

## 1.9. Atomic displacement parameters

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### 1.9.1. Introduction

Atomic thermal motion and positional disorder is at the origin of a systematic intensity reduction of Bragg reflections as a function of scattering vector  $\mathbf{Q}$ . The intensity reduction is given as the well known *Debye–Waller factor* (DWF); the DWF may be of purely thermal origin (*thermal DWF* or *temperature factor*) or it may contain contributions of static atomic disorder (*static DWF*). As atoms of chemically or isotopically different elements behave differently, the individual atomic contributions to the global DWF (describing the weakening of Bragg intensities) vary. Formally, one may split the global DWF into the individual atomic contributions. Crystallographic experiments usually measure the global weakening of Bragg intensities and the individual contributions have to be assessed by adjusting individual atomic parameters in a least-squares refinement.

The theory of lattice dynamics (see *e.g.* Willis & Pryor, 1975) shows that the atomic thermal DWF  $T_\alpha$  is given by an exponential of the form

$$T_\alpha(\mathbf{Q}) = \langle \exp(i\mathbf{Q}\mathbf{u}_\alpha) \rangle, \quad (1.9.1.1)$$

where  $\mathbf{u}_\alpha$  are the individual atomic displacement vectors and the brackets symbolize the thermodynamic (time–space) average over all contributions  $\mathbf{u}_\alpha$ . In the harmonic (Gaussian) approximation, (1.9.1.1) reduces to

$$T_\alpha(\mathbf{Q}) = \exp[(-1/2)\langle (\mathbf{Q}\mathbf{u}_\alpha)^2 \rangle]. \quad (1.9.1.2)$$

The thermodynamically averaged atomic mean-square displacements (of thermal origin) are given as  $U^{ij} = \langle u^i u^j \rangle$ , *i.e.* they are the thermodynamic average of the product of the displacements along the  $i$  and  $j$  coordinate directions. Thus (1.9.1.2) may be expressed with  $\mathbf{Q} = 4\pi\mathbf{h}|\mathbf{a}|$  in a form more familiar to the crystallographer as

$$T_\alpha(\mathbf{h}) = \exp(-2\pi^2 h_i |a^i| h_j |a^j| U_\alpha^{ij}), \quad (1.9.1.3)$$

where  $h_i$  are the covariant Miller indices,  $\mathbf{a}^i$  are the reciprocal-cell basis vectors and  $1 \leq i, j \leq 3$ . Here and in the following, tensor notation is employed; implicit summation over repeated indices is assumed unless stated otherwise. For computational convenience one often writes

$$T_\alpha(\mathbf{h}) = \exp(-h_i h_j \beta_\alpha^{ij}) \quad (1.9.1.4)$$

with  $\beta_\alpha^{ij} = 2\pi^2 |a^i| |a^j| U_\alpha^{ij}$  (no summation). Both  $\mathbf{h}$  and  $\beta$  are dimensionless tensorial quantities;  $\mathbf{h}$  transforms as a covariant tensor of rank 1,  $\beta$  as a contravariant tensor of rank 2 (for details of the mathematical notion of a tensor, see Chapter 1.1).

Similar formulations are found for the static atomic DWF  $S_\alpha$ , where the average of the atomic static displacements  $\Delta\mathbf{u}_\alpha$  may also be approximated [though with weaker theoretical justification, see Kuhs (1992)] by a Gaussian distribution:

$$S_\alpha(\mathbf{Q}) = \exp[(-1/2)\langle (\mathbf{Q}\Delta\mathbf{u}_\alpha)^2 \rangle]. \quad (1.9.1.5)$$

As in equation (1.9.1.3), the static atomic DWF may be formulated with the mean-square disorder displacements  $\Delta U^{ij} = \langle \Delta u^i \Delta u^j \rangle$  as

$$S_\alpha(\mathbf{h}) = \exp(-2\pi^2 h_i |a^i| h_j |a^j| \Delta U_\alpha^{ij}). \quad (1.9.1.6)$$

It is usually difficult to separate thermal and static contributions, and it is often wise to use the sum of both and call them simply (mean-square) atomic displacements. A separation may however be achieved by a temperature-dependent study of atomic displacements. A harmonic diagonal tensor component of purely thermal origin extrapolates linearly to zero at 0 K; zero-point motion causes a deviation from this linear behaviour at low temperatures, but an extrapolation from higher temperatures (where the contribution from zero-point motion becomes negligibly small) still yields a zero intercept. Any positive intercept in such extrapolations is then due to a (temperature-independent) static contribution to the total atomic displacements. Care has to be taken in such extrapolations, as pronounced anharmonicity (frequently encountered at temperatures higher than the Debye temperature) will change the slope, thus invalidating the linear extrapolation (see *e.g.* Willis & Pryor, 1975). Owing to the difficulty in separating thermal and static displacements in a standard crystallographic structure analysis, a subcommittee of the IUCr Commission on Crystallographic Nomenclature has recommended the use of the term *atomic displacement parameters* (ADPs) for  $U^{ij}$  and  $\beta^{ij}$  (Trueblood *et al.*, 1996).

### 1.9.2. The atomic displacement parameters (ADPs)

One notes that in the Gaussian approximation, the mean-square atomic displacements (composed of thermal and static contributions) are fully described by six coefficients  $\beta^{ij}$ , which transform on a change of the direct-lattice base (according to  $\mathbf{a}_k = A_{ki}\mathbf{a}_i$ ) as

$$\beta^{kl} = A_{ki} A_{lj} \beta^{ij}. \quad (1.9.2.1)$$

This is the transformation law of a tensor (see Section 1.1.3.2); the mean-square atomic displacements are thus tensorial properties of an atom  $\alpha$ . As the tensor is contravariant and in general is described in a (non-Cartesian) crystallographic basis system, its indices are written as superscripts. It is convenient for comparison purposes to quote the dimensionless coefficients  $\beta^{ij}$  as their dimensioned representations  $U^{ij}$ .

In the harmonic approximation, the atomic displacements are fully described by the fully symmetric second-order tensor given in (1.9.2.1). Anharmonicity and disorder, however, cause deviations from a Gaussian distribution of the atomic displacements around the atomic position. In fact, anharmonicity in the thermal motion also provokes a shift of the atomic position as a function of temperature. A generalized description of atomic displacements therefore also involves first-, third-, fourth- and even higher-order displacement terms. These terms are defined by a moment-generating function  $M(\mathbf{Q})$  which expresses  $\langle \exp(i\mathbf{Q}\mathbf{u}_\alpha) \rangle$  in terms of an infinite number of moments; for a Gaussian distribution of displacement vectors, all moments of order  $> 2$  are identically equal to zero. Thus

$$M(\mathbf{Q}) = \langle \exp(i\mathbf{Q}\mathbf{u}_\alpha) \rangle = \sum_{N=0}^{\infty} (i^N / N!) \langle (\mathbf{Q}\mathbf{u}_\alpha)^N \rangle. \quad (1.9.2.2)$$

The moments  $\langle (\mathbf{Q}\mathbf{u}_\alpha)^N \rangle$  of order  $N$  may be expressed in terms of cumulants  $\langle (\mathbf{Q}\mathbf{u}_\alpha)^N \rangle_{\text{cum}}$  by the identity

$$\sum_{N=0}^{\infty} (1/N!) \langle (\mathbf{Q}\mathbf{u}_\alpha)^N \rangle \equiv \exp \sum_{N=1}^{\infty} (1/N!) \langle (\mathbf{Q}\mathbf{u}_\alpha)^N \rangle_{\text{cum}}. \quad (1.9.2.3)$$

## 1.9. ATOMIC DISPLACEMENT PARAMETERS

Separating the powers of  $\mathbf{Q}$  and  $\mathbf{u}$  in (1.9.2.2) and (1.9.2.3), one may obtain expressions involving moments  $\mu$  and cumulants  $k$  explicitly as

$$M(\mathbf{Q}) = \sum_{N=0}^{\infty} (i^N/N!) Q_i Q_j Q_k \dots Q_n \mu^{ijk\dots n} \quad (1.9.2.4)$$

and the cumulant-generating function  $K(\mathbf{Q})$  as

$$K(\mathbf{Q}) = \exp[M(\mathbf{Q})] = \sum_{N=1}^{\infty} (I^N/N!) Q_i Q_j Q_k \dots Q_n k^{ijk\dots n}. \quad (1.9.2.5)$$

The indices  $i, j, k, \dots, n$  run in three-dimensional space from 1 to 3 and refer to the crystallographic basis system. Moments may be expressed in terms of cumulants (and *vice versa*); the transformation laws are given in *IT B* (2001), equation (1.2.12.9) and more completely in Kuhs (1988, 1992). The moment- and cumulant-generating functions are two ways of expressing the Fourier transform of the atomic probability density function (p.d.f.). If all terms up to infinity are taken into account,  $M(\mathbf{Q})$  and  $K(\mathbf{Q})$  are [by virtue of the identity  $\exp(i\mathbf{Q}) = \sum (i\mathbf{Q})^N/N!$ ] identical. For a finite series, however, the cumulants of order  $N$  carry implicit information on contributions of order  $N^2, N^3$  etc. in contrast to the moments. Equations (1.9.2.4) and (1.9.2.5) are useful, as they can be entered directly in a structure-factor equation (see Chapter 1.2 in *IT B*); however, the moments (and thus the cumulants) may also be calculated directly from the atomic p.d.f. as

$$\mu^{ijk\dots n} = \int u^i u^j u^k \dots u^n \text{p.d.f.}(\mathbf{u}) \, d\mathbf{u}. \quad (1.9.2.6)$$

The real-space expression of the p.d.f. obtained from a Fourier transform of (1.9.2.5) is called an *Edgeworth series* expansion. If one assumes that the underlying atomic p.d.f. is close to a Gaussian distribution, one may separate out the Gaussian contributions to the moment-generating function as suggested by Kuznetsov *et al.* (1960) and formulate a generating function for quasimoments as

$$\tilde{M}(\mathbf{Q}) = \exp[(1/2)\langle(\mathbf{Q}\mathbf{u})^2\rangle] \sum_{N=3}^{\infty} (i^N/N!) Q_i Q_j Q_k \dots Q_n \tilde{\mu}^{ijk\dots n}. \quad (1.9.2.7)$$

These quasimoments are especially useful in crystallographic structure-factor equations, as they just modify the harmonic case. The real-space expression of the p.d.f. obtained from a Fourier transformation of (1.9.2.7) is called a *Gram–Charlier* series expansion. Discussions of its merits as compared to the Edgeworth series are given in Zucker & Schulz (1982*a,b*), Kuhs (1983, 1988, 1992) and Scheringer (1985).

### 1.9.2.1. Tensorial properties of (quasi)moments and cumulants

By separating the powers of  $\mathbf{Q}$  and  $\mathbf{u}$ , one obtains in equations (1.9.2.4), (1.9.2.5) and (1.9.2.7) the higher-order displacement tensors in the form of moments, cumulants or quasimoments, which we shall denote in a general way as  $b^{ijk\dots}$ ; note that  $b^{ij}$  is identical to  $\beta^{ij}$ . They transform on a change of the direct-lattice base according to

$$b^{pqr\dots} = A_{pi} A_{qj} A_{rk} \dots b^{ijk\dots}. \quad (1.9.2.8)$$

The higher-order displacement tensors are fully symmetric with respect to the interchange of any of their indices; in the nomenclature of Jahn (1949), their tensor symmetry thus is  $[b^N]$ . The number of independent tensor coefficients depends on the site symmetry of the atom and is tabulated in Sirotnin (1960) as well as in Tables 1.9.3.1–1.9.3.6. For triclinic site symmetry, the numbers of independent tensor coefficients are 1, 3, 6, 10, 15, 21 and 28 for the zeroth to sixth order. Symmetry may further

reduce the number of independent coefficients, as discussed in Section 1.9.3.

In many least-squares programs for structure refinement, the atomic displacement parameters are used in a dimensionless form [as given in (1.9.1.4) for the harmonic case]. These dimensionless quantities may be transformed according to

$$U^{ijk\dots n} = [N!/(2\pi)^N] b^{ijk\dots n} |\mathbf{a}^i| |\mathbf{a}^j| |\mathbf{a}^k| \dots |\mathbf{a}^n| \quad (1.9.2.9)$$

(no summation) into quantities of units  $\text{\AA}^N$  (or  $\text{pm}^N$ );  $\mathbf{a}^i$  etc. are reciprocal-lattice vectors. Nowadays, the published structural results usually quote  $U^{ij}$  for the second-order terms; it would be good practice to publish only dimensioned atomic displacements for the higher-order terms as well.

### 1.9.2.2. Contraction, expansion and invariants of atomic displacement tensors

Anisotropic or higher-order atomic displacement tensors may contain a wealth of information. However, this information content is not always worth publishing in full, either because the physical meaning is not of importance or the significance is only marginal. Quantities of higher significance or better clarity are obtained by an operation known as tensor contraction. Likewise, lower-order terms may be expanded to higher order to impose certain (chemically implied) symmetries on the displacement tensors or to provide initial parameters for least-squares refinements. A contraction is obtained by multiplying the contravariant tensor components (referring to the real-space basis vectors) with the covariant components of the real-space metric tensor  $g_{ij}$ ; for further details on tensor contraction, see Section 1.1.3.3.3. In the general case of atomic displacement tensors of (even) rank  $N$ , one obtains

$${}^N I_0 = g_{ij} g_{kl} \dots g_{mn} b^{ijkl\dots mn}. \quad (1.9.2.10)$$

${}^N I_0$  is called the trace of a tensor of rank  $N$  and is a scalar invariant; it is given in units of  $\text{length}^N$  and provides an easily interpretable quantity: In the case of  ${}^4 I_0$ , a positive sign indicates that the corresponding (real-space) p.d.f. is peaked, a negative sign indicates flatness of the p.d.f. The larger  ${}^N I_0$ , the stronger the deviation from a Gaussian p.d.f. provoked by the atomic displacements of order  $N$ . The frequently quoted isotropic equivalent  $U$  value  $U_{\text{eq}}$  is also obtained by this contraction process. Noting that  $U^{ij}$  may be expressed in terms of  $b^{ij}$  ( $= \beta^{ij}$ ) according to (1.9.2.9) and that the trace of the matrix  $\mathbf{U}$  is given as  $\text{Tr}(\mathbf{U}) = (2\pi^2)^{-1.2} I_0$ , one obtains

$$U_{\text{eq}} = (1/3)(2\pi^2)^{-1} g_{ij} b^{ij}. \quad (1.9.2.11)$$

Note that in all non-orthogonal bases,  $\text{Tr}(\mathbf{U}) \neq U^{11} + U^{22} + U^{33}$ . In older literature, the isotropic equivalent displacement parameter is often quoted as  $B_{\text{eq}}$ , which is related to  $U_{\text{eq}}$  through the identity  $B_{\text{eq}} = 8\pi^2 U_{\text{eq}}$ . The use of  $B_{\text{eq}}$  is now discouraged (Trueblood *et al.*, 1996). Higher atomic displacement tensors of odd rank  $N$  may be reduced to simple vectors  $\mathbf{v}$  by the following contraction:

$${}^N v^i = g_{jk} g_{lm} \dots g_{np} b^{ijkl\dots np}. \quad (1.9.2.12)$$

where  $v^1$  is the 23 trace etc.  ${}^N v^i$  is sometimes called a vector invariant, as it can be uniquely assigned to the tensor in question (Pach & Frey, 1964) and its units are  $\text{length}^{N-1}$ . The vector  $\mathbf{v}$  is oriented along the line of maximum projected asymmetry for a given atom and vanishes for atoms with positional parameters fixed by symmetry; Johnson (1970) has named a vector closely related to  ${}^3 \mathbf{v}$  the vector of skew divergence. The calculation of  $\mathbf{v}$  is useful as it gives the direction of the largest antisymmetric displacements contained in odd-rank higher-order thermal-motion tensors.

# 1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

Table 1.9.3.1. Site-symmetry table giving key to Tables 1.9.3.2 to 1.9.3.6 for restrictions on the symmetry of various thermal-motion tensors

Hex denotes hexagonal axes.

Point symmetry at special position			Position <i>x, y, z</i>	Cross-reference for tensor tables					
Symmetry axes	Point-group generators			1B	1C	1D	1E	1F	
<i>m3m</i>		4[0, 0, 1] 3[1, 1, 1]	$\bar{1}$	0, 0, 0	B1	C0	D1	E0	F1
<i>43m</i>		4[0, 0, 1] 3[1, 1, 1]		0, 0, 0	B1	C1	D1	E1	F1
432		4[0, 0, 1] 3[1, 1, 1]		0, 0, 0	B1	C0	D1	E0	F1
<i>m3</i>		3[1, 1, 1] 2[0, 0, 1]	$\bar{1}$	0, 0, 0	B1	C0	D1	E0	F2
23		3[1, 1, 1] 2[0, 0, 1]		0, 0, 0	B1	C1	D1	E1	F2
<i>6/mmm</i>	Hex	6[0, 0, 1] 2[1, 0, 0]	$\bar{1}$	0, 0, 0	B9	C0	D2	E0	F3
<i>6m2</i>	Hex	6[0, 0, 1] 2[1, 0, 0]		0, 0, 0	B9	C9	D2	E5	F3
<i>6m2</i>	Hex	6[0, 0, 1] 2[1, 2, 0]		0, 0, 0	B9	C10	D2	E6	F3
<i>6mm</i>	Hex	6[0, 0, 1] 2[1, 0, 0]		0, 0, <i>z</i>	B9	C19	D2	E17	F3
622	Hex	6[0, 0, 1] 2[1, 0, 0]		0, 0, 0	B9	C0	D2	E0	F4
<i>6/m</i>	Hex	6[0, 0, 1] $\bar{1}$		0, 0, 0	B9	C0	D2	E0	F4
$\bar{6}$	Hex	6[0, 0, 1] $\bar{1}$		0, 0, 0	B9	C20	D2	E24	F4
6	Hex	6[0, 0, 1] $\bar{1}$		0, 0, <i>z</i>	B9	C19	D2	E17	F4
<i>4/mmm</i>		4[0, 0, 1] 2[1, 0, 0]	$\bar{1}$	0, 0, 0	B2	C0	D3	E0	F5
<i>4/mmm</i>		4[0, 1, 0] 2[0, 0, 1]	$\bar{1}$	0, 0, 0	B3	C0	D4	E0	F6
<i>4/mmm</i>		4[1, 0, 0] 2[0, 1, 0]	$\bar{1}$	0, 0, 0	B4	C0	D5	E0	F7
<i>42m</i>		4[0, 0, 1] 2[1, 0, 0]		0, 0, 0	B2	C1	D3	E7	F5
<i>42m</i>		4[0, 0, 1] 2[1, 1, 0]		0, 0, 0	B2	C2	D3	E8	F5
<i>42m</i>		4[0, 1, 0] 2[0, 0, 1]		0, 0, 0	B3	C1	D4	E9	F6
<i>42m</i>		4[0, 1, 0] 2[1, 0, 1]		0, 0, 0	B3	C3	D4	E10	F6
<i>42m</i>		4[1, 0, 0] 2[0, 1, 0]		0, 0, 0	B4	C1	D5	E11	F7
<i>42m</i>		4[1, 0, 0] 2[0, 1, 1]		0, 0, 0	B4	C4	D5	E12	F7
<i>4mm</i>		4[0, 0, 1] 2[1, 0, 0]		0, 0, <i>z</i>	B2	C13	D3	E25	F5
<i>4mm</i>		4[0, 1, 0] 2[0, 0, 1]		0, <i>y</i> , 0	B3	C14	D4	E26	F6
<i>4mm</i>		4[1, 0, 0] 2[0, 1, 0]		<i>x</i> , 0, 0	B4	C15	D5	E27	F7
422		4[0, 0, 1] 2[1, 0, 0]		0, 0, 0	B2	C0	D3	E2	F5
422		4[0, 1, 0] 2[0, 0, 1]		0, 0, 0	B3	C0	D4	E3	F6
422		4[1, 0, 0] 2[0, 1, 0]		0, 0, 0	B4	C0	D5	E4	F7
<i>4/m</i>		4[0, 0, 1] $\bar{1}$		0, 0, 0	B2	C0	D12	E0	F14
<i>4/m</i>		4[0, 1, 0] $\bar{1}$		0, 0, 0	B3	C0	D13	E0	F15
<i>4/m</i>		4[1, 0, 0] $\bar{1}$		0, 0, 0	B4	C0	D14	E0	F16
$\bar{4}$		4[0, 0, 1]		0, 0, 0	B2	C16	D12	E28	F14
$\bar{4}$		4[0, 1, 0]		0, 0, 0	B3	C17	D13	E29	F15
$\bar{4}$		4[1, 0, 0]		0, 0, 0	B4	C18	D14	E30	F16
4		4[0, 0, 1]		0, 0, <i>z</i>	B2	C13	D12	E31	F14
4		4[0, 1, 0]		0, <i>y</i> , 0	B3	C14	D13	E32	F15
4		4[1, 0, 0]		<i>x</i> , 0, 0	B4	C15	D14	E33	F16
<i>3m</i>		3[1, 1, 1] 2[1, $\bar{1}$ , 0]	$\bar{1}$	0, 0, 0	B5	C0	D6	E0	F8
<i>3m</i>		3[1, 1, $\bar{1}$ ] 2[1, $\bar{1}$ , 0]	$\bar{1}$	0, 0, 0	B6	C0	D7	E0	F9
<i>3m</i>		3[ $\bar{1}$ , 1, 1] 2[1, 1, 0]	$\bar{1}$	0, 0, 0	B7	C0	D8	E0	F10
<i>3m</i>		3[ $\bar{1}$ , 1, 1] 2[1, 1, 0]	$\bar{1}$	0, 0, 0	B8	C0	D9	E0	F11
<i>3m</i>	Hex	3[0, 0, 1] 2[1, 0, 0]	$\bar{1}$	0, 0, 0	B9	C0	D10	E0	F12
<i>3m</i>	Hex	3[0, 0, 1] 2[1, 2, 0]	$\bar{1}$	0, 0, 0	B9	C0	D11	E0	F13
<i>3m</i>		3[1, 1, 1] 2[1, $\bar{1}$ , 0]		<i>x, x, x</i>	B5	C33	D6	E34	F8
<i>3m</i>		3[1, 1, $\bar{1}$ ] 2[1, $\bar{1}$ , 0]		<i>x, x, <math>\bar{x}</math></i>	B6	C34	D7	E35	F9
<i>3m</i>		3[ $\bar{1}$ , 1, 1] 2[1, 1, 0]		<i>x, <math>\bar{x}</math>, x</i>	B7	C35	D8	E36	F10
<i>3m</i>		3[ $\bar{1}$ , 1, 1] 2[1, 1, 0]		$\bar{x}, x, x$	B8	C36	D9	D37	F11
<i>3m</i>	Hex	3[0, 0, 1] 2[1, 0, 0]		0, 0, <i>z</i>	B9	C37	D10	E38	F12
<i>3m</i>	Hex	3[0, 0, 1] 2[1, 2, 0]		0, 0, <i>z</i>	B9	C38	D11	E39	F13
32		3[1, 1, 1] 2[1, $\bar{1}$ , 0]		0, 0, 0	B5	C5	D6	E13	F8
32		3[1, 1, $\bar{1}$ ] 2[1, $\bar{1}$ , 0]		0, 0, 0	B6	C6	D7	E14	F9
32		3[ $\bar{1}$ , 1, 1] 2[1, 1, 0]		0, 0, 0	B7	C7	D8	E15	F10
32		3[ $\bar{1}$ , 1, 1] 2[1, 1, 0]		0, 0, 0	B8	C8	D9	E16	F11
32	Hex	3[0, 0, 1] 2[1, 0, 0]		0, 0, 0	B9	C9	D10	E5	F12
32	Hex	3[0, 0, 1] 2[1, 2, 0]		0, 0, 0	B9	C10	D11	E6	F13
$\bar{3}$		3[1, 1, 1]		0, 0, 0	B5	C0	D15	E0	F17
$\bar{3}$		3[1, 1, $\bar{1}$ ]		0, 0, 0	B6	C0	D16	E0	F18
$\bar{3}$		3[ $\bar{1}$ , 1, 1]		0, 0, 0	B7	C0	D17	E0	F19
$\bar{3}$		3[ $\bar{1}$ , 1, 1]		0, 0, 0	B8	C0	D18	E0	F20
$\bar{3}$	Hex	3[0, 0, 1]		0, 0, 0	B9	C0	D19	E0	F21
3		3[1, 1, 1]		<i>x, x, x</i>	B5	C54	D15	E58	F17
3		3[1, 1, $\bar{1}$ ]		<i>x, x, <math>\bar{x}</math></i>	B6	C55	D16	E59	F18
3		3[ $\bar{1}$ , 1, 1]		<i>x, <math>\bar{x}</math>, x</i>	B7	C56	D17	E60	F19
3	Hex	3[ $\bar{1}$ , 1, 1]		$\bar{x}, x, x$	B8	C57	D18	E61	F20
3		3[0, 0, 1]		0, 0, <i>z</i>	B9	C58	D19	E62	F21
<i>mmm</i>		2[0, 0, 1] 2[1, 0, 0]	$\bar{1}$	0, 0, 0	B10	C0	D20	E0	F22
<i>mmm</i>		2[0, 0, 1] 2[1, 1, 0]	$\bar{1}$	0, 0, 0	B11	C0	D21	E0	F23
<i>mmm</i>		2[0, 1, 0] 2[1, 0, 1]	$\bar{1}$	0, 0, 0	B12	C0	D22	E0	F24
<i>mmm</i>		2[1, 0, 0] 2[0, 1, 1]	$\bar{1}$	0, 0, 0	B13	C0	D23	E0	F25
<i>mmm</i>	Hex	2[0, 0, 1] 2[1, 0, 0]	$\bar{1}$	0, 0, 0	B14	C0	D24	E0	F26
<i>mmm</i>	Hex	2[0, 0, 1] 2[1, 1, 0]	$\bar{1}$	0, 0, 0	B11	C0	D21	E0	F23
<i>mmm</i>	Hex	2[0, 0, 1] 2[0, 1, 0]	$\bar{1}$	0, 0, 0	B15	C0	D25	E0	F27
<i>mm</i>		2[0, 0, 1] 2[1, 0, 0]		0, 0, <i>z</i>	B10	C21	D20	E40	F22
<i>mm</i>		2[0, 0, 1] 2[1, 1, 0]		0, 0, <i>z</i>	B11	C22	D21	E41	F23
<i>mm</i>		2[0, 1, 0] 2[0, 0, 1]		0, <i>y</i> , 0	B10	C23	D20	E42	F22
<i>mm</i>		2[0, 1, 0] 2[1, 0, 1]		0, <i>y</i> , 0	B12	C24	D22	E43	F24
<i>mm</i>		2[1, 0, 0] 2[0, 0, 1]		<i>x</i> , 0, 0	B10	C25	D20	E44	F22

1.9. ATOMIC DISPLACEMENT PARAMETERS

Table 1.9.3.1 (cont.)

Point symmetry at special position		Position <i>x, y, z</i>	Cross-reference for tensor tables					
Symmetry axes	Point-group generators		1B	1C	1D	1E	1F	
<i>mm</i>	$2[1, 0, 0]$	$\bar{2}[0, 1, 1]$	<i>x, 0, 0</i>	B13	C26	D23	E45	F25
<i>mm</i>	$2[1, 1, 0]$	$\bar{2}[0, 0, 1]$	<i>x, x, 0</i>	B11	C27	D21	E46	F23
<i>mm</i>	$2[1, \bar{1}, 0]$	$\bar{2}[0, 0, 1]$	<i>x, \bar{x}, 0</i>	B11	C28	D21	E47	F23
<i>mm</i>	$2[1, 0, 1]$	$\bar{2}[0, 1, 0]$	<i>x, 0, x</i>	B12	C29	D22	E48	F24
<i>mm</i>	$2[1, 0, \bar{1}]$	$\bar{2}[0, 1, 0]$	<i>x, 0, \bar{x}</i>	B12	C30	D22	E49	F24
<i>mm</i>	$2[0, 1, 1]$	$\bar{2}[0, 1, 0]$	<i>0, y, y</i>	B13	C31	D23	E50	F25
<i>mm</i>	$2[0, 1, \bar{1}]$	$\bar{2}[1, 0, 0]$	<i>0, y, \bar{y}</i>	B13	C32	D23	E51	F25
<i>mm</i>	Hex $2[0, 0, 1]$	$\bar{2}[1, 0, 0]$	<i>0, 0, z</i>	B14	C40	D24	E52	F26
<i>mm</i>	Hex $2[0, 0, 1]$	$\bar{2}[1, 1, 0]$	<i>0, 0, z</i>	B11	C22	D21	E41	F23
<i>mm</i>	Hex $2[0, 0, 1]$	$\bar{2}[0, 1, 0]$	<i>0, 0, z</i>	B15	C39	D25	E53	F27
<i>mm</i>	Hex $2[1, 0, 0]$	$\bar{2}[0, 0, 1]$	<i>x, 0, 0</i>	B14	C41	D24	E54	F26
<i>mm</i>	Hex $2[2, 1, 0]$	$\bar{2}[0, 0, 1]$	<i>2x, x, 0</i>	B15	C42	D25	E55	F27
<i>mm</i>	Hex $2[1, 1, 0]$	$\bar{2}[0, 0, 1]$	<i>x, x, 0</i>	B11	C27	D21	E46	F23
<i>mm</i>	Hex $2[1, 2, 0]$	$\bar{2}[0, 0, 1]$	<i>x, 2x, 0</i>	B14	C43	D24	E56	F26
<i>mm</i>	Hex $2[0, 1, 0]$	$\bar{2}[0, 0, 1]$	<i>0, y, 0</i>	B15	C44	D25	E57	F27
<i>mm</i>	Hex $2[1, \bar{1}, 0]$	$\bar{2}[0, 0, 1]$	<i>x, \bar{x}, 0</i>	B11	C28	D21	E47	F23
222	$2[0, 0, 1]$	$\bar{2}[1, 0, 0]$	<i>0, 0, 0</i>	B10	C1	D20	E18	F22
222	$2[0, 0, 1]$	$\bar{2}[1, 1, 0]$	<i>0, 0, 0</i>	B11	C2	D21	E19	F23
222	$2[0, 1, 0]$	$\bar{2}[1, 0, 1]$	<i>0, 0, 0</i>	B12	C3	D22	E20	F24
222	$2[1, 0, 0]$	$\bar{2}[0, 1, 1]$	<i>0, 0, 0</i>	B13	C4	D23	E21	F25
222	Hex $2[0, 0, 1]$	$\bar{2}[1, 0, 0]$	<i>0, 0, 0</i>	B14	C11	D24	E22	F26
222	Hex $2[0, 0, 1]$	$\bar{2}[1, 1, 0]$	<i>0, 0, 0</i>	B11	C2	D21	E19	F23
222	Hex $2[0, 0, 1]$	$\bar{2}[0, 1, 0]$	<i>0, 0, 0</i>	B15	C12	D25	E23	F27
2/m	$2[0, 0, 1]$	$\bar{1}$	<i>0, 0, 0</i>	B16	C0	D26	E0	F28
2/m	$2[0, 1, 0]$	$\bar{1}$	<i>0, 0, 0</i>	B17	C0	D27	E0	F29
2/m	$2[1, 0, 0]$	$\bar{1}$	<i>0, 0, 0</i>	B18	C0	D28	E0	F30
2/m	$2[1, 1, 0]$	$\bar{1}$	<i>0, 0, 0</i>	B19	C0	D29	E0	F31
2/m	$2[1, \bar{1}, 0]$	$\bar{1}$	<i>0, 0, 0</i>	B20	C0	D30	E0	F32
2/m	$2[1, 0, 1]$	$\bar{1}$	<i>0, 0, 0</i>	B21	C0	D31	E0	F33
2/m	$2[1, 0, \bar{1}]$	$\bar{1}$	<i>0, 0, 0</i>	B22	C0	D32	E0	F34
2/m	$2[0, 1, 1]$	$\bar{1}$	<i>0, 0, 0</i>	B23	C0	D33	E0	F35
2/m	$2[0, 1, \bar{1}]$	$\bar{1}$	<i>0, 0, 0</i>	B24	C0	D34	E0	F36
2/m	Hex $2[0, 0, 1]$	$\bar{1}$	<i>0, 0, 0</i>	B16	C0	D26	E0	F28
2/m	Hex $2[1, 0, 0]$	$\bar{1}$	<i>0, 0, 0</i>	B25	C0	D35	E0	F37
2/m	Hex $2[2, 1, 0]$	$\bar{1}$	<i>0, 0, 0</i>	B26	C0	D36	E0	F38
2/m	Hex $2[1, 1, 0]$	$\bar{1}$	<i>0, 0, 0</i>	B19	C0	D29	E0	F31
2/m	Hex $2[1, 2, 0]$	$\bar{1}$	<i>0, 0, 0</i>	B27	C0	D37	E0	F39
2/m	Hex $2[0, 1, 0]$	$\bar{1}$	<i>0, 0, 0</i>	B28	C0	D38	E0	F40
2/m	Hex $2[1, 1, 0]$	$\bar{1}$	<i>0, 0, 0</i>	B20	C0	D30	E0	F32
<i>m</i>	$\bar{2}[0, 1, 0]$		<i>x, 0, z</i>	B17	C64	D27	E77	F29
<i>m</i>	$\bar{2}[1, 0, 0]$		<i>0, y, z</i>	B18	C65	D28	E78	F30
<i>m</i>	$\bar{2}[1, \bar{1}, 0]$		<i>x, \bar{x}, z</i>	B19	C66	D29	E79	F31
<i>m</i>	$\bar{2}[1, 1, 0]$		<i>x, x, z</i>	B20	C67	D30	E80	F32
<i>m</i>	$\bar{2}[1, 0, 1]$		<i>x, y, \bar{x}</i>	B21	C68	D31	E81	F33
<i>m</i>	$\bar{2}[1, 0, \bar{1}]$		<i>x, y, x</i>	B22	C69	D32	E82	F34
<i>m</i>	$\bar{2}[0, 1, 1]$		<i>x, y, \bar{y}</i>	B23	C70	D33	E83	F35
<i>m</i>	$\bar{2}[0, 1, \bar{1}]$		<i>x, y, y</i>	B24	C71	D34	E84	F36
<i>m</i>	Hex $\bar{2}[0, 0, 1]$		<i>x, y, 0</i>	B16	C63	D26	E76	F28
<i>m</i>	Hex $\bar{2}[1, 0, 0]$		<i>x, 2x, z</i>	B25	C72	D35	E85	F37
<i>m</i>	Hex $\bar{2}[2, 1, 0]$		<i>0, y, z</i>	B26	C73	D36	E86	F38
<i>m</i>	Hex $\bar{2}[1, 1, 0]$		<i>x, \bar{x}, z</i>	B19	C66	D29	E79	F31
<i>m</i>	Hex $\bar{2}[1, 2, 0]$		<i>x, 0, z</i>	B27	C74	D37	E87	F39
<i>m</i>	Hex $\bar{2}[0, 1, 0]$		<i>2x, x, z</i>	B28	C75	D38	E88	F40
<i>m</i>	Hex $\bar{2}[1, \bar{1}, 0]$		<i>x, x, z</i>	B20	C67	D30	E80	F32
2	$\bar{2}[0, 0, 1]$		<i>0, 0, z</i>	B16	C45	D26	E63	F28
2	$\bar{2}[0, 1, 0]$		<i>0, y, 0</i>	B17	C46	D27	E64	F29
2	$\bar{2}[1, 0, 0]$		<i>x, 0, 0</i>	B18	C47	D28	E65	F30
2	$\bar{2}[1, 1, 0]$		<i>x, x, 0</i>	B19	C48	D29	E66	F31
2	$\bar{2}[1, \bar{1}, 0]$		<i>x, \bar{x}, 0</i>	B20	C49	D30	E67	F32
2	$\bar{2}[1, 0, 1]$		<i>x, 0, x</i>	B21	C50	D31	E68	F33
2	$\bar{2}[1, 0, \bar{1}]$		<i>x, 0, \bar{x}</i>	B22	C51	D32	E69	F34
2	$\bar{2}[0, 1, 1]$		<i>0, y, y</i>	B23	C52	D33	E70	F35
2	$\bar{2}[0, 1, \bar{1}]$		<i>0, y, \bar{y}</i>	B24	C53	D34	E71	F36
2	Hex $\bar{2}[0, 0, 1]$		<i>0, 0, z</i>	B16	C45	D26	E63	F28
2	Hex $\bar{2}[1, 0, 0]$		<i>x, 0, 0</i>	B25	C59	D35	E72	F37
2	Hex $\bar{2}[2, 1, 0]$		<i>2x, x, 0</i>	B26	C60	D36	E73	F38
2	Hex $\bar{2}[1, 1, 0]$		<i>x, x, 0</i>	B19	C48	D29	E66	F31
2	Hex $\bar{2}[1, 2, 0]$		<i>x, 2x, 0</i>	B27	C61	D37	E74	F39
2	Hex $\bar{2}[0, 1, 0]$		<i>0, y, 0</i>	B28	C62	D38	E75	F40
2	Hex $\bar{2}[1, \bar{1}, 0]$		<i>x, \bar{x}, 0</i>	B20	C49	D30	E67	F32
$\bar{1}$	$\bar{1}$		<i>0, 0, 0</i>	B29	C0	D39	E0	F41
$\bar{1}$	Hex $\bar{1}$		<i>0, 0, 0</i>	B29	C0	D39	E0	F41
1	1		<i>x, y, z</i>	B29	C76	D39	E89	F41
1	Hex 1		<i>x, y, z</i>	B29	C76	D39	E89	F41

## 1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

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* (1999), 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* (2002) 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