

## Symmetry Transformations of General Anisotropic Temperature Factors\*

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The effects of all possible crystallographic symmetry operations on general ellipsoidal atomic temperature factors are presented in tabular form. Examples of the application of these tables are given.

The availability of high-speed computers has made practicable detailed analysis of anisotropic thermal vibrations of atoms in crystals when the accuracy of the intensity data warrants it. The importance of the detailed study of temperature factors has been stressed by McWeeny (1954) in his discussion of 'bond corrections' to isolated-atom form factors, and anisotropic vibrations have been considered in a great many recent structure determinations. In all coding for crystallographic calculations on SWAC (Sparks, Prosen, Kruse & Trueblood, 1956), provision has been made for general ellipsoidal temperature factors for each separate atom in the structure, if desired. In the course of this work, the effects of all possible crystallographic symmetry operations on these general temperature factors have been derived, and since these relations should be of value to others working with anisotropic temperature factors in various space groups, they are presented here. The relations for the special case of centrosymmetric monoclinic crystals have been given previously by Rollett & Davies (1955), who also discussed the calculation of the constants of the vibration ellipsoid from the temperature-factor parameters.

The present results were derived by straightforward application of vector analysis to determine the effect of the symmetry operations upon the direction cosines of the principal axes of the temperature-factor ellipsoid

with respect to the reciprocal crystallographic axes. The general form of the temperature factor may be expressed as  $\exp[-\beta]$ , where

$$\beta = B_{11}h_1^2 + B_{22}h_2^2 + B_{33}h_3^2 + B_{12}h_1h_2 + B_{13}h_1h_3 + B_{23}h_2h_3. \quad (1)$$

Primed symbols, e.g.  $B'_{ik}$ , are used below to represent the corresponding terms after application of a symmetry operation. Although in practical application of (1) an additional subscript is needed to designate the particular atom in the asymmetric unit to which reference is made, this subscript is not needed in the present discussion and has therefore been omitted.

Translations and inversions are without effect upon the general form of the temperature factor because they do not alter the orientation of the vibration ellipsoid (which is itself centrosymmetric). Consequently, mirror planes and glide planes produce precisely the same effect as would a twofold axis normal to them, and thus need not be explicitly considered. Similarly, inversion axes of order higher than two, and all screw axes, have just the same effect as the corresponding simple rotation axes. Thus in the accompanying tabular presentations of the needed relationships the only operations explicitly listed are rotation axes of order 2, 3, 4 and 6.

Table 1 presents the results for crystals belonging to the monoclinic system and the various systems with orthogonal axes. Table 2 summarizes the results for crystals indexed in the hexagonal system; not all of these results are independent of one another, but in

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Table 1. *Temperature-factor transformations for monoclinic, orthorhombic, tetragonal and cubic systems*

Order of axis	Axis parallel to	$B'_{11}$	$B'_{22}$	$B'_{33}$	$B'_{12}$	$B'_{13}$	$B'_{23}$
2	$\mathbf{a}_1$	$B_{11}$	$B_{22}$	$B_{33}$	$-B_{12}$	$-B_{13}$	$+B_{23}$
2	$\mathbf{a}_2$	$B_{11}$	$B_{22}$	$B_{33}$	$-B_{12}$	$+B_{13}$	$-B_{23}$
2	$\mathbf{a}_3$	$B_{11}$	$B_{22}$	$B_{33}$	$+B_{12}$	$-B_{13}$	$-B_{23}$
2	$\mathbf{a}_1 + \mathbf{a}_2$	$B_{22}$	$B_{11}$	$B_{33}$	$+B_{12}$	$-B_{23}$	$-B_{13}$
2	$\mathbf{a}_2 + \mathbf{a}_3$	$B_{11}$	$B_{33}$	$B_{22}$	$-B_{13}$	$-B_{12}$	$+B_{23}$
2	$\mathbf{a}_3 + \mathbf{a}_1$	$B_{33}$	$B_{22}$	$B_{11}$	$-B_{23}$	$+B_{13}$	$-B_{12}$
3	$\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3$	$B_{33}$	$B_{11}$	$B_{22}$	$+B_{13}$	$+B_{23}$	$+B_{12}$
4	$\mathbf{a}_1$	$B_{11}$	$B_{33}$	$B_{22}$	$-B_{13}$	$+B_{12}$	$-B_{23}$
4	$\mathbf{a}_2$	$B_{33}$	$B_{22}$	$B_{11}$	$+B_{23}$	$-B_{13}$	$-B_{12}$
4	$\mathbf{a}_3$	$B_{22}$	$B_{11}$	$B_{33}$	$-B_{12}$	$-B_{23}$	$+B_{13}$

Table 2. *Temperature-factor transformations for the hexagonal system*

Order of axis	Axis parallel to	$B'_{11}$	$B'_{22}$	$B'_{33}$	$B'_{12}$	$B'_{13}$	$B'_{23}$
2	$\mathbf{a}_1$	$B_{11} + B_{22} - B_{12}$	$B_{22}$	$B_{33}$	$2B_{22} - B_{12}$	$B_{23} - B_{13}$	$+B_{23}$
2	$\mathbf{a}_2$	$B_{11}$	$B_{11} + B_{22} - B_{12}$	$B_{33}$	$2B_{11} - B_{12}$	$+B_{13}$	$B_{13} - B_{23}$
2	$\mathbf{a}_1 + \mathbf{a}_2$	$B_{22}$	$B_{11}$	$B_{33}$	$B_{12}$	$-B_{23}$	$-B_{13}$
2	$2\mathbf{a}_1 + \mathbf{a}_2$	$B_{11}$	$B_{11} + B_{22} - B_{12}$	$B_{33}$	$2B_{11} - B_{12}$	$-B_{13}$	$B_{23} - B_{13}$
2	$2\mathbf{a}_2 + \mathbf{a}_1$	$B_{11} + B_{22} - B_{12}$	$B_{22}$	$B_{33}$	$2B_{22} - B_{12}$	$B_{13} - B_{23}$	$-B_{23}$
6	$\mathbf{a}_3$	$B_{11} + B_{22} - B_{12}$	$B_{11}$	$B_{33}$	$2B_{11} - B_{12}$	$B_{13} - B_{23}$	$+B_{13}$

Table 3. *Temperature-factor transformations for the trigonal system\**

Order of axis:	3	2	2
Axis parallel to:	$(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)$	$(\mathbf{a}_1 - \mathbf{a}_2)$	$(\mathbf{a}_1 + \mathbf{a}_2 - 2\mathbf{a}_3)$
$B'_{11} =$	$B_{33}$	$B_{22}$	$\frac{1}{3}(4B_{11} + B_{22} + 4B_{33} - 2B_{12} + 4B_{13} - 2B_{23})$
$B'_{22} =$	$B_{11}$	$B_{11}$	$\frac{1}{3}(B_{11} + 4B_{22} + 4B_{33} - 2B_{12} - 2B_{13} + 4B_{23})$
$B'_{33} =$	$B_{22}$	$B_{33}$	$\frac{1}{3}(4B_{11} + 4B_{22} + B_{33} + 4B_{12} - 2B_{13} - 2B_{23})$
$B'_{12} =$	$+B_{13}$	$+B_{12}$	$\frac{1}{3}(-4B_{11} - 4B_{22} + 8B_{33} + 5B_{12} + 2B_{13} + 2B_{23})$
$B'_{13} =$	$+B_{23}$	$+B_{23}$	$\frac{1}{3}(8B_{11} - 4B_{22} - 4B_{33} + 2B_{12} + 2B_{13} + 5B_{23})$
$B'_{23} =$	$+B_{12}$	$+B_{13}$	$\frac{1}{3}(-4B_{11} + 8B_{22} - 4B_{33} + 2B_{12} + 5B_{13} + 2B_{23})$

\* With rhombohedral indexing.

practical application each of the relations is useful. Table 3, in which the arrangement is somewhat different because of the complexity of some of the expressions, gives the relations for rhombohedral indexing of trigonal crystals.

Only the result of the first application of each symmetry operation is given here. For operations of order higher than two, the expressions for positions related by several successive operations may be derived readily by applying the indicated relations an appropriate number of times. The following examples are illustrative; in each, we seek an expression for the temperature-factor exponent of an atom related by some symmetry operation, or combination of operations, to a standard atom at  $(x, y, z)$  and we wish this expression in terms of the coefficients for the standard atom as given in (1).

*Example I.*—Space group  $P6_3mc$ , position  $(\bar{y}, x - y, z)$ . This position is related to the standard position by two successive applications of the  $6_3$ -operation. Thus from Table 2 we use the relations for a sixfold axis parallel to  $\mathbf{a}_3$ . After the first application, we have

$$\begin{aligned} B'_{11} &= B_{11} + B_{22} - B_{12}, & B'_{12} &= 2B_{11} - B_{12}, \\ B'_{22} &= B_{11}, & B'_{13} &= B_{13} - B_{23}, \\ B'_{33} &= B_{33}, & B'_{23} &= B_{13}; \end{aligned}$$

and then application of the same relations again, this time to the  $B'_{ik}$ , leads to the desired relations:

$$\begin{aligned} B''_{11} &= B'_{11} + B'_{22} - B'_{12} = B_{22}, \\ B''_{22} &= B'_{11} = B_{11} + B_{22} - B_{12}, \\ B''_{33} &= B'_{33} = B_{33}, \\ B''_{12} &= 2B'_{11} - B'_{12} = 2B_{22} - B_{12}, \\ B''_{13} &= B'_{13} - B'_{23} = -B_{23}, \\ B''_{23} &= B'_{13} = B_{13} - B_{23}. \end{aligned}$$

*Example II.*—Space group  $P6_3mc$ , position  $(\bar{x}, y - x, \frac{1}{2} + z)$ . This position is related to  $(x, y, z)$  by the  $c$  glide normal to  $2\mathbf{a}_1 + \mathbf{a}_2$ . This glide-plane is equivalent for our purposes to a two-fold axis parallel to  $2\mathbf{a}_1 + \mathbf{a}_2$ , since translations and inversions have no effect on the vibration ellipsoid. Thus from Table 2 we find

$$\begin{aligned} B'_{11} &= B_{11}, & B'_{12} &= 2B_{11} - B_{12}, \\ B'_{22} &= B_{11} + B_{22} - B_{12}, & B'_{13} &= -B_{13}, \\ B'_{33} &= B_{33}, & B'_{23} &= B_{23} - B_{13}. \end{aligned}$$

Precisely these same relations may be obtained by application of the mirror-plane (equivalent here to a twofold axis parallel to  $\mathbf{a}_1$ ) followed by the  $6_3$ -axis, since this combination of operations also transforms  $(x, y, z)$  to  $(\bar{x}, y - x, \frac{1}{2} + z)$ .

*Example III.*—Space group  $P4_2/mbc$ , position  $(\frac{1}{2} - y, \frac{1}{2} - x, \frac{1}{2} - z)$ . This position is related to  $(x, y, z)$  by successive application of the  $c$ -glide and the mirror, which are equivalent for our purposes to twofold axes parallel to  $(\mathbf{a}_1 + \mathbf{a}_2)$  and  $(\mathbf{a}_3)$  respectively. Thus from Table 1, we obtain first

$$\begin{aligned} B'_{11} &= B_{22}, & B'_{12} &= +B_{12}, \\ B'_{22} &= B_{11}, & B'_{13} &= -B_{23}, \\ B'_{33} &= B_{33}, & B'_{23} &= -B_{13}; \end{aligned}$$

and finally

$$\begin{aligned} B''_{11} &= B'_{11} = B_{22}, & B''_{12} &= +B_{12} = +B_{12}, \\ B''_{22} &= B'_{22} = B_{11}, & B''_{13} &= -B'_{13} = +B_{23}, \\ B''_{33} &= B'_{33} = B_{33}, & B''_{23} &= -B'_{23} = +B_{13}. \end{aligned}$$

As before, these same relations may be derived by any other combination of operations, for example,  $b$ -glide,  $m$  and  $4_2$ , which converts  $(x, y, z)$  to the desired position.

All of our structure-factor coding utilizes the general form of the structure-factor expression so that no special coding is needed for particular space groups. Consequently, the above expressions may be used directly, in the form of 'code words' (Sparks *et al.*, 1956) appropriate for each particular equivalent position. This, of course, is not possible when the Lonsdale expressions are used.

Atoms in special positions are treated in the same manner as atoms in general positions, except that the form factor used in the former case is  $(m/N)f_i$ , where  $N$  is the order of the space group and  $m$  is the order of

the special position in question. This procedure avoids the need for using different sets of equivalent positions, and thus different code words, for atoms in positions of different symmetry.

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## The Crystal Structures of $\text{SrZn}_5$ and $\text{BaZn}_5$

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The crystal structures of  $\text{SrZn}_5$  and  $\text{BaZn}_5$  have been determined from Weissenberg and precession camera data. The orthorhombic unit-cell dimensions are for  $\text{SrZn}_5$ ,  $a = 5.32$ ,  $b = 6.72$ ,  $c = 13.15$  Å,  $Z = 4$ ,  $Pm\bar{c}n$ ; for  $\text{BaZn}_5$ ,  $a = 5.32$ ,  $b = 8.44$ ,  $c = 10.78$  Å,  $Amam$ . The structures are related to the  $\text{CaZn}_5$  structure.

### Introduction

The crystal structures of  $\text{SrZn}_5$  and  $\text{BaZn}_5$  were determined as part of a program of study of the compounds formed by major groups I and II and the rare earths (*A*) and minor group II (*B*) elements. In the barium-zinc and strontium-zinc systems, the structures of the corresponding  $AZn_{13}$  compounds have been determined (Zintl & Häucke, 1937, 1938; Ketelaar, 1937). In the calcium-zinc system, in addition to the  $\text{CaZn}_{13}$  compound, the structure of  $\text{CaZn}_5$  has been reported (Häucke, 1940). Investigation of the barium and strontium systems in this region led to the determination of two new structures which are related to the  $\text{CaZn}_5$  structure.

### Experimental procedure

A bomb made of  $1\frac{1}{2}$  in.  $\times$  6 in. steel pipe with a cap at each end containing an alundum crucible was used as the reaction vessel for the preparation of the  $AZn_5$  compounds by direct combination of their elements. An extra piece of group IIa metal was used outside the alundum crucible to act as a 'getter'. The bomb was heated in a resistance furnace to 1000° C. and allowed to cool slowly.

The crystals formed were brittle, shiny, and dulled very slowly in a moist atmosphere. If prepared with

an excess of group IIa metal in order to prevent welding by  $AZn_{13}$  or zinc, an abundance of crystals could be separated by placing the reaction product on a wire screen and flushing off the group IIa rich portion with water. A duplicate chemical analysis made on  $\text{BaZn}_5$  by precipitating the barium as the sulfate and the zinc as the pyrophosphate showed 28.5% (26.6%) barium and 69.6% (69.5%) zinc, indicating  $\text{BaZn}_{5.12}$ . X-ray analysis alone was used to determine the composition of  $\text{SrZn}_5$ .

Single crystals were chosen and mounted in 0.3 mm. diameter capillaries. Multiple-film Weissenberg ( $\text{Cu } K\alpha$ ) diagrams were taken of the zero to third levels of the [100] zone for both compounds. Precession ( $\text{Mo } K\alpha$ ) diagrams were taken for the ( $h$  $k$ 0) and ( $h$ 0 $l$ ) data. The intensities of the diffraction spots were estimated by visual comparison to a graded scale. Absorption corrections were made for the  $\text{Cu } K\alpha$  radiation by assuming a cylindrical shape of the crystals.

### Determination of the structures

The cell constants of the orthorhombic crystals are given in Table 1.

Patterson projections were made from ( $h$  $k$ 0), ( $h$ 0 $l$ ) and (0 $k$  $l$ ) data. Both structures appeared to have all atoms spaced by 0,  $\frac{1}{4}a$  or  $\frac{1}{2}a$  in the  $a$  direction.