

Weak absorption case

Using expressions (6) and (12) and tables of the elliptic integrals one can easily calculate the integral intensity in every concrete situation. However, in most cases of practical interest the expression (12) can be simplified. As a rule, with the exception of some of the cases near an absorption edge, the X-ray absorption is small, so that $Im\chi_0 \ll |\chi_0|$ and, if the structure factor F_h is not accidentally close to zero and if the polarization factor C is not too small, the quantity s is small compared with unity.

In such a case the parameter k is close to unity (note that $q \leq 1$ always). Now using the expressions of the full elliptic integrals of the first and second type (Gradstein & Ryzhik, 1963) and the expansion

$$(1-q^2)E(-q^2, k) \simeq \frac{1}{2} \ln \left(\frac{8}{1+q} \frac{1-q}{1-k} \right) + \frac{1-q}{4} \ln \frac{1+q}{1-q}, \dots \quad (1-k \ll 1) \quad (13)$$

we find

$$P(s, q) \simeq 1 - \frac{3\pi}{4} s(1-2q^2s^2) + 3s^2 \left[\frac{1+q^2}{2} \ln \frac{4}{s(1+q)} - \frac{1+3q^2}{4} + \frac{(1-q)^2}{4} \ln \frac{1+q}{1-q} \right]. \quad (14)$$

The formula (14) has the simple analytic form and, for $s \leq 0.2$ (which occurs for most real situations) it gives an accuracy of more than one per cent. For $s \lesssim 0.05$

the main terms in (14) are

$$P(s, q) \simeq 1 - \frac{3\pi}{4} s$$

and the integral reflexion takes the very simple form

$$R_i = \frac{8}{3 \sin 2\theta_B} \left(\sqrt{\left| \frac{\gamma_h \chi_h}{\gamma_0 \chi_{\bar{h}}} \right|} |C\chi_h| - \frac{3\pi}{4} \frac{\gamma_0 + |\gamma_h|}{2\gamma_0} \left| \frac{\chi_h}{\chi_{\bar{h}}} \right| Im\chi_0 \right). \quad (15)$$

This result is very close to the empirical result received by Hirsch & Ramachandran (1950), where instead of $3\pi/4$ they have 2.4. Setting $Im\chi_0 = 0$ we get the well-known Darwin result.

If $s > 0.2$ then one has to use the general expression (12) for $P(s, q)$. We have tabulated the function $P(s, q)$ and the results are given in Table 1.

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Representational Surfaces for Thermal Motion

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Representational surfaces for the mean-square displacement, and the root-mean-square displacement, are derived for atomic thermal motion in the harmonic approximation. It is shown how the form of these surfaces depends on the way in which 'mean-square displacement' is defined. It is concluded that to represent atomic thermal motion a different surface may be required from the second-order (ellipsoidal) surface usually presented in reports of crystal structure determinations.

Introduction

The purpose of this article is to clarify the meaning of the 'thermal vibration ellipsoids' presented graphically, stereographically, or parametrically in reports of crystal structure determinations to represent atomic thermal motion in the harmonic approximation.

Provided the forces acting on any atom are linear in the relative displacements of the atoms (the har-

monic approximation), it may be shown (Lipson & Cochran, 1966, p. 300) that the probability of the atomic centre lying within a volume element $dx_1 dx_2 dx_3$ is $p(x_1 x_2 x_3) dx_1 dx_2 dx_3$, where

$$p(x_1 x_2 x_3) = [(2\pi)^{3/2} u_1 u_2 u_3]^{-1} \exp [-(x_1^2/2u_1^2 + x_2^2/2u_2^2 + x_3^2/2u_3^2)]. \quad (1)$$

x_1 , x_2 , and x_3 are displacements along orthogonal axes

coincident with the principal axes of the family of ellipsoids

$$x_1^2/2u_1^2 + x_2^2/2u_2^2 + x_3^2/2u_3^2 = k, \quad (k > 0), \quad (2)$$

which represent surfaces of constant probability in direct space. u_i^2 ($i=1,2,3$) is the mean-square displacement (hereafter, m.s.d.) in the x_i direction, where the m.s.d. is defined by

$$\overline{x_i^2} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} x_i^2 p(x_1 x_2 x_3) dx_1 dx_2 dx_3, \quad i=1,2,3. \quad (3)$$

The semi-axes of the ellipsoidal surfaces (2) are proportional to the corresponding root-mean-square displacements (hereafter, r.m.s.d.). The 'thermal vibration ellipsoid' is a member of the family of ellipsoids (2) (see, for example, Lipson & Cochran, 1966, p. 300).

Definitions of mean-square displacement

Equation (3) formulates, along principal vibration axes, a particular definition of the m.s.d. of an atom. In fact,

$$\overline{x_i^2} = \frac{[(2\pi)^{3/2} u_1 u_2 u_3]^{-1} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} X_1^2 X_1^2 \exp[-X_1^2(n_1^2/2u_1^2 + n_2^2/2u_2^2 + n_3^2/2u_3^2)] dX_1 dX_2 dX_3}{[(2\pi)^{3/2} u_1 u_2 u_3]^{-1} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} X_1^2 \exp[-X_1^2(n_1^2/2u_1^2 + n_2^2/2u_2^2 + n_3^2/2u_3^2)] dX_1 dX_2 dX_3}, \quad (7)$$

there are *two* quite different definitions of m.s.d. implicit in the description given by crystallographers of crystal structures and elastic diffraction processes. A derivation of the possible representational surfaces and parameters for the description of atomic thermal motion, in terms of each of these two m.s.d.'s, clarifies the relationships between the surfaces and the parameters *actually* used.

In a general direction defined by the unit vector \mathbf{n} (always through the point $x_1=x_2=x_3=0$) the m.s.d. of an atom may be defined as either

(A) the mean value of the square of the projections onto the direction \mathbf{n} of *all* displacements, or

(B) the mean value of the square of the displacements lying within an elemental solid angle about the direction \mathbf{n} .

Equations (3), and hence u_1^2 , u_2^2 , and u_3^2 , correspond to definition (A).

Hereafter, the m.s.d.'s obtained under the two definitions (A) and (B) are denoted m.s.d.A. and m.s.d.B., respectively. Along \mathbf{n} , m.s.d.A. = $u_{\mathbf{A}}^2 = (\mathbf{x} \cdot \mathbf{n})^2$

$$= [(2\pi)^{3/2} u_1 u_2 u_3]^{-1} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} (\mathbf{x} \cdot \mathbf{n})^2 \exp[-(x_1^2/2u_1^2 + x_2^2/2u_2^2 + x_3^2/2u_3^2)] dx_1 dx_2 dx_3. \quad (4)$$

This reduces to

$$u_{\mathbf{A}}^2 = u_1^2 n_1^2 + u_2^2 n_2^2 + u_3^2 n_3^2, \quad (5)$$

where n_i is the component of \mathbf{n} along axis x_i , $i=1,2,3$.

To derive m.s.d.B. in the same direction \mathbf{n} , consider three orthogonal axes X_1, X_2, X_3 with X_1 and \mathbf{n} coincident, and an elemental solid angle about X_1 with a rectangular cross-section of sides δX_2 and δX_3 , subtending angles $\delta\alpha$ and $\delta\beta$ respectively at the origin. The probability of the atomic centre lying within a volume element $dX_1 \delta X_2 \delta X_3$ is $p(x_1 x_2 x_3) dX_1 \delta X_2 \delta X_3$. Now

$$x_i = n_i X_1, \quad i=1,2,3,$$

$$\delta X_2 = X_1 \cdot \delta\alpha,$$

$$\text{and} \quad \delta X_3 = X_1 \cdot \delta\beta.$$

Therefore,

$$p(x_1 x_2 x_3) dX_1 \delta X_2 \delta X_3 = p_{\mathbf{B}}(X_1) dX_1 = [(2\pi)^{3/2} u_1 u_2 u_3]^{-1} \exp[-X_1^2(n_1^2/2u_1^2 + n_2^2/2u_2^2 + n_3^2/2u_3^2)] X_1^2 dX_1 \delta\alpha \delta\beta, \quad (6)$$

defining $p_{\mathbf{B}}(X_1)$.

Thus,

$$\text{m.s.d.B.} = u_{\mathbf{B}}^2 = \overline{X_1^2}$$

which gives

$$3/u_{\mathbf{B}}^2 = n_1^2/u_1^2 + n_2^2/u_2^2 + n_3^2/u_3^2. \quad (8)$$

In the general direction \mathbf{n} , it may be shown that the one-dimensional distribution function for displacement-components parallel to \mathbf{n} [definition (A)] is Gaussian, while that for displacements within an elemental solid angle about \mathbf{n} [definition (B)] is of a different form. The distribution function corresponding to definition (A) is obtained by projecting the three-dimensional Gaussian function (1) onto a line parallel to \mathbf{n} . The resulting one-dimensional function is found to be

$$p_{\mathbf{A}}(X_1) = [(2\pi)^{1/2} (u_1^2 n_1^2 + u_2^2 n_2^2 + u_3^2 n_3^2)]^{-1} \exp\{(-X_1^2/2) [1/(u_1^2 n_1^2 + u_2^2 n_2^2 + u_3^2 n_3^2)]\}, \quad (9)$$

which is a normalized Gaussian function. The distribution function corresponding to definition (B) is given directly by equation (6), and is clearly not a Gaussian function; $p_{\mathbf{B}}(X_1) = 0$ at the origin ($x_1=x_2=x_3=0$).

It may be remarked that along the three principal axes, x_1, x_2 and x_3 , $u_{\mathbf{B}}^2 = 3u_{\mathbf{A}}^2$. This follows directly from equations (5) and (8).

Representational surfaces

The representational surfaces for the m.s.d. and r.m.s.d. of both definitions may now be derived. The surface whose radius $|\mathbf{r}|$, in any direction, is equal to

m.s.d.A. in that direction is given by

$$|\mathbf{r}| = (x_1^2 + x_2^2 + x_3^2)^{1/2} = u_A^2 = (x_1^2 + x_2^2 + x_3^2)^{-1}(u_1^2 x_1^2 + u_2^2 x_2^2 + u_3^2 x_3^2),$$

so that

$$(u_1^2 x_1^2 + u_2^2 x_2^2 + u_3^2 x_3^2)^2 = (x_1^2 + x_2^2 + x_3^2)^3, \quad (10)$$

which describes a sixth-order surface (always excluding the pathological solution $x_1 = x_2 = x_3 = 0$) known as an ovaloid (Nye, 1957, p.48). The surface whose radius $|\mathbf{r}|$ equals the corresponding r.m.s.d.A. is given by

$$|\mathbf{r}|^2 = x_1^2 + x_2^2 + x_3^2 = u_A^2,$$

so that

$$u_1^2 x_1^2 + u_2^2 x_2^2 + u_3^2 x_3^2 = (x_1^2 + x_2^2 + x_3^2)^2. \quad (11)$$

This is a fourth-order, or quartic, surface.

On the other hand, if $|\mathbf{r}|$ is equal to m.s.d.B. in any direction, then

$$|\mathbf{r}| = (x_1^2 + x_2^2 + x_3^2)^{1/2} = u_B^2 = 3(x_1^2 + x_2^2 + x_3^2)(x_1^2/u_1^2 + x_2^2/u_2^2 + x_3^2/u_3^2)^{-1},$$

and

$$(x_1^2/u_1^2 + x_2^2/u_2^2 + x_3^2/u_3^2)^2 = 9(x_1^2 + x_2^2 + x_3^2), \quad (12)$$

which describes a fourth-order, or quartic surface of a different form from (11). If $|\mathbf{r}|$ is equal to r.m.s.d.B., then

$$|\mathbf{r}|^2 = (x_1^2 + x_2^2 + x_3^2) = u_B^2,$$

and

$$x_1^2/u_1^2 + x_2^2/u_2^2 + x_3^2/u_3^2 = 3. \quad (13)$$

This is an ellipsoid, and coincides with a surface of constant probability in $p(x_1, x_2, x_3)$ [equations (1) and (2)].

Equations (10) to (13) describe surfaces in direct space; their radii have the dimension L (length). The surface whose radius is equal to (r.m.s.d.A.)⁻¹ is given by

$$|\mathbf{r}|^2 = (x_1^2 + x_2^2 + x_3^2) = u_A^{-2},$$

so that

$$u_1^2 x_1^2 + u_2^2 x_2^2 + u_3^2 x_3^2 = 1. \quad (14)$$

Equation (14) describes an ellipsoidal surface in reciprocal space (having radii of dimension L⁻¹), which may be identified with an 'ellipsoid of constant temperature factor'. This identification follows from the fact that the temperature factor is the Fourier transform of $p(x_1, x_2, x_3)$ [equation (1)], and is thus given by

$$\exp[-2\pi^2(u_1^2 H_1^2 + u_2^2 H_2^2 + u_3^2 H_3^2)], \quad (15)$$

where H_1, H_2, H_3 are the projections of the reciprocal lattice vector \mathbf{H} onto axes parallel to x_1, x_2, x_3 (see, for example, Lipson & Cochran, 1966, p.300).

Hence:

(i) the surfaces of constant temperature factor are ellipsoids in reciprocal space whose principal semi-axes are proportional to (r.m.s.d.A.)⁻¹; these surfaces represent constant values of the distribution function (15), and it is in terms of this function in reciprocal space that the elastic diffraction process 'detects' the thermal behaviour of the atoms comprising a crystal structure;

(ii) the 'inverse surface', which arises in Fourier transformation, is the quartic surface (11) whose radius is proportional to r.m.s.d.A.;

(iii) the 'square' of the latter surface is the ovaloid (10) whose radius is proportional to m.s.d.A.

Thus, of the parameters of thermal vibration discussed, the m.s.d. (or r.m.s.d.)A.'s are those most directly related to function (15), and, as commented below, it is indeed usual in representing thermal motion to use the principal r.m.s.d.A.'s, u_1, u_2 and u_3 . The m.s.d.B. and r.m.s.d.B. are, of course, also related to (15) but in a more complex way.

Conclusions

It becomes clear that the direct space 'thermal vibration ellipsoid' presented in reports of crystal structure determinations represents either

(i) a surface of constant probability in the function $p(x_1, x_2, x_3)$ [equations (1) and (2)], or,

(ii) the r.m.s.d. (definition B) of the atom, which, as remarked earlier, is a particular case of (i).

However, if the intention is to represent thermal motion in terms of the r.m.s.d.A. of an atom, then this is properly described either by the quartic surface (11), whose radius is equal to r.m.s.d.A. in any direction, or by the ellipsoidal surface (14), whose radius is equal to (r.m.s.d.A.)⁻¹ in any direction.

The ellipsoid (14), having radii of dimension L⁻¹, is, of course, to be distinguished from the 'thermal vibration ellipsoid' with radii of dimension L. The latter surface is usually derived (see, for example, Lipson & Cochran, 1966, chapter 11) by finding the directions of its principal axes, and the r.m.s.d.A.'s, u_1, u_2 , and u_3 , from the thermal vibration constants determined in least-squares refinement. The ellipsoid is drawn, or must be imagined, with semi-axial lengths proportional to the corresponding r.m.s.d.A.'s. This surface only represents the relative magnitudes of the r.m.s.d.A.'s of the atom along the principal vibration directions, and is otherwise related to the thermal motion of the atom in an unspecified way, unless the particular surface of constant probability depicted is stated. This is rarely done (it is, for example, in Nilsson, Liminga & Olovsson, 1968, where the ellipses bounding the projections of the 'thermal vibration ellipsoids' are scaled to enclose 50% probability). A recent paper (Sirota, Olekhovich & Olekhovich, 1968) shows 'ellipsoids of mean-square vibration displacements', and neither m.s.d.A. nor m.s.d.B. lies on an ellipsoidal surface (see (ii) and (iv) below).

The representational surfaces derived above may be summarized as follows:

(i) constant probability lies on an ellipsoid in direct space [equation (2)];

(ii) m.s.d.A. lies on an ovaloid in direct space [equation (10)];

(iii) r.m.s.d.A. lies on a quartic surface in direct space [equation (11)];

(iv) m.s.d.B. lies on a quartic surface in direct space [equation (12)];

(v) r.m.s.d.B. lies on an ellipsoid in direct space [equation (13)];

(vi) constant temperature factor lies on an ellipsoid in reciprocal space [equation (15)];

(vii) $(\text{r.m.s.d.A})^{-1}$ lies on an ellipsoid in reciprocal space [equation (14)].

Ellipsoids (i) and (v) are members of the same family of surfaces defined by equation (2). Ellipsoids (vi) and (vii) are both members of another family of surfaces [equations (14) and (15)].

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Méthode Générale d'Etude des Couplages entre Polarisation, Aimantation et Tensions dans les Cristaux

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An extension of Bertaut's macroscopic theory of magnetic and magnetoelectric couplings is presented. The components of electric and magnetic moments and the stress tensor are classified according to the irreducible representations of the crystal's magnetic group; couplings are possible only within a representation.

Couplages dans les cristaux paramagnétiques

Soit \mathbf{T}_A un tenseur d'ordre n représentant une grandeur physique A , ses 3^n composantes se transforment dans une rotation suivant la représentation $\Gamma_A = \mathbf{V}^n$ ou $\bar{\mathbf{V}}^n$, \mathbf{V} et $\bar{\mathbf{V}}$ étant respectivement les représentations vectorielles polaire et axiale du groupe des rotations (dans un cristal paramagnétique, donc invariant dans le renversement du temps, une grandeur magnétique A couplée à d'autres grandeurs non magnétiques intervient nécessairement un nombre pair p de fois, et par suite $\mathbf{V}^{np} = \bar{\mathbf{V}}^{np}$). Soit G le groupe ponctuel du cristal; Γ_A est réductible suivant les représentations irréductibles Γ_α de G et par suite on peut classer les composantes de \mathbf{T}_A , ou des combinaisons linéaires de ces composantes, suivant les représentations Γ_α .

Une manière simple d'effectuer cette classification consiste à utiliser la méthode de l'opérateur de projection (Melvin, 1956), quelles que soient les dimensions des représentations Γ_α , après avoir déterminé les propriétés de transformation des composantes de \mathbf{T}_A , A étant la polarisation \mathbf{P} , le tenseur des contraintes $\bar{\sigma}$, le tenseur des déformations $\bar{\mathbf{d}}$. Le théorème d'Unsöld (Tinkham, 1964) fournit alors des invariants tensoriels d'ordre 2 couplant deux grandeurs A et B : ce sont les

produits scalaires des vecteurs de base d'une même représentation extraits respectivement de l'espace des coordonnées des tenseurs \mathbf{T}_A et \mathbf{T}_B ; le terme énergétique $T_{Aijk} \cdot T_{Blmn}$ est invariant dans G si T_{Aijk} et T_{Blmn} appartiennent à la même représentation.

Le nombre d'invariants indépendants couplant les grandeurs A et B est égal au nombre d'interventions de la représentation identité Γ_1 de G dans la réduction de $\Gamma_A \times \Gamma_B$, ou encore au nombre de composantes irréductibles réelles communes à Γ_A et Γ_B (Sivardière & Waintal, 1969, à paraître).

La méthode ci-dessus généralise la théorie des couplages ferro et antiferro électriques et magnétiques développée par Bertaut (Bertaut, 1968). Elle permet de déterminer les couplages physiques autorisés par la symétrie G , c'est-à-dire de construire une fonction thermodynamique (énergie libre F) invariante dans G , combinaison linéaire des invariants indépendants d'Unsöld:

$$F = \sum_{ijk,lmn} T_{Aijk,lmn} T_{Aijk} T_{Blmn}.$$

Par des dérivations convenables, tenant compte de la symétrie intrinsèque du tenseur \mathbf{T}_a (souvent supérieure à celle du tenseur $\mathbf{T}_A \times \mathbf{T}_B$), on en déduit l'expression du tenseur \mathbf{T}_a décrivant les couplages entre