

## 1.9. ATOMIC DISPLACEMENT PARAMETERS

Atomic displacement tensors may also be partially contracted or expanded; rules for these operations are found in Kuhs (1992).

## 1.9.3. Site-symmetry restrictions

Atoms (or molecules) situated on special positions of a space group exhibit (time-space averaged) probability distributions with a symmetry corresponding to the site symmetry. The p.d.f.'s describing these distributions contain the atomic displacement tensors. The displacement tensors enter into the structure-factor equation, which is the Fourier transform of the scattering density of the unit cell, *via* the atomic Debye–Waller factor, which is the Fourier transform of the atomic p.d.f. (see Chapter 1.2 of *IT B*). As discussed above, the tensor is fully symmetric with respect to the interchange of indices (*inner symmetry*). The site-symmetry restrictions (*outer symmetry*) of atomic displacement tensors of rank 2 are given in Chapter 8.3 of *IT C* (2004), where the tabulation of the constraints on the tensor coefficients are quoted for every Wyckoff position in each space group. Here the constraints for atomic displacement tensors of ranks 2, 3, 4, 5 and 6 for any crystallographic site symmetry are tabulated; some restrictions for tensors of rank 7 and 8 can be found in Kuhs (1984). To use these tables, first the site symmetry has to be identified. The site symmetries are given in *IT A* (2005) for the first equipoint of every Wyckoff position in each space group. The tabulated constraints may be introduced in least-squares refinements (some programs have the constraints of second-order displacement tensor components already imbedded). It should also be remembered that, due to arbitrary phase shifts in the structure-factor equation in a least-squares refinement of a noncentrosymmetric structure, for all odd-order tensors *one* coefficient corresponding to a nonzero entry for the corresponding acentric space group has to be kept fixed (in very much the same way as for positional parameters); *e.g.* the term  $b^{123}$  has to be kept fixed for *one* atom for all refinements in all space groups belonging to the point groups  $43m$  or  $23$ , while all other terms  $b^{ijk}$  are allowed to vary freely for all atoms (Hazell & Willis, 1978). Even if this is strictly true only for the Edgeworth-series expansion, it also holds in practice for the Gram–Charlier case (Kuhs, 1992).

## 1.9.3.1. Calculation procedures

Levy (1956) and Peterse & Palm (1966) have given algorithms for determining the constraints on anisotropic displacement tensor coefficients, which are also applicable to higher-order tensors. The basic idea is that a tensor transformation according to the symmetry operation of the site symmetry under consideration (represented by the point-group generators) should leave the tensor unchanged. For symmetries higher than the identity 1, this only holds true if some of the tensor coefficients are either zero or interrelated. The constraints may be obtained explicitly from solving the homogeneous system of equations of tensor transformations (with one equation for each coefficient).

## 1.9.3.2. Key to tables

After identification of the site symmetry of the atomic site under consideration, the entry point (cross-reference) for the tabulation of the displacement tensors of a given rank (Tables 1.9.3.2–1.9.3.6) needs to be looked up in Table 1.9.3.1. The line entry corresponding to the cross-reference number in Tables 1.9.3.2–1.9.3.6 holds the information on the constraints imposed by the outer symmetry on the tensor coefficients. The order of assignment of independency of the coefficients is as for increasing indices of the coefficients (first 1, then 2, then 3, where 1, 2 and 3 refer to the three crystallographic axes), except for the unmixed coefficients, which have highest priority in every case; this order of priority is the same as the order in the tables reading from left to right. For better readability, each coefficient is assigned a letter (or 0 if the component is equal to zero by symmetry). Constraints

Table 1.9.3.2. Symmetry restrictions on coefficients in second-order tensors

Cross-reference	No. of independent variables	Symbols and coefficient indices					
		A	B	C	D	E	F
		(1) (1)	(2) (2)	(3) (3)	(1) (2)	(1) (3)	(2) (3)
B1	1	A	A	A	0	0	0
B2	2	A	A	C	0	0	0
B3	2	A	B	A	0	0	0
B4	2	A	B	B	0	0	0
B5	2	A	A	A	D	D	D
B6	2	A	A	A	D	–D	–D
B7	2	A	A	A	D	–D	D
B8	2	A	A	A	D	D	–D
B9	2	A	A	C	A/2	0	0
B10	3	A	B	C	0	0	0
B11	3	A	A	C	D	0	0
B12	3	A	B	A	0	E	0
B13	3	A	B	B	0	0	F
B14	3	A	B	C	B/2	0	0
B15	3	A	B	C	A/2	0	0
B16	4	A	B	C	D	0	0
B17	4	A	B	C	0	E	0
B18	4	A	B	C	0	0	F
B19	4	A	A	C	D	E	–E
B20	4	A	A	C	D	E	E
B21	4	A	B	A	D	E	–D
B22	4	A	B	A	D	E	D
B23	4	A	B	B	D	–D	F
B24	4	A	B	B	D	D	F
B25	4	A	B	C	B/2	E	2E
B26	4	A	B	C	A/2	0	F
B27	4	A	B	C	B/2	E	0
B28	4	A	B	C	A/2	E	E/2
B29	6	A	B	C	D	E	F

thus read as algebraic relations between letter variables. Some more complicated constraint relations are quoted as footnotes to the tables.

## 1.9.4. Graphical representation

Atomic displacement tensors (ADTs) described by their tensor coefficients may be represented graphically to clarify their physical meaning. Different graphical representations exist and will be discussed separately for second- and higher-order tensors in the following.

## 1.9.4.1. Representation surfaces of second-order ADTs

Numerous examples of graphical representations of thermal-motion tensors (or, more generally speaking, atomic displacement tensors) have appeared in the literature since the early days of the computer program *ORTEP* written by C. K. Johnson (1965), yet the equal-probability surface usually displayed is only one of the possible representations of a second-order atomic displacement tensor. Representation surfaces are usually calculated in a Cartesian coordinate system. Accordingly, one has to transform the second-order ADT  $\mathbf{b}$  into  $\mathbf{U}_C$  described in a Cartesian frame:

$$\mathbf{U}_C = (2\pi^2)^{-1} \mathbf{F}^T \mathbf{b} \mathbf{F}. \quad (1.9.4.1)$$

The transformation matrix depends on the choice of Cartesian axes  $\mathbf{e}_i$  with respect to the reciprocal-cell axes  $\mathbf{a}^i$  (or equally well with respect to the direct axes  $\mathbf{a}_i$ ). Choosing  $\mathbf{e}_1$  along  $\mathbf{a}^1$ ,  $\mathbf{e}_2$  in the  $\mathbf{a}^1\mathbf{a}^2$  plane and  $\mathbf{e}_3$  completing the right-handed set, one obtains for the transformation matrix  $\mathbf{F}$  (see also Willis & Pryor, 1975)

$$\mathbf{F} = \begin{pmatrix} 1/a^1 & a^2 \cos \gamma^* & a^3 \cos \beta^* \\ 0 & a^2 \sin \gamma^* & -a^3 \sin \beta^* \cos \alpha \\ 0 & 0 & 1/a_3 \end{pmatrix}. \quad (1.9.4.2)$$

Clearly, there is an infinite number of possible choices for relating a Cartesian frame to a crystallographic coordinate