Table 6.1.1.8. *Cubic harmonics $K_{lj}(\theta, \varphi)$ for cubic site symmetries*

$K_{lj}(\theta, \varphi)$	N_{l^2j}	Site symmetry				
		23	$m3$	432	$\bar{4}3m$	$m3m$
$K_0 = Y_{00+} = 1$	4π	×	×	×	×	×
$K_3 = Y_{32-}$	$\frac{240\pi}{7}$	×			×	
$K_4 = Y_{40+} + \frac{1}{168} Y_{44+}$	$\frac{16\pi}{21}$	×	×	×	×	×
$K_{6,1} = Y_{60+} - \frac{1}{360} Y_{64+}$	$\frac{32\pi}{13}$	×	×	×	×	×
$K_{6,2} = Y_{62+} - \frac{1}{792} Y_{66+}$	$\frac{512\pi}{13} \cdot \frac{105}{11}$	×	×			
$K_7 = Y_{72-} + \frac{1}{1560} Y_{76-}$	$\frac{256\pi}{15} \cdot \frac{567}{13}$	×			×	
$K_8 = Y_{80+} + \frac{1}{5940}(Y_{84+} + \frac{1}{672} Y_{88+})$	$\frac{256\pi}{17 \cdot 33}$	×	×	×	×	×
$K_{9,1} = Y_{92-} - \frac{1}{2520} Y_{96-}$	$\frac{512\pi}{19} \cdot 165$	×			×	
$K_{9,2} = Y_{94-} - \frac{1}{4080} Y_{98-}$	$\frac{2048\pi}{19} \cdot \frac{243 \cdot 5005}{17}$	×		×		
$K_{10,1} = Y_{10,0+} - \frac{1}{5460}(Y_{10,4} + \frac{1}{4320} Y_{10,8+})$	$\frac{512\pi}{21} \cdot \frac{3}{65}$	×	×	×	×	×
$K_{10,2} = Y_{10,2+} + \frac{1}{43680}(Y_{10,6+} + \frac{1}{456} Y_{10,10+})$	$\frac{2048\pi}{21} \cdot \frac{4455}{247}$	×	×			

The mean-square displacement of the atom from its mean position in the direction of the vector $\mathbf{v}$ is given by

$$\langle \mathbf{u}^2 \rangle_{\mathbf{v}} = \mathbf{v}^T \mathbf{g}^T \boldsymbol{\sigma}_{\mathbf{u}} \mathbf{g} \mathbf{v} / (\mathbf{v}^T \mathbf{g} \mathbf{v}), \tag{6.1.1.32}$$

where g_{ij} is the covariant metric tensor with the scalar products of the unit-cell vectors $\mathbf{a}_i \cdot \mathbf{a}_j$ as components.

The thermal motion for atoms in crystals is often displayed as surfaces of constant probability density. The surface for the thermal displacement $\mathbf{u}$ is defined by

$$\mathbf{u}^T \boldsymbol{\sigma}_{\mathbf{u}}^{-1} \mathbf{u} = C^2. \tag{6.1.1.33}$$

The square of the distance from the origin to the equiprobability surface in the direction $\mathbf{v}$ is

$$C^2 \mathbf{v}^T \mathbf{g} \mathbf{v} / (\mathbf{v}^T \boldsymbol{\sigma}_{\mathbf{u}}^{-1} \mathbf{v}). \tag{6.1.1.34}$$

This is equal to (6.1.1.32) for C unity only if $\mathbf{v}$ coincides with a principal axis of the vibration ellipsoid.

The probability that a displacement falls within the ellipsoid defined by C is

$$(2/\pi)^{1/2} \int_0^C q^2 \exp(-q^2/2)\, \mathrm{d}q. \tag{6.1.1.35}$$

6.1.1.6. *The generalized temperature factor*

The Gaussian model of the probability density function (p.d.f.) $\rho_o(\mathbf{u})$ for atomic thermal motion defined in (6.1.1.30) is adequate in many cases. Where anharmonicity or curvilinear motion is important, however, more elaborate models are needed.

In the classical (high-temperature) regime, the generalized temperature factor is given by the Fourier transform of the one-particle p.d.f:

$$\rho(\mathbf{u}) = N^{-1} \exp[-V(\mathbf{u})/kT], \tag{6.1.1.36}$$

where

$$N = \int \exp[-V(\mathbf{u})/kT]\, \mathrm{d}\mathbf{u}. \tag{6.1.1.37}$$

In the cases where the potential function $V(\mathbf{u})$ is a close approximation to the Gaussian (harmonic) potential, series expansions based on a perturbation treatment of the anharmonic terms provide a satisfactory representation of the temperature factors. That is, if the deviations from the Gaussian shape are small, approximations obtained by adding higher-order corrections to the Gaussian model are satisfactory.

In an arbitrary coordinate system, the number of significant high-order tensor coefficients for the correction is large. It may be helpful to choose coordinates parallel to the principal axes for the harmonic approximation so that

$$V(\mathbf{u})/kT = 1/2 \sum_{i=1}^{3} (B_i u_i)^2, \tag{6.1.1.38}$$

in which case (6.1.1.36) may be written as

$$\rho_o(\mathbf{u}) = \frac{1}{N_0} \exp\left[-1/2 \sum_i (B_i u_i)^2 \right], \tag{6.1.1.39}$$

where

$$N_0 = \frac{B_1 B_2 B_3}{8\pi^3}. \tag{6.1.1.40}$$

The harmonic temperature factor is

$$T_o(\mathbf{S}) = \exp\left[-1/2 \sum_i (b_i S_i)^2 \right], \tag{6.1.1.41}$$

where b_i and B_i are related by the reciprocity condition

$$b_i B_i = 1. \tag{6.1.1.42}$$

references