

THE METRICAL MATRIX IN TEACHING MINERALOGY

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INTRODUCTION

The calculation of the d -spacings, the angles between planes and zones, the bond lengths and angles and other important geometric relationships for a mineral can be a tedious task both for the student and the instructor, particularly when completed with the large assortment of trigonometric identities and algebraic formulae that are available (cf. Crystal Geometry (1959), Donnay and Donnay, International Tables for Crystallography, Vol. II, Section 3, The Kynoch Press, 101–158). However, such calculations are straightforward and relatively easy to do when completed with the metrical matrix and the interactive software MATOP. Several applications of the matrix are presented below, each of which is worked out in detail and which is designed to teach you its use in the study of crystal geometry.

SOME PRELIMINARY COMMENTS

We begin our discussion of the matrix with a brief examination of the properties of the geometric three dimensional space, S , in which we live and in which minerals and rocks occur. For our purposes, it will be convenient to view S as the set of all vectors that radiate from a common origin to each point in space. In constructing a model for S , we chose three noncoplanar, coordinate axes denoted X , Y and Z , each radiating from the origin, $\mathbf{0}$. Next, we place three nonzero vectors denoted \mathbf{a} , \mathbf{b} and \mathbf{c} along X , Y and Z , respectively, likewise radiating from $\mathbf{0}$. Since the vectors $D = \{\mathbf{a}, \mathbf{b}, \mathbf{c}\}$ are nonzero, noncoplanar vectors, they qualify as basis vectors for S . This means that for each vector \mathbf{v} in S there exist three real numbers x, y and z such that \mathbf{v} can be written uniquely as $\mathbf{v} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c}$.

In the study of minerals, the coordinate X -, Y - and Z -axes and the basis vectors are chosen to coincide with three intersecting, noncoplanar edges of a representative block (parallelepiped) of the crystal structure called the unit cell. The magnitudes (lengths) of the basis vectors, \mathbf{a} , \mathbf{b} and \mathbf{c} , denoted a, b and c , respectively, are each taken as equal to the lengths of the three edges of the cell. In many cases, the cell edges are different in length such that $a \neq b \neq c$. The angles between the basis vectors $\alpha = \angle \mathbf{b} \wedge \mathbf{c}$, $\beta = \angle \mathbf{a} \wedge \mathbf{c}$ and $\gamma = \angle \mathbf{a} \wedge \mathbf{b}$ are taken as the interaxial angles; angles other than $90^\circ, 60^\circ, 120^\circ, 109.47^\circ$ etc., are often encountered. (cf. Fig 2.3, MSA Reviews in Mineralogy, Vol. 15, by Boisen and Gibbs, 1990 (B&G)). Once the size, shape and orientation of a unit cell is determined in an X-ray diffraction experiment, the choice of the origin, the coordinates axes and the basis vectors for a mineral is completely determined.

As it is difficult to enter a directed line segment \mathbf{v} directly into a computer, a correspondence is established between each vector $\mathbf{v} \in S$ and its triple representative $[\mathbf{v}]_D$. A set of three real numbers x, y and z form a triple representation of each vector $\mathbf{v} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c} \in S$ symbolized as

$$\mathbf{v} \iff [\mathbf{v}]_D = \begin{bmatrix} x \\ y \\ z \end{bmatrix}.$$

As the components of the triple are real numbers, they can be easily read into the computer or used in a calculation with a hand-held calculator (B&G, 21–25).

In most math courses, S is usually defined in terms of the well-known Cartesian basis $C = \{\mathbf{i}, \mathbf{j}, \mathbf{k}\}$ such that each vector $\mathbf{v} \in S$ can be written uniquely as $\mathbf{v} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k}$ where x, y and z are again real numbers. The triple representative for a vector \mathbf{v} , written in terms of the C -basis, is denoted as

$$[\mathbf{v}]_C = \begin{bmatrix} x \\ y \\ z \end{bmatrix}.$$

Although the components of the triples $[\mathbf{v}]_C$ and $[\mathbf{v}]_D$ are identical in appearance, the subscripts tell us that they can represent quite different vectors in S , one written in terms of the C -basis and the other in terms of the D -basis. When we use these components in a calculation or enter them into a computer, we require a metrical matrix, denoted G , that completely characterizes the geometry of the basis vectors and makes the arithmetic come out right regardless of whether one is using the natural basis in studying minerals or the Cartesian basis in studying mathematics.

The metrical matrix is found by evaluating the inner (dot) product of the nonzero vectors

$$\mathbf{v} = v_1\mathbf{a} + v_2\mathbf{b} + v_3\mathbf{c} \quad \text{and} \quad \mathbf{w} = w_1\mathbf{a} + w_2\mathbf{b} + w_3\mathbf{c}$$

where the product, denoted $\mathbf{v} \cdot \mathbf{w}$, is defined to be $\mathbf{v} \cdot \mathbf{w} = vw \cos \theta$, where θ is the angle between \mathbf{v} and \mathbf{w} such that $0^\circ \leq \theta \leq 180^\circ$ and where v and w are the lengths of \mathbf{v} and \mathbf{w} , respectively. Hence, the angle between the two vectors is given by the expression $\cos \theta = (\mathbf{v} \cdot \mathbf{w}) / (vw)$. The length of a vector \mathbf{v} , for example, is found by forming the inner product $\mathbf{v} \cdot \mathbf{v} = v^2 \cos 0^\circ = v^2$. When written in terms of the triple representative of \mathbf{v} , $[\mathbf{v}]_D$ (cf. B&G, 25-28),

$$\mathbf{v} \cdot \mathbf{v} = v^2 = [\mathbf{v}]_D^t G [\mathbf{v}]_D$$

where

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

and where $[\mathbf{v}]_D^t = [v_1 \ v_2 \ v_3]$ and $[\mathbf{v}]_D = \begin{bmatrix} v_1 \\ v_2 \\ v_3 \end{bmatrix}$. By evaluating $(\mathbf{v} \cdot \mathbf{v})^{1/2} = ([\mathbf{v}]_D^t G [\mathbf{v}]_D)^{1/2}$, the length of the vector \mathbf{v} is found. Likewise, $\mathbf{v} \cdot \mathbf{w} = [\mathbf{v}]_D^t G [\mathbf{w}]_D$ and since

$$\mathbf{v} \cdot \mathbf{w} = vw \cos \theta = ([\mathbf{v}]_D^t G [\mathbf{v}]_D)^{1/2} ([\mathbf{w}]_D^t G [\mathbf{w}]_D)^{1/2} \cos \theta = [\mathbf{v}]_D^t G [\mathbf{w}]_D,$$

it follows that

$$\cos \theta = \frac{([\mathbf{v}]_D^t G [\mathbf{w}]_D)}{([\mathbf{v}]_D^t G [\mathbf{v}]_D)^{1/2} ([\mathbf{w}]_D^t G [\mathbf{w}]_D)^{1/2}}$$

where $[\mathbf{v}]_D^t = [v_1 \ v_2 \ v_3]$, $[\mathbf{w}]_D^t = [w_1 \ w_2 \ w_3]$, $[\mathbf{v}]_D = \begin{bmatrix} v_1 \\ v_2 \\ v_3 \end{bmatrix}$ and $[\mathbf{w}]_D = \begin{bmatrix} w_1 \\ w_2 \\ w_3 \end{bmatrix}$.

For a Cartesian basis, the metrical matrix G is equal to the identity matrix I_3 ; $G = I_3$ because \mathbf{i}, \mathbf{j} and \mathbf{k} are mutually perpendicular, unit length vectors. Hence, the inner product of a vector $\mathbf{v} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k}$, written in terms of a Cartesian basis, becomes

$$\mathbf{v} \cdot \mathbf{v} = [\mathbf{v}]_C^t I_3 [\mathbf{v}]_C = [x \ y \ z] \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = [x \ y \ z] \begin{bmatrix} x \\ y \\ z \end{bmatrix} = x^2 + y^2 + z^2.$$

As indicated above, a unit cell, an origin, a set of basis vectors and a coordinate system is defined, in a crystal structure analysis, in a natural way for each mineral. Without these constructs and the model for S , the study of the geometry and symmetry of minerals becomes a qualitative chore, providing little meaningful insight into the nature of their properties and their possible uses. The C -basis is not without its use in studying minerals. For example, it can be used to generate the ϕ and ρ angles for plotting face poles and zones in stereographic projection (cf. B&G, 75–83).

Miller indices, zone axes and the positions of the atoms in the unit cell are defined in terms of the basis vectors and the coordinate system that correspond with those of the lattice representation, L_D , of the periodic symmetry of a mineral. Mineralogy students are often taught this but they may not appreciate the full power and convenience of basis vectors unless they attempt to calculate the angular and spatial relationships that exists among the faces and zones for a triclinic mineral like kyanite. In this note, a number of worked examples of useful crystallographic calculations are presented that could be included in mineralogy lectures or homework assignments. If you would like to convince your students that unit cells, zones and Miller indices are really useful, read on. In the pages that follow, interzonal and interfacial angles, $d_{(hkl)}$ -spacings, bond lengths and angles and unit cell volumes are calculated, each with the metrical matrix. The calculations entail adding, subtracting and multiplying vectors and matrices (evaluating inner products). These are relatively simple operations for a system defined in terms of a Cartesian basis and surprisingly straightforward operations when completed for the natural basis of a mineral. The derivation of the expressions used in this note together with a number of additional problems and examples can be found in B&G. Also, a review of matrices and determinants and the rules of matrix multiplication and matrix inversion are given in Appendix 2 of B&G or in almost any text on linear algebra.

As is well-known, crystallographic calculations are usually time consuming and open to error when completed by hand or with a calculator. To avoid these problems, the program MATOP was written for our students at Virginia Tech and for anyone else who has need of it. MATOP is an interactive program that begins by asking the user for the cell dimensions of a mineral. It then proceeds by calculating the metrical matrix G and its inverse, G^{-1} . Up to three 3×3 matrices can be entered into MATOP. Upon request, it multiplies and inverts these matrices including the metrical matrix, it multiplies a matrix by a triple (a vector), it evaluates inner and cross products of vectors, etc. With MATOP, the problems in this note and those in B&G can be completed rapidly and with little effort (See Boisen, Jr., M.B. and G.V. Gibbs, (1988), *MATOP: An interactive FORTRAN 77 Program for Solving Problems in Geometrical Crystallography*. Computers & Geosciences, 14, 37-53; problems similar to those worked here as well as others are solved step by step in this paper with MATOP). The note ends with a brief discussion of the connection that exist between the periodic crystal structure of a mineral and its lattice representation together with a discussion of the connection that exists between planes and lines of the lattice and faces and zones of the mineral. A simple rule is given that can be used to find the equation of a lattice (crystal) plane and its Miller indices.

APPLICATIONS OF THE METRICAL MATRIX

EXAMPLE 1: Constructing a metrical matrix

Suppose that the unit cell dimensions of a triclinic rhodonite crystal are $a = 10.497\text{\AA}$, $b = 9.797\text{\AA}$, $c = 12.185\text{\AA}$, $\alpha = 103.00^\circ$, $\beta = 108.51^\circ$ and $\gamma = 82.50^\circ$. With this information, the metrical matrix becomes

$$G = \begin{bmatrix} 110.187009 & 13.423197 & -40.606321 \\ 13.423197 & 95.981209 & -26.853857 \\ -40.606321 & -26.853857 & 148.474225 \end{bmatrix}.$$

PROBLEM 1: Calculate the metrical matrix for an orthorhombic crystal with cell dimensions $a = 3.397\text{\AA}$, $b = 11.321\text{\AA}$, $c = 6.516\text{\AA}$, $\alpha = 90.00^\circ$, $\beta = 90.00^\circ$ and $\gamma = 90.00^\circ$.

SOLUTION

$$G = \begin{bmatrix} 11.539609 & 0.0 & 0.0 \\ 0.0 & 128.165041 & 0.0 \\ 0.0 & 0.0 & 42.458256 \end{bmatrix}$$

DEFINITION 1: An expression for calculating the angle between two zones

Suppose that $[u_1 \ v_1 \ w_1]$ and $[u_2 \ v_2 \ w_2]$ are the indices of two zones defined by the vectors $\mathbf{r}_1 = u_1\mathbf{a} + v_1\mathbf{b} + w_1\mathbf{c}$ and $\mathbf{r}_2 = u_2\mathbf{a} + v_2\mathbf{b} + w_2\mathbf{c}$, respectively, in a crystal, then the angle δ between the two is given by the expression

$$\cos \delta = \mathbf{r}_1 \cdot \mathbf{r}_2 / (r_1 r_2) = \frac{([\mathbf{r}_1]_D^t G [\mathbf{r}_2]_D)}{([\mathbf{r}_1]_D^t G [\mathbf{r}_1]_D)^{1/2} ([\mathbf{r}_2]_D^t G [\mathbf{r}_2]_D)^{1/2}}.$$

EXAMPLE 2: A calculation of the angle between two zones

Given the unit cell dimensions for rhodonite (Example 1), calculate the angle δ between the zones $[-1 \ 1 \ 2]$ and $[2 \ 1 \ 3]$. To find the angle, the following three expressions are evaluated: $([\mathbf{r}_1]_D^t G [\mathbf{r}_2]_D)$, $([\mathbf{r}_1]_D^t G [\mathbf{r}_1]_D)^{1/2}$ and $([\mathbf{r}_2]_D^t G [\mathbf{r}_2]_D)^{1/2}$. Setting $[\mathbf{r}_1]_D^t = [u_1 \ v_1 \ w_1] = [-1 \ 1 \ 2]$ and $[\mathbf{r}_2]_D^t = [u_2 \ v_2 \ w_2] = [2 \ 1 \ 3]$, we can write

$$([\mathbf{r}_1]_D^t G [\mathbf{r}_2]_D) = [-1 \ 1 \ 2] \begin{bmatrix} 110.187009 & 13.423197 & -40.606321 \\ 13.423197 & 95.981209 & -26.853857 \\ -40.606321 & -26.853857 & 148.474225 \end{bmatrix} \begin{bmatrix} 2 \\ 1 \\ 3 \end{bmatrix} =$$

$$[-1 \ 1 \ 2] \begin{bmatrix} 111.9782508 \\ 42.2660321 \\ 337.3561748 \end{bmatrix} = 605.000131,$$

$$([\mathbf{r}_1]_D^t G [\mathbf{r}_1]_D) = [-1 \ 1 \ 2] \begin{bmatrix} 110.187009 & 13.423197 & -40.606321 \\ 13.423197 & 95.981209 & -26.853857 \\ -40.606321 & -26.853857 & 148.474225 \end{bmatrix} \begin{bmatrix} -1 \\ 1 \\ 2 \end{bmatrix} =$$

$$[-1 \ 1 \ 2] \begin{bmatrix} -177.9764547 \\ 28.8502974 \\ 310.7009143 \end{bmatrix} = 828.228581,$$

$$([\mathbf{r}_2]_D^t G [\mathbf{r}_2]_D) = [2 \ 1 \ 3] \begin{bmatrix} 110.187009 & 13.423197 & -40.606321 \\ 13.423197 & 95.981209 & -26.853857 \\ -40.606321 & -26.853857 & 148.474225 \end{bmatrix} \begin{bmatrix} 2 \\ 1 \\ 3 \end{bmatrix} =$$

$$[2 \ 1 \ 3] \begin{bmatrix} 111.9782508 \\ 42.2660321 \\ 337.3561748 \end{bmatrix} = 1278.291058.$$

Recalling that

$$\cos \delta = \frac{([\mathbf{r}_1]_D^t G [\mathbf{r}_2]_D)}{([\mathbf{r}_1]_D^t G [\mathbf{r}_1]_D)^{1/2} ([\mathbf{r}_2]_D^t G [\mathbf{r}_2]_D)^{1/2}},$$

$$\cos \delta = \frac{605.000131}{(828.228581)^{1/2} (1278.291058)^{1/2}} = 0.587984.$$

Hence, $\delta = 53.99^\circ$.

PROBLEM 2: Calculate the angle between the zones $[1 \ -1 \ 2]$ and $[3 \ 1 \ 1]$ for the orthorhombic crystal described in Problem 1.

SOLUTION

91.70°

DEFINITION 2: An expression for calculating $d_{(hkl)}$ -spacings

Given the indices h, k and l of a lattice plane and a set of unit cell dimensions, the $d_{(hkl)}$ -spacing of the plane can be found with the quadratic expression

$$Q_{(hkl)} = 1/d_{hkl}^2 = [\mathbf{s}]_{D^*}^t \mathbf{G}^{-1} [\mathbf{s}]_{D^*}$$

where $[\mathbf{s}]_{D^*}^t = [h \ k \ l]$ and $[\mathbf{s}]_{D^*} = \begin{bmatrix} h \\ k \\ l \end{bmatrix}$. Hence, it follows that

$$1/d_{(hkl)}^2 = [h \ k \ l] \begin{bmatrix} a^2 & ab \cos \gamma & ac \cos \beta \\ ab \cos \gamma & b^2 & bc \cos \alpha \\ ac \cos \beta & bc \cos \alpha & c^2 \end{bmatrix}^{-1} \begin{bmatrix} h \\ k \\ l \end{bmatrix}.$$

The subscript D^* denotes an important set of basis vectors $D^* = \{\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*\}$ defined on S that play a central role in the interpretation of the X-diffraction record of a mineral and the solution of its crystal structure. The geometry of the D^* -basis is completely defined by $\mathbf{G}^* = \mathbf{G}^{-1}$ just as that of the D -basis is defined by \mathbf{G} . It is important to note that there exists a vector $\mathbf{s} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ perpendicular to each potential plane (hkl) of a mineral. In addition, the vector \mathbf{s} has the length $s = 1/d_{(hkl)}$ such that the inner product $\mathbf{s} \cdot \mathbf{s} = 1/d_{(hkl)}^2 = [\mathbf{s}]_{D^*}^t \mathbf{G}^* [\mathbf{s}]_{D^*}$. The reciprocal metrix matrix

$$\mathbf{G}^* = \begin{bmatrix} a^{*2} & a^*b^* \cos \gamma^* & a^*c^* \cos \beta^* \\ a^*b^* \cos \gamma^* & b^{*2} & b^*c^* \cos \alpha^* \\ a^*c^* \cos \beta^* & b^*c^* \cos \alpha^* & c^{*2} \end{bmatrix}$$

completely defines the geometry of the reciprocal lattice, L_{D^*} , just as \mathbf{G} defines the geometry of the direct lattice, L_D .

EXAMPLE 3: A calculation of a $d_{(hkl)}$ -spacing

Given the cell dimensions for kyanite $a = 7.126\text{\AA}$, $b = 7.852\text{\AA}$, $c = 5.572\text{\AA}$, $\alpha = 89.99^\circ$, $\beta = 101.11^\circ$ and $\gamma = 106.03^\circ$, calculate the d -spacing for the plane $(2 \ -3 \ 1)$.

SOLUTION

As defined above,

$$1/d_{(hkl)}^2 = [h \ k \ l] \begin{bmatrix} a^2 & ab \cos \gamma & ac \cos \beta \\ ab \cos \gamma & b^2 & bc \cos \alpha \\ ac \cos \beta & bc \cos \alpha & c^2 \end{bmatrix}^{-1} \begin{bmatrix} h \\ k \\ l \end{bmatrix}.$$

Replacing the entries of the matrix with the given cell dimensions and h, k and l by 2, -3 and 1, respectively, we have

$$1/d_{(2-31)}^2 = [2 \ -3 \ 1] \begin{bmatrix} 50.779876 & -15.450994 & -7.651091 \\ -15.450994 & 61.653904 & 0.007636 \\ -7.651091 & 0.007636 & 31.047184 \end{bmatrix}^{-1} \begin{bmatrix} 2 \\ -3 \\ 1 \end{bmatrix}.$$

Next, inverting the G matrix to obtain G^{-1} ,

$$\begin{aligned} 1/d_{(2-31)}^2 &= [2 \quad -3 \quad 1] \begin{bmatrix} 0.022211 & 0.005566 & 0.005472 \\ 0.005566 & 0.017614 & 0.001367 \\ 0.005472 & 0.001367 & 0.033557 \end{bmatrix} \begin{bmatrix} 2 \\ -3 \\ 1 \end{bmatrix} = \\ & [2 \quad -3 \quad 1] \begin{bmatrix} 0.0331971 \\ -0.0403442 \\ 0.0403999 \end{bmatrix} = 0.22783. \end{aligned}$$

Hence, $d_{(2-31)} = 2.095\text{\AA}$.

PROBLEM 3: Calculate the $d_{(123)}$ -spacing for the plane (123) for the orthorhombic crystal discussed in Problem 1.

SOLUTION

$$d_{(123)} = 1.741\text{\AA}$$

DEFINITION 3: An expression for calculating the angle between two face poles.

Suppose that (h_1, k_1, l_1) and (h_2, k_2, l_2) are two planes of a crystal, then the angle, Δ , between the poles to these faces is given by the expression

$$\cos \Delta = \frac{([\mathbf{s}_1]_{D^*}^t G^{-1} [\mathbf{s}_2]_{D^*})}{([\mathbf{s}_1]_{D^*}^t G^{-1} [\mathbf{s}_1]_{D^*})^{1/2} ([\mathbf{s}_2]_{D^*}^t G^{-1} [\mathbf{s}_2]_{D^*})^{1/2}}$$

where $[\mathbf{s}_1]_{D^*}^t = [h_1 \ k_1 \ l_1]$, $[\mathbf{s}_2]_{D^*}^t = [h_2 \ k_2 \ l_2]$, $[\mathbf{s}_1]_{D^*} = \begin{bmatrix} h_1 \\ k_1 \\ l_1 \end{bmatrix}$ and $[\mathbf{s}_2]_{D^*} = \begin{bmatrix} h_2 \\ k_2 \\ l_2 \end{bmatrix}$.

EXAMPLE 4: Calculation of the interfacial angle between two planes

The structure of kyanite can be viewed as based on a cubic close-packed array of oxide anions with close-packed monolayers layers paralleling (110), (-122) , $(0-11)$ and $(3-20)$ (cf. B&G, 65-71). Determine the interfacial angle Δ between the planes (-122) and $(3-20)$.

SOLUTION

Our task is to evaluate

$$\cos \Delta = \frac{([\mathbf{s}_1]_{D^*}^t G^{-1} [\mathbf{s}_2]_{D^*})}{([\mathbf{s}_1]_{D^*}^t G^{-1} [\mathbf{s}_1]_{D^*})^{1/2} ([\mathbf{s}_2]_{D^*}^t G^{-1} [\mathbf{s}_2]_{D^*})^{1/2}}$$

which is done by evaluating $[\mathbf{s}_1]_{D^*}^t G^{-1} [\mathbf{s}_2]_{D^*}$, $([\mathbf{s}_1]_{D^*}^t G^{-1} [\mathbf{s}_1]_{D^*})^{1/2}$ and $([\mathbf{s}_2]_{D^*}^t G^{-1} [\mathbf{s}_2]_{D^*})^{1/2}$. With $h_1 = -1$, $k_1 = 2$, $l_1 = 2$, $h_2 = 3$, $k_2 = -2$ and $l_2 = 0$ and with the cell dimensions of kyanite (Example 3),

$$[\mathbf{s}_1]_{D^*}^t G^{-1} [\mathbf{s}_1]_{D^*} = [-1 \quad 2 \quad 2] \begin{bmatrix} 50.779876 & -15.450994 & -7.651091 \\ -15.450994 & 61.653904 & 0.007636 \\ -7.651091 & 0.007636 & 31.047184 \end{bmatrix}^{-1} \begin{bmatrix} -1 \\ 2 \\ 2 \end{bmatrix}.$$

Next, inverting the G matrix,

$$[\mathbf{s}_1]_{D^*}^t G^{-1} [\mathbf{s}_1]_{D^*} = [-1 \quad 2 \quad 2] \begin{bmatrix} 0.022211 & 0.005566 & 0.005472 \\ 0.005566 & 0.017614 & 0.001367 \\ 0.005472 & 0.001367 & 0.033557 \end{bmatrix} \begin{bmatrix} -1 \\ 2 \\ 2 \end{bmatrix} = 0.193683,$$

$$[s_2]_{D^*}^t G^{-1} [s_2]_{D^*} = [3 \quad -2 \quad 0] \begin{bmatrix} 0.022211 & 0.005566 & 0.005472 \\ 0.005566 & 0.017614 & 0.001367 \\ 0.005472 & 0.001367 & 0.033557 \end{bmatrix} \begin{bmatrix} 3 \\ -2 \\ 0 \end{bmatrix} = 0.203567,$$

$$[s_2]_{D^*}^t G^{-1} [s_2]_{D^*} = [-1 \quad 2 \quad 2] \begin{bmatrix} 0.022211 & 0.005566 & 0.005472 \\ 0.005566 & 0.017614 & 0.001367 \\ 0.005472 & 0.001367 & 0.033557 \end{bmatrix} \begin{bmatrix} 3 \\ -2 \\ 0 \end{bmatrix} = -0.065201.$$

Hence, $\cos \Delta = -0.065201 / ((0.193683)^{1/2} \times (0.203567)^{1/2})$ and $\Delta = 109.17^\circ$. This angle is closed to the ideal tetrahedra angle of 109.47° that would have obtained if the oxide anions in the kyanite structure were ideally cubic close-packed.

PROBLEM 4: Calculate the angle between the close-packed monolayers of oxide anions that parallel (-122) and (3-20) in kyanite.

SOLUTION

$$\Delta = 109.17^\circ$$

DEFINITION 4: An expression for calculating the angle between a face pole and a zone

The angle, ϵ , between a face pole (hkl) and a zone $[uvw]$ is given by the expression

$$\cos \epsilon = \frac{[s]_{D^*}^t [r]_D}{([s]_{D^*}^t G^{-1} [s]_{D^*})^{1/2} ([r]_D^t G [r]_D)^{1/2}}$$

where $[s]_{D^*}^t = [h \ k \ l]$ and $[r]_D = \begin{bmatrix} u \\ v \\ w \end{bmatrix}$.

EXAMPLE 5: Calculation of the angle between a zone and a face pole

Calculate the angle, ϵ , between the close-packed plane (-1 2 2) and the zone [8 7 2] of kyanite where [8 7 2] defines a zone that is perpendicular to one of the oxide monolayers in the cubic close-packed structure. The angle is given by the expression

$$\cos \epsilon = \frac{hu + kv + lw}{([s]_{D^*}^t G^{-1} [s]_{D^*})^{1/2} ([r]_D^t G [r]_D)^{1/2}}$$

SOLUTION

$$\cos \epsilon = \frac{10}{(0.193883)^{1/2} (4420.009648)^{1/2}} = 0.341601$$

and $\epsilon = 70.03^\circ$. This angle is close to the ideal angle of 70.53° expected between a vector perpendicular to an oxide anion monolayer and another monolayer in a cubic close-packed structure.

PROBLEM 5: Calculate the angle between the monolayer of oxide anions that parallels the (1 1 0) plane and the [0 1 2] zone in kyanite.

SOLUTION

71.04°

DEFINITION 5: An expression for calculating the unit cell volume

The volume v of the unit cell is given by the expression

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

EXAMPLE 6: Calculation of the volume of the unit cell

Given that the cell dimensions of coesite, a high pressure monoclinic form of silica, are $a = 7.135 \text{ \AA}$, $b = 12.372 \text{ \AA}$, $c = 7.173 \text{ \AA}$, $\alpha = \gamma = 90^\circ$ and $\beta = 120.36^\circ$, calculate the volume of its unit cell. The unit cell volume of coesite is obtained using the expression

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

which for coesite becomes

$$\det \begin{bmatrix} 50.908225 & 0.0 & -25.867658 \\ 0.0 & 153.066384 & 0.0 \\ -25.867658 & 0.0 & 51.45192 \end{bmatrix} =$$

$$153.066384(50.908225 \times 51.45192 - 25.867658 \times 25.867658) = (546.36)^2 \text{ \AA}^6$$

Hence, the volume of the unit cell of coesite is $v = 546.36 \text{ \AA}^3$.

PROBLEM 6: Calculate the volume of the unit cell in quartz given that $a = b = 4.914 \text{ \AA}$, $c = 5.409 \text{ \AA}$, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$.

SOLUTION

113.114 \AA^3

BOND LENGTH AND ANGLE CALCULATIONS

A close connection exists between crystal chemistry of a mineral and the bond lengths and angles exhibited by its crystal structure. Indeed, a knowledge of the bond lengths and angles is necessary for determining the likely coordination numbers of the atoms, for a description of the structure and for an understanding of certain physical properties. This example illustrates how the SiO bond lengths in two corner sharing silicate tetrahedra and the SiOSi angle that links the tetrahedra into a chain in pectolite can be calculated with the metrical matrix. The cell dimensions of pectolite are $a = 7.988 \text{ \AA}$, $b = 7.040 \text{ \AA}$, $c = 7.025 \text{ \AA}$, $\alpha = 90.51^\circ$, $\beta = 95.18^\circ$ and $\gamma = 102.47^\circ$. A structure analysis of the mineral shows that the fractional positional coordinates (x, y, z) of the two Si atoms, (denoted Si₂ and Si₃) are (0.2150, 0.9544, 0.3440) and (0.4505, 0.7353, 0.1447), respectively, while that of the O atom (denoted O₈) is (0.3955, 0.9092, 0.2746). In this example, the separations (bond lengths) between Si₂ and O₈ and Si₃ and O₈ and the Si₂O₈Si₃ angle are calculated. The two bond lengths, denoted $R(\text{Si}_2\text{O}_8)$ and $R(\text{Si}_3\text{O}_8)$, are calculated below in three steps followed by a calculation of the angle.

EXAMPLE 7: Calculation of SiO bond lengths

Step 1: Calculation of the metrical matrix for pectolite:

$$G = \begin{bmatrix} a^2 & ab \cos \gamma & ac \cos \beta \\ ab \cos \gamma & b^2 & bc \cos \alpha \\ ac \cos \beta & bc \cos \alpha & c^2 \end{bmatrix} = \begin{bmatrix} 63.808144 & -12.142846 & -5.066403 \\ -12.142846 & 49.561600 & -0.440211 \\ -5.066403 & -0.440211 & 49.350625 \end{bmatrix}$$

Step 2: If we denote the vectors that radiate from the origin of the unit cell, $\mathbf{0}$, to O_8 , Si_2 and Si_3 , to be \mathbf{v}_1 , \mathbf{v}_2 and \mathbf{v}_3 respectively, and those that radiate from O_8 to Si_2 and Si_3 to be \mathbf{v}_4 and \mathbf{v}_5 , respectively, then the lengths of the Si_2O_8 and the Si_3O_8 bonds are equal to $|\mathbf{v}_4|$ and $|\mathbf{v}_5|$, respectively. The triple representatives of these vectors are:

$$[\mathbf{v}_1]_D = \begin{bmatrix} 0.3955 \\ 0.9092 \\ 0.2746 \end{bmatrix}, [\mathbf{v}_2]_D = \begin{bmatrix} 0.2150 \\ 0.9544 \\ 0.3440 \end{bmatrix} \text{ and } [\mathbf{v}_3]_D = \begin{bmatrix} 0.4505 \\ 0.7353 \\ 0.1447 \end{bmatrix},$$

$$[\mathbf{v}_4]_D = [\mathbf{v}_2]_D - [\mathbf{v}_1]_D = \begin{bmatrix} 0.2150 \\ 0.9544 \\ 0.3440 \end{bmatrix} - \begin{bmatrix} 0.3955 \\ 0.9092 \\ 0.2746 \end{bmatrix} = \begin{bmatrix} -0.1805 \\ 0.0452 \\ 0.0694 \end{bmatrix} \text{ and}$$

$$[\mathbf{v}_5]_D = [\mathbf{v}_3]_D - [\mathbf{v}_1]_D = \begin{bmatrix} 0.4505 \\ 0.7353 \\ 0.1447 \end{bmatrix} - \begin{bmatrix} 0.3955 \\ 0.9092 \\ 0.2746 \end{bmatrix} = \begin{bmatrix} 0.0550 \\ -0.1739 \\ -0.1299 \end{bmatrix}.$$

Step 3: With the triples for $[\mathbf{v}_4]_D$ and $[\mathbf{v}_5]_D$ and the metrical matrix G , we can write the equality

$$\begin{aligned} |\mathbf{v}_4|^2 &= R(Si_2O_8)^2 = [\mathbf{v}_4]_D^t G [\mathbf{v}_4]_D = \\ & \begin{bmatrix} -0.1805 & 0.0452 & 0.0694 \end{bmatrix} \begin{bmatrix} 63.808144 & -12.142846 & -5.066403 \\ -12.142846 & 49.561600 & -0.440211 \\ -5.066403 & -0.440211 & 49.350625 \end{bmatrix} \begin{bmatrix} -0.1805 \\ 0.0452 \\ 0.0694 \end{bmatrix} \\ & \begin{bmatrix} -0.1805 & 0.0452 & 0.0694 \end{bmatrix} \begin{bmatrix} -12.4178350 \\ 4.4014173 \\ 4.3195216 \end{bmatrix} = (1.655336)^2. \end{aligned}$$

$$\begin{aligned} |\mathbf{v}_5|^2 &= R(Si_3O_8)^2 = [\mathbf{v}_5]_D^t G [\mathbf{v}_5]_D = \\ & \begin{bmatrix} 0.0550 & -0.1739 & -0.1299 \end{bmatrix} \begin{bmatrix} 63.808144 & -12.142846 & -5.066403 \\ -12.142846 & 49.561600 & -0.440211 \\ -5.066403 & -0.440211 & 49.350625 \end{bmatrix} \begin{bmatrix} 0.0550 \\ -0.1739 \\ -0.1299 \end{bmatrix} \\ & \begin{bmatrix} 0.0550 & -0.1739 & -0.1299 \end{bmatrix} \begin{bmatrix} 6.2792145 \\ -9.2294354 \\ -6.6127457 \end{bmatrix} = (1.676112)^2 \text{ and} \end{aligned}$$

hence, the lengths of the Si_2O_8 and Si_3O_8 bonds are 1.655Å and 1.676Å, respectively.

EXAMPLE 8: A calculation of the SiOSi angle

Step 1. The SiOSi angle is calculated with the expression

$$\cos \angle (Si_3O_8Si_2) = ([\mathbf{v}_5]_D^t G [\mathbf{v}_4]_D) / (([\mathbf{v}_5]_D^t G [\mathbf{v}_5]_D)^{1/2} ([\mathbf{v}_4]_D^t G [\mathbf{v}_4]_D)^{1/2}) =$$

$$([\mathbf{v}_5]_D^t G[\mathbf{v}_4]_D) / (R(\text{Si}_3\text{O}_8) \times R(\text{Si}_2\text{O}_8)).$$

We next evaluate

$$([\mathbf{v}_5]_D^t G[\mathbf{v}_4]_D),$$

and obtain

$$\begin{bmatrix} 0.0550 & -0.1739 & -0.1299 \end{bmatrix} \begin{bmatrix} 63.808144 & -12.142846 & -5.066403 \\ -12.142846 & 49.561600 & -0.440211 \\ -5.066403 & -0.440211 & 49.350625 \end{bmatrix} \begin{bmatrix} -0.1805 \\ 0.0452 \\ 0.0694 \end{bmatrix} = -2.009493.$$

Hence,

$$\cos \angle (\text{Si}_3\text{O}_8\text{Si}_2) = -2.009493 / (1.676112 \times 1.655336)$$

from which it follows that

$$\angle (\text{Si}_3\text{O}_8\text{Si}_2) = 136.408^\circ.$$

PROBLEM 7: Calculate the Si_1O_3 and the Si_1O_4 bond lengths and the $\text{O}_3\text{Si}_1\text{O}_4$ angle for coesite given that $a = 7.1367\text{\AA}$, $b = 12.3695\text{\AA}$, $c = 7.1742\text{\AA}$, $\alpha = \gamma = 90^\circ$ and $\beta = 120.337^\circ$ and that the fraction coordinates of Si_1 , O_3 and O_4 are $(0.14034, 0.10832, 0.07233)$, $(0.26628, 0.12309, -0.05990)$ and $(0.31097, 0.10374, 0.32799)$, respectively.

SOLUTION

$$R(\text{Si}_1\text{O}_3) = 1.613\text{\AA}; R(\text{Si}_1\text{O}_4) = 1.611\text{\AA}; \angle \text{O}_3\text{Si}_1\text{O}_4 = 110.38^\circ$$

CRYSTAL FACES, LATTICE PLANES AND MILLER INDICES

Lattices play a fundamental role in the study of crystals in that they can be used to represent the translational symmetry and the periodic structure of a crystal. For our purposes, a crystal can be defined as an array of bonded atoms that repeats at regular intervals along parallel lines in S . By replacing each such array of atoms by a lattice point, a 3D lattice L_D results. In other words, a lattice is an array of lattice points that repeats at regular intervals along parallel lines in S . As the points in a lattice are all translationally equivalent, the environment about each array of atoms represented by a lattice point is identical to each other such array in the crystal.

Each plane of lattice points (lattice plane) in L_D parallels a potential face on a crystal and each line of lattice points parallels the line formed by two or more such intersecting lattice (crystal) planes. As lattice (crystal) planes and their lines of intersection are defined by lattice points in S , they are defined by sets of three integers referred to as indices. The line formed by the intersection of two or more nonparallel lattice planes is called a zone denoted $[uvw]$ where u, v and w are integers (zone indices), while the lattice planes themselves are defined by three integers (hkl) , referred to as the Miller indices of the plane.

EXAMPLE 9: A derivation of the equation of a lattice (crystal) plane and its Miller indices

RULE: Suppose that the expression $v_1x + v_2y + v_3z = 1$ defines a plane in S where x, y and z are indeterminants and v_1, v_2 and v_3 are real numbers. If the end point of a vector $\mathbf{v} = p\mathbf{a} + q\mathbf{b} + r\mathbf{c}$ lies on a plane P , then the equation of the plane is found by simply replacing the indeterminates x, y and z in the expression $v_1x + v_2y + v_3z = 1$ by p, q and r , respectively, to yield the equation $v_1p + v_2q + v_3r = 1$. Stated another way, the end point of a vector $\mathbf{v} = p\mathbf{a} + q\mathbf{b} + r\mathbf{c}$ lies on a plane $v_1x + v_2y + v_3z = 1$ if and only if $x = p, y = q$ and $z = r$.

For a plane to qualify as a lattice plane in S , it must pass through the end-points of three noncoplanar lattice vectors in L_D . Hence, if P is a lattice plane, then there must exist three such lattice vectors $\mathbf{p} = p_1\mathbf{a} + p_2\mathbf{b} + p_3\mathbf{c}$, $\mathbf{q} = q_1\mathbf{a} + q_2\mathbf{b} + q_3\mathbf{c}$ and $\mathbf{r} = r_1\mathbf{a} + r_2\mathbf{b} + r_3\mathbf{c}$ in L_D whose end-points lie on P where p_i , q_i and r_i are integers. As the end-points of these vectors are each on P , then the indeterminants x, y and z of the expression $v_1x + v_2y + v_3z = 1$ can be replaced successively by the coefficients of \mathbf{a} , \mathbf{b} and \mathbf{c} for each of the three vectors to yield the following three equations: $v_1p_1 + v_2p_2 + v_3p_3 = 1$, $v_1q_1 + v_2q_2 + v_3q_3 = 1$, and $v_1r_1 + v_2r_2 + v_3r_3 = 1$. Simultaneously solving these equations for v_1, v_2 and v_3 yields three rational numbers which can be easily converted into the integers h, k and l by multiplying both sides of the equation by a common factor and clearing the resulting fractions to obtain the Miller indices of the plane P .

EXAMPLE 10: A determination of the Miller indices for a lattice plane

Suppose that the end-points of the following three noncoplanar lattice vectors $\mathbf{p} = 2\mathbf{a} - 3\mathbf{b} + \mathbf{c}$, $\mathbf{q} = -\mathbf{a} + \mathbf{b} - 2\mathbf{c}$ and $\mathbf{r} = -3\mathbf{a} + 2\mathbf{b} + 3\mathbf{c}$ in L_D lie on some lattice plane P , find the equation and its Miller indices.

SOLUTION

As observed above, the equation of a plane in S can be written as $v_1x + v_2y + v_3z = 1$ and since the end point of the three lattice vectors \mathbf{p} , \mathbf{q} and \mathbf{r} lie on a lattice plane, P , we can write the following three equations $v_1(2) + v_2(-3) + v_3(1) = 1$, $v_1(-1) + v_2(1) + v_3(-2) = 1$ and $v_1(-3) + v_2(2) + v_3(3) = 1$. Simultaneously solving these equations, we find that $v_1 = -23/12$, $v_2 = -7/4$ and $v_3 = -5/12$. Substituting these values into the equation $v_1x + v_2y + v_3z = 1$, we obtain $-23/12x - 7/4y - 5/12z = 1$. Multiplying both sides of the equation by each of the denominators of v_1, v_2 and v_3 and clearing fractions, we obtain $-23x - 21y - 5z = 12$ as the equation of P where $h = -23, k = -21$ and $l = -5$ are the Miller indices of the plane.

In general, it can be shown that the equation of a lattice plane in L_D is of the form $hx + ky + lz = m$ where h, k, l and m can adopt all possible integer values, resulting in as many planes. For example, the equation $hx + ky + lz = m$ defines, for a given set of integers h, k and l , an infinite number of equally spaced, parallel planes, one for each integer value of m . It can be shown that each such plane is translationally equivalent to the plane $hx + ky + lz = 1$. The spacing between each of these planes is the well-known $d_{(hkl)}$ -spacing for the plane (hkl) . The plane $hx + ky + lz = 1$ intercepts the X -axis of the crystal at \mathbf{a}/h , the Y -axis at \mathbf{b}/k and the Z -axis at \mathbf{c}/l . The plane defined by $hx + ky + lz = m$ intercepts the X -axis of the crystal at $m\mathbf{a}/h$, the Y -axis at $m\mathbf{b}/k$ and the Z -axis at $m\mathbf{c}/l$ whereas the plane defined by the equation $hx + ky + lz = 0$ passes through the origin, $\mathbf{0}$, of the unit cell (cf. Fig. 2.3, B&G). In other words, the plane defined by the equation $hx + ky + lz = m$ is m times as far from the origin as the plane defined by the equation $hx + ky + lz = 1$. As the plane $hx + ky + lz = 1$ is translationally equivalent to each of the planes defined by the equations $hx + ky + lz = m$, it is taken as the representative plane for this infinite set of equally spaced, parallel planes in the lattice. By convention, whenever a plane with indices h, k and l is discussed, it is assumed by convention to be the plane defined by the equation $hx + ky + lz = 1$, located at a distance of $d_{(hkl)}$ from the origin of the unit cell. For another but similar development of the equation of a lattice plane, Miller indices and a derivation of an expression for the $d_{(hkl)}$ -spacing see B&G (p. 42-47 and Appendix 5).

PROBLEM 8: Determine the equation of the lattice plane in L_D that passes through the end-points of the vectors $\mathbf{p} = 3\mathbf{a}$, $\mathbf{q} = -\mathbf{b}$ and $\mathbf{r} = 2\mathbf{c}$.

SOLUTION

In this example, we want to find the equation of a plane that passes through the end-

points of the three vectors \mathbf{p} , \mathbf{q} and \mathbf{r} that lie along the X -, Y - and Z -coordination axes, respectively. With the information given, the following three equations can be written: $3v_1 = 1$, $-1v_2 = 1$ and $2v_3 = 1$. It follows that $v_1 = 1/3$, $v_2 = -1$ and $v_3 = 1/2$. Replacing v_1 , v_2 and v_3 in $v_1x + v_2y + v_3z = 1$ by $1/3$, -1 and $1/2$, respectively, the equation $1/3x - y + 1/2z = 1$ is obtained. Multiplying both sides of the equation by 6 and clearing fractions, $2x - 6y + 3z = 6$ results as the equation of the plane that passes through the end-points of the lattice vectors $3\mathbf{a}$, $-1\mathbf{b}$ and $2\mathbf{c}$. The Miller indices of this plane are $(2\ -6\ 3)$.

PROBLEM 9: Determine the equation and the Miller indices of a lattice plane that passes through the end-points of the following three noncoplanar lattice vectors $\mathbf{v}_1 = 1\mathbf{a} + 2\mathbf{b} + 5\mathbf{c}$, $\mathbf{v}_2 = 2\mathbf{a} - 1\mathbf{b} - 6\mathbf{c}$ and $\mathbf{v}_3 = -1\mathbf{a} - 1\mathbf{b} + 0\mathbf{c}$.

SOLUTION

$$(2, -3\ 1) \text{ and } 2x - 3y + z = 1$$

CONCLUDING REMARKS

The selection of a set of basis vectors in an X-ray diffraction study is an important first step in the study of the geometrical properties of a mineral. Once this is done, the metrical matrix is easily computed and the geometry of the mineral is completely characterized. With the matrix and a knowledge of the rules of matrix multiplication and matrix inversion, a variety of relatively difficult crystallographic problems can be solved with surprisingly little effort, particularly when the computations are completed with the program MATOP. Also, with a simple rule for determining the equation of a plane, the Miller indices of a lattice (crystal) plane can be determined in a straightforward way. With the use of the rule, one avoids using Weiss parameters which have not only outlived their usefulness but should be purged from the mineralogical literature.

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