) has as its conventional basis the conventional basis ($\mathbf{a_I}$,$\mathbf{b_I}$,$\mathbf{c_I}$) of a primitive cubic lattice, but the lattice also contains the centring vector $1/2\mathbf{a_I}+1/2\mathbf{b_I}+1/2\mathbf{c_I}$ which points to the centre of the conventional cell.

Calculate the coefficients of the metric tensor for the body-centred cubic lattice:

(i) for the conventional basis ($\mathbf{a_I}$,$\mathbf{b_I}$,$\mathbf{c_I}$);

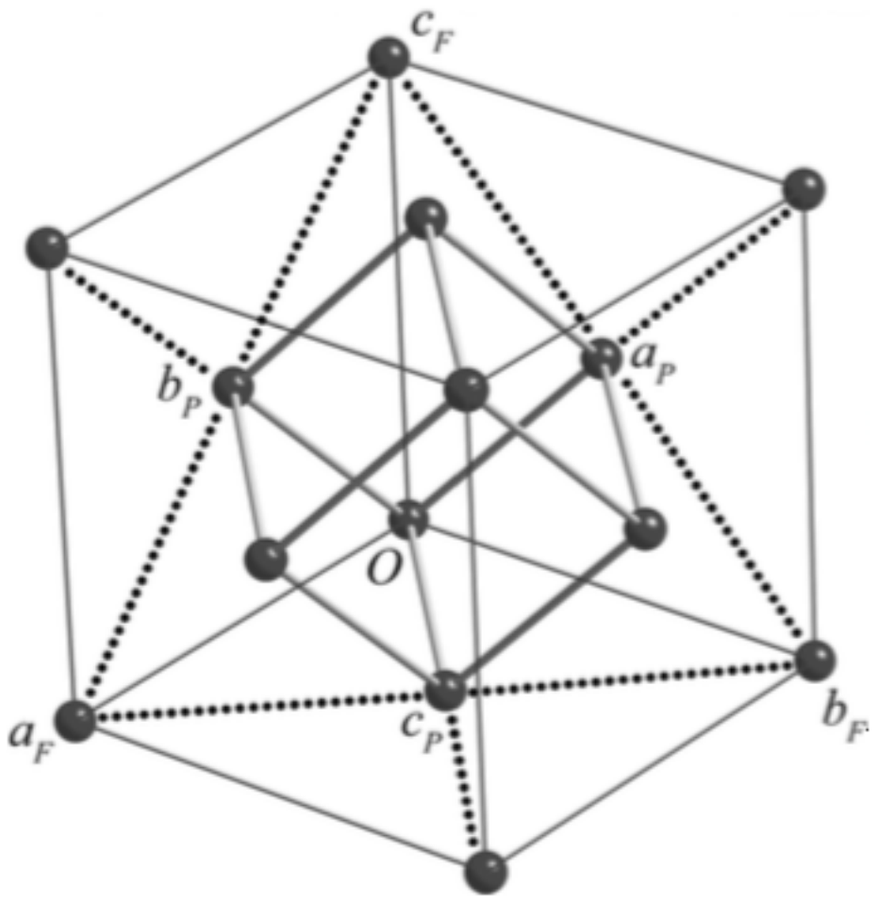
(ii) for the primitive basis:

$\mathbf{a_P}=1/2(-\mathbf{a_I}+\mathbf{b_I}+\mathbf{c_I})$, $\mathbf{b_P}=1/2(\mathbf{a_I}-\mathbf{b_I}+\mathbf{c_I})$, $\mathbf{c_P}=1/2(\mathbf{a_I}+\mathbf{b_I}-\mathbf{c_I})$

(iii) determine the lattice parameters of the primitive cell if a_I=4 Å

EXERCISES

Problem 2.4.7



A face-centred cubic lattice (*cF*) has as its conventional basis the conventional basis (**a**$_F$,**b**$_F$,**c**$_F$) of a primitive cubic lattice, but the lattice also contains the centring vectors 1/2**b**$_F$+1/2**c**$_F$, 1/2**a**$_F$+1/2**c**$_F$, 1/2**a**$_F$+1/2**b**$_F$, which point to the centres of the faces of the conventional cell.

Calculate the coefficients of the metric tensor for the face-centred cubic lattice:

(i) for the conventional basis (**a**$_F$,**b**$_F$,**c**$_F$);

(ii) for the primitive basis:

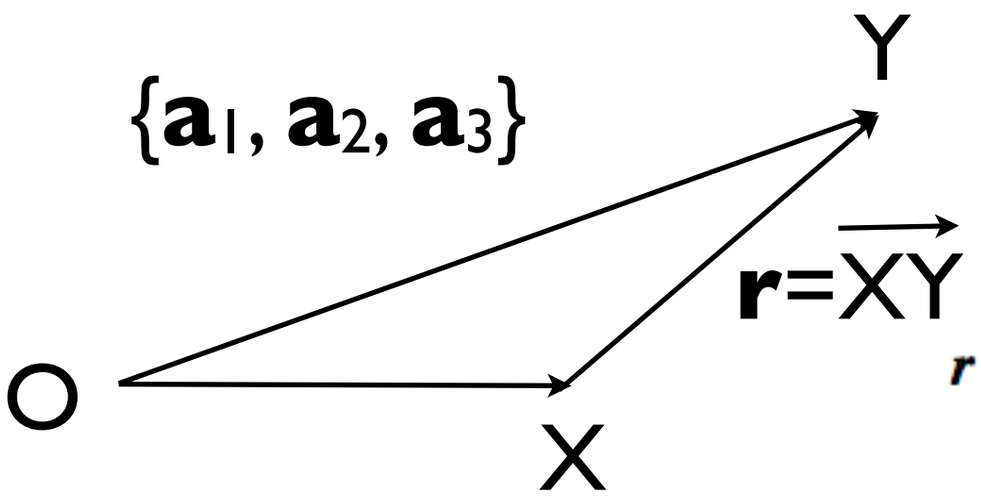
a$_P$=1/2(**b**$_F$+**c**$_F$), **b**$_P$=1/2(**a**$_F$+**c**$_F$), **c**$_P$=1/2(**a**$_F$+**b**$_F$)

(iii) determine the lattice parameters of the primitive cell if a_F=4 Å

BOND LENGTHS

BONDING ANGLES

Crystallographic calculations: Distances or Lengths



$$\mathbf{r}=\overrightarrow{XY}=r_1\mathbf{a}_1+r_2\mathbf{a}_2+r_3\mathbf{a}_3,\ r_i\in\mathbb{R}$$

$$\boldsymbol{r} = \begin{pmatrix} y_1 - x_1 \\ y_2 - x_2 \\ y_3 - x_3 \end{pmatrix}, \text{ where } \boldsymbol{x} = \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} \text{ and } \boldsymbol{y} = \begin{pmatrix} y_1 \\ y_2 \\ y_3 \end{pmatrix}$$

length r of r: $r^2=(\mathbf{r}, \mathbf{r})=(r_1\mathbf{a}_1+r_2\mathbf{a}_2+r_3\mathbf{a}_3,\ r_1\mathbf{a}_1+r_2\mathbf{a}_2+r_3\mathbf{a}_3)$

$$r^2=(r_1\mathbf{a}_1,r_1\mathbf{a}_1)+(r_2\mathbf{a}_2,r_2\mathbf{a}_2)+(r_3\mathbf{a}_3,r_3\mathbf{a}_3)+2(r_2\mathbf{a}_2,r_3\mathbf{a}_3)+2(r_3\mathbf{a}_3,r_1\mathbf{a}_1)+2(r_1\mathbf{a}_1,r_2\mathbf{a}_2)$$

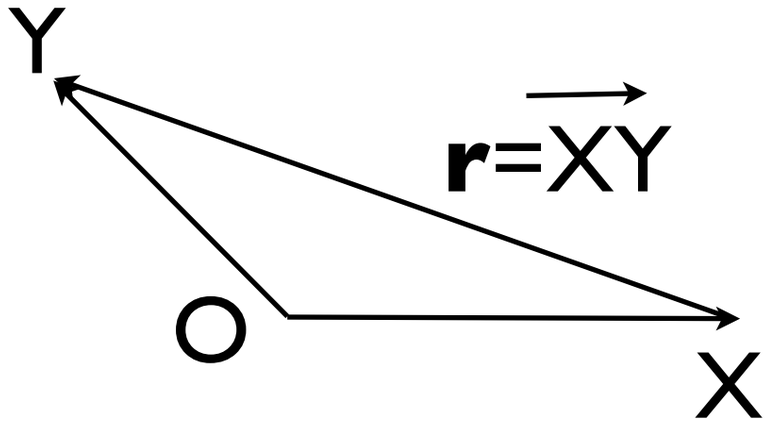
$$r^2=r_1^2a_1^2+r_2^2a_2^2+r_3^2a_3^2+2r_2r_3a_2a_3\cos\alpha_1+2r_3r_1a_3a_1\cos\alpha_2+2r_1r_2a_1a_2\cos\alpha_3$$

orthonormal basis ($a_1=a_2=a_3=1$, $\alpha_1=\alpha_2=\alpha_3=90$):

$$r^2=r_1^2+r_2^2+r_3^2$$

Crystallographic calculations: Distances or Lengths

Given a basis:
$\{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3\}$



length r of **r**: $r^2=(\mathbf{r},\mathbf{r})$

$$r^2=r_1^2a_1^2+r_2^2a_2^2+r_3^2a_3^2+2r_2r_3a_2a_3\cos\alpha_1+2r_3r_1a_3a_1\cos\alpha_2+2r_1r_2a_1a_2\cos\alpha_3$$

Fundamental matrix (metric tensor)

$\boldsymbol{G}=$

G_{11}	G_{12}	G_{13}
G_{21}	G_{22}	G_{23}
G_{31}	G_{32}	G_{33}

$\boldsymbol{G}_{ik}=(\mathbf{a}_i,\mathbf{a}_k)=a_ia_k\cos\alpha_j,$

$\boldsymbol{G}_{ik}=\boldsymbol{G}_{ki}$

length of a vector:

$r^2=(\mathbf{r}, \mathbf{r})=\mathbf{r}^T\boldsymbol{G}\mathbf{r}$

orthonormal basis

$(a_1=a_2=a_3=1, \alpha_1=\alpha_2=\alpha_3=90)$: $\boldsymbol{G}=\boldsymbol{I}$

$r^2=\mathbf{r}^T\boldsymbol{G}\mathbf{r}=\mathbf{r}^T\mathbf{r}$

EXERCISE

Problem 2.1.7a

For a crystal with lattice parameters {3Å, 4Å, 6Å, 90°, 120°, 90°} (i.e. a monoclinic crystal), compute the length of the main body diagonal of the unit cell.

Calculate the volume of the unit cell.

EXERCISE

Problem 2.1.7b

A crystal with lattice parameters
{2Å, 2Å, 3Å, 90°, 90°, 90°} contains among others,
atoms at positions with fractional coordinates
(1/2,1/3,1/4) and (1/3,1/2,3/4).

Compute the distance between the two atoms.

Hint: the distance between any two points in a crystal equals the length of the vector connecting those two points

Crystallographic calculations: Bonding angle

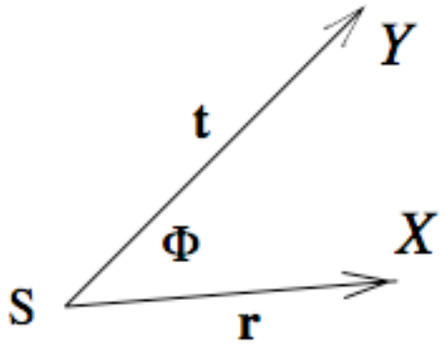


Fig. 1.6.1 The bonding angle Φ between the bond vectors $\overrightarrow{SX} = \mathbf{r}$ and $\overrightarrow{SY} = \mathbf{t}$.

$$(\mathbf{r}\,,\,\mathbf{t}) = |\mathbf{r}|\,|\mathbf{t}|\,\cos\Phi = r\,t\,\cos\Phi,$$

$$r_1\,t_1\,a_1^2 + r_2\,t_2\,a_2^2 + r_3\,t_3\,a_3^2 + (r_2\,t_3 + r_3\,t_2)\,a_2\,a_3\cos\alpha_1 + \\ + (r_3\,t_1 + r_1\,t_3)\,a_1\,a_3\cos\alpha_2 + (r_1\,t_2 + r_2\,t_1)\,a_1\,a_2\cos\alpha_3.$$

$$\cos\Phi = \Big(\sum_{i,k=1}^{3} G_{ik}\,r_i\,r_k\Big)^{-1/2}\Big(\sum_{i,k=1}^{3} G_{ik}\,t_i\,t_k\Big)^{-1/2}\sum_{i,k=1}^{3} G_{ik}\,r_i\,t_k$$

orthonormal basis:

$$r\,t\cos\Phi = r_1\,t_1 + r_2\,t_2 + r_3\,t_3,$$

$$\cos\Phi = \frac{r_1 t_1 + r_2 t_2 + r_3 t_3}{r\,t}$$

Crystallographic calculations: Bonding angle

Given a basis:

$\{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3\}$

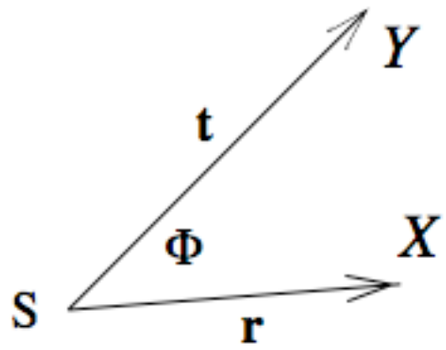


Fig. 1.6.1 The bonding angle Φ between the bond vectors $\overrightarrow{SX} = \mathbf{r}$ and $\overrightarrow{SY} = \mathbf{t}$.

Fundamental matrix (metric tensor)

$$\boldsymbol{G} = \begin{pmatrix} G_{11} & G_{12} & G_{13} \\ G_{21} & G_{22} & G_{23} \\ G_{31} & G_{32} & G_{33} \end{pmatrix}$$

$\boldsymbol{G}_{ik}=(\mathbf{a}_i,\mathbf{a}_k)=a_i a_k \cos\alpha_j,$

$\boldsymbol{G}_{ik}=\boldsymbol{G}_{ki}$

bonding angle:

$$(\mathbf{r}\,,\,\mathbf{t}) = |\mathbf{r}|\,|\mathbf{t}|\,\cos\Phi = r\,t\,\cos\Phi,$$

$$(\mathbf{r},\mathbf{t})=\mathbf{r}^{\mathrm{T}}\boldsymbol{G}\mathbf{t}$$

$$\cos\Phi = (\boldsymbol{r}^{\mathrm{T}}\,\boldsymbol{G}\,\boldsymbol{r})^{-1/2}\,(\boldsymbol{t}^{\mathrm{T}}\,\boldsymbol{G}\,\boldsymbol{t})^{-1/2}\,\boldsymbol{r}^{\mathrm{T}}\,\boldsymbol{G}\,\boldsymbol{t}.$$

EXERCISE

Problem 2.1.8

In a cubic crystal with lattice parameter *a*, an oxygen atom is present at the position (0,0,0); this atom is bonded to two titanium atoms, located at the positions (1/2,1/2,0) and (1/2,0,1/2). Compute the angle between these two bonds.

Hint: The angle between the two bonds corresponds to the angle between the two direction vectors parallel to these bonds; in this case the direction vectors are **r**= (1/2,1/2,0) and **t**= (1/2,0,1/2).

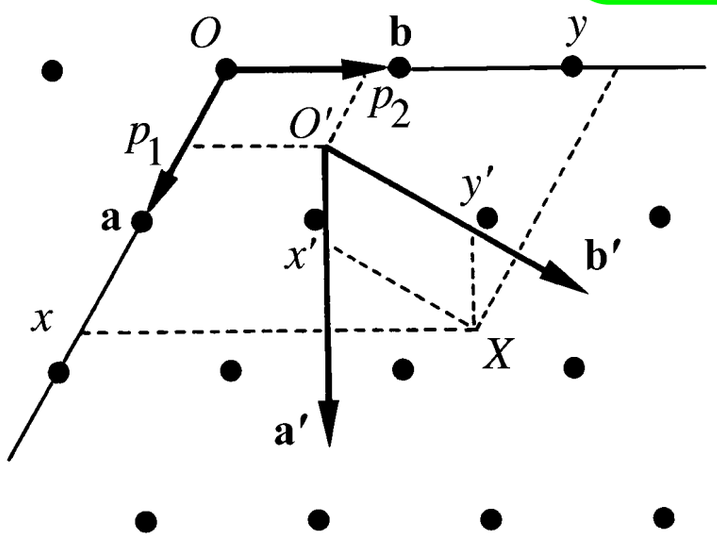
EXERCISE

Problem 2.1.8

Consider a monoclinic crystal with lattice parameter a=4Å, b=6Å, c=5Å and ß= 120°. What is the angle between the [101] and [$\bar{2}$01] directions?

COORDINATE TRANSFORMATIONS IN CRYSTALLOGRAPHY

Co-ordinate transformations



3-dimensional space

$(\mathbf{a}, \mathbf{b}, \mathbf{c})$, origin O: point $\mathrm{X}(x, y, z)$

(P,p) ↓

$(\mathbf{a}', \mathbf{b}', \mathbf{c}')$, origin O': point $\mathrm{X}(x', y', z')$

Transformation matrix-column pair (P,p)

(i) linear part: change of orientation or length:

$$(\mathbf{a}', \mathbf{b}', \mathbf{c}') = (\mathbf{a}, \mathbf{b}, \mathbf{c})\boldsymbol{P}$$

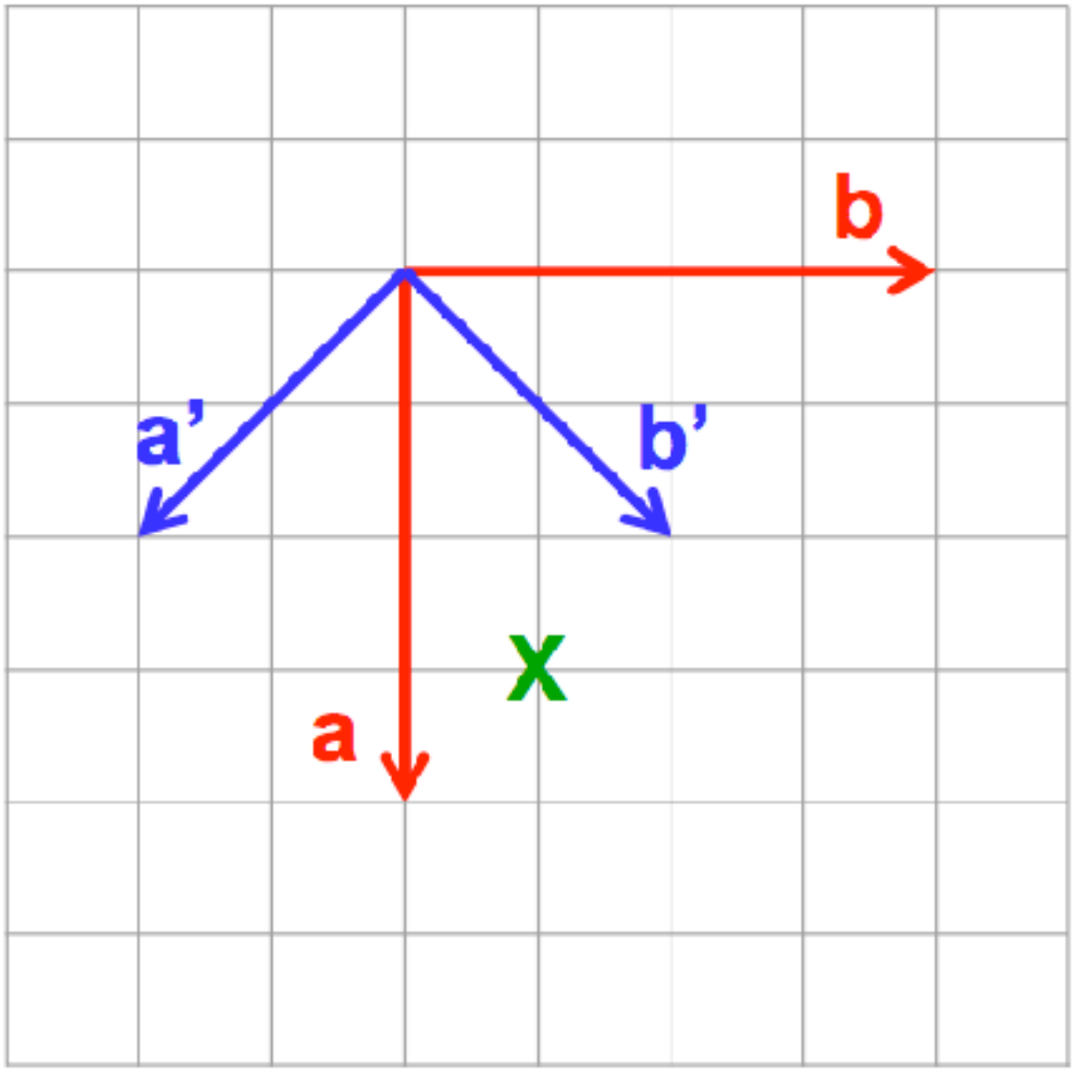
$$= (\mathbf{a}, \mathbf{b}, \mathbf{c}) \begin{pmatrix} P_{11} & P_{12} & P_{13} \\ P_{21} & P_{22} & P_{23} \\ P_{31} & P_{32} & P_{33} \end{pmatrix} = (P_{11}\mathbf{a} + P_{21}\mathbf{b} + P_{31}\mathbf{c}, \quad P_{12}\mathbf{a} + P_{22}\mathbf{b} + P_{32}\mathbf{c}, \quad P_{13}\mathbf{a} + P_{23}\mathbf{b} + P_{33}\mathbf{c}).$$

(ii) origin shift by a shift vector $\boldsymbol{p}(p_1,p_2,p_3)$:

$$\boldsymbol{O' = O + p}$$

the origin ***O'*** has coordinates (p_1,p_2,p_3) in the old coordinate system

EXAMPLE



$$(a',b',c') = (a,b,c)\begin{pmatrix} ? \end{pmatrix}$$

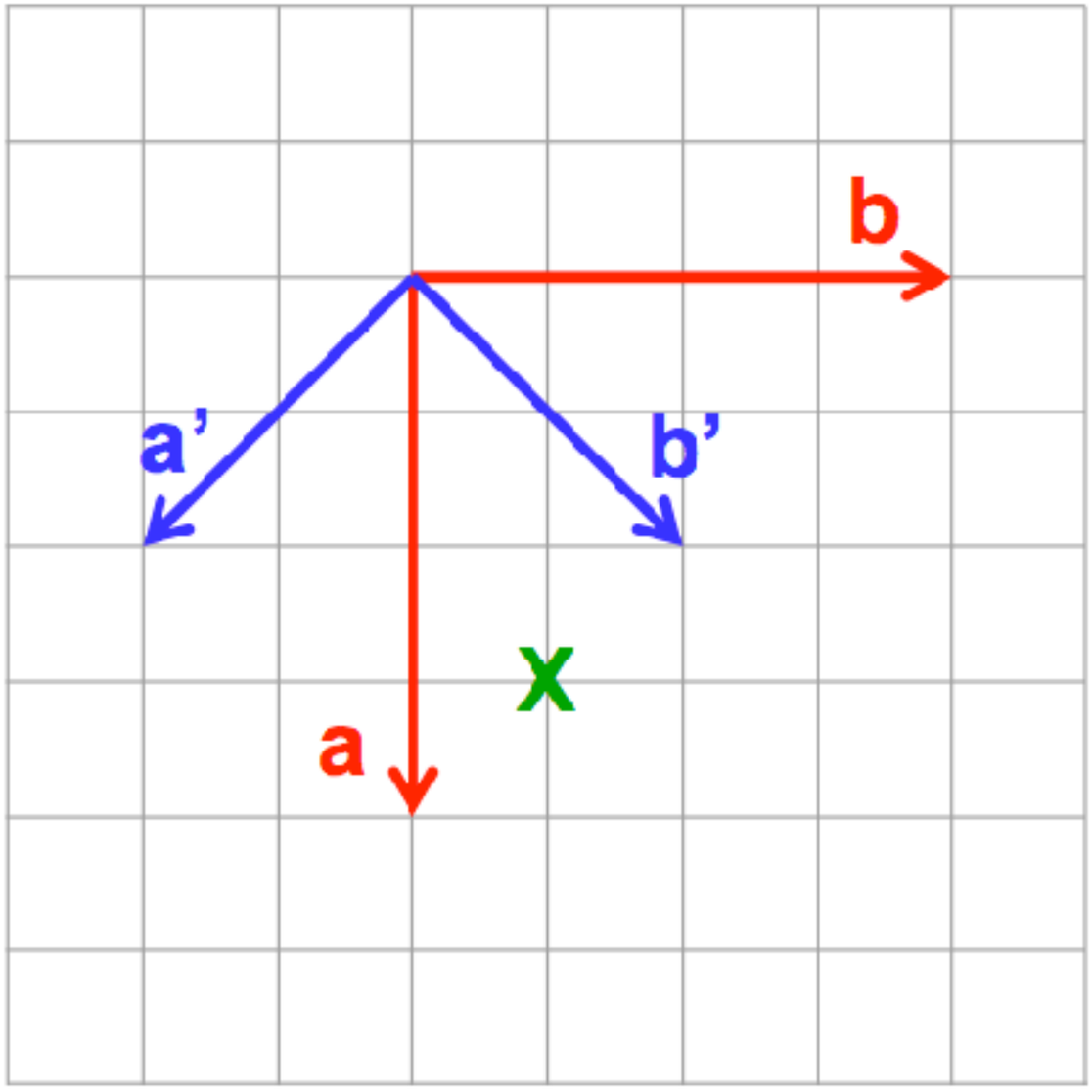
$$(a,b,c) = (a',b',c')\begin{pmatrix} ? \end{pmatrix}$$

$$X = (3/4,1/4,0)$$

$$X' = (\ ?\ )$$

Write "new in terms of old" as column vectors.

EXAMPLE



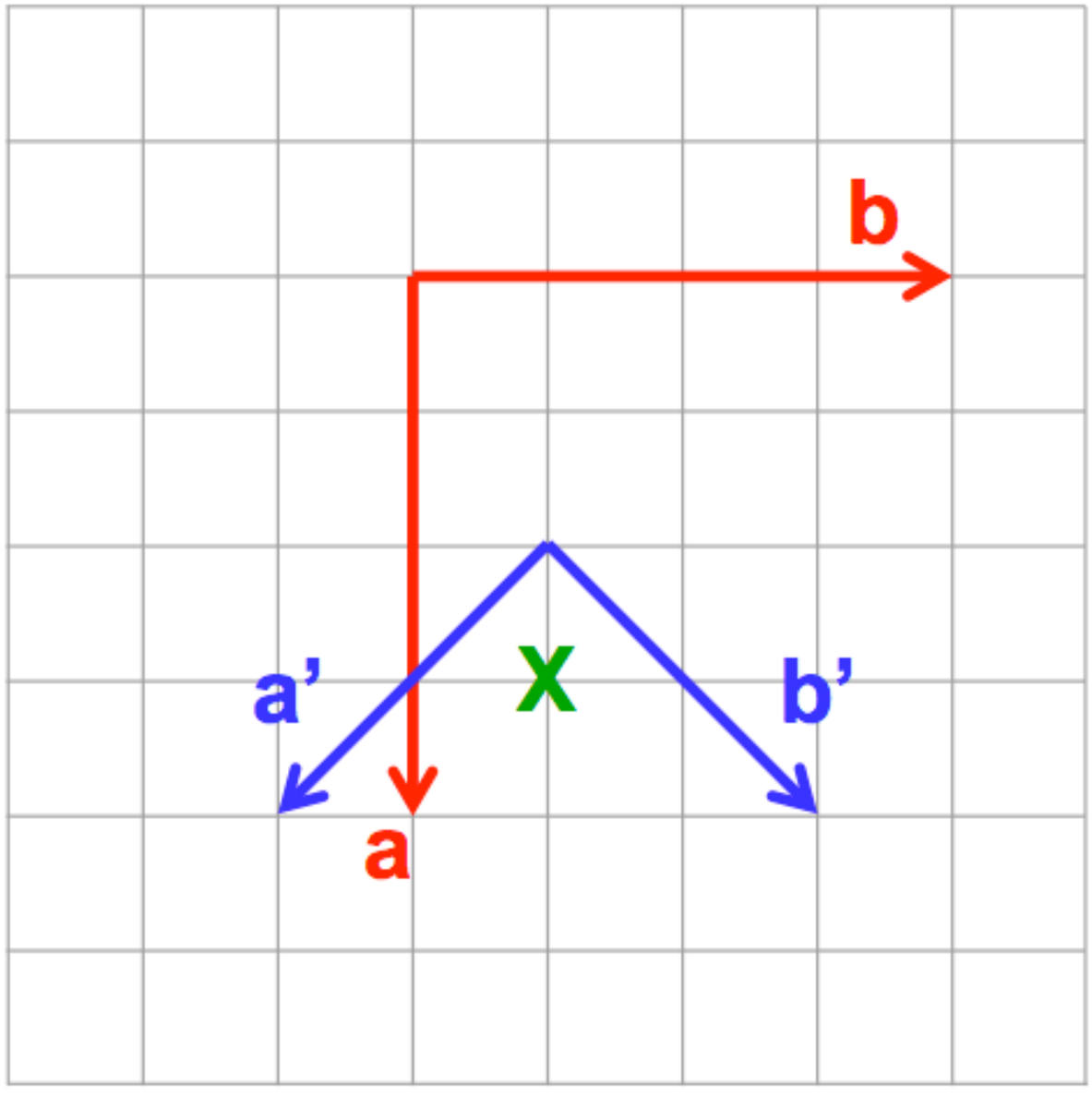
$$(\boldsymbol{a}',\boldsymbol{b}',\boldsymbol{c}') = (\boldsymbol{a},\boldsymbol{b},\boldsymbol{c}) \begin{pmatrix} 1/2 & 1/2 & 0 \\ -1/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$(\boldsymbol{a},\boldsymbol{b},\boldsymbol{c}) = (\boldsymbol{a}',\boldsymbol{b}',\boldsymbol{c}') \begin{pmatrix} 1 & -1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\boldsymbol{X} = (3/4,1/4,0)$$

$$\boldsymbol{X}' = (1/2,1,0)$$

EXAMPLE



$$p = \begin{pmatrix} ? \end{pmatrix}$$

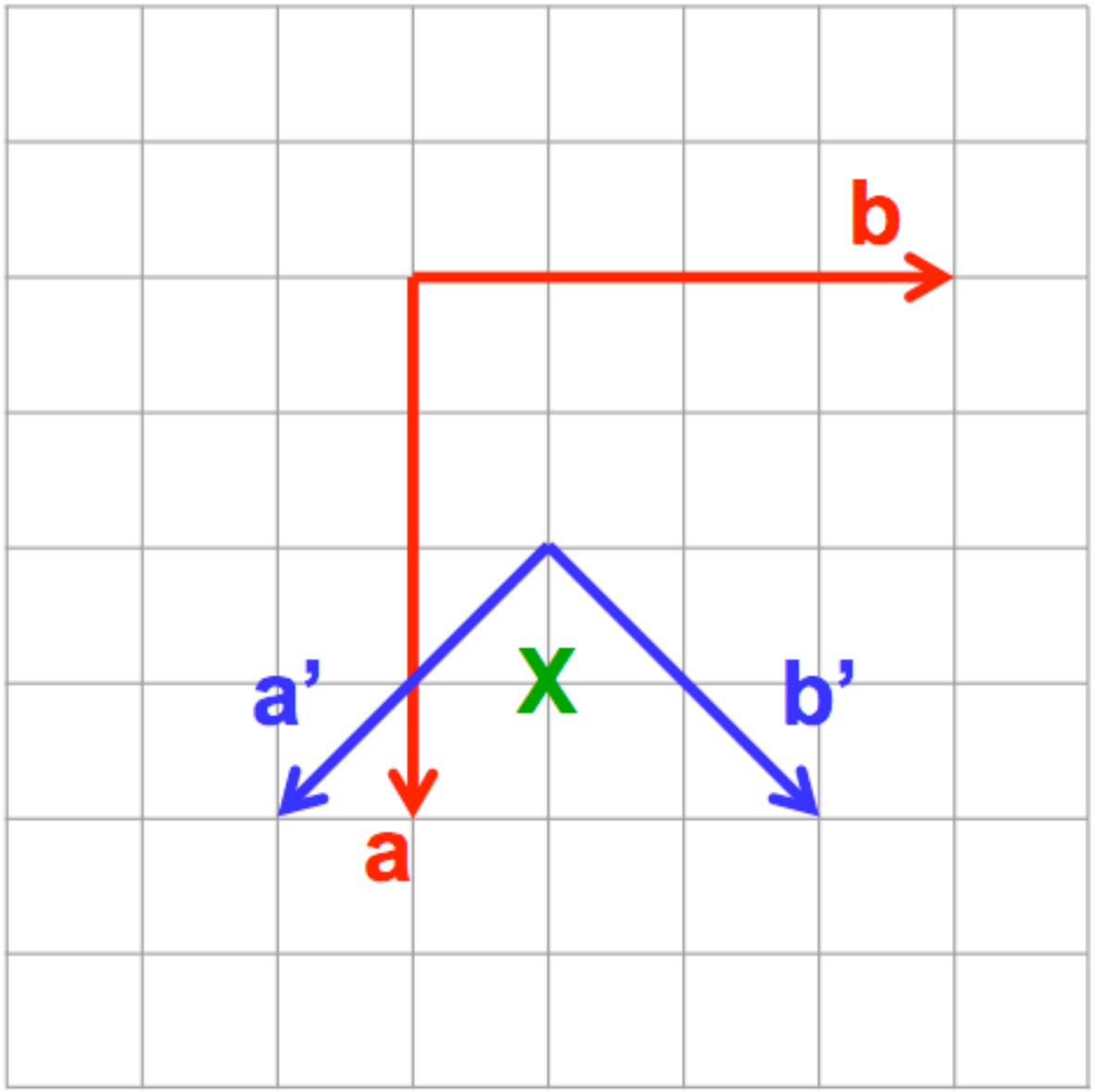
$$q = \begin{pmatrix} ? \end{pmatrix}$$

$$X = (3/4, 1/4, 0)$$

$$X' = (\ ?\ )$$

Linear parts as before.

EXAMPLE



$$\boldsymbol{p} = \begin{pmatrix} 1/2 \\ 1/4 \\ 0 \end{pmatrix}$$

$$\boldsymbol{q} = \begin{pmatrix} -1/4 \\ -3/4 \\ 0 \end{pmatrix}$$

$$\boldsymbol{X} = (3/4, 1/4, 0)$$

$$\boldsymbol{X}' = (1/4, 1/4, 0)$$

Linear parts as before.

Transformation matrix-column pair (*P,p*)

$$(P,p)=\left(\begin{array}{ccc|c} 1/2 & 1/2 & 0 & 1/2 \\ -1/2 & 1/2 & 0 & 1/4 \\ 0 & 0 & 1 & 0 \end{array}\right)$$

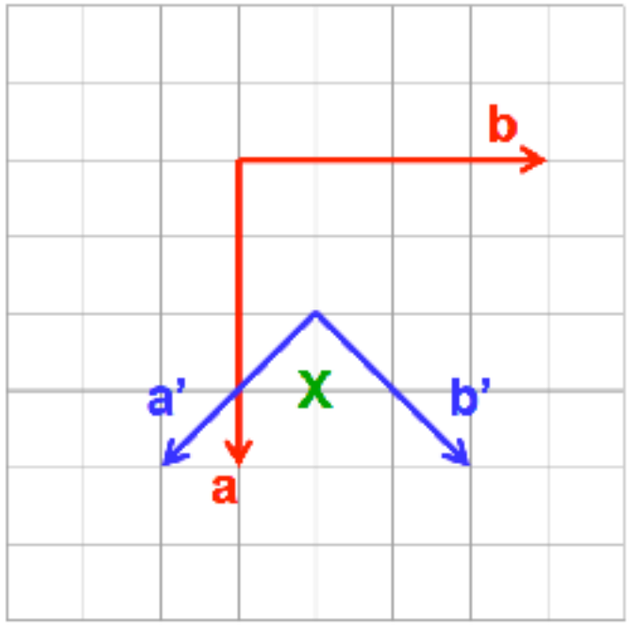
$$(P,p)^{-1}=\left(\begin{array}{ccc|c} 1 & -1 & 0 & -1/4 \\ 1 & 1 & 0 & -3/4 \\ 0 & 0 & 1 & 0 \end{array}\right)$$

$$a'=1/2a-1/2b$$

$$b'=1/2a+1/2b$$

$$c'=c$$

$$O'=O+\begin{array}{|c|}\hline 1/2 \\ \hline 1/4 \\ \hline 0 \\ \hline \end{array}$$



$$a=a'+b'$$

$$b=-a'+b'$$

$$c=c'$$

$$O=O'+\begin{array}{|c|}\hline -1/4 \\ \hline -3/4 \\ \hline 0 \\ \hline \end{array}$$

Transformation of the coordinates of a point X(x,y,z):

$$(X') = (P,p)^{-1}(X) = (P^{-1}, -P^{-1}p)(X)$$

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \left(\begin{array}{ccc|c} P_{11} & P_{12} & P_{13} & p1 \\ P_{21} & P_{22} & P_{23} & p2 \\ P_{31} & P_{32} & P_{33} & p3 \end{array} \right)^{-1} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

special cases

-origin shift (***P***=***I***):

$$x' = x - p$$

-change of basis (***p***=***o***) :

$$x' = P^{-1}x$$

Transformation of symmetry operations (*W*,*w*):

$$(W',w') = (P,p)^{-1}(W,w)(P,p)$$

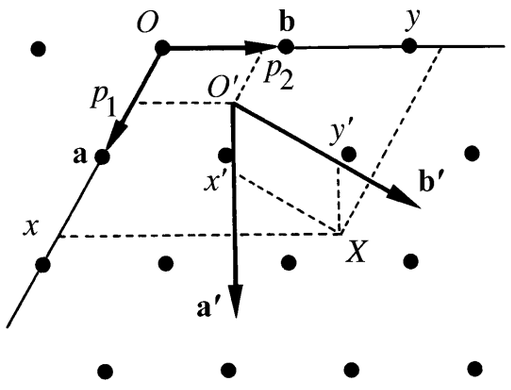
Transformation by (***P***,***p***) of the unit cell parameters:

metric tensor ***G***:

$$G' = P^t\, G\, P$$

Short-hand notation for the description of transformation matrices

Transformation matrix:



(a,b,c), origin O

$$(P,p)=\left(\begin{array}{ccc|c} P_{11} & P_{12} & P_{13} & p1 \\ P_{21} & P_{22} & P_{23} & p2 \\ P_{31} & P_{32} & P_{33} & p3 \end{array}\right)$$

(a',b',c'), origin O'

notation rules:

-written by columns
-coefficients 0, +1, -1
-different columns in one line
-origin shift

example:

1	-1		-1/4
1	1		-3/4
		1	0

→ { a+b, -a+b, c;-1/4,-3/4,0

EXERCISES

Problem 2.1.14

The following matrix-column pairs (W,w) are referred with respect to a basis (**a**,**b**,**c**):

(1) x,y,z (2) -x,y+1/2,-z+1/2

(3) -x,-y,-z (4) x,-y+1/2, z+1/2

Determine the corresponding matrix-column pairs (W',w') with respect to the basis (**a'**,**b'**,**c'**)= (**a**,**b**,**c**)**P**, with **P**=**c**,**a**,**b**.

Determine the coordinates X' of a point X= with respect to the new basis (**a'**,**b'**,**c'**).

0,70
0,31
0,95