Table 5. *Bond lengths with their standard deviations*

	Bond	M–O Distance	σ
Si–O	A	1·646 Å	0·014 Å
Si–O	B	1·611	0·013
Si–O	C	1·580	0·018
Si–O	D	1·566	0·017
Average:		1·601	0·008*
Al–O	E	1·762	0·014
Be–O	F	1·608	0·012

* Taken as the average of σ divided by the square root of the numbers of independent determinations, as suggested by Smith & Bailey (1963).

Smith & Bailey (1963) give as best values for Si–O and Al–O 1·61 Å and 1·75 Å respectively, and our values agree within the experimental error. Only a few Be–O distances have been reported in the literature, but the value found in tugtupite falls within the interval given by *International Tables for X-ray Crystallography* (1962, p.260). The question of the space group of sodalite, $Na_8Al_6Si_6O_{24}Cl_2$, is still open. In the paper of Pauling (1930) it was given as $P\bar{4}3n$, while Barth (1932) argued for $P\bar{4}3m$. Later Saalfeld (1961) discussed the matter in relation to other members of the sodalite group and proposed the space group $P\bar{4}3n$. With the technique used in the early structure determinations it was not possible to determine the Si–O and Al–O distances with sufficient accuracy to decide whether the 6 Al and 6 Si are in two different special positions ($P\bar{4}3n$) or statistically distributed in a 12-fold position ($P\bar{4}3m$).

In view of the ordered arrangement of the cations of tugtupite it seems worth while to re-examine the structure of sodalite. We hope to be able to do so in the near future.

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On the Equivalence of Structure Invariants*

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The triangle in reciprocal space associated with a given structure invariant is defined and the concept of the equivalence of structure invariants is introduced. It is assumed that many of the interatomic triangles (especially the smaller ones) in a crystal structure are congruent to each other and that the triangles in each collection of congruent interatomic triangles are more or less randomly oriented in space. Under these assumptions the values of equivalent structure invariants are approximately equal, especially if the sides of the associated triangle are small. This result facilitates the solution of the problem of direct phase determination for structures satisfying our assumptions.

1. Introduction

The structure invariants are those entities whose values are uniquely determined by a crystal structure. They play a fundamental role in the problem of direct phase

determination. An important set of structure invariants consists of the linear combinations of the phases

$$\varphi_1 + \varphi_2 + \varphi_3 , \tag{1·1}$$

in which the abbreviations

$$\varphi_i = \varphi_{\mathbf{h}_i} , \quad i = 1, 2, 3 , \tag{1·2}$$

have been used and the assumption

$$\mathbf{h}_1 + \mathbf{h}_2 + \mathbf{h}_3 = 0 \tag{1·3}$$

has been made. The phase $\varphi_{\mathbf{h}}$ of the normalized structure factor $E_{\mathbf{h}}$ is defined by

$$E_{\mathbf{h}} = |E_{\mathbf{h}}| \exp(i\varphi_{\mathbf{h}})$$
$$= (1/\sigma_2^{1/2}) \sum_{j=1}^{N} Z_j \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_j) \tag{1·4}$$

where

$$\sigma_n = \sum_{j=1}^{N} Z_j^n, \tag{1·5}$$

N is the number of atoms in the unit cell, and Z_j is the atomic number of the jth atom the position vector of which is $\mathbf{r}_j$.

We shall be primarily concerned with the following variant of (1·1):

$$V_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3} = |E_1 E_2 E_3| \cos(\varphi_1 + \varphi_2 + \varphi_3), \tag{1·6}$$

in which the abbreviations

$$E_i = E_{\mathbf{h}_i}, \quad i = 1, 2, 3 \tag{1·7}$$

have been employed. Under the assumption (1·3), the expression (1·6), like (1·1), is evidently a structure invariant. The elements of the set (1·6) are important because their values lead directly, by means of space-group dependent procedures for fixing the origin and enantiomorph described elsewhere (e.g. Karle & Hauptman, 1956, 1957), to the values of the phases $\varphi_{\mathbf{h}}$. Hence the phase problem is solved if, by making use of the magnitudes of the normalized structure factors, $|E_{\mathbf{h}}|$, the values of (1·6) are determined.

It is the purpose of this paper to study the structure of the set of invariants (1·6) in order to facilitate the direct determination of phase. We shall introduce the notion of the equivalence of two structure invariants. In this way the collection of invariants (1·6) is decomposed into mutually exclusive subsets, the equivalence classes, having the property that any two invariants belonging to the same equivalence class are equivalent (approximately) to each other; two invariants chosen from different equivalence classes are not equivalent to each other. The importance of the concept of equivalence lies in the fact that, under suitable conditions, equivalent structure invariants are equal (approximately) to each other. Hence knowledge of the equivalence classes facilitates the solution of the problem of direct phase determination.

2. The equivalence concept

Def. 2·1. In view of (1·3), the invariant $V_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$ determines a triangle, $\varDelta_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$, said to be the triangle associated with $V_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$, having a definite orientation in reciprocal space and sides $\mathbf{h}_1$, $\mathbf{h}_2$, $\mathbf{h}_3$. The lengths of the sides of this triangle are denoted by

$$q_{\mathbf{h}_i} = |\mathbf{h}_i|, \quad i = 1, 2, 3. \tag{2·1}$$

Def. 2.2. Two invariants $V_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$ and $V_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}$ are said to be equivalent if their associated triangles $\varDelta_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$ and

$\varDelta_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}$ are congruent, *i.e.* if $q_{\mathbf{h}_i} = q_{\mathbf{k}_i}$, $i = 1, 2, 3$. (Implicit in this definition, naturally, is the assumption that $\mathbf{h}_1 + \mathbf{h}_2 + \mathbf{h}_3 = \mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 = 0$.)

In application the notion of approximate equivalence is of particular importance. This means that $V_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$ and $V_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}$ are considered to be equivalent if $q_{\mathbf{h}_i}$ and $q_{\mathbf{k}_i}$, $i = 1, 2, 3$, are approximately equal to each other so that the triangles $\varDelta_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$ and $\varDelta_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}$ are almost congruent.

3. The structure invariants $V_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$

We begin with the following expression for the invariant (1·6) in terms of the interatomic vectors (Hauptman & Karle, 1962):

$$|E_{\mathbf{h}_1} E_{\mathbf{h}_2} E_{\mathbf{h}_3}| \cos(\varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_3})$$
$$\approx 1/\sigma_2^{3/2} \sum_{\substack{\mu \neq \nu \neq \varrho \neq \mu \\ 1}}^{N} Z_{\mu\nu\rho} \cos 2\pi (\mathbf{h}_1 \cdot \mathbf{r}_{\mu\nu} - \mathbf{h}_3 \cdot \mathbf{r}_{\nu\rho})$$
$$+ (\sigma_3/\sigma_2^{3/2})(|E_{\mathbf{h}_1}|^2 + |E_{\mathbf{h}_2}|^2 + |E_{\mathbf{h}_3}|^2 - 2), \tag{3.1}$$

where

$$Z_{\mu\nu\rho} = Z_\mu Z_\nu Z_\rho, \tag{3.2}$$

$$\mathbf{r}_{\mu\nu} = \mathbf{r}_\mu - \mathbf{r}_\nu, \quad \mathbf{r}_{\nu\rho} = \mathbf{r}_\nu - \mathbf{r}_\rho. \tag{3.3}$$

We assume, without essential loss of generality (except for structures containing 'heavy atoms'), that all atoms are identical so that (3.1) reduces to

$$V_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3} - \frac{1}{N^{\frac{1}{2}}}(|E_{\mathbf{h}_1}|^2 + |E_{\mathbf{h}_2}|^2 + |E_{\mathbf{h}_3}|^2 - 2)$$
$$= \frac{(N-1)(N-2)}{N^{\frac{1}{2}}} \langle \cos 2\pi (h_1 \cdot r_{\mu\nu} - h_3 \cdot r_{\nu\rho}) \rangle_{\mu\nu\rho} \tag{3·4}$$

in which the average of the cosine is defined by

$$\langle \cos 2\pi (\mathbf{h}_1 \cdot \mathbf{r}_{\mu\nu} - \mathbf{h}_3 \cdot \mathbf{r}_{\nu\rho}) \rangle_{\mu\nu\rho}$$
$$= \frac{\displaystyle\sum_{\substack{\mu \neq \nu \neq \varrho \neq \mu \\ 1}}^{N} \cos 2\pi (\mathbf{h}_1 \cdot \mathbf{r}_{\mu\nu} - \mathbf{h}_3 \cdot \mathbf{r}_{\nu\rho})}{N(N-1)(N-2)}. \tag{3·5}$$

Next we attempt to estimate the average (3.5) by replacing each term in the sum on the right hand side by its average value. Which average shall we choose? In order to answer this question we observe that there corresponds to each term in the sum an interatomic triangle having sides $\mathbf{r}_{\mu\nu}$, $\mathbf{r}_{\nu\rho}$, $\mathbf{r}_{\rho\mu}$ since, in view of (3.3),

$$\mathbf{r}_{\mu\nu} + \mathbf{r}_{\nu\rho} + \mathbf{r}_{\rho\mu} = 0. \tag{3·6}$$

In short the sum in (3.5) is taken over all the interatomic triangles. Since the crystal structure is fixed, the magnitudes of the interatomic vectors and the angle between any pair of them, while perhaps not known, are nevertheless also fixed. These facts suggest that we fix the vectors $\mathbf{h}_1$, $\mathbf{h}_3$ and the magnitudes r and r' of the vectors $\mathbf{r}$ and $\mathbf{r}'$ respectively (to be identified later with a pair of adjacent interatomic vectors), as well as the angle φ_r between $\mathbf{r}$ and $\mathbf{r}'$. We imagine all orientations in space of the triangle determined by r, r', and φ_r to be

equally probable and, under these conditions, require the average value of cos $2\pi(\mathbf{h}_1 . \mathbf{r} - \mathbf{h}_3 . \mathbf{r}')$. This average has already been found to be (Hauptman, 1965)

$$\langle \cos 2\pi(\mathbf{h}_1 . \mathbf{r} - \mathbf{h}_3 . \mathbf{r}') \rangle = B(z, t)$$

$$= \sqrt{\frac{\pi}{2z}} \sum_{n=0}^{\infty} \frac{t^{2n}}{(n!)^2} J_{\frac{4n+1}{2}}(z) , \quad (3.7)$$

where

$$z = 2\pi \sqrt{q_{\mathbf{h}_1}^2 r^2 + 2q_{\mathbf{h}_1} q_{\mathbf{h}_3} rr' \cos \varphi_h \cos \varphi_r + q_{\mathbf{h}_3}^2 r'^2} , \quad (3.8)$$

$$t = \frac{1}{z} (2\pi^2 q_{\mathbf{h}_1} q_{\mathbf{h}_3} rr' \sin \varphi_h \sin \varphi_r) , \quad (3.9)$$

$q_{\mathbf{h}_i}$ is given by (2.1), φ_h is the angle between $\mathbf{h}_1$ and $-\mathbf{h}_3$, and r, r', and φ_r have already been defined. Substituting from (3·7) into (3.4) we find

$$V_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3} - \frac{1}{N^{\frac{1}{2}}} (|E_{\mathbf{h}_1}|^2 + |E_{\mathbf{h}_2}|^2 + |E_{\mathbf{h}_3}|^2 - 2)$$

$$\approx \frac{(N-1)(N-2)}{N^{\frac{1}{2}}} \langle B(z_{\mu\nu\rho}, t_{\mu\nu\rho}) \rangle_{\mu\nu\rho} \quad (3.10)$$

where $B(z_{\mu\nu\rho}, t_{\mu\nu\rho})$ is obtained from (3.7); $z_{\mu\nu\rho}$ and $t_{\mu\nu\rho}$ are found from (3.8) and (3.9) respectively by replacing r by $r_{\mu\nu} = |\mathbf{r}_{\mu\nu}|$, r' by $r_{\nu\rho} = |\mathbf{r}_{\nu\rho}|$, and φ_r by $\varphi_{\mu\nu\rho}$, the angle between $\mathbf{r}_{\mu\nu}$ and $\mathbf{r}_{\nu\rho}$; and the average of $B(z_{\mu\nu\rho}, t_{\mu\nu\rho})$ is defined by

$$\langle B(z_{\mu\nu\rho}, t_{\mu\nu\rho}) \rangle_{\mu\nu\rho} = \frac{\sum\limits_{\substack{\mu \ne \nu \ne \rho \ne \mu \\ 1}}^{N} B(z_{\mu\nu\rho}, t_{\mu\nu\rho})}{N(N-1)(N-2)} . \quad (3.11)$$

We have yet to determine under what circumstances the identification of the average (3.7) with that appearing in (3.4) is justified. In view of the meaning of the average in (3.7) we make the following:

Hypothesis. Each interatomic triangle in the crystal structure belongs to a set of congruent interatomic triangles, and the interatomic triangles in each such set are randomly oriented in space (so that the number of congruent interatomic triangles in each such set is large).

Under this hypothesis (3·10) is almost exactly correct; the only source of error arises from the use in (3.5) of the finite sample, consisting of the existing interatomic triangles, from the hypothetical infinite population which is the finite union of families of randomly oriented triangles, the triangles in each family all being congruent to the same interatomic triangle while triangles chosen from different families are incongruent to each other. In order to prove this it is sufficient to group the terms in the numerator of the right side of (3.5) into sets, the terms in each set corresponding to all those interatomic triangles which are congruent to some specified one. Since the triangles in any such set are assumed to be randomly oriented in space (*Hypothesis*), the sum of the cosine terms corresponding to each such set in the numerator of (3·5) is equal to the number of terms in the set multiplied by

the appropriate average, $B(z_{\mu\nu\rho}, t_{\mu\nu\rho})$. In this way we arrive at (3·10) and (3·11).

Even if our hypothesis is relaxed somewhat, in particular for the larger interatomic triangles whose corresponding terms in (3.5) would then tend to cancel each other and for which computation shows that the values of $B(z_{\mu\nu\rho}, t_{\mu\nu\rho})$ are relatively small (Hauptman, 1964), it is clear that (3·10) retains approximate validity.

There remains only the problem of showing that, for structures satisfying our hypothesis, the right hand side of (3.10) has the same value for equivalent structure invariants. To this end let $V_{k_1k_1k_3}$ be any structure invariant equivalent to $V_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$ so that $\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 = 0$ and $|\mathbf{k}_i| = |\mathbf{h}_i|$, $i = 1, 2, 3$. For this invariant (3.10) becomes

$$V_{k_1k_2k_3} - \frac{1}{N^{\frac{1}{2}}} (|E_{k_1}|^2 + |E_{k_2}|^2 + |E_{k_3}|^2 - 2)$$

$$\approx \frac{(N-1)(N-2)}{N^{\frac{1}{2}}} \langle B(z'_{\mu\nu\rho}, t'_{\mu\nu\rho}) \rangle_{\mu\nu\rho} \quad (3.12)$$

where $z'_{\mu\nu\rho}$ and $t'_{\mu\nu\rho}$ are obtained from $z_{\mu\nu\rho}$ and $t_{\mu\nu\rho}$ respectively by replacing $\mathbf{h}_1$ by $\mathbf{k}_1$ and $\mathbf{h}_3$ by $\mathbf{k}_3$, *i.e.* by replacing $q_{\mathbf{h}_1}$ by q_{k_1}, $q_{\mathbf{h}_3}$ by q_{k_3}, and φ_h, the angle between $\mathbf{h}_1$ and $-\mathbf{h}_3$, by φ_k, the angle between $\mathbf{k}_1$ and $-\mathbf{k}_3$. Since $V_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$ and $V_{k_1k_2k_3}$ are equivalent, the associated triangles $\Delta_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$ and $\Delta_{k_1k_2k_3}$ are congruent so that $q_{k_1} = q_{\mathbf{h}_1}$, $q_{k_3} = q_{\mathbf{h}_3}$, and $\varphi_k = \varphi_h$. Hence, in view of (3.8) and (3.9), $z'_{\mu\nu\rho} = z_{\mu\nu\rho}$ and $t'_{\mu\nu\rho} = t_{\mu\nu\rho}$ for all μ, ν, ϱ. The right hand sides of (3.10) and (3.12) are therefore equal. Since, for large N, the second terms of the left sides of (3.10) and (3.12) are relatively small, we arrive at the main result of this paper:

Theorem. For structures satisfying our hypothesis, equivalent structure invariants are approximately equal to each other.

It has already been noted that this result retains approximate validity even if the hypothesis is relaxed. We remark next that the error made by relaxing the hypothesis is particularly small if the sides of the associated triangle are small. This fact becomes intuitively clear if we observe that interatomic triangles which are approximately congruent 'appear' to be more accurately congruent when viewed from the low resolution implied by the small associated triangle $\mathbf{h}_1$, $\mathbf{h}_2$, $\mathbf{h}_3$. More rigorously, we note that two contributors to the sum in (3.5) which correspond to approximately congruent interatomic triangles remain almost unchanged in value under the small transformation which replaces approximate congruence by exact congruence, provided that the associated triangle is small. Hence, in effect, interatomic triangles which are only approximately congruent may then be lumped into the same set, so that the conditions of our hypothesis are more accurately fulfilled.

Conversely, the theorem tends to lose validity as the sides of the associated triangle increase since, in practice, the hypothesis can never be exactly fulfilled so that two contributors to (3.5) corresponding to almost congruent interatomic triangles 'appear' to arise from

completely unrelated interatomic triangles if the associated triangle is sufficiently large. More precisely, if the associated triangle is large, it is no longer permissible to consider interatomic triangles which are only approximately congruent as belonging to the same set since the deviations from congruence are exaggerated by multiplying by the large magnitudes $|h_1|$ and $|h_3|$ of (3.5). Hence the conditions of our hypothesis are not, in this case, approximately fulfilled even though interatomic triangles may be almost congruent.

4. Concluding remarks

The power of the direct methods of phase determination depends on the extent to which *a priori* structural knowledge can be utilized. Thus, the earliest methods employed the positivity of the electron density to yield inequality relationships among the structure factors, while the essential discreteness of the electron density function later led to relationships of equality. Recently (Hauptman, 1964) it was shown how previous knowledge of partial or complete molecular structure could be used. In the present paper we have found new relationships among the structure factors that are valid for structures satisfying our hypothesis. If, in addition, partial or complete knowledge of molecular structure is also available, (3.10) may be employed directly to obtain a first estimate of the structure invariant $V_{h_1h_2h_3}$, since the function $B(z, t)$ has already been tabulated (Hauptman, 1964). Standard techniques may then be used to find the phases themselves. In future publications it will be shown how to exploit other kinds of structural information as aids in phase determination, *e.g.* the tendency for interatomic distances to coincide, the existence of coplanar groupings in the crystal structure, *etc.*

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The Crystal Structure of the High Temperature Form of Barium Borate, BaO.B₂O₃

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The crystal structure of the high temperature form of BaO.B₂O₃ (m.p. $1095 \pm 5°C$) was determined by conventional three-dimensional Patterson and electron-density syntheses. The heavy atom technique was used to establish the initial phases. BaO.B₂O₃ crystallizes in the trigonal system, space group $R\bar{3}c$, with 18 formula units per hexagonal cell. Unit-cell dimensions, referred to hexagonal axes, are $a=b=7.235$, $c=39.192$ Å. Least-squares refinement with 498 independent reflections yielded a reliability index of 5.7 %, based on the observed data only. The anion in the structure is a nearly planar $[B_3O_6]^{3-}$ group constructed of three BO₃ triangles each of which shares two of the three corners. The structure contains two crystallographically distinct barium atoms located in positions having point symmetries 32 and 3. About the barium in the 32 point symmetry position the oxygens are arranged in a trigonal prism. About the barium which lies in the 3 point symmetry position the oxygen coordination is ninefold.

Introduction

As part of a continuing program aimed at achieving a better understanding of the structural principles of anhydrous borate compounds, the structure of the high temperature form of BaO.B₂O₃ was selected for study. Levin & McMurdie (1949) have investigated the BaO–B₂O₃ system and found that BaO.B₂O₃ exists as the primary phase in mixtures containing approximately 56 to 78% BaO. They reported that this compound

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existed in two polymorphic forms, but the inversion temperature was not determined since the transition occurred over a range of 100°C to 400°C. The crystalline high temperature form of BaO.B₂O₃ (m.p. 1095 ± 5 °C) can be quenched and studied at room temperature. McMurdie & Levin found this crystalline form to be highly birefringent, uniaxial negative, with $N_e = 1.528$ and $N_o = 1.667$. Preliminary unit-cell dimensions and possible space groups have been reported by Block, Perloff & Weir (1964), and the infrared spectrum has been investigated by Weir & Schroeder (1964), who suggested the presence of a $[B_3O_6]^{3-}$ ring.