

1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

Table 1.9.3.6. Symmetry restrictions on coefficients in sixth-rank symmetric polar tensors

(a) A–N.

Cross-reference	No. of independent parameters	Symbols and coefficient indices														
		A	B	C	D	E	F	G	H	I	J	K	L	M	N	
	1	2	3	1	1	1	1	1	1	1	1	1	1	1	1	
	1	2	3	1	1	1	1	1	1	1	1	1	1	1	1	
	1	2	3	1	1	1	1	1	1	1	1	1	1	2	2	
	1	2	3	1	1	1	1	1	2	2	2	2	3	2	2	
	1	2	3	1	1	2	2	3	2	2	3	3	3	2	2	
	1	2	3	2	3	2	3	3	2	3	3	3	3	2	3	
F1	3	A	A	A	0	0	F	0	F	0	0	0	0	F	0	
F2	4	A	A	A	0	0	F	0	H	0	0	0	0	H	0	
F3	5	A	A	C	A/2	0	F	0	H	(1)†	0	H/2	0	F	0	
F4	6	A	A	C	D	0	F	0	H	(2)†	0	H/2	0	(5)†	0	
F5	6	A	A	C	0	0	F	0	H	0	0	0	0	F	0	
F6	6	A	B	A	0	0	F	0	H	0	0	0	0	M	0	
F7	6	A	B	B	0	0	F	0	F	0	0	0	0	M	0	
F8	7	A	A	A	D	D	F	G	F	I	J	J	I	F	J	
F9	7	A	A	A	D	-D	F	G	F	I	J	-J	-I	F	J	
F10	7	A	A	A	D	-D	F	G	F	I	J	-J	-I	F	-J	
F11	7	A	A	A	D	D	F	G	F	I	J	J	I	F	-J	
F12	7	A	A	C	A/2	E	F	E/2	H	(1)†	E/10	H/2	I	F	-E/10	
F13	7	A	A	C	A/2	0	F	G	H	(1)†	G	H/2	0	F	G	
F14	8	A	A	C	D	0	F	0	H	0	0	K	0	F	0	
F15	8	A	B	A	0	E	F	0	H	0	J	0	0	M	0	
F16	8	A	B	B	0	0	F	0	H	0	0	0	0	M	N	
F17	10	A	A	A	D	E	F	G	H	I	J	K	I	H	K	
F18	10	A	A	A	D	E	F	G	H	I	J	K	-I	H	-K	
F19	10	A	A	A	D	E	F	G	H	I	J	K	-I	H	K	
F20	10	A	A	A	D	E	F	G	H	I	J	K	I	H	-K	
F21	10	A	A	C	D	E	F	G	H	(2)†	(4)†	H/2	L	(5)†	(7)†	
F22	10	A	B	C	0	0	F	0	H	0	0	0	0	M	0	
F23	10	A	A	C	D	0	F	0	H	I	0	K	0	F	0	
F24	10	A	B	A	0	E	F	0	H	0	J	0	L	M	0	
F25	10	A	B	B	0	0	F	G	F	0	0	0	0	M	N	
F26	10	A	B	C	D	0	F	0	H	(3)†	0	K	0	(6)†	0	
F27	10	A	B	C	A/2	0	F	0	H	(1)†	0	H/2	0	M	0	
F28	16	A	B	C	D	0	F	0	H	I	0	K	0	M	0	
F29	16	A	B	C	0	E	F	0	H	0	J	0	L	M	0	
F30	16	A	B	C	0	0	F	G	H	0	0	0	0	M	N	
F31	16	A	A	C	D	E	F	G	H	I	J	K	L	F	-J	
F32	16	A	A	C	D	E	F	G	H	I	J	K	L	F	J	
F33	16	A	B	A	D	E	F	G	H	I	J	K	L	M	N	
F34	16	A	B	A	D	E	F	G	H	I	J	K	L	M	N	
F35	16	A	B	B	D	-D	F	G	F	I	J	-J	-I	M	N	
F36	16	A	B	B	D	D	F	G	F	I	J	J	I	M	N	
F37	16	A	B	C	D	E	F	G	H	(3)†	J	K	L	(6)†	(8)†	
F38	16	A	B	C	A/2	0	F	G	H	(1)†	G	H/2	0	M	N	
F39	16	A	B	C	D	E	F	G	H	(3)†	J	K	L	(6)†	(9)†	
F40	16	A	B	C	A/2	E	F	E/2	H	(1)†	J	H/2	L	M	(10)†	
F41	28	A	B	C	D	E	F	G	H	I	J	K	L	M	N	

(b) P–c.

Cross-reference	No. of independent parameters	Symbols and coefficient indices														
		P	Q	R	S	T	U	V	W	X	Y	Z	a	b	c	
	1	1	1	1	1	1	1	1	1	2	2	2	2	2	2	
	1	1	1	2	2	2	2	2	2	3	2	2	2	2	3	
	2	2	3	2	2	2	2	2	3	3	2	2	2	3	3	
	2	3	3	3	2	2	2	3	3	3	2	2	3	3	3	
	3	3	3	3	2	2	3	3	3	3	2	3	3	3	3	
F1	3	P	0	F	0	0	0	0	0	0	0	F	0	F	0	
F2	4	P	0	F	0	0	0	0	0	0	0	F	0	H	0	
F3	5	H/2	0	R	A/2	0	H/2	0	R/2	0	0	H	0	R	0	
F4	6	H/2	0	R	(11)†	0	H/2	0	R/2	0	0	H	0	R	0	
F5	6	P	0	R	0	0	0	0	0	0	0	H	0	R	0	
F6	6	P	0	H	0	0	0	0	0	0	0	M	0	F	0	
F7	6	P	0	M	0	0	0	0	0	0	0	Z	0	Z	0	
F8	7	P	J	F	D	G	J	J	G	D	D	F	I	F	D	
F9	7	P	J	F	D	G	-J	J	-G	-D	-D	F	-I	F	-D	
F10	7	P	-J	F	D	-G	-J	-J	G	-D	D	F	I	F	D	
F11	7	P	-J	F	D	-G	J	-J	-G	D	-D	F	-I	F	-D	
F12	7	H/2	I/2	R	A/2	-E/2	H/2	-I/2	R/2	0	-E	H	-I	R	0	
F13	7	H/2	Q	R	A/2	G	H/2	Q	R/2	0	0	H	0	R	0	
F14	8	P	0	R	-D	0	-K	0	0	0	0	H	0	R	0	
F15	8	P	0	H	0	0	0	-J	0	-E	0	M	0	F	0	
F16	8	P	-N	M	0	0	0	0	0	0	0	Y	Z	0	Z	-Y
F17	10	P	J	F	E	G	J	K	G	D	D	F	I	H	E	
F18	10	P	J	F	-E	G	-J	-K	-G	-D	-D	F	-I	H	E	

1.9. ATOMIC DISPLACEMENT PARAMETERS

Table 1.9.3.6 (cont.)

Cross-reference	No. of independent parameters	Symbols and coefficient indices														
		P	Q	R	S	T	U	V	W	X	Y	Z	a	b	c	
F21	1	1	1	1	1	1	1	1	1	2	2	2	2	2	2	
	1	1	1	2	2	2	2	2	3	2	2	2	2	2	3	
	2	2	3	2	2	2	2	3	3	2	2	2	3	3	3	
	2	3	3	2	2	2	3	3	3	2	2	3	3	3	3	
	3	3	3	2	2	3	3	3	3	2	3	3	3	3	3	
	3	3	3	2	3	3	3	3	3	3	3	3	3	3	3	
F19	10	P	-J	F	-E	-G	-J	-K	G	-D	D	F	I	H	-E	
F20	10	P	-J	F	E	-G	J	K	-G	D	-D	F	-I	H	-E	
F21	10	H/2	Q	R	(11)†	(13)†	H/2	(18)†	R/2	0	-E	H	-L	R	0	
F22	10	P	0	R	0	0	0	0	0	0	0	Z	0	b	0	
F23	10	P	0	R	D	0	K	0	W	0	0	H	0	R	0	
F24	10	P	0	H	0	T	0	J	0	E	0	M	0	F	0	
F25	10	P	N	M	0	0	0	0	0	0	Y	Z	a	Z	Y	
F26	10	P	0	R	B/2	0	(16)†	0	W	0	0	(22)†	0	2W	0	
F27	10	P	0	R	(12)†	0	(17)†	0	R/2	0	0	Z	0	b	0	
F28	16	P	0	R	S	0	U	0	W	0	0	Z	0	b	0	
F29	16	P	0	R	0	T	0	V	0	X	0	Z	0	b	0	
F30	16	P	Q	R	0	0	0	0	0	0	Y	Z	a	b	c	
F31	16	P	Q	R	D	-G	K	-Q	W	X	-E	H	-L	R	-X	
F32	16	P	Q	R	D	G	K	Q	W	X	E	H	L	R	X	
F33	16	P	-K	H	S	T	-N	J	-G	E	-S	M	-I	F	-D	
F34	16	P	K	H	S	T	N	J	G	E	S	M	I	F	D	
F35	16	P	N	M	S	T	U	-U	-T	-S	Y	Z	a	Z	Y	
F36	16	P	N	M	S	T	U	U	T	S	Y	Z	a	Z	Y	
F37	16	P	Q	R	B/2	(14)†	(16)†	(19)†	W	X	(20)†	(22)†	(23)†	2W	2X	
F38	16	P	Q	R	(12)†	(15)†	(17)†	Q	R/2	0	Y	Z	a	b	c	
F39	16	P	Q	R	B/2	(9)†	(16)†	Q	W	X	0	(22)†	0	2W	0	
F40	16	P	L/2	R	(12)†	T	(17)†	V	R/2	X	(21)†	Z	(24)†	b	X/2	
F41	28	P	Q	R	S	T	U	V	W	X	Y	Z	a	b	c	

† (1) $-A/4 + F/2$; (2) $A/2 - 3D/2 + 3F/2$; (3) $B/20 - 3D/5 + 3F/2$; (4) $-2E/5 + G$; (5) $A - 2D + F$; (6) $B/5 - 2D/5 + F$; (7) $-3E/5 + G$; (8) $2E - 5G + 4J$; (9) $-G + 2J$; (10) $-E/4 + 3J/2$; (11) $A - D$; (12) $A/2 - 5F/2 + 5M/2$; (13) $-E + G$; (14) $6E - 15G + 10J$; (15) $-G + 2N$; (16) $-2K + 3P$; (17) $-H/4 + 3P/2$; (18) $-L + Q$; (19) $-2L + 3Q$; (20) $12E - 30G + 20J$; (21) $E/2 - 5J/2 + 5T/2$; (22) $-4K + 6P$; (23) $-4L + 6Q$; (24) $-L/4 + 3V/2$.

system with correspondingly different transformation matrices \mathbf{F} (see e.g. Chapter 1.1 of *IT B*). The most useful representation surface of the second-order atomic displacement tensor \mathbf{U}_C is the representation quadric defined by the tensor invariant

$$^2I_0 = \mathbf{u}^T \mathbf{U}_C^{-1} \mathbf{u} \quad (1.9.4.3)$$

where \mathbf{u} is a displacement vector; \mathbf{U}_C^{-1} is often called the *variance-covariance matrix* and has (in a general axes frame) covariant components. Under the conditions of *positive definiteness*,

$$\left. \begin{array}{l} \text{Det}(\mathbf{U}_C) \\ \mathbf{U}_C^{ij} \end{array} \right\} \text{all positive,} \quad (1.9.4.4)$$

the surface of the representation quadric is an ellipsoid whose semi-major axes (for $^2I_0 = 0$) are of lengths equal to the root-mean-square displacements (r.m.s.d.'s) along the axes directions. The *thermal vibration ellipsoids* calculated in *ORTEP* are related to this surface; considering the discussion in Section 1.9.1, they should more appropriately be called *atomic displacement ellipsoids* or simply *ORTEP ellipsoids*. One notes that the Fourier transform of the atomic DWF, the atomic probability density function $P(\mathbf{u})$, is given in the case of a second-order tensor as a trivariate Gaussian distribution,

$$P(\mathbf{u}) = \frac{[\text{Det}(\mathbf{U}_C^{-1})]^{1/2}}{(2\pi)^{3/2}} \exp\left\{-\frac{1}{2}\mathbf{u}^T \mathbf{U}_C^{-1} \mathbf{u}\right\}. \quad (1.9.4.5)$$

On comparing (1.9.4.3) and (1.9.4.5), it is evident that (1.9.4.3) defines a surface of constant probability of finding a (displaced) atom. The integral of (1.9.4.5) over the volume inside the ellipsoid is a constant. For $^2I_0 = C^2$ with the integration limit $C = 1.5382$ (2.5003), the integral is equal to one half (nine tenths), and the ellipsoid is then called a 50 (90) per cent probability ellipsoid.

Other representation surfaces can be defined and are useful for special considerations. The quantities of interest are either the r.m.s.d.'s or the mean-square displacements (m.s.d.'s) defined in direct space. Here a distinction has to be made between the averaged squared displacement along a certain direction and the average for all squared displacements of an atom projected onto a given direction. Representation surfaces may also be calculated in reciprocal space, related to surfaces in direct space by Fourier transformation. For further details, see Nelmés (1969) and Hummel *et al.* (1990).

1.9.4.2. Higher-order representations

Representation surfaces of higher-order tensors may be calculated from their invariants. While for second-order tensors surfaces can be found that fully describe the directional aspects of the tensor involved, higher-order tensors need several different surfaces for a full description (see e.g. Wondratschek, 1958; Sirotin, 1961). This makes the graphical representation of the displacements somewhat cumbersome and it is therefore rarely used. Instead, the probability density functions [given in equations (6.1.1.46), (6.1.1.48) or (6.1.1.49) of *IT C*] are calculated from the tensor coefficients and displayed in sections or as three-dimensional surfaces. If the higher-order terms are small, it is more appropriate to display only the difference between the total p.d.f. and the related Gaussian p.d.f., which may be calculated from the second-order displacement tensor using equation (1.9.4.5). Here, the second-order terms that were refined together with the higher-order terms are usually used (not the best-fitting second-order terms of a fit in the harmonic approximation):

$$P_{\text{deformation}}(\mathbf{u}) = P_{\text{general}}(\mathbf{u}) - P_{\text{Gaussian}}(\mathbf{u}). \quad (1.9.4.6)$$

The resulting *anharmonic deformation densities* (or *disorder deformation densities* in the case of static disorder) $P_{\text{deformation}}(\mathbf{u})$ may be displayed in a similar way to the total p.d.f.'s $P_{\text{general}}(\mathbf{u})$. The graphical representations appropriate for displaying those densities are similar to those used for electronic deformation