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## The Absorption-Correction Factor of Multifaceted Crystals

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### Abstract

A mathematical analysis of the evaluation of the absorption-correction factors in convex polyhedral crystals is made. Formulae are given that permit the exact evaluation of the factors and their derivatives and that do not depend on the subdivision of the crystal into tetrahedra. A new method of defining the Howells polyhedra as the included volume of a set of planes is also described. The method allows additional constraints to be introduced, which could be used to deal with inhomogeneities in either the crystal or the incident beam. Computation based on these ideas gives rapid and exact evaluation of both the absorption-correction factor and its derivatives, with negligible rounding-error problems. In addition, a formula is given for scattering by a general tetrahedron with a wide range of orientations that can be used as a test of computer programs.

### Introduction

The transmission (or absorption-correction) factor of a multifaceted crystal has been found in the past either by a numerical method (Busing & Levy, 1957; Hamilton, 1963) or by subdivision of the crystal into elemental tetrahedra (de Meulenaer & Tompa, 1965) and analytic evaluation of the absorption over a tetrahedron. Similar methods that use triangles and parallelograms have been used in the case of two-dimensional crystals (Howells, 1950; Braibanti & Tiripicchio, 1965). The two techniques have been compared many times, most recently by Blanc, Schwarzenbach & Flack (1991). In principle, the analytic method should give an exact answer but the subdivision into tetrahedra leads to problems with rounding errors and to extended computing time for

multifaceted crystals. The rounding-error problems have been largely overcome by the improvements suggested by Alcock (1970, 1974) and by Blanc, Schwarzenbach & Flack (1991). Nevertheless, the subdivision into tetrahedra is totally unnecessary because analytic expressions for the transmission factor can be found for any simple shape. In this paper, mathematical expressions are provided that avoid this unnecessary subdivision. All that is required is the evaluation of geometric factors for the edges of each Howells polyhedron. In addition, a method of finding these edges is described that results in an unambiguous determination of each edge. The expressions given in this paper allow the volume of the whole crystal and that of each of the Howells polyhedra to be evaluated separately.

This paper is divided into three sections. The first section derives the mathematical expressions. The one following that explains how the concept of the included volume of a set of planes can be used to simplify the definitions of the Howells polyhedra. Finally, a simple way of deriving the transmission factors for crystals that each consist of a single Howells polyhedron is given.

### The transmission factor

The transmission factor is defined by

$$T = V^{-1} \int_V d\tau \exp[-\mu L(\mathbf{r})], \quad (1)$$

where  $L(\mathbf{r})$  is the total path length within the crystal of a ray that is scattered once at  $\mathbf{r}$ . Because  $L(\mathbf{r})$  is a linear function of the scattering position  $\mathbf{r}$ , one can write

$$-\mu L(\mathbf{r}) = -\mu(\mathbf{a} \cdot \mathbf{r} + c) \quad (2)$$

and  $T = V^{-1} \exp(-\mu c)I$ , reducing the problem to the evaluation of the integral

$$I = \int_V d\tau \exp(-\mu \mathbf{a} \cdot \mathbf{r}). \quad (3)$$

Because the path  $L(\mathbf{r})$  depends on both the distance from the face of the crystal through which the ray entered and the distance from that through which it leaves, the crystal has to be subdivided into polyhedra (the Howells polyhedra) over which the vector  $\mathbf{a}$  is a constant. If the emerging ray is reversed then a single Howells polyhedron is that volume which is 'lit' through single faces by both the incident beam (beam 1) and the reversed scattered beam (beam 2). When these two beams have directions given by unit vectors  $\mathbf{t}_1$  and  $\mathbf{t}_2$  and each crystal face is defined by  $\mathbf{n} \cdot \mathbf{r} = D$  (where  $\mathbf{n}$  is the outward normal to the face and  $D = \mathbf{n} \cdot \mathbf{r}_0$ , with  $\mathbf{r}_0$  any point on the face) then it is straightforward to show that the constants in (2) are

$$\begin{aligned} a_{ij} &= \mathbf{n}_j / (\mathbf{n}_i \cdot \mathbf{t}_1) + \mathbf{n}_j / (\mathbf{n}_j \cdot \mathbf{t}_2), \\ c_{ij} &= -D_i / (\mathbf{n}_j \cdot \mathbf{t}_1) - D_j / (\mathbf{n}_j \cdot \mathbf{t}_2). \end{aligned} \quad (4)$$

Here, the subscript  $i$  refers to the crystal face through which beam 1 enters and the subscript  $j$  to that through which beam 2 enters.

In the mathematics that follow we shall consider only one Howells polyhedron and, for clarity, drop the subscripts  $i$  and  $j$ . We shall also let  $-\mu \mathbf{a} = \mathbf{b}$ . Gauss's theorem,

$$\int_V \nabla \cdot \mathbf{u} \, dV = \int_S \mathbf{u} \cdot \mathbf{n} \, dS, \quad (5)$$

with  $\mathbf{u} = \mathbf{b} \exp(\mathbf{b} \cdot \mathbf{r})$ , allows us to re-express the integral over the volume of each polyhedron (over which  $\mathbf{b}$  is constant, by definition) as an integral over the faces of that polyhedron.

$$\begin{aligned} I &= \int_V \exp(\mathbf{b} \cdot \mathbf{r}) \, d\tau \\ &= (1/b^2) \sum_k \mathbf{n}_k \cdot \mathbf{b} \int_{S_k} \exp(\mathbf{b} \cdot \mathbf{r}) \, dS, \end{aligned} \quad (6)$$

where the sum is over all faces of the polyhedron and  $\mathbf{n}_k$  is the outward normal to the  $k$ th face. In addition, we can reduce the integral over each face by using a companion theorem to Stokes's theorem,

$$\int_S \nabla \times \mathbf{u} \cdot \mathbf{n} \, dS = \int \mathbf{u} \cdot d\mathbf{l}. \quad (7)$$

This is obtained by putting  $\mathbf{u} = \Psi(\mathbf{r})\mathbf{e}$ , where  $\mathbf{e}$  is any constant vector, and is

$$\int_S \mathbf{n} \times \nabla \Psi \, dS = \int_C \Psi \, d\mathbf{l}. \quad (8)$$

With  $\Psi = \exp(\mathbf{b} \cdot \mathbf{r})$ ,

$$\int_C \exp(\mathbf{b} \cdot \mathbf{r}) \, d\mathbf{l} = (\mathbf{n} \times \mathbf{b}) \int_S \exp(\mathbf{b} \cdot \mathbf{r}) \, dS, \quad (9)$$

or

$$\int_S \exp(\mathbf{b} \cdot \mathbf{r}) \, dS = (\mathbf{n} \times \mathbf{b}) / |\mathbf{n} \times \mathbf{b}|^2 \cdot \int_C \exp(\mathbf{b} \cdot \mathbf{r}) \, d\mathbf{l}. \quad (10)$$

Finally, the line integral round the perimeter  $C$  of the face  $S$  may be expressed as a sum over the edges of the face.

$$\int_C \exp(\mathbf{b} \cdot \mathbf{r}) \, d\mathbf{l} = \sum_j \int_{\mathbf{r}_{j1}}^{\mathbf{r}_{j2}} \exp(\mathbf{b} \cdot \mathbf{r}) \, d\mathbf{l}, \quad (11)$$

where  $\mathbf{r}_{j1}$  and  $\mathbf{r}_{j2}$  are the vertices at the ends of edge  $j$ . Because the line along edge  $j$  is  $\mathbf{r} = \mathbf{r}_{j1} + \lambda(\mathbf{r}_{j2} - \mathbf{r}_{j1})$ ,

$$\begin{aligned} \int_{\mathbf{r}_{j1}}^{\mathbf{r}_{j2}} \exp(\mathbf{b} \cdot \mathbf{r}) \, d\mathbf{l} &= \mathbf{d}_j \int_0^1 \exp(\mathbf{b} \cdot \mathbf{r}_{j1} + \lambda \mathbf{d}_j) \, d\lambda \\ &= (\mathbf{d}_j / \mathbf{b} \cdot \mathbf{d}_j) [\exp(\mathbf{b} \cdot \mathbf{r}_{j2}) \\ &\quad - \exp(\mathbf{b} \cdot \mathbf{r}_{j1})], \end{aligned} \quad (12)$$

where  $\mathbf{d}_j = \mathbf{r}_{j2} - \mathbf{r}_{j1}$ . The integral  $I$  is now reduced to a sum of terms evaluated over the edges of the polyhedron.

$$\begin{aligned} I &= \sum_k \mathbf{n}_k \cdot \mathbf{b} / (b^2 |\mathbf{n}_k \times \mathbf{b}|^2) \sum_j (\mathbf{n}_k \cdot \mathbf{b}, \mathbf{d}_j) / \mathbf{b} \cdot \mathbf{d}_j \\ &\quad \times [\exp(\mathbf{b} \cdot \mathbf{r}_{j2}) - \exp(\mathbf{b} \cdot \mathbf{r}_{j1})], \end{aligned} \quad (13)$$

where  $(\mathbf{n}, \mathbf{b}, \mathbf{d})$  is the triple scalar product  $\mathbf{n} \times \mathbf{b} \cdot \mathbf{d}$  and the sum over  $k$  is over all faces. The sum over  $j$  is round the perimeter of each face in the usual anti-clockwise direction around the outward normal to the face.

In the above, we have assumed that  $b^2$ ,  $|\mathbf{n}_k \times \mathbf{b}|^2$  and  $\mathbf{b} \cdot \mathbf{d}_j$  are not zero. We now consider these three special cases, which are, of course, precisely the three special cases that led de Meulenaer & Tompa (1965) to introduce their function  $h(u)$ .

(a)  $b^2 = 0$ . If  $\mathbf{b}$  is a null vector, then either  $\mu = 0$  or the path length,  $L(\mathbf{r})$ , is constant over the whole polyhedron. The latter will occur whenever  $\mathbf{n}_i = -\mathbf{n}_j$  and  $\mathbf{n}_i \cdot \mathbf{t}_1 = \mathbf{n}_j \cdot \mathbf{t}_2$ , i.e. the two crystal faces defining the polyhedron are parallel and the angles the two beams make with the faces are equal. In this case,

$$\begin{aligned} \int_V \exp[-\mu L(\mathbf{r})] \, d\tau &= \exp(-\mu c) \int_V d\tau \\ &= \exp(-\mu c) V. \end{aligned} \quad (14)$$

The volume  $V$  of any polyhedron can be expressed as a sum over the edges of the polyhedron by repeating the above analysis with  $\mathbf{u} = \mathbf{r}/3$  in Gauss's theorem and  $\mathbf{u} = \mathbf{n} \times \mathbf{r}$  in Stokes's theorem. This gives

$$V = (1/6) \sum_k \sum_j \mathbf{n}_k \cdot \mathbf{R}_j(\mathbf{n}_k, \mathbf{R}_j, \mathbf{d}_j), \quad (15)$$

where  $\mathbf{R}_j = (1/2)(\mathbf{r}_{j2} + \mathbf{r}_{j1})$  is the midpoint of edge  $j$ . With the properties of the triple scalar product and

the equation  $\mathbf{n}_k \cdot \mathbf{r} = D_k$  defining face  $k$ , this can be re-expressed more simply as

$$V = (1/6) \sum_k \sum_j D_k(\mathbf{n}_k, \mathbf{r}_{j1}, \mathbf{r}_{j2}). \quad (16)$$

(b)  $\mathbf{n}_k \times \mathbf{b} = 0$ . This will occur if  $L(\mathbf{r})$  is constant over the whole of face  $k$  of the polyhedron. Then, for any point  $\mathbf{r}_0$  on the face,

$$\begin{aligned} \int_S \exp(\mathbf{b} \cdot \mathbf{r}) dS \\ = \exp(\mathbf{b} \cdot \mathbf{r}_0) \text{ multiplied by the area of face } k \\ = \sum_j (1/2)(\mathbf{n}_k, \mathbf{r}_{j1}, \mathbf{r}_{j2}) \exp(\mathbf{b} \cdot \mathbf{r}_{j1}). \end{aligned} \quad (17)$$

(c)  $\mathbf{b} \cdot \mathbf{d}_j = 0$ . This occurs if  $L(\mathbf{r})$  is constant along edge  $j$ , then

$$\int \exp(\mathbf{b} \cdot \mathbf{r}) d\mathbf{l} = \exp(\mathbf{b} \cdot \mathbf{r}_{j1}) \mathbf{d}_j. \quad (18)$$

Note that on a face for which  $\mathbf{n}_k \times \mathbf{b} = 0$ , necessarily  $\mathbf{b} \cdot \mathbf{d}_j = 0$  over all its edges.

Because each edge will be counted twice if the sum is taken round the perimeters of all faces, it is better to rearrange the sum as a sum over all edges taken only once. This leads to the final expression for  $T$ , which can be summarized as follows:

Let  $\mathbf{n}_1$  and  $\mathbf{n}_2$  be the unit normals to two faces that intersect at an edge and  $D_1$  and  $D_2$  be the constants associated with these two faces. Let  $\mathbf{r}_1$  and  $\mathbf{r}_2$  be the vertices at the ends of the edge, ordered such that  $\mathbf{d} = \mathbf{r}_2 - \mathbf{r}_1$  is parallel to  $\mathbf{n}_1 \times \mathbf{n}_2$ . Then

$$\begin{aligned} T = (1/V) \sum \{ (1/\mu)^{p_1} f_1 \exp[-\mu L(\mathbf{r}_1)] \\ - (1/\mu)^{p_2} f_2 \exp[-\mu L(\mathbf{r}_2)] \}, \end{aligned} \quad (19)$$

where the sum is taken over all edges of each Howells polyhedron and over all the polyhedra. The geometric factors  $f$  and the powers  $p$  are given by:

(i) if  $a^2 = 0$ ,  $p_1 = p_2 = 0$ ,

$$\begin{aligned} f_1 = (1/6) D_1(\mathbf{n}_1, \mathbf{r}_1, \mathbf{r}_2), \\ f_2 = (1/6) D_2(\mathbf{n}_2, \mathbf{r}_1, \mathbf{r}_2); \end{aligned} \quad (20)$$

(ii) if  $\mathbf{a} \cdot \mathbf{d} = 0$ ,  $p_1 = p_2 = 2$ ,

$$\begin{aligned} f_1 = (1/a^2) \frac{\mathbf{n}_1 \cdot \mathbf{a}}{|\mathbf{n}_1 \times \mathbf{a}|^2} (\mathbf{n}_1, \mathbf{a}, \mathbf{d}) \\ f_2 = (1/a^2) \frac{\mathbf{n}_2 \cdot \mathbf{a}}{|\mathbf{n}_2 \times \mathbf{a}|^2} (\mathbf{n}_2, \mathbf{a}, \mathbf{d}), \end{aligned} \quad (21)$$

unless either (a)  $|\mathbf{n}_1 \times \mathbf{a}|^2 = 0$  when  $p_1 = 1$  and

$$f_1 = -(1/2a^2)(\mathbf{n}_1 \cdot \mathbf{a})[(\mathbf{n}_1, \mathbf{r}_1, \mathbf{r}_2)]$$

or (b)  $|\mathbf{n}_2 \times \mathbf{a}|^2 = 0$  when  $p_2 = 1$  and

$$f_2 = -(1/2a^2)(\mathbf{n}_2 \cdot \mathbf{a})(\mathbf{n}_2, \mathbf{r}_1, \mathbf{r}_2); \quad (22)$$

(iii) otherwise,  $p_1 = p_2 = 3$  and

$$\begin{aligned} f_1 = (1/a^2) \{ [(\mathbf{n}_1 \cdot \mathbf{a})/|\mathbf{n}_1 \times \mathbf{a}|^2][(\mathbf{n}_1, \mathbf{a}, \mathbf{d})/(\mathbf{a} \cdot \mathbf{d})] \\ - [(\mathbf{n}_2 \cdot \mathbf{a})/|\mathbf{n}_2 \times \mathbf{a}|^2][(\mathbf{n}_2, \mathbf{a}, \mathbf{d})/(\mathbf{a} \cdot \mathbf{d})] \} \end{aligned} \quad (23)$$

$$f_2 = f_1.$$

Note that, in (23),  $\mathbf{d}$  could be replaced by  $\mathbf{n}_1 \times \mathbf{n}_2$  and  $f_1$  and  $f_2$  made demonstrably independent of the vertices  $\mathbf{r}_1$  and  $\mathbf{r}_2$ . This, together with the simple result of de Meulenaer & Tompa (1965) for a tetrahedron, leads one to suspect that an equally simple result akin to theirs could be found if the sum over edges were replaced by a sum over vertices. Note that, for computational purposes, this is a retrograde step because of the special cases arising from constant  $L(\mathbf{r})$ . Edges are much more easily handled than vertices when computing  $T$ . However, for completeness, one can point out that after a little vector algebra we can show from (23) that there will be a term of the form

$$(1/\mu^3) \frac{(\mathbf{d}_1, \mathbf{d}_2, \mathbf{d}_3)}{\Delta L_1 \Delta L_2 \Delta L_3} \exp[-\mu L(\mathbf{r})], \quad (24)$$

provided  $\Delta L$ , the change in  $L(\mathbf{r})$  over an edge, is nonzero on three edges that meet at a vertex  $\mathbf{r}$ . This is the result used by de Meulenaer & Tompa (1965).

### Derivatives of $T$

As pointed out by J. S. Reid (private communication), the analytic expression for  $T$  allows the derivatives of  $T$  with respect to  $\mu$  to be evaluated in a similar manner.

$$\begin{aligned} (dT/d\mu) = -(1/V) \sum \{ (1/\mu)^{p_1} f_1 \exp[-\mu L(\mathbf{r}_1)] \\ \times [(p_1/\mu) + L(\mathbf{r}_1)] \\ - (1/\mu)^{p_2} f_2 \exp[-\mu L(\mathbf{r}_2)] \\ \times [(p_2/\mu) + L(\mathbf{r}_2)] \}. \end{aligned} \quad (25)$$

Thus, the absorption weighted mean path length,

$$\bar{T} = -(1/T)(dT/d\mu), \quad (26)$$

can be calculated with minimum extra effort along with  $T$  once the edges of the Howells polyhedron have been defined. Higher derivatives can also be found if required.

Blanc, Schwarzenbach & Flack (1991) have given expressions for derivatives of  $T$  with respect to changes in the distance  $d_j$  of the  $j$ th crystal face from the origin. Because their expressions are in terms of the integrals of  $\exp[-\mu L(\mathbf{r})]$  over individual Howells polyhedra and over the  $j$ th face of the crystal, it is clear that they also can be calculated by the above method.

### The Howells polyhedra as included volumes

When a computer program is constructed to evaluate the transmission factor, the Howells polyhedra have

to be clearly defined. We have found that the concept of the included volume of a set of planes is simple, unambiguous and gives directly the required edges and vertices.

Any plane  $\mathbf{n} \cdot \mathbf{r} = D$  divides space into two regions: (i) the included region, that part of space in which  $(\mathbf{n} \cdot \mathbf{r} - D)$  is negative; and (ii) the excluded region, that part in which  $(\mathbf{n} \cdot \mathbf{r} - D)$  is positive. The origin, for example, is included if  $D$  is positive and excluded if  $D$  is negative. With the usual definition of outward-going normals, a given crystal volume is that region of space not excluded by any member of the set of planes that combine to make up its faces. Other planes added to this set may or may not exclude it. A crystal in a laboratory is the included volume of the set of planes that contains the crystal faces and the walls of the laboratory. It is excluded by any set containing the walls of the laboratory next door - provided, of course, that the normals to the walls point outward from the room enclosed.

Viewed in this manner, any one Howells polyhedron is the included volume of the set of planes made up of (a) the planes that define the faces of the crystal; (b) the planes parallel to  $\mathbf{t}_1$  that outline the face through which beam 1 passes - the shadows of the edges round that face with normals outward from the face; and (c) the planes parallel to  $\mathbf{t}_2$  that outline the face through which beam 2 passes. An included volume of this total set will only be nonzero if the two parts of the beams so defined meet inside the crystal. If an included volume does exist, it is one of the Howells polyhedra.

The edges of the polyhedron are found by considering the line of intersection between any pair of planes in the set and the points where this line meets the other planes in the set. Any such point will be a vertex of the polyhedron only if, for all planes in the set,  $(\mathbf{n} \cdot \mathbf{r} - D) \leq 0$ . Otherwise this point is excluded by some planes of the set.

If, for any line of intersection, two such points are found, then the line is an edge of the included volume and the two points are the associated vertices. Care must be taken to order  $\mathbf{r}_1$  and  $\mathbf{r}_2$  so that  $(\mathbf{r}_2 - \mathbf{r}_1)$  is parallel to  $\mathbf{n}_1 \times \mathbf{n}_2$ . Once this is done, the factors  $f_1, f_2, p_1, p_2, L(\mathbf{r}_1)$  and  $L(\mathbf{r}_2)$  required for the evaluation of  $T$  can be calculated directly.

Despite the simplicity of the above method of defining the Howells polyhedra, some precautions must be taken in defining the set of planes. No two planes can be either identical or face to face (i.e.  $\mathbf{n}_1 = -\mathbf{n}_2$  and  $D_1 = -D_2$ ). In the former case, any edge will be counted twice as 'not excluded' by either plane. In the latter, no included volume is possible, but the program will spend time computing zero. Such 'ghost' volumes should be eliminated. Finally, a common line of intersection between three planes, if not excluded by another member of the set of planes, will be counted three times (as the 'edge' defined by three

different pairs of planes) and, similarly, one common to four planes will be counted six times. A simple algorithm to see which pair of planes (of three) is the pair that defines the edge of the included volume and which plane is merely another plane through this edge follows.

Let  $\mathbf{n}_1, \mathbf{n}_2$  and  $\mathbf{n}_3$  be the normals to three planes with a common line.

Define  $\alpha_1 = (\mathbf{n}_1 \times \mathbf{n}_2) \cdot (\mathbf{n}_1 \times \mathbf{n}_3)$  and  $\alpha_2 = (\mathbf{n}_2 \times \mathbf{n}_3) \cdot (\mathbf{n}_1 \times \mathbf{n}_3)$  and determine whether  $\alpha_1$  and  $\alpha_2$  are positive or negative.

The following chart shows which plane of the three is *not* a face of the included volume:

| $\alpha_1$ | $\alpha_2$ | Plane not required           |
|------------|------------|------------------------------|
| +          | +          | 2                            |
| +          | -          | 3                            |
| -          | +          | 1                            |
| -          | -          | No included volume possible. |

Many of the above points have been made in different forms by Blanc, Schwarzenbach & Flack (1991). However, they construct a list of edges for each polyhedron because they then have to divide it up into elementary irregular tetrahedra. As shown above, this is not necessary and, once any edge is found from the set of planes, the required factors can immediately be evaluated.

The concept of the included volume of a set of planes makes it easy to introduce further constraints on the Howells polyhedra. The incident beam may be restricted so that, instead of the whole of the crystal, only a small section of it is illuminated. It is easy to add to the set of planes that defines the included volume of the Howells polyhedra, the set that determines the outline of the incident beam. This will be further discussed in a subsequent paper (Clark & Reid, in preparation).

Limitation of the beam size could be used to overcome inhomogeneities in the beam (Markov, Fetsov & Zhukov, 1990) or in the crystal itself.

### Standard tests

Alcock (1974), Cahen & Ibers (1972) and Flack, Vincent & Alcock (1980) have emphasized the need for standard tests. The easiest tests to apply are those of Cahen & Ibers but unfortunately their formulae do not test the terms with factors  $\mu^{-3}$  above, or the dependence on  $2\theta$ . Equation (19) is an analytic expression for  $T$  and is perfectly feasibly evaluated by hand in simple cases but, for a tetrahedron with the particular beam directions that imply that the whole tetrahedron is a single Howells polyhedron, the transmission factor can be deduced from general considerations alone. Using these, we can give an analytic expression for scattering by a tetrahedron  $ABCD$ . If the directions of the incident beam and the

scattered beam are such that both beams pass through face  $ABC$ , say, the transmission factor is

$$T = 6\{(1/2\mu\beta) - (1/\mu^2\beta^2) + (1/\mu^3\beta^3)[1 - \exp(-\mu\beta)]\}, \quad (27)$$

where  $\beta$  is the path length  $L(\mathbf{r}_D)$ .

The above result could be derived from (19) to (23) but is more simply derived from the following argument. There is only one effective length in the problem, namely  $\beta$ .  $T$  must be a function of  $\mu\beta$  as it is dimensionless. In order that it tends to zero as  $\mu$  tends to  $\infty$ ,  $T$  must be expressible in terms of  $\exp(-\mu\beta)$  and powers of  $(\mu\beta)^{-1}$ . With (24), the coefficient of  $\exp(-\mu\beta)$  is  $(\mu\beta)^{-3}$ . No powers of  $(\mu\beta)^{-1}$  higher than three will enter in any other term. Because  $T$  tends to 1 as  $\mu$  tends to 0, it can only be of the form

$$3!(\mu\beta)^{-3}[1 - \mu\beta + (1/2)\mu^2\beta^2 - \exp(-\mu\beta)]. \quad (28)$$

This is the expression we have given above. Note that (27) is correct only if the beams pass in and out of a single face. Simple forms could be derived for other configurations.

A similar argument applies to two-dimensional shapes, leading to the form

$$-2!(\mu\beta)^{-2}[1 - \mu\beta - \exp(-\mu\beta)]. \quad (29)$$

A special case of this result is one of the test formulae of Cahen & Ibers (1972). Note, however, that their result is for fixed angles of the incident and scattered beams, while (27) and (29) apply to all angles and crystal orientations for which both beams pass through a single face. If  $D$  is taken as the origin and  $\mathbf{n}_4$  and  $D_4$  describe face  $ABC$ ,  $\beta$  is given by

$$\beta = -D_4[(\mathbf{n}_4 \cdot \mathbf{t}_1)^{-1} + (\mathbf{n}_4 \cdot \mathbf{t}_2)^{-1}]. \quad (30)$$

### Concluding remarks

We have shown how to calculate transmission factors and their derivatives analytically without subdividing the Howells polyhedra into tetrahedra. The computational method, based on the idea of these polyhedra as the included volumes of sets of well defined planes, is fast, efficient and accurate. The calculation of the geometric factors need only be performed once for each orientation of the crystal. Thereafter, a single sum over terms gives the transmission factor for any value of  $\mu$  very quickly.

The reader may note that the method applied above to integrate  $\exp(-\mu L)$  over the crystal volume can equally well be applied to any function of  $L$ ,  $f(L)$ , which can be written as the third derivative of another function,  $g(L)$ . This allows a simple check on the accuracy of any computer program because  $g(L) = L^3/6$  generates the volume of the crystal using the same factors  $f_1, f_2, p_1, p_2$  etc. that are used to find the

transmission factor. The result can be compared with the volume calculated independently using (16). In all tests of a program making this comparison (Clark & Reid, in preparation), the two results differ only in the 14th decimal place. Another consequence is that any  $g(L)$  whose third derivative is  $\exp(-\mu L)$  can be used to find the transmission factor. A better  $g(L)$  than that used in the above analysis is

$$g(L) = [1/(-\mu)^3] \times [\exp(-\mu L) - 1 + \mu L - (1/2)(\mu L)^2], \quad (31)$$

which does not diverge as  $\mu \rightarrow 0$ . This form of  $g(L)$  gives greater accuracy of  $T$  and  $\bar{T}$  for small  $\mu$ . Full details will be given in the subsequent paper (Clark & Reid, in preparation).

The number of geometric factors that have to be calculated depends on the number of faces of the crystal that are lit by the two beam directions. An estimate can be made in the case of a crystal with many faces. A crystal with  $f$  faces will have  $e$  edges, where  $3f/2 \leq e \leq 3(f-2)$ . When  $f$  is large, the mean number of edges per face is close to its maximum value, six, so each Howells polyhedron will average 12 faces and approximately 30 edges. Because the number of polyhedra will be about  $\frac{1}{2}(\frac{1}{2}f)^2$ , an estimate of the number of edges for which geometric factors have to be found is  $4f^2$ . The number of points that must be checked to find the edges of the Howells polyhedra in principle increases rapidly for large  $f$  because every polyhedron is defined by a set containing at least  $f$  planes and the vertex of every triplet of planes in the set has to be found. However, a large proportion of these triplets can be flagged as meeting outside the crystal and, therefore, not computed more than once. Elimination of the division of each polyhedron into tetrahedra followed by the calculation of results for each of these achieves considerable savings in computing time and storage. Separation out of the  $\mu$  dependence in the calculation means that the geometric factors do not have to be re-evaluated for different values of  $\mu$ , so wavelength dependence in  $\mu$  can be easily handled. Restrictions on the incident-beam shape can also be accommodated.

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## The Determination of Rigid-Unit Modes as Potential Soft Modes for Displacive Phase Transitions in Framework Crystal Structures

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### Abstract

This paper describes a computational method for the determination of all possible phonon modes in framework crystal structures that leave the fundamental structural units (tetrahedra and octahedra) undistorted. Such rigid-unit modes (RUMs) are prime candidates as soft modes for displacive phase transitions, such as in the perovskite structure, and this computational method can be used to rationalize the phase transitions in any framework structure. The method has been programmed for general use. The RUM approach is illustrated by consideration of the perovskite, quartz and cristobalite structures.

### 1. The concept of rigid-unit modes

Many silicate crystal structures are composed of  $\text{SiO}_4$  tetrahedra that are linked to other tetrahedra by corner-sharing oxygen atoms to give a semi-infinite framework connectivity. Quartz is one well known example of what we call a *framework structure*. Such framework structures are not confined to silicates:  $\text{AlPO}_4$  and  $\text{As}_2\text{O}_5$  are examples of nonsilicate framework structures. Many framework structures are found to undergo displacive phase transitions (Carpenter, 1988; Salje, 1988). In some respects this

might seem to be counter-intuitive, because Si–O bonds are strong and the tetrahedra are difficult to distort. However, such phase transitions can occur without any significant distortions of the  $\text{SiO}_4$  tetrahedra. Quartz is a good example of this (Megaw, 1973; Grimm & Dorner, 1975; Boysen, Dorner, Frey & Grimm, 1980; Berge, Baccheimer, Dolino, Vallade & Zeyen, 1985; Vallade, Berge & Dolino, 1992). The high-temperature ( $\beta$ ) phase of quartz (Fig. 1a) has hexagonal symmetry and the low-temperature ( $\alpha$ ) phase (Fig. 1b) has trigonal symmetry. In the quartz structure, the  $\text{SiO}_4$  tetrahedra are connected as linked spirals and at the phase transition the spirals are distorted by rotations and displacements of the tetrahedra. Megaw (1973) has discussed the structures

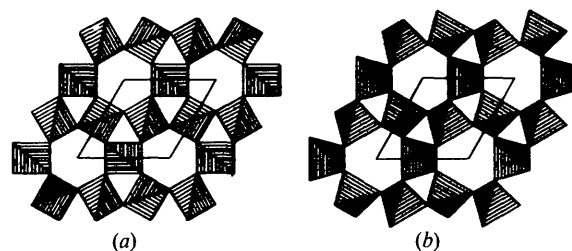


Fig. 1. (a) Projection of the hexagonal phase of quartz down [001], in which the  $\text{SiO}_4$  tetrahedra are shown as shaded units. (b) Projection of the trigonal phase of quartz down [001].

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