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_α is given by an exponential of the form

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

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

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

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

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

where h_i are the covariant Miller indices, $\mathbf{a}^i$ are the reciprocal-cell basis vectors and $1 \le \iota, \varphi \le 3$. 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

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

with $\beta_\alpha^{ij} = 2\pi^2|\mathbf{a}^i||\mathbf{a}^j|U_\alpha^{ij}$ (no summation). Both $\mathbf{h}$ and $\boldsymbol{\beta}$ are dimensionless tensorial quantities; $\mathbf{h}$ transforms as a covariant tensor of rank 1, $\boldsymbol{\beta}$ 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_α, 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:

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

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

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

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 β^{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 β^{ij}, which transform on a change of the direct-lattice base (according to $\mathbf{a}_k = A_{ki}\mathbf{a}_i$) as

$$\beta^{kl} = A_{ki}A_{lj}\beta^{ij}. \tag{1.9.2.1}$$

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 α. 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 β^{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

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

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

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

references