

# The Explicit Expression of the Atomic Thermal Parameters

William P. Jensen and Il-Hwan Suh\*

Chemistry Department, South Dakota State University, Brookings, SD 57007-0896 U.S.A.

\*Department of Physics, Chungnam National University, Taejeon 305-764, Korea

## 原子的 溫度 媒介變數의 正確한 表現

William P. Jensen · 徐日煥\*

Chemistry Department, South Dakota State University, Brookings, SD 57007-0896 U.S.A.

\*忠南大學校 物理學科, 大田 305-764, 大韓民國

### Abstract

The accurate expression of the anisotropic thermal parameters is either  $\exp(-2\pi^2 < h^2 \frac{u_x^2}{a^2} + k^2 \frac{u_y^2}{b^2} + l^2 \frac{u_z^2}{c^2} + 2hk \frac{u_x}{a} \frac{u_y}{b} + 2hl \frac{u_x}{a} \frac{u_z}{c} + 2kl \frac{u_y}{b} \frac{u_z}{c} >)$  with the small displacements  $u_x, u_y, u_z$  in absolute measure or  $\exp(-2\pi^2 < h^2 u_x^2 + k^2 u_y^2 + l^2 u_z^2 + 2hku_x u_y + 2hlu_x u_z + 2klu_y u_z >)$  with the small displacements  $u_x, u_y, u_z$  in fractional measure.

### 要 約

非等方性 溫度 媒介變數의 正確한 表現은 微小變位  $u_x, u_y, u_z$ 가 絶對量(Å單位)으로 測定되었을 때는  $\exp(-2\pi^2 < h^2 \frac{u_x^2}{a^2} + k^2 \frac{u_y^2}{b^2} + l^2 \frac{u_z^2}{c^2} + 2hk \frac{u_x}{a} \frac{u_y}{b} + 2hl \frac{u_x}{a} \frac{u_z}{c} + 2kl \frac{u_y}{b} \frac{u_z}{c} >)$ 이고, 微小變位  $u_x, u_y, u_z$ 가 分數量으로 測定되었을 때는  $\exp(-2\pi^2 < h^2 u_x^2 + k^2 u_y^2 + l^2 u_z^2 + 2hku_x u_y + 2hlu_x u_z + 2klu_y u_z >)$ 이다.

## 1. Introduction

The many different and ambiguous expressions for the anisotropic thermal parameters:

$$\exp[-(\alpha_1 h^2 a^{*2} + \beta_1 k^2 b^{*2} + \gamma_1 l^2 c^{*2} + \delta_1 hka^* b^* + \epsilon_1 hlb^* c^* + \eta_1 hla^* c^*)]^{(1)},$$

$$\exp[-2\pi^2(u_{11}^* x^{*2} + u_{22}^* y^{*2} + u_{33}^* z^{*2} + 2u_{12}^* x^* y^* + 2u_{13}^* x^* z^* + 2u_{23}^* y^* z^*)]^{(2)},$$

$$\exp[-(b_r^{11} h_1 h_1 + b_r^{22} h_2 h_2 + b_r^{33} h_3 h_3 + 2b_r^{12} h_1 h_2 + 2b_r^{13} h_1 h_3 + 2b_r^{23} h_2 h_3)]^{(3)},$$

$$\exp[-(\sum_{i=1}^3 \sum_{j=1}^3 h_i h_j \beta_{ij})]^{(4)},$$

$$\exp[-2\pi^2 \overline{u_j^2} h_j h_j]^{(5)},$$

$$\exp(-\frac{1}{2}(Q_1^2 \langle u_1^2 \rangle + Q_2^2 \langle u_2^2 \rangle + Q_3^2 \langle u_3^2 \rangle + 2Q_1 Q_2 \langle u_1 u_2 \rangle$$

$$+ 2Q_1 Q_3 \langle u_1 u_3 \rangle + 2Q_2 Q_3 \langle u_2 u_3 \rangle))^{(6)},$$

$$\exp[-2\pi^2 < h^2 a^{*2} u_x^2 + k^2 b^{*2} u_y^2 + l^2 c^{*2} u_z^2 + 2kha^* b^* u_x u_y$$

$$+ 2hla^* c^* u_x u_z + 2klb^* c^* u_y u_z >]^{(7)},$$

$$\exp[-2\pi^2(U_{11} h^2 a^{*2} + U_{22} k^2 b^{*2} + U_{33} l^2 c^{*2}$$

$$+ 2U_{12} hka^* b^* + 2U_{13} hla^* c^* + 2U_{23} klb^* c^*)]^{(8,9)},$$

and some wrong expressions for them:

$$\exp[-\frac{1}{4}(B_{11} h^2 a^{*2} + B_{22} k^2 b^{*2} + B_{33} l^2 c^{*2}$$

$$+ 2B_{12} hka^* b^* \cos \gamma^* + 2B_{13} hla^* c^* \cos \beta^*$$

$$+ 2B_{23} klb^* c^* \cos \alpha^*)]^{(10,11)},$$

make it difficult for us to identify their correct

expression. In this paper, the explicit expressions of the anisotropic and isotropic thermal factors are shown.

## 2. Theory

We assume that a set of lattice planes (hkl) satisfies the Bragg condition  $2d(\text{hkl}) \sin\theta(\text{hkl}) = \lambda$ , where  $d(\text{hkl})$  is an interplanar distance of planes (hkl),  $\theta$ : Bragg angle and  $\lambda$ : wave length. The vector  $\vec{d}^*(\text{hkl}) = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$  is parallel to the scattering vector of the planes (hkl) and therefore perpendicular to the planes (hkl) and the relation  $|\vec{d}^*(\text{hkl})| = \frac{1}{d(\text{hkl})}$  holds.

When an atom is lying at an arbitrary point P (x, y, z), where x, y, z are fractional coordinates in a unit cell, the vector from an origin to P is  $\vec{r} = x\vec{a} + y\vec{b} + z\vec{c}$ .

Since reflections from all points in one plane are in phase, it is necessary to consider only the distance perpendicular to the plane in dealing with the phase problem.

The magnitude of  $\vec{r}$  projected on  $\vec{d}^*$  is

$$\begin{aligned} \frac{\vec{d}^*}{d^*} \cdot \vec{r} &= \frac{1}{d^*} (h\vec{a}^* + k\vec{b}^* + l\vec{c}^*) \cdot (x\vec{a} + y\vec{b} + z\vec{c}) \\ &= d(hx + ky + lz) \end{aligned}$$

The path difference introduced by this distance for the same incident angle  $\theta$  is

$$2\left(\frac{\vec{d}^*}{d^*} \cdot \vec{r}\right) \sin\theta = 2d(hx + ky + lz) \sin\theta$$

and the phase difference in radians caused by this path difference for the given wave length  $\lambda$  is

$$\begin{aligned} \phi &= 2d(hx + ky + lz) \sin\theta \frac{2\pi}{\lambda} = \lambda(hx + ky + lz) \frac{2\pi}{\lambda} \\ &= 2\pi(hx + ky + lz) \end{aligned}$$

where the Bragg condition is employed.

The structure factor F is the resultant amplitude of diffracted waves with phases  $\phi_j$  and is expressed as a complex number.

$$F = \sum_j^n f_j \exp(i\phi_j)$$

If the atom lying at P(x, y, z) undergoes small displacements  $\frac{u_x}{a}, \frac{u_y}{b}, \frac{u_z}{c}$  by thermal agitation, the expression for F is

$$F = \sum_j^n f_j \exp[2\pi i(h\frac{u_x}{a} + k\frac{u_y}{b} + l\frac{u_z}{c})] \exp(i\phi_j) \quad (1)$$

and the first exponential factor in Eq. (1) is the temperature factor.

**2-1.** When the small displacements  $u_x, u_y, u_z$  are absolute measure, the displacement vector is

$$\vec{U} = \frac{u_x}{a}\vec{a} + \frac{u_y}{b}\vec{b} + \frac{u_z}{c}\vec{c}$$

and the magnitude of  $\vec{U}$  projected on  $\vec{d}^*$  is

$$\begin{aligned} \frac{\vec{d}^*}{d^*} \cdot \vec{U} &= d(h\vec{a}^* + k\vec{b}^* + l\vec{c}^*) \cdot \left(\frac{u_x}{a}\vec{a} + \frac{u_y}{b}\vec{b} + \frac{u_z}{c}\vec{c}\right) \\ &= d\left(h\frac{u_x}{a} + k\frac{u_y}{b} + l\frac{u_z}{c}\right) \end{aligned}$$

and the path difference introduced by the magnitude for the same incident angle  $\theta$  is

$$2d\left(h\frac{u_x}{a} + k\frac{u_y}{b} + l\frac{u_z}{c}\right) \sin\theta.$$

Employing the Bragg condition, the corresponding phase difference introduced by the path difference is given as

$$\begin{aligned} \phi &= 2d\left(h\frac{u_x}{a} + k\frac{u_y}{b} + l\frac{u_z}{c}\right) \sin\theta \frac{2\pi}{\lambda} \\ &= \lambda\left(h\frac{u_x}{a} + k\frac{u_y}{b} + l\frac{u_z}{c}\right) \frac{2\pi}{\lambda} \\ &= 2\pi\left(h\frac{u_x}{a} + k\frac{u_y}{b} + l\frac{u_z}{c}\right) = 2\pi(\vec{d}^* \cdot \vec{U}) \end{aligned}$$

and therefore the atomic temperature factor in Eq. (1) can be written as a time-average of  $\exp[2\pi i(\vec{d}^* \cdot \vec{U})]$ , i.e.,

$$\langle \exp[2\pi i(\vec{d}^* \cdot \vec{U})] \rangle \quad (2)$$

where  $\langle \dots \rangle$  denotes the time average.

Eq. (2) can be expanded as a power of  $\vec{d}^* \cdot \vec{U}$ :

$$\langle \exp(2\pi i \vec{d}^* \cdot \vec{U}) \rangle \equiv \langle \exp(2\pi i M) \rangle \\ = 1 + \frac{2\pi i \langle M \rangle}{1!} - \frac{4\pi^2 \langle M^2 \rangle}{2!} - \dots$$

where  $\langle M \rangle = 0$  since  $M$  are equally probable to be plus and minus for the time average of the phase change. So for sufficiently small displacements we have

$$\langle \exp(2\pi i \vec{d}^* \cdot \vec{U}) \rangle \doteq 1 - 2\pi^2 \langle (\vec{d}^* \cdot \vec{U})^2 \rangle \quad (3)$$

The first two terms of Eq. (3) are identical with the first two terms of the expansion

$$\exp(-\langle 2\pi^2 (\vec{d}^* \cdot \vec{U})^2 \rangle) \equiv \exp(-\langle 2\pi^2 P \rangle) \\ = 1 - 2\pi^2 \frac{\langle P \rangle}{1!} + \dots \doteq 1 - 2\pi^2 \langle (\vec{d}^* \cdot \vec{U})^2 \rangle$$

and so the atomic temperature factor for sufficiently small displacements can be written as follows neglecting terms higher than the quadratic in products of displacements

$$\langle \exp(2\pi i \vec{d}^* \cdot \vec{U}) \rangle = \exp(-2\pi^2 \langle (\vec{d}^* \cdot \vec{U})^2 \rangle) \quad (4)$$

where

$$\langle (\vec{d}^* \cdot \vec{U})^2 \rangle = \langle (h \frac{u_x}{a} + k \frac{u_y}{b} + l \frac{u_z}{c})^2 \rangle \\ = \langle h^2 \frac{u_x^2}{a^2} + k^2 \frac{u_y^2}{b^2} + l^2 \frac{u_z^2}{c^2} + 2hk \frac{u_x}{a} \frac{u_y}{b} \\ + 2hl \frac{u_x}{a} \frac{u_z}{c} + 2kl \frac{u_y}{b} \frac{u_z}{c} \rangle$$

Therefore the anisotropic temperature factor is

$$\exp[-2\pi^2 \langle h^2 \frac{u_x^2}{a^2} + k^2 \frac{u_y^2}{b^2} + l^2 \frac{u_z^2}{c^2} + 2hk \frac{u_x}{a} \frac{u_y}{b} \\ + 2hl \frac{u_x}{a} \frac{u_z}{c} + 2kl \frac{u_y}{b} \frac{u_z}{c} \rangle] \quad (5)$$

Since  $a = \frac{1}{a^*}$ ,  $b = \frac{1}{b^*}$ ,  $c = \frac{1}{c^*}$  for orthogonal crystal systems, Eq. (5) becomes for orthogonal crystal systems:

$$\exp(-2\pi^2 \langle h^2 a^{*2} u_x^2 + k^2 b^{*2} u_y^2 + l^2 c^{*2} u_z^2 + 2hka^* b^* u_x u_y \\ + 2hla^* c^* u_x u_z + 2klb^* c^* u_y u_z \rangle)$$

**2-2.** When the small displacements  $u_x$ ,  $u_y$ ,  $u_z$  are the fractional measure, the displacement vector is

$$\vec{U} = u_x \vec{a} + u_y \vec{b} + u_z \vec{c}$$

and the magnitude of  $\vec{U}$  projected on  $\vec{d}^*$  is

$$\frac{\vec{d}^*}{d^*} \cdot \vec{U} = d(ha^* + kb^* + lc^*) \cdot (u_x \vec{a} + u_y \vec{b} + u_z \vec{c}) \\ = d(hu_x + ku_y + lu_z)$$

The path difference introduced by this displacement for an incident angle  $\theta$  is

$$2d(hu_x + ku_y + lu_z) \sin \theta$$

and the corresponding phase difference for an incident wave length  $\lambda$  is

$$\phi = 2d(hu_x + ku_y + lu_z) \sin \theta \frac{2\pi}{\lambda} \\ = 2\pi(hu_x + ku_y + lu_z) = 2\pi(\vec{d}^* \cdot \vec{U})$$

Just like Eq. (4), the temperature factor is expressed as

$$\langle \exp(2\pi i \vec{d}^* \cdot \vec{U}) \rangle = \exp(-2\pi^2 \langle (\vec{d}^* \cdot \vec{U})^2 \rangle)$$

where

$$\langle (\vec{d}^* \cdot \vec{U})^2 \rangle = \langle (hu_x + ku_y + lu_z)^2 \rangle \\ = \langle h^2 u_x^2 + k^2 u_y^2 + l^2 u_z^2 + 2hku_x u_y + 2hlu_x u_z + 2klu_y u_z \rangle$$

Therefore the anisotropic temperature factor is

$$\exp(-2\pi^2 \langle h^2 u_x^2 + k^2 u_y^2 + l^2 u_z^2 + 2hku_x u_y \\ + 2hlu_x u_z + 2klu_y u_z \rangle)$$

**2-3.** The isotropic thermal vibration means the magnitude of an atomic vibrational amplitude is the same in all directions. Therefore the fraction  $\frac{u}{d(hkl)}$  is a function of  $(hkl)$ . The atomic vibrational amplitude  $u$  in absolute measure introduces a path difference and accordingly a phase difference for the Bragg angle  $\theta$

$$2d(hkl) \frac{u}{d(hkl)} \sin \theta = \lambda \frac{u}{d(hkl)} = 2\pi \frac{u}{d(hkl)}$$

Like Eq. (4), we get

$$\langle \exp(2\pi i \frac{u}{d}) \rangle = \exp[-2\pi^2 \frac{\langle u^2 \rangle}{d^2}]$$

The isotropic temperature factor can be expressed in two different ways:

$$\exp[-2\pi^2 \frac{\langle u^2 \rangle}{d^2}] = \exp[-8\pi^2 \langle u^2 \rangle \frac{\sin^2 \theta (hkl)}{\lambda^2}]$$

using the Bragg condition and

$$\exp[-2\pi^2 \frac{\langle u^2 \rangle}{d^2}] = \exp[-2\pi^2 \langle u^2 \rangle (h^2 a^{-2} + k^2 b^{-2} + l^2 c^{-2} + 2hka^* b^* \cos \gamma^* + 2hla^* c^* \cos \beta^* + 2klb^* c^* \cos \alpha^*)]$$

using the formula for interplanar spacing.

### 3. Conclusion

The general expression for the anisotropic temperature factor is either

$$\exp(-2\pi^2 \langle h^2 \frac{u_x^2}{a^2} + k^2 \frac{u_y^2}{b^2} + l^2 \frac{u_z^2}{c^2} + 2hk \frac{u_x}{a} \frac{u_y}{b} + 2hl \frac{u_x}{a} \frac{u_z}{c} + 2kl \frac{u_y}{b} \frac{u_z}{c} \rangle)$$

with the small displacements  $u_x$ ,  $u_y$ ,  $u_z$  in absolute measure or

$$\exp(-2\pi^2 \langle h^2 u_x^2 + k^2 u_y^2 + l^2 u_z^2 + 2hku_x u_y + 2hlu_x u_z + 2klu_y u_z \rangle)$$

with the small displacements  $u_x$ ,  $u_y$ ,  $u_z$  in fractional measure.

Specifically for orthogonal crystal systems, it is expressed as

$$\exp(-2\pi^2 \langle h^2 a^{-2} u_x^2 + k^2 b^{-2} u_y^2 + l^2 c^{-2} u_z^2 + 2hka^* b^* u_x u_y + 2hla^* c^* u_x u_z + 2klb^* c^* u_y u_z \rangle)$$

with the small displacements  $u_x$ ,  $u_y$ ,  $u_z$  in absolute measure.

The two expressions for the isotropic temperature factor are

$$\exp(-8\pi^2 \langle u^2 \rangle \frac{\sin^2 \theta}{\lambda^2})$$

and

$$\exp[-2\pi^2 \langle u^2 \rangle (h^2 a^{-2} + k^2 b^{-2} + l^2 c^{-2} + 2hka^* b^* \cos \gamma^* + 2hla^* c^* \cos \beta^* + 2klb^* c^* \cos \alpha^*)]$$

where  $u$  is an absolute measure.

### References

- 1) Davies, D. R. and Blum, J. J., *Acta Cryst.* **8**, 129-136 (1955).
- 2) Giacovazzo, C., Monaco, H. L., Viterbo, D., Scordari, F., Gilli, G., Zanotti, G. and Catti, M. pp. 148-149, pp. 186-188, International Union of Crystallography, Oxford University Press, New York (1992).
- 3) Ibers, J. A. and Hamilton, W. C., International Tables for X-Ray Crystallography. Vol. IV, p. 314, The Kynoch Press, Birmingham, England (1974).
- 4) Peterse, W. J. A. M. and Palm, J. H., *Acta Cryst.* **20**, 147-150 (1966).
- 5) Sands, D. E., Vectors and Tensors in Crystallography. pp. 69-72, Addison-Wesley Publishing Company, London · Amsterdam · Don Mills, Ontario · Sydney · Tokyo (1982).
- 6) Willis, B. T. M. and Pryor, A. W., Thermal Vibrations in Crystallography. pp. 81-102, Cambridge University Press, London · New York (1975).
- 7) Prince, E., Mathematical Techniques in Crystallography and Materials Science, 2nd Ed., pp. 62-65. Springer-Verlag, Berlin · Heidelberg · New York · London · Paris · Tokyo · Hong Kong · Barcelona · Budapest (1994).
- 8) Ladd, M. F. C. and Palmer, R. A., Structure Determination by X-Ray Crystallography, 2nd Edition, p. 418, Plenum Press, New York and London (1994).
- 9) Sheldrick, G. M., SHELXL93 Manual, p. 64. Program for the Refinement for the Refinement of Crystal Structure. University of Goettingen, Germany (1993).
- 10) Luger, P., Modern X-Ray Analysis on Single Crystals. pp. 151-152, Walter de Gruyter. Berlin · New York (1980).
- 11) Stout, G. H. and Jensen, L. H., X-ray structure determination, 2nd Ed., pp. 424-425, John Wiley and Sons, New York · Chichester · Brisbane · Toronto · Singapore (1989).