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# Atomic displacement parameters and anisotropic thermal ellipsoid lengths and angles

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Relations between direct and reciprocal basis vectors and the atomic displacement matrix and anisotropic temperature-factor matrix are provided for generic dimension $n$, introducing a few new symbols. The moments of the probability distribution of the anisotropic thermal ellipsoids are provided as functions of dimension $n$. For specific dimensions $n = 2$ and $n = 3$, new explicit formulas for the semi-axis lengths and rotation angles of the thermal ellipsoids are derived from the atomic displacement matrix, taking into account certain special cases. For dimension $n = 3$, the Euler angles are defined. The resulting formulas can be used, for example, to display the thermal ellipsoids of atoms or for further analysis of molecular vibrations.

## 1. Introduction

The dimension $n$ of a diffracting object need not necessarily be $n = 3$. Dimension $n = 1$ can be used for describing diffraction by a line (Brussaard *et al.*, 2002), dimension $n = 2$ for diffraction by a surface (Robinson, 1998), dimension $n = 3$ for diffraction by a volume, described in many textbooks, and dimension $n > 3$ for diffraction by aperiodic crystals (de Wolff, 1974; Janner *et al.*, 1983; Janssen *et al.*, 1992; Steurer & Haibach, 2001). A description of the crystallographic symmetries for generic dimension $n$ has been provided (Janssen *et al.*, 1999, 2002). The formulas for the direct and reciprocal basis vectors, the atomic displacement matrix, the anisotropic temperature-factor matrix and the symmetry restrictions can be derived for generic dimension $n$. The semi-axis lengths and rotation angles of the thermal ellipsoids can be obtained by numerical diagonalization of the atomic displacement matrix (Waser, 1955*b*; Cerrini, 1971; Willis & Pryor, 1975; Prince, 1982; Trueblood *et al.*, 1996; Grosse-Kunstleve & Adams, 2002; Press *et al.*, 2002). In this paper, however, for specific dimensions $n = 2$ and $n = 3$, new explicit formulas for the semi-axis lengths and rotation angles of the thermal ellipsoid are derived from the atomic displacement matrix, taking into account certain special cases, and ready to be used for example for displaying the thermal ellipsoid, as in *ORTEP* (Burnett & Johnson, 1996), or for further interpretation in terms of molecular vibrations (Cruickshank, 1956*a*,*b*; Schomaker & Trueblood, 1968; Willis & Pryor, 1975; Tanaka & Marumo, 1983; Dunitz *et al.*, 1988; Bürgi, 1995).

The content of this paper is organized as follows. The generic direct and reciprocal basis vectors are defined in §2, and their mutual relation is derived, introducing a few new symbols. A derivation is provided in §3 of the generic atomic displacement matrix and anisotropic temperature-factor matrix. The symmetry restrictions of the atomic displacement matrix are discussed in §4. Specific explicit formulas are derived in §5 for the semi-axis lengths and rotation angles of the anisotropic thermal ellipsoid up to dimension $n = 3$, including their symmetries and taking into account certain special cases. The Euler angles for dimension $n = 3$ are derived in Appendix *A*.

## 2. Direct and reciprocal basis vectors

For describing the $n$-dimensional thermal ellipsoids, it is convenient to provide a few new symbols relating to the direct and reciprocal basis vectors. Let $i = 1, \ldots, n$ be the index over the dimensions, and let $\{\mathbf{e}_i\}$ be an orthonormal basis in $n$-dimensional space, which means that

$$\mathbf{e}_i \cdot \mathbf{e}_j = \delta_{ij}, \tag{1}$$

where $\delta_{ij}$ is the Kronecker delta:

$$\delta_{ij} = \begin{cases} 1 & \text{if} \quad i = j \\ 0 & \text{if} \quad i \neq j. \end{cases} \tag{2}$$

In practice, this fixed non-crystallographic orthonormal basis specifies a chosen reference orientation in the experimental set-up, and the crystallographic direct and reciprocal basis vectors as well as the anisotropic thermal ellipsoid semi-axis lengths and rotation angles have coordinates on this fixed orthonormal basis. Let the matrices $A = \{A_{ij}\}$ and $A^* = \{A^*_{ij}\}$ have as columns the coordinates on this orthonormal basis of two sets of basis vectors $\{\mathbf{a}_i\}$ and $\{\mathbf{a}^*_i\}$, respectively, so that (Trueblood *et al.*, 1996)

$$A_{ij} = \mathbf{e}_i \cdot \mathbf{a}_j \tag{3}$$

$$A^*_{ij} = \mathbf{e}_i \cdot \mathbf{a}^*_j. \tag{4}$$

Let the vector **r** have coordinates on the orthonormal basis $\{\mathbf{e}_i\}$ and let the vectors **x** and $\mathbf{x}^*$ be the same as vector **r**, but with coordinates on the basis $\{\mathbf{a}_i\}$ and $\{\mathbf{a}_i^*\}$, respectively (Sands, 1982; Giacovazzo, 1992; Shmueli, 1993a). Then,

$$\mathbf{r} = A \cdot \mathbf{x} = A^* \cdot \mathbf{x}^*. \tag{5}$$

From (5) follows

$$\mathbf{x}^* = A^{*-1} \cdot A \cdot \mathbf{x}. \tag{6}$$

Let the lengths of and the mutual angles between the $\{\mathbf{a}_i\}$ and $\{\mathbf{a}_i^*\}$ be given, that is the following matrices are given:

$$G = A^T \cdot A \tag{7}$$

$$G^* = A^{*T} \cdot A^* \tag{8}$$

$$Q = A^T \cdot A^*. \tag{9}$$

The matrices $G$ and $G^*$ are the metric matrices (Giacovazzo, 1992) and the matrix $Q$ is the mixed matrix (Shmueli, 1993a). Then (6) can also be written as (Shmueli, 1993a)

$$\mathbf{x}^* = Q^{-1} \cdot G \cdot \mathbf{x} \tag{10}$$

and as

$$\mathbf{x}^* = G^{*-1} \cdot Q^T \cdot \mathbf{x}. \tag{11}$$

Combination of (10) and (11) yields

$$G^* = Q^T \cdot G^{-1} \cdot Q \tag{12}$$

and equivalently

$$G = Q \cdot G^{*-1} \cdot Q^T. \tag{13}$$

The formulas above are valid for any two sets of basis vectors $\{\mathbf{a}_i\}$ and $\{\mathbf{a}_i^*\}$. If $\{\mathbf{a}_i\}$ and $\{\mathbf{a}_i^*\}$ are both orthonormal, then $G = G^* = I$, and $A$, $A^*$ and $Q$ are orthogonal matrices. For the crystallographic direct and reciprocal basis vectors, $\{\mathbf{a}_i\}$ and $\{\mathbf{a}_i^*\}$ are mutually reciprocal:

$$\mathbf{a}_i \cdot \mathbf{a}_j^* = \delta_{ij}, \tag{14}$$

which means that (Shmueli, 1993a)

$$Q = I \tag{15}$$

and (9) yields

$$A^* = (A^{-1})^T \tag{16}$$

and equivalently

$$A = (A^{*-1})^T. \tag{17}$$

For any dimension $n$, (16) and (17) give the generic relations between mutually reciprocal crystallographic basis vectors $\{\mathbf{a}_i\}$ as columns of $A$ and $\{\mathbf{a}_i^*\}$ as columns of $A^*$. With (5), this yields:

$$\mathbf{r} \cdot \mathbf{r} = \mathbf{x} \cdot \mathbf{x}^*. \tag{18}$$

This means that **x** and $\mathbf{x}^*$ are covariant and contravariant components of the vector **r** (Borisenko & Tarapov, 1968; Sands, 1982, 1993; Shmueli, 1993a). Now let the direct unit cell of an $n$-dimensional crystal lattice be spanned by the crystallographic direct basis $\{\mathbf{a}_i\}$. This direct unit cell may be composed of more than one asymmetric unit cell, depending

on the space group. The vector **x** of the fractional coordinates of vector **r** in this direct unit cell, which are the coordinates on the crystallographic direct basis $\{\mathbf{a}_i\}$, becomes with (5):

$$\mathbf{x} = A^{-1} \cdot \mathbf{r}. \tag{19}$$

The $n$-dimensional volume of this direct unit cell is

$$V = |\det(A)|. \tag{20}$$

The symbols defined above can also be used in Fourier analysis. The Fourier transform of the electron density of a number of atoms evaluates to (Giacovazzo, 1992; Shmueli, 1993a; Trueblood et al., 1996)

$$\mathcal{F}(\mathbf{h}) = \sum_{\nu=1}^{N} f_\nu(|\mathbf{h}|) T_\nu(\mathbf{h}) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_\nu), \tag{21}$$

where $N$ is the number of atoms, $\nu = 1, \ldots, N$ is the index over the atoms, **h** is the diffraction vector (Shmueli, 1993a), $\mathbf{r}_\nu$ is the position of atom $\nu$, and the $f_\nu(|\mathbf{h}|)$ are the spherical atomic scattering factors (Coppens, 1993; Trueblood et al., 1996), which are tabulated (Maslen et al., 1992). The atomic temperature factor $T_\nu(\mathbf{h})$ is the Fourier transform of the thermal probability distribution of the individual atom (Coppens, 1993; Trueblood et al., 1996). For an $n$-dimensional crystal lattice, the diffraction vector **h** in (21) is restricted to the reciprocal lattice (Giacovazzo, 1992; Bricogne, 1993; Shmueli, 1993a):

$$\mathbf{h} = \sum_{i=1}^{n} h_i \mathbf{a}_i^*, \tag{22}$$

where the $\{h_i\}$ is any set of $n$ integers, which are the Miller indices. The number of atoms $N$ in (21) is now restricted to the number of atoms in the unit cell. Let the vector $\mathbf{h}^*$ be the vector of this set of Miller indices, which are the coordinates of the diffraction vector on the crystallographic reciprocal basis $\{\mathbf{a}_i^*\}$:

$$\mathbf{h}^* = \begin{pmatrix} h_1 \\ \vdots \\ h_n \end{pmatrix} \tag{23}$$

and (22) becomes:

$$\mathbf{h} = A^* \cdot \mathbf{h}^*. \tag{24}$$

Combination of (5), (16) and (24) yields

$$\mathbf{h} \cdot \mathbf{r} = \mathbf{h}^* \cdot \mathbf{x}. \tag{25}$$

The $n$-dimensional volume of the reciprocal unit cell is

$$V^* = |\det(A^*)|, \tag{26}$$

which with (16) and (20) becomes

$$V^* = 1/V. \tag{27}$$

## 3. Atomic displacement parameters

In this section, a description is provided of the $n$-dimensional atomic displacement matrix, which determines the semi-axis

lengths and rotation angles of the $n$-dimensional thermal ellipsoid. The atomic displacement parameters are the elements of this matrix. In general, the thermal motion of atoms in matter should be assumed anisotropic because of the binding forces. Isotropic thermal motion is a special case. Let $n$ be the dimension of the diffracting object, and let $\{\mathbf{e}_i\}$ be the orthonormal reference basis as above. Let the matrix $C$ transform the $n$-dimensional anisotropic thermal ellipsoid into an $n$-dimensional unit sphere:

$$C = \text{diag}(\{1/\lambda_i\}) \cdot D. \tag{28}$$

The $\{\lambda_i\}$ are the lengths of the $n$ mutually perpendicular semi-axes of the ellipsoid and $D$ is the orthogonal rotation matrix that rotates each semi-axis of length $\lambda_i$ onto reference axis $\mathbf{e}_i$. The thermal probability distribution of the $n$-dimensional atomic displacement vector $\mathbf{u}$ for anisotropic thermal motion is a normalized $n$-dimensional ellipsoidal normal distribution (Willis & Pryor, 1975; Prince, 1982):

$$P(\mathbf{u}) = \sqrt{\frac{\det(W)}{(2\pi)^n}} \exp(-\tfrac{1}{2}\mathbf{u} \cdot W \cdot \mathbf{u}), \tag{29}$$

where the matrix $W$ is

$$W = C^T \cdot C. \tag{30}$$

From (30), it follows that $W$ is symmetric and that $\det(W) > 0$. The thermal probability distribution (29) is normalized:

$$1 = \int_{\mathbf{u}} P(\mathbf{u}) \, d^n\mathbf{u}. \tag{31}$$

The coordinates of the displacement vector are

$$u_i = \mathbf{e}_i \cdot \mathbf{u}. \tag{32}$$

The expectation value $\langle u_i u_j \rangle$ is, by definition,

$$\langle u_i u_j \rangle = \int_{\mathbf{u}} u_i u_j P(\mathbf{u}) \, d^n\mathbf{u}. \tag{33}$$

Let the atomic displacement matrix $U = \{U_{ij}\}$ be defined by (Lipson & Cochran, 1966; Willis & Pryor, 1975)

$$U_{ij} = \langle u_i u_j \rangle. \tag{34}$$

Let the elements of matrix $W$ be defined as $W = \{W_{ij}\}$. For the exponential in (29), it follows that

$$\frac{\partial}{\partial W_{ij}} \exp(-\tfrac{1}{2}\mathbf{u} \cdot W \cdot \mathbf{u}) = -\tfrac{1}{2} u_i u_j \exp(-\tfrac{1}{2}\mathbf{u} \cdot W \cdot \mathbf{u}). \tag{35}$$

As $W$ is symmetric, expansion of $\det(W)$ in cofactors (Gradshteyn & Ryzhik, 1980) yields

$$\frac{\partial}{\partial W_{ij}} \det(W) = (W^{-1})_{ij} \det(W). \tag{36}$$

Combination of (29), (31), (33), (34), (35) and (36) proves that the atomic displacement matrix $U$ is the inverse of $W$:

$$U = W^{-1}. \tag{37}$$

As $W$ is symmetric, $U$ is also symmetric and, as $\det(W) > 0$, $\det(U) > 0$. The total mean square displacement is

$$\langle |\mathbf{u}|^2 \rangle = \text{trace}(U). \tag{38}$$

Evaluation of (37) with (28) and (30) yields

$$U = D^T \cdot \text{diag}(\{\lambda_i^2\}) \cdot D. \tag{39}$$

This means that the $\{\lambda_i^2\}$ are the eigenvalues of $U$. From (39), it follows that

$$\sum_{i=1}^{n} \lambda_i^2 = n\mu^2, \tag{40}$$

where

$$\mu = \sqrt{\frac{\text{trace}(U)}{n}}. \tag{41}$$

From (38) and (41), it follows that $\mu^2$ is the mean square displacement per dimension, also called $U_{\text{eq}}$ (Trueblood et al., 1996). For isotropic thermal motion, $D = I$, $\lambda_i = \mu$ and $U = \text{diag}(\mu^2)$. From (29), it follows that the following ellipsoids have constant probability (Willis & Pryor, 1975):

$$\mathbf{u} \cdot W \cdot \mathbf{u} = c^2. \tag{42}$$

The ellipsoid with $c = 1$ has semi-axes with lengths $\lambda_i$. The probability distribution of $c$, which is $P(c)$, is proportional to (29) times the surface of an $n$-dimensional sphere:

$$P(c) = \frac{2^{1-n/2}c^{n-1}}{\Gamma(n/2)} \exp(-\tfrac{1}{2}c^2), \tag{43}$$

where $\Gamma(x)$ is the Gamma function (Gradshteyn & Ryzhik, 1980). The expectation values of the powers of $c$, which are the moments of $P(c)$, are functions of dimension $n$:

$$\langle c^m \rangle = \frac{\Gamma([n+m]/2)}{\Gamma(n/2)} 2^{m/2}. \tag{44}$$

When displaying the thermal ellipsoid of an atom, it seems reasonable to display the ellipsoid with semi-axis lengths $\langle c \rangle \lambda_i$, with $\langle c \rangle$ computed from (44). For dimension $n = 1$, $\langle c \rangle \simeq 0.7979$. For dimension $n = 2$, $\langle c \rangle \simeq 1.2533$. For dimension $n = 3$, $\langle c \rangle \simeq 1.5958$, which is close to the value of $c = 1.5382$ (Willis & Pryor, 1975) of an ellipsoid that encloses half of the total probability. The Fourier transform of the thermal probability distribution (29) yields (Bricogne, 1993; Trueblood et al., 1996)

$$T(\mathbf{h}) = \exp(-2\pi^2 \mathbf{h} \cdot U \cdot \mathbf{h}), \tag{45}$$

which is the atomic temperature factor to be substituted in (21). Combination with (21) yields the following expectation value (Wilson, 1942):

$$\langle |\mathcal{F}(\mathbf{h})|^2 \rangle = \sum_{\nu=1}^{N} f_\nu^2(|\mathbf{h}|) \exp(-4\pi^2 \mathbf{h} \cdot U_\nu \cdot \mathbf{h}). \tag{46}$$

The dimensionless matrix $\beta$, which is the anisotropic temperature-factor matrix (Willis & Pryor, 1975; Trueblood et al., 1996), can be defined in terms of matrices $A$ and $A^*$ defined in (3) and (4):

$$\beta = 2\pi^2 A^{*T} \cdot U \cdot A^* \tag{47}$$

and equivalently with (16):

$$U = \frac{1}{2\pi^2} A \cdot \beta \cdot A^T. \qquad (48)$$

On crystallographic axes, the Fourier transform (21) becomes, with (24), (25), (45) and (48) (Shmueli, 1993a),

$$\mathcal{F}(\mathbf{h}^*) = \sum_{v=1}^{N} f_v(|\mathbf{h}|) \exp(-\mathbf{h}^* \cdot \beta_v \cdot \mathbf{h}^*) \exp(2\pi i \mathbf{h}^* \cdot \mathbf{x}_v), \qquad (49)$$

where $\mathbf{h}^*$ is the vector of Miller indices defined by (23), $\mathbf{h}$ is given by (24), $\beta_v$ is the anisotropic temperature-factor matrix of atom $v$ and $\mathbf{x}_v$ is the vector with the fractional coordinates in the crystallographic direct unit cell of atom $v$, which is given by (19).

## 4. Symmetry restrictions

For understanding the symmetries of the thermal ellipsoids, first the symmetry restrictions of the atomic displacement matrix are provided in terms of the new symbols defined in the previous sections. A symmetry operation $S$ of a space group operates on vector $\mathbf{x}$ of the fractional coordinates on the crystallographic direct unit-cell basis $\{\mathbf{a}_i\}$, defined in (5) and (19):

$$S(\mathbf{x}) = R \cdot \mathbf{x} + \mathbf{t}, \qquad (50)$$

where the orthogonal matrix $R$ is the rotation and/or inversion part and the vector $\mathbf{t}$ is the translation part of the symmetry operation, which are tabulated (Hahn, 1983; Janssen et al., 1999, 2002). The symmetry operator $S'$, equivalent to $S$ in (50) but operating on vector $\mathbf{r}$ with coordinates on the orthonormal reference basis $\{\mathbf{e}_i\}$, becomes with (5) and (50):

$$S'(\mathbf{r}) = R' \cdot \mathbf{r} + A \cdot \mathbf{t}, \qquad (51)$$

where the matrix $R'$ is

$$R' = A \cdot R \cdot A^{-1} \qquad (52)$$

and where $A$ and $\mathbf{r}$ are defined in (3) and (5). The symmetry operation equivalent to $S$ in (50) in reciprocal space on the crystallographic reciprocal basis $\{\mathbf{a}_i^*\}$ is (Shmueli, 1993b)

$$S^*(\mathbf{h}^*) = (R^{-1})^T \cdot \mathbf{h}^* = R \cdot \mathbf{h}^* \qquad (53)$$

and with (17) and (52) on the orthonormal basis $\{\mathbf{e}_i\}$:

$$S^{*\prime}(\mathbf{h}) = (R'^{-1})^T \cdot \mathbf{h} = A^* \cdot R \cdot A^{*-1} \cdot \mathbf{h}. \qquad (54)$$

Any symmetry operator $S'$ of the space group on the orthonormal basis in direct space, defined by (51), leaves the electron density invariant:

$$\rho(\mathbf{r}) = \rho(S'(\mathbf{r})), \qquad (55)$$

from which follows for the Fourier transform (49) with (53) (Waser, 1955a; Giacovazzo, 1992; Shmueli, 1993b):

$$\mathcal{F}(R \cdot \mathbf{h}^*) = \mathcal{F}(\mathbf{h}^*) \exp(2\pi i \mathbf{h}^* \cdot \mathbf{t}), \qquad (56)$$

where $R$ and $\mathbf{t}$ are defined in (50). From this equation, the restricted phase reflections and systematic absences can be derived (Giacovazzo, 1992; Shmueli, 1993b). In addition, on the special positions of the space group in the direct unit cell, the thermal probability distribution (29) must be invariant to any symmetry-operator matrix $R'$, defined by (52), of the point group of the special position (Giacovazzo, 1992):

$$P(\mathbf{u}) = P(R'(\mathbf{u})). \qquad (57)$$

Combination of (29), (37), (48), (52) and (57) yields

$$\beta = R^T \cdot \beta \cdot R, \qquad (58)$$

where $\beta$ is the anisotropic temperature-factor matrix of the atom on the special position, and where the orthogonal matrix $R$ is any symmetry-operator matrix on the crystallographic basis in direct space belonging to the point group of the special position, which are tabulated (Hahn, 1983; Janssen et al., 1999, 2002). As the thermal distribution (29) itself is centrosymmetric, the number of symmetries considered is reduced (Giacovazzo, 1992). The resulting restrictions on the $\beta$ matrix for dimension $n = 3$ can be found in the literature (Willis & Pryor, 1975; Giacovazzo, 1992; Prince et al., 1992).

The symmetry restrictions described in this section restrict the possible values of the anisotropic temperature-factor matrix and the atomic displacement matrix. In addition, depending on the degeneracy of their eigenvalues, symmetry is present in the possible semi-axis lengths and rotation angles of the thermal ellipsoid, which is described in the next section.

## 5. Thermal ellipsoid lengths and angles

In this section, the semi-axis lengths and rotation angles of the thermal ellipsoid of an atom are derived for specific dimensions, given that the atomic displacement matrix $U = \{U_{ij}\}$ of that atom has been experimentally determined. The semi-axis lengths are directly related to the eigenvalues of $U$ and the orientation of the ellipsoid can be described by the eigenvectors of $U$ (Cerrini, 1971; Prince, 1982). As the lengths of the eigenvectors are already given by the eigenvalues, the only new parameters are their rotation angles. Furthermore, the resulting formulas for the rotation angles can be simplified in certain special cases, depending on the degeneracy of the eigenvalues.

For dimension $n = 1$, (39) yields $\mu = \lambda = \sqrt{U_{11}}$ and $D = I$.

For dimension $n = 2$, the matrix $D$ is a two-dimensional rotation matrix:

$$D = R(\phi) = \begin{pmatrix} \cos(\phi) & \sin(\phi) \\ -\sin(\phi) & \cos(\phi) \end{pmatrix}, \qquad (59)$$

where $\phi$ is the clockwise rotation angle which rotates each ellipse semi-axis of length $\lambda_i$ onto reference axis $\mathbf{e}_i$. The clockwise angle of the ellipse axes with respect to the reference basis is $-\phi$. Then, solving (39) with (59) yields

# research papers

$$\mu = \sqrt{\frac{U_{11} + U_{22}}{2}} \tag{60}$$

$$\lambda_1 = \mu\sqrt{1 + \frac{\text{sign}(U_{11} - U_{22})}{U_{11} + U_{22}}\sqrt{(U_{11} - U_{22})^2 + 4U_{12}^2}} \tag{61}$$

$$\lambda_2 = \mu\sqrt{1 - \frac{\text{sign}(U_{11} - U_{22})}{U_{11} + U_{22}}\sqrt{(U_{11} - U_{22})^2 + 4U_{12}^2}} \tag{62}$$

$$\phi = \tfrac{1}{2}\arctan\left(\frac{2U_{12}}{U_{11} - U_{22}}\right), \tag{63}$$

where $\text{sign}(x)$ is the sign of $x$. Note that interchanging $U_{11}$ and $U_{22}$ leads to interchanging $\lambda_1$ and $\lambda_2$ and changing the sign of $\phi$. A special case occurs when $U_{11} = U_{22}$ and $U_{12} = 0$, in which case $\lambda_1 = \lambda_2 = \mu$ and $\phi = 0$ (isotropic thermal vibration). In this case, the ellipse becomes a circle.

For dimension $n = 3$, the matrix $D$ is a three-dimensional rotation matrix, which is a product of three rotation matrices around the fixed reference axes:

$$D = R_3(\phi_3) \cdot R_2(\phi_2) \cdot R_1(\phi_1), \tag{64}$$

where $R_i(\phi_i)$ is the rotation matrix around the fixed reference axis $\mathbf{e}_i$ with the clockwise angle $\phi_i$:

$$R_1(\phi_1) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos(\phi_1) & \sin(\phi_1) \\ 0 & -\sin(\phi_1) & \cos(\phi_1) \end{pmatrix} \tag{65}$$

$$R_2(\phi_2) = \begin{pmatrix} \cos(\phi_2) & 0 & -\sin(\phi_2) \\ 0 & 1 & 0 \\ \sin(\phi_2) & 0 & \cos(\phi_2) \end{pmatrix} \tag{66}$$

$$R_3(\phi_3) = \begin{pmatrix} \cos(\phi_3) & \sin(\phi_3) & 0 \\ -\sin(\phi_3) & \cos(\phi_3) & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{67}$$

As mentioned, $D$ rotates each semi-axis of length $\lambda_i$ onto reference axis $\mathbf{e}_i$. Solving (39) with (64) yields

$$p = \tfrac{1}{2}[(U_{11} - U_{22})^2 + (U_{11} - U_{33})^2 + (U_{22} - U_{33})^2] + 3(U_{12}^2 + U_{13}^2 + U_{23}^2) \tag{68}$$

$$\begin{aligned} q &= 3(U_{11} + U_{22})(U_{11} + U_{33})(U_{22} + U_{33}) \\ &\quad - 2(U_{11}^3 + U_{22}^3 + U_{33}^3) \\ &\quad - 18(U_{11}U_{22}U_{33} + 3U_{12}U_{13}U_{23}) \\ &\quad - 9(U_{11} + U_{22} + U_{33})(U_{12}^2 + U_{13}^2 + U_{23}^2) \\ &\quad + 27(U_{11}U_{23}^2 + U_{22}U_{13}^2 + U_{33}U_{12}^2) \end{aligned} \tag{69}$$

$$\mu = \sqrt{\frac{U_{11} + U_{22} + U_{33}}{3}} \tag{70}$$

$$\Delta = \arccos\left(\frac{q}{2\sqrt{p^3}}\right) \tag{71}$$

$$\lambda_1 = \mu\sqrt{1 - \frac{2\sqrt{p}}{U_{11} + U_{22} + U_{33}}\cos\left(\frac{\Delta}{3}\right)} \tag{72}$$

$$\lambda_2 = \mu\sqrt{1 - \frac{2\sqrt{p}}{U_{11} + U_{22} + U_{33}}\cos\left(\frac{\Delta + 2\pi}{3}\right)} \tag{73}$$

$$\lambda_3 = \mu\sqrt{1 - \frac{2\sqrt{p}}{U_{11} + U_{22} + U_{33}}\cos\left(\frac{\Delta - 2\pi}{3}\right)} \tag{74}$$

$$v = \frac{U_{12}^2 + U_{13}^2 + (U_{11} - \lambda_3^2)(U_{11} + \lambda_3^2 - \lambda_1^2 - \lambda_2^2)}{(\lambda_2^2 - \lambda_3^2)(\lambda_3^2 - \lambda_1^2)} \tag{75}$$

$$w = \frac{U_{11} - \lambda_3^2 + (\lambda_3^2 - \lambda_2^2)v}{(\lambda_1^2 - \lambda_2^2)v}. \tag{76}$$

In the case that $v = 0$, then $w = 1$. The angles $\phi_2$ and $\phi_3$ are

$$\phi_2 = \pm\arccos(\sqrt{v}) \tag{77}$$

$$\phi_3 = \pm\arccos(\sqrt{w}). \tag{78}$$

The signs of $\phi_2$ and $\phi_3$ are determined below. Let the two-dimensional vectors $\mathbf{f}_1$, $\mathbf{f}_2$, $\mathbf{g}_1$ and $\mathbf{g}_2$ be

$$\mathbf{f}_1 = \begin{pmatrix} U_{12} \\ -U_{13} \end{pmatrix} \tag{79}$$

$$\mathbf{f}_2 = \begin{pmatrix} U_{22} - U_{33} \\ -2U_{23} \end{pmatrix} \tag{80}$$

$$\mathbf{g}_1 = \begin{pmatrix} \tfrac{1}{2}(\lambda_1^2 - \lambda_2^2)\cos(\phi_2)\sin(2\phi_3) \\ \tfrac{1}{2}[(\lambda_1^2 - \lambda_2^2)w + \lambda_2^2 - \lambda_3^2]\sin(2\phi_2) \end{pmatrix} \tag{81}$$

$$\mathbf{g}_2 = \begin{pmatrix} (\lambda_1^2 - \lambda_2^2)[1 + (v - 2)w] + (\lambda_2^2 - \lambda_3^2)v \\ (\lambda_1^2 - \lambda_2^2)\sin(\phi_2)\sin(2\phi_3) \end{pmatrix}. \tag{82}$$

For the lengths of these vectors,

$$|\mathbf{g}_1| = |\mathbf{f}_1| \tag{83}$$

$$|\mathbf{g}_2| = |\mathbf{f}_2|. \tag{84}$$

Let angle($\mathbf{v}$) be the angle of a two-dimensional vector $\mathbf{v}$ with respect to the positive $x$ axis, and let the angles $\psi_1$ and $\psi_2$ be

$$\psi_1 = \text{angle}(\mathbf{f}_1) \tag{85}$$

$$\psi_2 = \text{angle}(\mathbf{f}_2). \tag{86}$$

Let $R(\phi)$ be the two-dimensional rotation matrix defined in (59). Then $\phi_1$ is given by two equations:

$$\phi_{1(1)} = \text{angle}(R(\psi_1) \cdot \mathbf{g}_1) \tag{87}$$

$$\phi_{1(2)} = \tfrac{1}{2}\text{angle}(R(\psi_2) \cdot \mathbf{g}_2). \tag{88}$$

For solving the angles, of the four sign combinations of $\phi_2$ and $\phi_3$ in (77) and (78), the sign combination with the smallest difference between $\phi_{1(1)}$ and $\phi_{1(2)}$ is selected. Because $|\mathbf{f}_1|$ or $|\mathbf{f}_2|$ can be zero, one is selected:

$$\phi_1 = \begin{cases} \phi_{1(1)} & \text{if} \quad |\mathbf{f}_1| \geq |\mathbf{f}_2| \\ \phi_{1(2)} & \text{if} \quad |\mathbf{f}_1| < |\mathbf{f}_2|. \end{cases} \tag{89}$$

The clockwise Euler angles in the $xyz$ sequence (Kuipers, 1999) of the axes of the ellipsoid with respect to the reference basis are $\{-\phi_1, -\phi_2, -\phi_3\}$ (see Appendix A). The fourfold rotation symmetry of the ellipsoid is generated by adding $\pi$ to

the angles $\phi_2$ and/or $\phi_3$ in (77) and (78). In the previous equations, changing the order of $\lambda_1$, $\lambda_2$ and $\lambda_3$ is compensated by change of the resulting angles $\phi_1$, $\phi_2$ and $\phi_3$, thus always generating the identical ellipsoid belonging to the atomic displacement matrix $U = \{U_{ij}\}$.

A special case occurs when $p = 0$, in which case $q = 0$, $\lambda_1 = \lambda_2 = \lambda_3 = \mu$ and $\phi_1 = \phi_2 = \phi_3 = 0$. In this case, the ellipsoid becomes a sphere (isotropic thermal vibration).

Another special case occurs when $q^2 = 4p^3 \neq 0$, in which case two of the three $\lambda_i$ values are equal. In this case, the ellipsoid becomes a spheroid, also called ellipsoid of revolution. In this case, choosing the order of $\lambda_1$, $\lambda_2$ and $\lambda_3$ such that

$$\lambda_1 = \lambda_2 = \lambda \tag{90}$$

yields the following equations for the angles:

$$s = \frac{U_{11} - \lambda_3^2}{\lambda^2 - \lambda_3^2} \tag{91}$$

$$\phi_2 = \pm \arccos(\sqrt{s}) \tag{92}$$

$$\phi_3 = 0 \tag{93}$$

$$\mathbf{g}_1 = \begin{pmatrix} 0 \\ \frac{1}{2}(\lambda^2 - \lambda_3^2)\sin(2\phi_2) \end{pmatrix} \tag{94}$$

$$\mathbf{g}_2 = \begin{pmatrix} (\lambda^2 - \lambda_3^2)s \\ 0 \end{pmatrix}. \tag{95}$$

The other equations are identical to the general case, except that only two sign combinations in (92) are possible. The twofold rotation symmetry of this type of ellipsoid is generated by adding $\pi$ to the angles $\phi_2$ in (92).

The two special cases mentioned can occur coincidentally for atoms on general positions or systematically because of symmetry elements for atoms on certain special positions. The effect of the latter is already accounted for when determining the atomic displacement matrix itself (see previous section), so for the formulas above no symmetry considerations other than the ones mentioned are needed.

A computer program has been developed that uses the formulas in this section to compute the semi-axis lengths and Euler angles of the thermal ellipsoid of any atomic displacement matrix for dimension $n = 3$. This computer program can be obtained from the author via e-mail.

## 6. Conclusions

The matrix $A^*$ and the vector $\mathbf{h}^*$ are useful for describing the atomic displacement matrix and anisotropic temperature-factor matrix for generic dimension $n$. The moments of the probability distribution of the anisotropic thermal ellipsoids have been expressed as functions of dimension $n$. The semi-axis lengths and rotation angles of the ellipsoids have been expressed as functions of the atomic displacement matrix for specific dimensions $n = 2$ and $n = 3$, taking into account the special cases.

## APPENDIX A
### Euler angles

A three-dimensional rotation can always be written as a sequence of three rotations around the fixed reference axes as in (64):

$$D = R_3(\phi_3) \cdot R_2(\phi_2) \cdot R_1(\phi_1). \tag{96}$$

Such a rotation can also be written as a sequence of three rotations around reference axes that are themselves also rotated. This type of rotation is called an Euler rotation sequence (Altmann & Ryzhik, 1986; Kuipers, 1999). When the first rotation $R_1(\phi_1)$ around the $\mathbf{e}_1$ axis or $x$ axis also rotates the other reference axes, then the second rotation is a rotation around the new rotated $\mathbf{e}_2$ axis or $y$ axis, which is denoted with a prime: $R_2'(\phi_2)$. This new rotation is

$$R_2'(\phi_2) = R_1(\phi_1) \cdot R_2(\phi_2) \cdot R_1(\phi_1)^{-1}. \tag{97}$$

When this second rotation also rotates the other reference axes, then the third rotation around the new rotated $\mathbf{e}_3$ axis or $z$ axis yields a similar identity. The resulting complete Euler rotation sequence is

$$R_3''(\phi_3) \cdot R_2'(\phi_2) \cdot R_1(\phi_1) = R_1(\phi_1) \cdot R_2(\phi_2) \cdot R_3(\phi_3). \tag{98}$$

The left-hand side is an Euler rotation in the $xyz$ sequence (Kuipers, 1999), with angles $\{\phi_1, \phi_2, \phi_3\}$. This equation means that a rotation sequence around fixed reference axes is equal to an Euler rotation sequence around rotating reference axes with identical angles but in reverse order. As the resulting rotation $D$ in (64) rotates the ellipsoid axes onto the reference axes, the orientation of the ellipsoid with respect to the reference axes is the inverse of $D$. For this, the following identity is used:

$$R(\phi)^{-1} = R(-\phi), \tag{99}$$

which yields with (96)

$$D^{-1} = R_1(-\phi_1) \cdot R_2(-\phi_2) \cdot R_3(-\phi_3) \tag{100}$$

and which with (98) is equal to

$$D^{-1} = R_3''(-\phi_3) \cdot R_2'(-\phi_2) \cdot R_1(-\phi_1). \tag{101}$$

The Euler rotation angles in the $xyz$ sequence that give the orientation of the ellipsoid with respect to the reference axes thus are $\{-\phi_1, -\phi_2, -\phi_3\}$.

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