Acta Cryst A FOUNDATIONS ADVANCES

ISSN 2053-2733

The atomic anisotropic displacement tensor – completing the picture

Gunnar Thorkildsen* and Helge B. Larsen

Department of Mathematics and Natural Science, University of Stavanger, N-4036 Stavanger, Norway. *Correspondence e-mail: gunnar.thorkildsen@uis.no

Received 30 January 2015
Accepted 28 April 2015

Edited by W. F. Kuhs, Georg-August University Göttingen, Germany

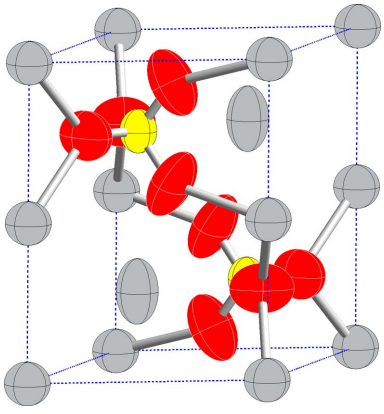
Keywords: anisotropic displacement tensor; transformations among tensor representations; site-symmetry restrictions; equivalent isotropic displacement parameter.

Supporting information: this article has supporting information at journals.iucr.org/a

A simplified approach for calculating the equivalent isotropic displacement parameter is presented and the transformation property of the tensor representation **U** to point-group operations is analysed. Complete tables have been compiled for the restrictions imposed upon the tensor owing to the site symmetry associated with all special positions as listed in Hahn [(2011), *International Tables for Crystallography*, Vol. A, *Space-group Symmetry*, 5th revised ed. Chichester: John Wiley and Sons, Ltd].

1. Introduction

The basis for this work is the important report by Trueblood *et al.* (1996), hereafter referred to as T. Symbols for key quantities are used accordingly. In the present communication some features of the atomic anisotropic displacement tensor are further elucidated. §2 summarizes the basic relations among the tensor representations $\boldsymbol{\beta}$, **U** and $\mathbf{U}^{C}$. These relations mainly serve the other sections. As matrices are used throughout, one should also consult Grosse-Kunstleve & Adams (2002). In §3 we point to an alternative, simplified method for calculating the equivalent isotropic displacement parameter, U_{eq}, based on $\boldsymbol{\beta}$ or **U**, using a statement by Wigner (1959): *The trace of a product of two matrices does not depend on the order of the two factors*. In §4 it is explicitly shown that, in relation to point-group operations, **U** and $\boldsymbol{\beta}$ obey identical transformation rules. §5 provides updated and extended information (see the supporting information) regarding site-symmetry restrictions imposed upon the displacement tensor (Peterse & Palm, 1966; Johnson & Levy, 1974; Willis & Pryor, 1975; Kuhs, 1984, 2010).



2. Transformations among the basic tensor representations

The atomic anisotropic displacement tensor is linked to the variance–covariance matrix of the components of the atomic displacement vector. Different choices of bases result in alternative forms of representations of this tensor. Expanding the displacement vector in the basis of direct lattice vectors, (**a**, **b**, **c**), leads to a dimensionless representation ($\boldsymbol{\beta}$). On the other hand, the bases ($a^{\star}\mathbf{a}$, $b^{\star}\mathbf{b}$, $c^{\star}\mathbf{c}$) and ($\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$), the latter a general Cartesian one, result in representations (**U** and $\mathbf{U}^{C}$) having components with dimensions of (length)^2. $a^{\star}$, $b^{\star}$ and $c^{\star}$ are the norms of the basis vectors of reciprocal space. Transformations among these representations are readily obtained.

Given $\boldsymbol{\beta}$, $\mathbf{U}$ and $\mathbf{U}^{\rm C}$ are determined from

$$\mathbf{U} = \frac{1}{2\pi^2}(\mathbf{D}^\star)^{-1}\boldsymbol{\beta}(\mathbf{D}^\star)^{-1}, \qquad \text{(T25)(1}a\text{)}$$

$$\mathbf{U}^{\rm C} = \frac{1}{2\pi^2}\mathbf{A}\,\boldsymbol{\beta}\,\mathbf{A}^T. \qquad \text{(T44)(1}b\text{)}$$

Given $\mathbf{U}$, $\boldsymbol{\beta}$ and $\mathbf{U}^{\rm C}$ are determined from

$$\boldsymbol{\beta} = 2\pi^2\,\mathbf{D}^\star\,\mathbf{U}\,\mathbf{D}^\star \qquad (2a)$$

$$\mathbf{U}^{\rm C} = (\mathbf{A}\,\mathbf{D}^\star)\mathbf{U}\,(\mathbf{A}\,\mathbf{D}^\star)^T, \qquad (2b)$$

$\mathbf{D}^\star$ is the diagonal matrix:

$$\mathbf{D}^\star = \mathrm{diag}[a^\star, b^\star, c^\star]. \qquad (3)$$

The standard representation of $\mathbf{A}$, (T50), is determined by a Cholesky decomposition of the metric matrix, $\mathbf{g}$, in direct space:

$$\mathbf{g} = \mathbf{A}^T\mathbf{A}. \qquad (4)$$

Equations (2a), (2b) directly follow from equations (1a), (1b).

3. The equivalent isotropic displacement parameter

The equivalent isotropic displacement parameter[1] is calculated from the anisotropic displacement parameters. Values obtained for a set of corresponding atoms serve the purpose of providing a first-order comparison of their state of displacements (Merritt, 1999). The parameter may be defined by the equation

$$U_{\rm eq} = \frac{1}{3}\mathrm{tr}(\mathbf{U}^{\rm C}). \qquad \text{(T51)(5)}$$

As matrices in a product may be cycled without affecting the value of its trace (Wigner, 1959), it is immediately deduced from equations (1b) and (2b), by applying equation (4), that

$$U_{\rm eq} = \frac{1}{6\pi^2}\mathrm{tr}(\mathbf{g}\,\boldsymbol{\beta}), \qquad \text{(T53)(6}a\text{)}$$

$$U_{\rm eq} = \frac{1}{3}\mathrm{tr}(\mathbf{D}^\star\,\mathbf{g}\,\mathbf{D}^\star\,\mathbf{U}). \qquad (6b)$$

Equation (6b) is equivalent to (T55), *cf.* Fischer & Tillmanns (1988). The present approach makes the deduction of these formulas very transparent.

4. Symmetry restrictions

Previous works in the literature (Peterse & Palm, 1966; Johnson & Levy, 1974; Willis & Pryor, 1975; Kuhs, 1984) on the subject of symmetry restrictions on the anisotropic displacement tensor involve the tensor representation $\boldsymbol{\beta}$. The tensor's invariance properties under symmetry transformations are evaluated on the basis of

$$\boldsymbol{\beta}_s = \mathbf{R}_s\boldsymbol{\beta}\mathbf{R}_s^T, \qquad (7a)$$

Table 1
Changes in ITA for space group No. 224.

Origin at centre ($\bar{3}m$) at $\frac{1}{4},\frac{1}{4},\frac{1}{4}$ from $\bar{4}3m$. *W* symbolizes a Wyckoff letter, $\beta_{\rm c}$ a key for $\boldsymbol{\beta}$-restrictions (Peterse & Palm, 1966). As to year published, consult IUCr (2015).

W	1952 → 1976	$\beta_{\rm c}$	1983 → 1989	$\beta_{\rm c}$	1992 →	$\beta_{\rm c}$
j	$\frac{1}{2}, \frac{1}{4}+x, \frac{3}{4}+x$	11	$\frac{1}{2}, y, y+\frac{1}{2}$	11	$\frac{1}{2}, y, -y$	10
i	$\frac{1}{2}, \frac{1}{4}+x, \frac{3}{4}-x$	10	$\frac{1}{2}, y, -y$	10	$\frac{1}{2}, y, y+\frac{1}{2}$	11

$$\boldsymbol{\beta}_s \equiv \boldsymbol{\beta}. \qquad (7b)$$

$\mathbf{R}_s$ is the matrix representation of the point-group symmetry operation *s*. The reader should consult Sands (1995), ch. 4.10, for a discussion of coordinate transformations *versus* symmetry operations in the context of second-rank tensors. In the present context, $\boldsymbol{\beta}$ has to be left invariant by the elements of a certain subgroup, $\mathcal{H}$, of the point group, $\mathcal{P}$, associated with the actual space group, $\mathcal{G}$. This subgroup is the site-symmetry group of the point (the special position) in question. In light of the comments of Trueblood *et al.* (1996) regarding transformation properties of $\boldsymbol{\beta}$ and $\mathbf{U}$, equations (T32) and (T33), it seems essential to explicitly verify that the transformation rule stated in equation (7a) also applies to $\mathbf{U}$. On combining equations (1a) and (2a) one obtains

$$\mathbf{U}_s = [(\mathbf{D}^\star)^{-1}\mathbf{R}_s\mathbf{D}^\star]\mathbf{U}[(\mathbf{D}^\star)^{-1}\mathbf{R}_s\mathbf{D}^\star]^T = \mathbf{R}_s\mathbf{U}\mathbf{R}_s^T. \qquad (8)$$

Here, the commutation relation,

$$\mathbf{R}_s\mathbf{D}^\star = \mathbf{D}^\star\mathbf{R}_s, \qquad (9)$$

is applied in the final step of equation (8). Its validity is trivial for triclinic, monoclinic and orthorhombic space groups where every element, $\mathbf{R}_s \in \mathcal{H}$, is represented by diagonal matrices. Furthermore, it is obviously fulfilled for cubic and rhombohedral space groups, where $\mathbf{D}^\star = a^\star\mathbf{I}$, with $\mathbf{I}$ being the 3×3 identity matrix. For tetrahedral, trigonal (hexagonal setting) and hexagonal space groups every element, $\mathbf{R}_s$, is represented by a matrix of the generic type $\{\{*,*,0\},\{*,*,0\},\{0,0,*\}\}$, and equation (9) is fulfilled since $\mathbf{D}^\star = \mathrm{diag}[a^\star, a^\star, c^\star]$.

5. Site-symmetry restrictions imposed – updated and extended tables

In the table, '*Nature of the* $\boldsymbol{\beta}$*-restrictions*', provided by Peterse & Palm (1966) and reproduced[2] by Willis & Pryor (1975), a correction should be made for space group No. 224, $Pn\bar{3}m$, thereby accommodating the interchange (Hahn, 1993) of the positions 24*i* and 24*j* (origin choice 2). Table 1 shows the amendments made to *International Tables for Crystallography* (ITA) from Henry & Lonsdale (1952) to Hahn (2011) for these positions.

Furthermore, for space groups in which there are two possible choices of origin, the $\boldsymbol{\beta}$-restrictions were originally processed for the unit cells having their origins on a centre of

[1] In coreCIF: atom_site_U_iso_or_equiv.

[2] Two transcription errors are spotted concerning the space groups 80 and 227.

Table 2
Space groups that exhibit a different pattern for $\boldsymbol{\beta}$-symmetry restrictions when origin choice 1 is selected.

Positions where changes occur are put in bold. Numeric labels (keys) as in Peterse & Palm (1966).

Space group	No.	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*j*	*k*	*l*	*m*	*n*
$P4/nbm$	125	8	8	8	8	7	7	8	5	7	7	3	3	**6**	
$P4/nmm$	129	8	8	8	**7**	**7**	4	**7**	**7**	3	6				
$P4/ncc$	130	5	8	8		2	**7**								
$P4_2/nnm$	134	8	8	4	5	**6**	**6**	5	2	3	3	7	7	**6**	
$P4_2/nmc$	137	8	8	4	4		**7**	3							
$P4_2/ncm$	138	5	8	**7**	**7**	5	2	**7**	**7**	6					
$I4_1/acd$	142	8	5		2	**1**	7								
$Pn\bar{3}m$	224	17	18	18	12	18	9	9	3	**10**	**11**	6			

symmetry only (origin choice 2). Based on origin choice 1 some changes, *cf.* Table 2, must be implemented.

We have undertaken a complete examination of all 230 space groups in order to reveal site symmetries and hence the restrictions on symmetry of the anisotropic displacement tensor ($\boldsymbol{\beta}$-restrictions) for atoms in special positions. A self-contained account, mainly tabulated material, is available as supporting information for this article.

A one-to-one correspondence exists between the compiled tables and the sequences of coordinate triplets listed in the fifth edition of ITA (Hahn, 2011). Thus any possible changes in those sequences, *e.g.* in future editions of ITA, will require a rebuilding of the tables. The procedure followed is as outlined by Müller (2013) and Janssen (2010, pp. 52–53). The implementation is accomplished within the mathematical software system *Mathematica* version 9.0.1 (Wolfram Research, 2013). Site symmetries are labelled both conventionally and by the subgroup notations given by Janovec & Přívratská (2010), *cf.* Nespolo & Souvignier (2009) for a discussion of site-symmetry groups for positions of the same Wyckoff set. The keys used to label symmetry restrictions are as given by Kuhs (2010) and Giacovazzo *et al.* (2011). Table 3 is an example of the information compiled.

The $\boldsymbol{\beta}$-restrictions deduced are identical to those reported by Peterse & Palm (1966) for the first entry of coordinates in the Wyckoff sets. Based on this information alone, the $\boldsymbol{\beta}$-restrictions for all the remaining symmetry-equivalent positions in the sets may also be directly deduced using equation (7*a*). These calculations have been carried out. They verify the results of our general procedure which comprises the explicit determination of the site-symmetry groups of all special atomic positions.

6. Concluding remarks

Some points regarding the atomic anisotropic displacement tensor are added to the exhaustive expositions already existing in the literature. The tables available as supporting information are intended to be both look-up tables and sources of reference. References are made from the supporting information to Fischer *et al.* (2011), Giacovazzo *et al.* (2011), Glazer *et al.* (2014), Hahn (2011), Hahn & Looijenga-Vos (2011), Janovec & Přívratská (2010), Janssen (2010), Johnson & Levy (1974), Kuhs (2010), Müller (2013), Peterse & Palm (1966), Prince *et al.* (2011), Scheringer (1979), Willis & Prior (1975) and Wolfram Research (2013).

Table 3
Space group No. 223, $Pm\bar{3}n$, arbitrarily chosen.

All equivalent positions associated with Wyckoff letter *e*. Ordering of entries as in ITA. Site symmetries and labels associated with restrictions on the symmetry of the atomic displacement tensors are tabulated.

$\frac{1}{4},\frac{1}{4},\frac{1}{4}$	$\frac{3}{4},\frac{3}{4},\frac{1}{4}$	$\frac{3}{4},\frac{1}{4},\frac{3}{4}$	$\frac{1}{4},\frac{3}{4},\frac{3}{4}$	$\frac{3}{4},\frac{3}{4},\frac{3}{4}$	$\frac{1}{4},\frac{1}{4},\frac{3}{4}$	$\frac{1}{4},\frac{3}{4},\frac{1}{4}$	$\frac{3}{4},\frac{1}{4},\frac{1}{4}$
$3_p2_{x\bar{y}}$	$3_q2_{x\bar{y}}$	3_s2_{xy}	3_r2_{xy}	$3_p2_{x\bar{y}}$	$3_q2_{x\bar{y}}$	3_s2_{xy}	3_r2_{xy}
B5	B6	B7	B8	B5	B6	B7	B8

Acknowledgements

The authors would like to thank Professors Th. Hahn and M. Aroyo for the information provided regarding the changes in ITA that have emerged for space group No. 224.

References

Fischer, R. X. & Tillmanns, E. (1988). *Acta Cryst.* C**44**, 775–776.
Fischer, W., Koch, E. & Arnold, H. (2011). *International Tables for Crystallography*, Vol. A, *Space-group Symmetry*, 5th revised ed., ch. 11.2. Chichester: John Wiley and Sons, Ltd.
Giacovazzo, C., Monaco, H. L., Artioli, G., Viterbo, D., Milanesio, M., Ferraris, G., Gilli, G., Gilli, P., Zanotti, G. & Catti, M. (2011). *Fundamentals of Crystallography*, edited by C. Giacoavzzo, 3rd ed., ch. 3.B.3, pp. 209–211. Oxford University Press.
Glazer, A. M., Aroyo, M. I. & Authier, A. (2014). *Acta Cryst.* A**70**, 300–302.
Grosse-Kunstleve, R. W. & Adams, P. D. (2002). *J. Appl. Cryst.* **35**, 477–480.
Hahn, Th. (1993). *Acta Cryst.* A**49**, 592–593.
Hahn, Th. (2011). Editor. *International Tables for Crystallography*, Vol. A, *Space-group Symmetry*, 5th revised ed. Chichester: John Wiley and Sons, Ltd.
Hahn, Th. & Looijenga-Vos, A. (2011). *International Tables for Crystallography*, Vol. A, *Space-group Symmetry*, 5th revised ed., ch. 2.2. Chichester: John Wiley and Sons, Ltd.
Henry, N. F. M. & Lonsdale, K. (1952). *International Tables for X-ray Crystallography*, Vol. I, *Symmetry Groups*, 1st ed. Birmingham: Kynoch Press.
IUCr (2015). *International Tables for Crystallography*, all editions and editors. http://www.iucr.org/resources/commissions/international-tables/editions.

Janovec, V. & Přívratská, J. (2010). *International Tables for Crystallography*, edited by A. Authier, Vol. D, ch. 3.4, pp. 449–505, 1st revised ed. Chichester: John Wiley and Sons, Ltd.
Janssen, T. (2010). *International Tables for Crystallography*, edited by A. Authier, Vol. D, ch. 1.2, 1st revised ed. Chichester: John Wiley and Sons, Ltd.
Johnson, C. K. & Levy, H. A. (1974). *International Tables for X-ray Crystallography*, edited by J. A. Ibers & W. C. Hamilton, Vol. IV, ch. 5, pp. 311–336, 3rd revised ed. Birmingham: Kynoch Press.
Kuhs, W. F. (1984). *Acta Cryst.* A**40**, 133–137.
Kuhs, W. F. (2010). *International Tables for Crystallography*, edited by A. Authier, Vol. D, ch. 1.9, pp. 228–242, 1st revised ed. Chichester: John Wiley and Sons, Ltd.
Merritt, E. A. (1999). *Acta Cryst.* D**55**, 1997–2004.
Müller, U. (2013). *Symmetry Relationships between Crystal Structures.* Oxford University Press.
Nespolo, M. & Souvignier, B. (2009). *Z. Kristallogr.* **224**, 127–136.
Peterse, W. J. A. M. & Palm, J. H. (1966). *Acta Cryst.* **20**, 147–150.
Prince, E., Finger, L. W. & Konnert, J. H. (2011). *International Tables for Crystallography*, Vol. C, *Mathematical, Physical and Chemical Tables*, ch. 8.3, 3rd revised ed. Chichester: John Wiley and Sons, Ltd.
Sands, D. E. (1995). *Vectors and Tensors in Crystallography*, first corrected reprint edition. New York: Dover Publications, Inc.
Scheringer, C. (1979). *Acta Cryst.* A**35**, 700.
Trueblood, K. N., Bürgi, H.-B., Burzlaff, H., Dunitz, J. D., Gramaccioli, C. M., Schulz, H. H., Shmueli, U. & Abrahams, S. C. (1996). *Acta Cryst.* A**52**, 770–781.
Wigner, E. P. (1959). *Group Theory and its Application to the Quantum Mechanics of Atomic Spectra.* New York: Academic Press.
Willis, B. T. M. & Pryor, A. W. (1975). *Thermal Vibrations in Crystallography*. Cambridge University Press.
Wolfram Research (2013). *Mathematica*, version 9.0.1. Champaign, Illinois: Wolfram Research, Inc.