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Symmetry relations among coefficients of the anisotropic temperature factor.

By Henri A. Levy,
Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.

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In the least-squares refinement of crystal structures involving anisotropic temperature motion, individual atom temperature factors $\exp(-M_{\mathbf{h}})$ are conveniently introduced by expressing $M_{\mathbf{h}}$ in the form

$$M_{\mathbf{h}} = \sum_{i=1}^{3}\sum_{j=1}^{3}\beta_{ij}h_ih_j,\ \beta_{ij} = \beta_{ji}\,, \qquad (1)$$

where $\mathbf{h} = \sum_{i=1}^{3} h_i\mathbf{b}_i$ is the reciprocal-lattice vector for the reflection. Two problems which arise are (1) the determination of relations among the β_{ij} for symmetry-related atoms, and (2) the determination of restrictions among the β_{ij} for an atom in a position of special symmetry. A derivation of these relations applicable to any type of position in any space group is given here, and examples are presented.

Temperature factor (1) corresponds to a Gaussian distribution of scattering matter in three dimensions having a mean-square component of displacement in any direction $\mathbf{h}$ given by a sum of squares of components in the three orthogonal principal axis directions:

$$\langle\mu_{\mathbf{h}}^2\rangle_{\text{av.}} = \sum_{r=1}^{3}(\boldsymbol{\mu}^{(r)}\cdot\mathbf{h}/|\mathbf{h}|)^2\,. \qquad (2)$$

Here $\boldsymbol{\mu}^{(r)}$ is a vector parallel to principal displacement r whose magnitude is the root-mean-square displacement in that direction. The problem of finding the vectors $\boldsymbol{\mu}^{(r)}$ from the coefficients β_{ij} is discussed by Waser (1955). In the present discussion, the formulation of the β_{ij} in terms of the components $\varrho_i^{(r)}$, $i = 1, 2, 3$, of $\boldsymbol{\mu}^{(r)}$ resolved along the crystal axes $\mathbf{a}_i$ is desired:

$$\boldsymbol{\mu}^{(r)} = \sum_{i=1}^{3}\varrho_i^{(r)}\mathbf{a}_i,\ r = 1, 2, 3\,. \qquad (3)$$

If now $\mathbf{h}$ is identified as a reciprocal-lattice vector, equation (2) becomes

$$\langle\mu_{\mathbf{h}}^2\rangle_{\text{av.}} = \frac{1}{|\mathbf{h}|^2}\sum_{r=1}^{3}\left(\sum_{i=1}^{3}h_i\varrho_i^{(r)}\right)^2 = \frac{1}{|\mathbf{h}|^2}\sum_{i=1}^{3}\sum_{j=1}^{3}h_ih_j\sum_{r=1}^{3}\varrho_i^{(r)}\varrho_j^{(r)}\,.$$

The temperature factor exponent (see, for example, James, 1954) is given by

$$M_{\mathbf{h}} = 2\pi^2|\mathbf{h}|^2\langle\mu_{\mathbf{h}}^2\rangle_{\text{av.}}\,,$$

so that the β_{ij} in (1) are related to the crystal axis components of the principal root-mean-square thermal displacements by

$$\beta_{ij} = 2\pi^2\sum_{r=1}^{3}\varrho_i^{(r)}\varrho_j^{(r)}\,. \qquad (4)$$

The components $\varrho_i^{(r)}$ transform under symmetry operations as do the coordinates of general positions x_i in the unit cell, except of course that there are no translational components. The behavior of the β_{ij} can conveniently be found, in accord with equation (4), by examining the transformation of the quadratic products x_ix_j in which translational terms are ignored.

The following rules thus give the desired relationships:

Rule 1.—The quantities β_{ij} for distinct positions, general or special, related by a symmetry operation are related as are the quadratic products of atomic coordinates, translational terms being ignored, for general positions related by the symmetry operation.

Rule 2.—The quantities β_{ij} associated with a position of special symmetry are restricted as required by the invariance of all β_{ij}, when transformed as described by Rule 1 above, under all symmetry operations leaving the position invariant.

The use of these rules is illustrated by the following examples. In space group D_{6h}^4–$6_3/mmc$, (x, y, z) is a general position of set (l) and β_{ij} are the associated temperature factor coefficients. The coefficients β'_{ij} associated with two other positions of the set are listed in Table 1.

Table 1

	Position x, y, z transforms to $y-x, y, z$		Position x, y, z transforms to $x-y, x, \frac{1}{2}+z$	
ij	$x'_ix'_j$	β'_{ij}	$x'_ix'_j$	β'_{ij}
11	$y^2-2xy+x^2$	$\beta_{22}-2\beta_{12}+\beta_{11}$	$x^2-2xy+y^2$	$\beta_{11}-2\beta_{12}+\beta_{22}$
22	y^2	β_{22}	x^2	β_{11}
33	z^2	β_{33}	z^2	β_{33}
12	y^2-xy	$\beta_{22}-\beta_{12}$	x^2-xy	$\beta_{11}-\beta_{12}$
23	yz	β_{23}	xz	β_{31}
31	$yz-xz$	$\beta_{23}-\beta_{31}$	$xz-yz$	$\beta_{31}-\beta_{32}$

Consider now the special position $(x, 2x, z)$ of set (k) of the same space group. This position lies in a mirror plane whose operation transforms the general atomic coordinates as in the left-hand half of the preceding table. According to Rule 2, the β_{ij} must remain invariant to the transformation. Thus

$$\begin{aligned}\beta_{11} &= \beta_{22}-2\beta_{12}+\beta_{11}\,,\\ \beta_{12} &= \beta_{22}-\beta_{12}\,,\\ \beta_{31} &= \beta_{23}-\beta_{31}\,.\end{aligned}$$

These equalities require that the β_{ij} be restricted by

$$\beta_{12} = \tfrac{1}{2}\beta_{22},\ \beta_{31} = \tfrac{1}{2}\beta_{23}\,,$$

so that only four independent coefficients exist for positions of set (k). These restrictions correspond to fixing the direction of one principal axis of displacement normal to the mirror plane.

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References

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