Moments of the Probability Density Function of R_2 Approached *Via* Conditional Probabilities. V. Incorporation of the *A Priori* Knowledge of Atomic Coordinates in the Evaluation of Moments of R_2

By W. K. L. Van Havere and A. T. H. Lenstra

University of Antwerp (UIA), Department of Chemistry, Universiteitsplein 1, B-2610 Wilrijk, Belgium

Abstract

First and second moments of $P(R_2)$ are evaluated for models denoted symbolically by $\{g,f;a\}$, containing a atoms known *a priori* to be correct, g (new) atoms correctly and f (new) atoms incorrectly placed. Formulas are derived, valid for the space groups $P1$ and $P\bar{1}$, using explicitly the set of observed reflections as well as the *a priori* knowledge about the a atoms. It is demonstrated that the implementation of the latter information decreases $\sigma(R_2)$ and enhances considerably the resolving power of R_2-based criteria to discriminate between a correct and an incorrect model.

1. Introduction

Our research on automated crystal-structure determination is centered around the study of mathematical criteria which indicate the correctness of a tentative model. As mathematical indicator function we use R_2, defined as

$$R_2 \equiv \sum_H (E_o^2 - \eta^2 E_c^2)^2 / \sum_H E_o^4, \qquad (1.1)$$

where E_o and E_c are the normalized structure factors for the observed N-atom structure and the tentative n-atom model ($n \leq N$), respectively. For point atoms with equal scattering power η^2 can be written as

$$\eta^2 \equiv \eta_c^2 / \eta_o^2 = n/N. \qquad (1.2)$$

So far, R_2-controlled structure evaluation routines (*e.g.* Van de Mieroop, 1978) used only the first moment of the probability density function $P(R_2)$. The decision whether a model is correct or not is based on the comparison of the actual R_2 value of the model with an appropriate theoretical estimate of R_2. This somewhat simplistic approach had to be taken, instead of a more sophisticated and powerful one based on statistical decision procedures, for want of a theory to evaluate the higher moments of $P(R_2)$. Recently, we showed (Van Havere & Lenstra, 1983a, b; referred to hereafter as parts I and II) that higher moments can only be evaluated by taking the finiteness of data sets explicitly into account through the concept of conditional probabilities. In this way we could remove the inconsistencies of older theories, which assumed the existence of infinite data sets.

The goal of an X-ray determination is a complete and correct structural model or an $\{N,0\}$ model in a nomenclature where $\{g, f\}$ represents a model with g correctly and f incorrectly placed atoms ($g + f \leq N$). In practice one may attain $\{N,0\}$ by two different approaches: (i) from a complete but only partially correct starting model or (ii) from an incomplete but correct one. The first, which may be called the rearranging or random-atom approach, starts in the worst possible case from $\{0,N\}$, rearranges atomic positions, sifts out incorrect atoms and proceeds *via* intermediate models $\{i, N-i\}$ to the final structure. A starting model may be obtained from one of the many direct-methods programs. The second, which may be called the additive or zero-atom approach, starts from a partial model, independently known to be correct $\{g,0\}$. Then, new atoms are added iteratively and tested, thereby avoiding the addition of incorrect atoms. The starting model may be obtained from a Patterson map, while possible new atomic coordinates are generated from a heavy-atom Fourier synthesis or from procedures such as *DIRDIF* (Beurskens & Noordik, 1972). In the zero-atom approach one strives for a test procedure which allows g to start from zero: the $\{0,0\}$ model.

In part III (Van Havere & Lenstra, 1983c) of this series we demonstrated that, using R_2 as an indicator function, the zero-atom approach has the better chance of being successful. This followed from a study of the resolving power S of R_2, defined as

$$S = \frac{\langle R_2\{\text{incorrect}\}\rangle - \langle R_2\{\text{correct}\}\rangle}{3[\sigma(R_2\{\text{incorrect}\}) + \sigma(R_2\{\text{correct}\})]}. \qquad (1.3)$$

Clearly, the resolving power increases if one lowers the spread of $P(R_2)$. An improvement, not yet considered, is to use the information about the atoms already known to be correct. We will do so by using the set of structure-factor amplitudes, $\mathscr{E}_a \equiv \{E_a(H)\}$, associated with the known part of the model as an extra condition in the calculus of probabilities. The other, normal, condition is the set of E values observed for the structure, $\mathscr{E}_o \equiv \{E_o(H)\}$. We will proceed to evaluate $\langle R_2; \mathscr{E}_o, \mathscr{E}_a \rangle$ and $\sigma^2(R_2; \mathscr{E}_a, \mathscr{E}_o)$ for the space groups $P1$ and $P\bar{1}$. The implications of the a priori knowledge will be discussed for three different situations: (i) all added, trial atoms are badly misplaced; (ii) all added, trial atoms are correctly positioned; (iii) some added atoms are correct, the others are incorrect.

To incorporate the a priori known atoms we modify our model nomenclature to $\{g, f; a\}$, where a denotes the a priori known atoms, g the correctly and f the incorrectly positioned ones. Within the present framework we will limit ourselves to calculate the first and second moments of $P(R_2)$, since $P(R_2)$ can be approximated as a Gaussian with sufficient accuracy (part I).

$$\langle R_2; \mathscr{E}_o, \mathscr{E}_a \rangle = 1 + \eta^4 \frac{\sum_H \langle E_c^4; E_o, E_a \rangle}{\sum_H E_o^4}$$

$$- 2\eta^2 \frac{\sum_H E_o^2 \langle E_c^2; E_o, E_a \rangle}{\sum_H E_o^4} \qquad (1.4)$$

$$\sigma^2(R_2; \mathscr{E}_o, \mathscr{E}_a) = \{\sum_H \eta^8 (\langle E_c^8; E_o, E_a \rangle - \langle E_c^4; E_o, E_a \rangle^2)$$

$$- \sum_H 4\eta^6 E_o^2 (\langle E_c^6; E_o, E_a \rangle$$

$$- \langle E_c^4; E_o, E_a \rangle \langle E_c^2; E_o, E_a \rangle)$$

$$+ \sum_H 4\eta^4 E_o^4 (\langle E_c^4; E_o, E_a \rangle$$

$$- \langle E_c^2; E_o, E_a \rangle^2)\} / \{\sum_H E_o^4\}^2. \qquad (1.5)$$

Formulas (1.4) and (1.5) reflect the approximation of $\langle E_c^n; \mathscr{E}_o, \mathscr{E}_a \rangle$ by $\langle E_c^n; E_o, E_a \rangle$, i.e. we ignore the correlation between two points in reciprocal space. The necessity to do so as well as the implications are analyzed in part I. It was shown that this approximation leads to negligible errors.

2. The added atoms are incorrect

2.1. Space group $P1$

Fig. 1 depicts the relations between structure factors associated with the different constituents of the total

structure. The distribution needed to evaluate formulas (1.4) and (1.5) is $P(E_c; E_o, E_a)$. Realizing that for point atoms

$$E_H = N^{-1/2} F_H, \qquad (2.1.1)$$

where F_H is defined as usual as

$$F_H = \sum_{j=1}^{N} f_j \exp(-2\pi i H r_j), \qquad (2.1.2)$$

and realizing that for added incorrect atoms E_o and E_c are statistically independent variables, one can write

$$P(E_c; E_o, E_a) = \frac{P(E_c, E_o; E_a)}{P(E_o; E_a)}.$$

If it is assumed that

$$P(E_c, E_o; E_a) = P(E_c; E_a) P(E_o; E_a),$$

then

$$P(E_c; E_o, E_a) = P(E_c; E_a). \qquad (2.1.3)$$

If we then assume that the atoms in the rest structure and in the added model are both randomly placed, we can use the formulas derived by Srinivasan & Parthasarathy (1976) for large structures:

$$P(E_c; E_a) = \frac{2E_c \eta_c^2}{\eta_c^2 - \eta_a^2} \exp\left(-\frac{\eta_c^2 E_c^2 + \eta_a^2 E_a^2}{\eta_c^2 - \eta_a^2}\right)$$

$$\times I_0 \left(\frac{2\eta_c \eta_a E_c E_a}{\eta_c^2 - \eta_a^2}\right), \qquad (2.1.4)$$

where I_0 is a modified Bessel function of the first kind and order zero. η_c^2 and η_a^2 are respectively the number of atoms in the total model and the number of atoms known a priori. The moments of this distribution can be written as (see Appendix A)
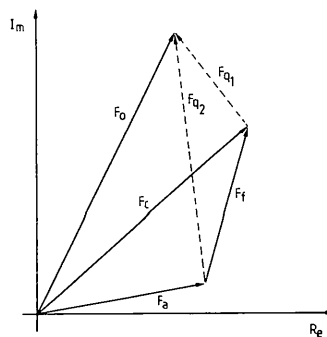

Fig. 1. Relation between structure factors of an N-atom structure (F_o) and an n-atom model (F_c), in which f atoms (F_f) are incorrectly placed and a atoms are placed on correct positions, known a priori $F(a)$; i.e. the situation $\{0, f; a\}$. The figure also gives the relation between structure factors of an N-atom structure in the situation $\{g, 0; a\}$ if one reads F_g in place of F_f. F_{q_1} and F_{q_2} are taken to arise from random rest structures.

$$\langle E_c^{2n}; E_a \rangle = n! \left(\frac{\eta_c^2 - \eta_a^2}{\eta_c^2}\right)^n {}_1F_1\left(-n; 1; -\frac{\eta_a^2 E_a^2}{\eta_c^2 - \eta_a^2}\right),$$

(2.1.5)

in which ${}_1F_1(\alpha; \beta; x)$ is a confluent hypergeometric function (Bateman, 1953). Since in our case $\alpha = -n$ (α a negative integer), (2.1.5) reduces to a polyomial in E_a^2, which gives after substitution in (1.4)

$$\langle R_2; \mathscr{E}_o, \mathscr{E}_a \rangle$$

$$= \left\{ \sum_H E_o^4 \right.$$

$$- \sum_H 2 \frac{\eta_c^2}{\eta_o^2} E_o^2 \left[\frac{\eta_a^2}{\eta_c^2} E_a^2 + \left(1 - \frac{\eta_a^2}{\eta_c^2}\right)\right]$$

$$+ \sum_H \frac{\eta_c^4}{\eta_o^4} \left[\frac{\eta_a^4}{\eta_c^4} E_a^4 + 4 \frac{\eta_a^2}{\eta_c^2} \left(1 - \frac{\eta_a^2}{\eta_c^2}\right) E_a^2\right.$$

$$+ \left. 2 \left(1 - \frac{\eta_a^2}{\eta_c^2}\right)^2 \right] \right\} \bigg/ \sum_H E_o^4,$$

(2.1.6)

and, after substitution in (1.5),

$$\sigma^2(R_2; \mathscr{E}_o, \mathscr{E}_a)$$

$$= \left\{ \sum_H \frac{\eta_c^8}{\eta_o^8} \left[8 \frac{\eta_a^6}{\eta_c^6} \left(1 - \frac{\eta_a^2}{\eta_c^2}\right) E_a^6 \right.\right.$$

$$+ 52 \frac{\eta_a^4}{\eta_c^4} \left(1 - \frac{\eta_a^2}{\eta_c^2}\right)^2 E_a^4$$

$$+ \left. 80 \frac{\eta_a^2}{\eta_c^2} \left(1 - \frac{\eta_a^2}{\eta_c^2}\right)^3 E_a^2 + 20 \left(1 - \frac{\eta_a^2}{\eta_c^2}\right)^4\right]$$

$$- \sum_H 4 \frac{\eta_c^6}{\eta_o^6} E_o^2 \left[4 \frac{\eta_a^4}{\eta_c^4} \left(1 - \frac{\eta_a^2}{\eta_c^2}\right) E_a^4 \right.$$

$$+ \left. 12 \frac{\eta_a^2}{\eta_c^2} \left(1 - \frac{\eta_a^2}{\eta_c^2}\right)^2 E_a^2 + 4 \left(1 - \frac{\eta_a^2}{\eta_c^2}\right)^3\right]$$

$$+ \sum_H 4 \frac{\eta_c^4}{\eta_o^4} E_o^4 \left[2 \frac{\eta_a^2}{\eta_c^2} \left(1 - \frac{\eta_a^2}{\eta_c^2}\right) E_a^2 \right.$$

$$+ \left.\left. \left(1 - \frac{\eta_a^2}{\eta_c^2}\right)^2\right] \right\} \bigg/ \left\{\sum_H E_o^4\right\}^2.$$

(2.1.7)

2.2. Space group $P\bar{1}$

For space group $P\bar{1}$ we define E_H as

$$E_H = (2/N)^{1/2} \sum_{j=1}^{N} \cos(2\pi H r_j),$$

(2.2.1)

where N is the number of atoms in the asymmetric part of the unit cell. Completely analogously to $P1$ we take

the distribution given by Srinivasan & Parthasarathy (1976):

$$P(E_c; E_a)$$

$$= \left(\frac{2\eta_c^2}{\pi(\eta_c^2 - \eta_a^2)}\right)^{1/2} \exp\left\{-\frac{\eta_c^2 E_c^2 + \eta_a^2 E_a^2}{2(\eta_c^2 - \eta_a^2)}\right\}$$

$$\times \cosh\left\{\frac{\eta_c \eta_a E_c E_a}{\eta_c^2 - \eta_a^2}\right\}.$$

(2.2.2)

Its moments can be written as (see Appendix B)

$$\langle E_c^{2n}; E_a \rangle = 2^n \frac{\Gamma(n + \frac{1}{2})}{\Gamma(\frac{1}{2})} \left(\frac{\eta_c^2 - \eta_a^2}{\eta_c^2}\right)^n$$

$$\times {}_1F_1\left(-n; \frac{1}{2}; -\frac{1}{2} \frac{\eta_a^2 E_a^2}{\eta_c^2 - \eta_a^2}\right).$$

(2.2.3)

Again, the hypergeometric function reduces to polynomials in E_a^2 and substitution in (1.4) and (1.5) gives

$$\langle R_2; \mathscr{E}_o, \mathscr{E}_a \rangle$$

$$= \left\{ \sum_H E_o^4 \right.$$

$$- \sum_H 2 \frac{\eta_c^2}{\eta_o^2} E_o^2 \left[\frac{\eta_a^2}{\eta_c^2} E_a^2 + \left(1 - \frac{\eta_a^2}{\eta_c^2}\right)\right]$$

$$+ \sum_H \frac{\eta_c^4}{\eta_o^4} \left[\frac{\eta_a^4}{\eta_c^4} E_a^4 + 6 \frac{\eta_a^2}{\eta_c^2} \left(1 - \frac{\eta_a^2}{\eta_c^2}\right) E_a^2\right.$$

$$+ \left. 3 \left(1 - \frac{\eta_a^2}{\eta_c^2}\right)^2\right] \right\} \bigg/ \sum_H E_o^4$$

(2.2.4)

$$\sigma^2(R_2; \mathscr{E}_o, \mathscr{E}_a)$$

$$= \left\{ \sum_H \frac{\eta_c^8}{\eta_o^8} \left[6 \frac{\eta_a^6}{\eta_c^6} \left(1 - \frac{\eta_a^2}{\eta_c^2}\right) E_a^6\right.\right.$$

$$+ 168 \frac{\eta_a^4}{\eta_c^4} \left(1 - \frac{\eta_a^2}{\eta_c^2}\right)^2 E_a^4$$

$$+ \left. 384 \frac{\eta_a^2}{\eta_c^2} \left(1 - \frac{\eta_a^2}{\eta_c^2}\right)^3 E_a^2 + 96 \left(1 - \frac{\eta_a^2}{\eta_c^2}\right)^4\right]$$

$$- \sum_H 4 \frac{\eta_c^6}{\eta_o^6} E_o^2 \left[8 \frac{\eta_a^4}{\eta_c^4} \left(1 - \frac{\eta_a^2}{\eta_c^2}\right) E_a^4\right.$$

$$+ \left. 36 \frac{\eta_a^2}{\eta_c^2} \left(1 - \frac{\eta_a^2}{\eta_c^2}\right)^2 E_a^2 + 12 \left(1 - \frac{\eta_a^2}{\eta_c^2}\right)^3\right]$$

$$+ \sum_H 4 \frac{\eta_c^4}{\eta_o^4} E_o^4 \left[4 \frac{\eta_a^2}{\eta_c^2} \left(1 - \frac{\eta_a^2}{\eta_c^2}\right) E_a^2\right.$$

$$+ \left.\left. 2 \left(1 - \frac{\eta_a^2}{\eta_c^2}\right)^2\right] \right\} \bigg/ \left\{\sum_H E_o^4\right\}^2.$$

(2.2.5)

3. The added atoms are correct

3.1. *Space group* P1

The relations between the contributions to the structure factors are illustrated in Fig. 2. Again we have to know the distribution function $P(E_c;E_o,E_a)$. Now, however, the correlation between E_c and E_o does not vanish and thus the distribution will be more complex. Using the theorem of Bayes, we have

$$P(E_c;E_o,E_a) = \frac{P(E_o;E_c,E_a)\,P(E_c;E_a)}{P(E_o;E_a)}. \quad (3.1.1)$$

$P(E_c;E_a)$ is given by (2.1.4) and $P(E_o;E_a)$ is again given by (2.1.4) provided E_o and η_o replace E_c and η_c. The distribution $P(E_o;E_c,E_a)$ is equal to $P(E_o;E_c)$ because the condition towards E_a includes the one towards E_c. Again $P(E_o;\ E_c)$ is given by (2.1.4) by suitable change of parameters. Substitution of the relevant formulas into (3.1.1) gives

$$P(E_c;E_o,E_a)$$

$$= \frac{2\eta_c^2(\eta_o^2-\eta_a^2)E_c}{(\eta_o^2-\eta_c^2)(\eta_c^2-\eta_a^2)} I_0^{-1}\left(\frac{2\eta_o\eta_a E_o E_a}{\eta_o^2-\eta_a^2}\right)$$

$$\times \exp\{-[(\eta_c^2-\eta_a^2)^2\eta_o^2 E_o^2 + (\eta_o^2-\eta_a^2)^2\eta_c^2 E_c^2$$

$$+ (\eta_o^2-\eta_c^2)^2\eta_a^2 E_a^2]$$

$$\times [(\eta_o^2-\eta_a^2)(\eta_c^2-\eta_a^2)(\eta_o^2-\eta_c^2)]^{-1}\}$$

$$\times I_0\left(\frac{2\eta_o\eta_c E_o E_c}{\eta_o^2-\eta_c^2}\right) I_0\left(\frac{2\eta_c\eta_a E_c E_a}{\eta_c^2-\eta_a^2}\right). \quad (3.1.2)$$

The intensity moments necessary to calculate the first and second moment of R_2 for this situation are

$$\langle E_c^2;E_o,E_a\rangle = \eta_1^2 E_o^2 + \eta_2^2 E_a^2 + \eta_3$$

$$+ \{2\eta_1\eta_2 E_o E_a\}\frac{I_1(2\eta_4 E_o E_a)}{I_0(2\eta_4 E_o E_a)}$$

$$\langle E_c^4;E_o,E_a\rangle$$

$$= \eta_1^4 E_o^4 + 6\eta_1^2\eta_2^2 E_o^2 E_a^2 + \eta_2^4 E_a^4$$

$$+ 4\eta_1^2\eta_3 E_o^2 + 4\eta_2^2\eta_3 E_a^2 + 2\eta_3^2$$

$$+ \{4\eta_1^3\eta_2 E_o^3 E_a + 4\eta_1\eta_2^3 E_o E_a^3 + 6\eta_1\eta_2\eta_3 E_o E_a\}$$

$$\times \frac{I_1(2\eta_4 E_o E_a)}{I_0(2\eta_4 E_o E_a)}$$

$$\langle E_c^6;E_o,E_a\rangle$$

$$= \eta_1^6 E_o^6 + 15\eta_1^4\eta_2^2 E_o^4 E_a^2 + 15\eta_1^2\eta_2^4 E_o^2 E_a^4 + \eta_2^6 E_a^6$$

$$+ 9\eta_1^4\eta_3 E_o^4 + 50\eta_1^2\eta_2^2\eta_3 E_o^2 E_a^2 + 9\eta_2^4\eta_3 E_a^4$$

$$+ 18\eta_1^2\eta_3^2 E_o^2 + 18\eta_2^2\eta_3^2 E_a^2 + 6\eta_3^3$$

$$+ \{6\eta_1^5\eta_2 E_o^5 E_a + 6\eta_1\eta_2^5 E_o E_a^5 + 20\eta_1^3\eta_2^3 E_o^3 E_a^3$$

$$+ 30\eta_1^3\eta_2\eta_3 E_o^3 E_a + 30\eta_1\eta_2^3\eta_3 E_o E_a^3$$

$$+ 22\eta_1\eta_2\eta_3^2 E_o E_a\}\frac{I_1(2\eta_4 E_o E_a)}{I_0(2\eta_4 E_o E_a)}$$

$$\langle E_c^8;E_o,E_a\rangle$$

$$= \eta_1^8 E_o^8 + 28\eta_1^6\eta_2^2 E_o^6 E_a^2 + 70\eta_1^4\eta_2^4 E_o^4 E_a^4$$

$$+ 28\eta_1^2\eta_2^6 E_o^2 E_a^6 + \eta_2^8 E_a^8$$

$$+ 16\eta_1^6\eta_3 E_o^6 + 224\eta_1^4\eta_2^2\eta_3 E_o^4 E_a^2$$

$$+ 224\eta_1^2\eta_2^4\eta_3 E_o^2 E_a^4 + 16\eta_2^6\eta_3 E_a^6$$

$$+ 72\eta_1^4\eta_3^2 E_o^4 + 380\eta_1^2\eta_2^2\eta_3^2 E_o^2 E_a^2 + 72\eta_2^4\eta_3^2 E_a^4$$

$$+ 96\eta_1^2\eta_3^3 E_o^2 + 96\eta_2^2\eta_3^3 E_a^2 + 24\eta_3^4$$

$$+ \{8\eta_1^7\eta_2 E_o^7 E_a + 8\eta_1\eta_2^7 E_o E_a^7 + 280\eta_1^3\eta_2^3\eta_3 E_o^3 E_a^3$$

$$+ 56\eta_1^5\eta_2 E_o^5 E_a^3 + 56\eta_1^3\eta_2^5 E_o^3 E_a^5$$

$$+ 84\eta_1^5\eta_2\eta_3 E_o^5 E_a + 84\eta_1\eta_2^5\eta_3 E_o E_a^5$$

$$+ 208\eta_1^3\eta_2\eta_3^2 E_o^3 E_a + 208\eta_1\eta_2^3\eta_3^2 E_o E_a^3$$

$$+ 100\eta_1\eta_2\eta_3^3 E_o E_a\}\frac{I_1(2\eta_4 E_o E_a)}{I_0(2\eta_4 E_o E_a)}, \quad (3.1.3)$$

where

$$\eta_1 = \frac{(\eta_c^2-\eta_a^2)\eta_o}{(\eta_o^2-\eta_a^2)\eta_c}, \quad \eta_2 = \frac{(\eta_o^2-\eta_c^2)\eta_a}{(\eta_o^2-\eta_a^2)\eta_c},$$

$$\eta_3 = \frac{(\eta_o^2-\eta_c^2)(\eta_c^2-\eta_a^2)}{(\eta_o^2-\eta_a^2)\eta_c^2}, \quad \eta_4 = \frac{\eta_o\eta_a}{(\eta_o^2-\eta_a^2)}. \quad (3.1.4)$$

I_1 and I_0 are modified Bessel functions of the first kind respectively of order one and zero. The general procedures to obtain these moments are discussed in Appendix C. Substitution of these moments in (1.4) and (1.5) would give the wanted expressions. The expressions are rather lengthy and will be omitted. Their evaluation, however, is a trivial matter using a computer.

3.2. *Space group* P1̄

The moments of the conditional probability distribution in P1̄ are calculated in an analogous way to those in P1, starting from (3.1.1).

In P1̄ the distributions $P(E_o;E_a)$, $P(E_c;E_a)$ and $P(E_o;E_c)$ are readily obtained by suitable changes of parameters in (2.2.2). Then, substitution into (3.1.1) gives

$$P(E_c;E_o,E_a)$$

$$= \left(\frac{2}{\pi}\frac{\eta_c^2(\eta_o^2-\eta_a^2)}{(\eta_o^2-\eta_c^2)(\eta_c^2-\eta_a^2)}\right)^{1/2}\cosh^{-1}\left(\frac{\eta_o\eta_a E_o E_a}{\eta_o^2-\eta_a^2}\right)$$

$$\times \exp\{-\tfrac{1}{2}[(\eta_c^2-\eta_a^2)^2\eta_o^2 E_o^2 + (\eta_o^2-\eta_a^2)^2\eta_c^2 E_c^2$$

$$+ (\eta_o^2-\eta_c^2)^2\eta_a^2 E_a^2]$$

$$\times [(\eta_o^2-\eta_c^2)(\eta_c^2-\eta_a^2)(\eta_o^2-\eta_a^2)]^{-1}\}$$

$$\times \cosh\left(\frac{\eta_o\eta_c E_o E_c}{\eta_o^2-\eta_c^2}\right)\cosh\left(\frac{\eta_c\eta_a E_c E_a}{\eta_c^2-\eta_a^2}\right). \quad (3.2.1)$$

The intensity moments necessary to calculate the first and second moments of R_2 for this situation are

$$\langle E_c{}^2; E_o, E_a \rangle = \eta_1^2 E_o^2 + \eta_2^2 E_a^2 + \eta_3$$
$$+ \{\eta_1 h_2 E_o E_a\} \tanh(\eta_4 E_o E_a)$$

$$\langle E_c^4; E_o E_a \rangle$$
$$= \eta_1^4 E_o^4 + 6\eta_1^2\eta_2^2 E_o^2 E_a^2 + \eta_2^4 E_a^4$$
$$+ 6\eta_1^2\eta_3 E_o^2 + 6\eta_2^2\eta_3 E_a^2 + 3\eta_3^2$$
$$+ \{4\eta_1^3\eta_2 E_o^3 E_a + 4\eta_1\eta_2^3 E_o E_a^3$$
$$+ 12\eta_1\eta_2\eta_3 E_o E_a\} \tanh(\eta_4 E_o E_a)$$

$$\langle E_c^6; E_o, E_a \rangle$$
$$= \eta_1^6 E_o^6 + 15\eta_1^4\eta_2^2 E_o^4 E_a^2 + 15\eta_1^2\eta_2^4 E_o^2 E_a^4 + \eta_2^6 E_a^6$$
$$+ 15\eta_1^4\eta_3 E_o^4 + 90\eta_1^2\eta_2^2\eta_3 E_o^2 E_a^2 + 15\eta_2^4\eta_3 E_a^4$$
$$+ 45\eta_1^2\eta_3^2 E_o^2 + 45\eta_2^2\eta_3^2 E_a^2 + 15\eta_3^3$$
$$+ \{6\eta_1^5\eta_2 E_o^5 E_a + 6\eta_1\eta_2^5 E_o E_a^5 + 20\eta_1^3\eta_2^3 E_o^3 E_a^3$$
$$+ 60\eta_1^3\eta_2\eta_3 E_o^3 E_a + 60\eta_1\eta_2^3\eta_3 E_o E_a^3$$
$$+ 90\eta_1\eta_2\eta_3^2 E_o E_a\} \tanh(\eta_4 E_o E_a)$$

$$\langle E_c^8; E_o, E_a \rangle$$
$$= \eta_1^8 E_o^8 + 28\eta_1^6\eta_2^2 E_o^6 E_a^2 + 70\eta_1^4\eta_2^4 E_o^4 E_a^4$$
$$+ 28\eta_1^2\eta_2^6 E_o^2 E_a^6 + \eta_2^8 E_o^8$$
$$+ 28\eta_1^6\eta_3 E_o^6 + 420\eta_1^4\eta_2^2\eta_3 E_o^4 E_a^2$$
$$+ 420\eta_1^2\eta_2^4\eta_3 E_o^2 E_a^4 + 28\eta_2^6\eta_3 E_a^6$$
$$+ 210\eta_1^4\eta_3^2 E_o^4 + 1260\eta_1^2\eta_2^2\eta_3^2 E_o^2 E_a^2 + 210\eta_2^4\eta_3^2 E_a^4$$
$$+ 420\eta_1^2\eta_3^3 E_o^2 + 420\eta_2^2\eta_3^3 E_a^2 + 105\eta_3^4$$
$$+ \{8\eta_1^7\eta_2 E_o^7 E_a + 8\eta_1\eta_2^7 E_o E_a^7 + 560\eta_1^3\eta_2^3\eta_3 E_o^3 E_a^3$$
$$+ 56\eta_1^5\eta_2^3 E_o^5 E_a^3 + 56\eta_1^3\eta_2^5 E_o^3 E_a^5$$
$$+ 168\eta_1^5\eta_2\eta_3 E_o^5 E_a + 168\eta_1\eta_2^5\eta_3 E_o E_a^5$$
$$+ 840\eta_1^3\eta_2\eta_3^2 E_o^3 E_a + 840\eta_1\eta_2^3\eta_3^2 E_o E_a^3$$
$$+ 840\eta_1\eta_2\eta_3^3 E_o E_a\} \tanh(\eta_4 E_o E_a). \tag{3.2.2}$$

The general procedure to obtain these moments is discussed in Appendix D. Substitution of these moments in (1.4) and (1.5) gives the wanted expressions for the average value and spread of R_2.

4. Some added atoms are correct, others are incorrect

4.1. Space group $P1$

Let the added fragment contain, besides the a a priori known atoms, g atoms at their correct position and f atoms which are incorrectly placed. In terms of structure factors the relations are depicted in Fig. 2.

The derivation of $P(E_c; E_o, E_a)$ is analogous to that described in part III (Van Havere & Lenstra, 1983c).

$$P(E_c; E_o, E_o) = \int_0^\infty P(E_c, E_p; E_o, E_a) \, dE_p. \tag{4.1.1}$$

From the theorem of Bayes we know that

$$P(E_c; E_o, E_a) = \int_0^\infty P(E_c; E_p, E_o, E_a) P(E_p; E_o, E_a) dE_p. \tag{4.1.2}$$

Using the arguments used in part III one can easily see that

$$P(E_c; E_p, E_a, E_o) = P(E_c; E_p, E_o) = \frac{P(E_c, E_o; E_p)}{P(E_o; E_p)}.$$

Under the assumption that E_c and E_o are statistically independent variables we have

$$P(E_c; E_p, E_o, E_a) = P(E_c; E_p). \tag{4.1.3}$$

It is also easy to see that (4.1.3) has the same form as (2.1.4), whereas $P(E_p; E_o, E_a)$ is analogous to (3.1.2). The integral resulting from substitution of these distributions in (4.1.2) can be expressed directly as a confluent form of a Lauricella function (Exton, 1978). We have, however, obtained the moments of this distribution in an indirect way, which allows us to use the formulas derived for the cases where either the added atoms are completely correctly or completely incorrectly positioned. From (4.1.2) and (4.1.3) one sees that the moments can be written as

$$\langle E_c^{2n}; E_o, E_a \rangle = \int_0^\infty \int_0^\infty E_c^{2n} P(E_c; E_p)$$
$$\times P(E_p; E_o, E_a) \, dE_p dE_c. \tag{4.1.4}$$

Integrating first over E_c gives

$$\langle E_c^{2n}; E_o, E_a \rangle = \int_0^\infty \langle E_c^{2n}; E_p \rangle$$
$$\times P(E_p; E_o, E_a) \, dE_p, \tag{4.1.5}$$

where $\langle E_c^{2n}; E_p \rangle$ is equivalent to (2.1.5). Inserting this moment, which is a polynomial in E_p^2, in (4.1.5) shows
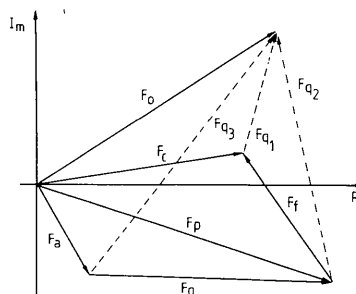

Fig. 2. Relation between structure factors of an N-atom structure (F_a) and an n-atom model (F_c), in which g and f atoms are placed respectively correct and incorrect. a atoms are placed a priori. The contribution of all correct atoms is denoted $p = a + g$.

us that (4.1.5) also reduces to a polynomial but now one in moments of $P(E_p;E_o,E_a)$. These moments are of the same form as (3.1.3). It would be a laborious task to perform all further substitutions by hand. Fortunately, the fully expanded formulas are not needed to calculate the numbers needed to describe these models.

4.2. Space Group $P\bar{1}$

The formulas for this space group can be obtained in an identical way as for $P1$, by simply using everywhere in the calculations the moments of $P\bar{1}$ given in §§ 2.2 and 3.2.

5. Discussion

The aim of this work is to improve the usefulness of the R_2 criterion in the zero-atom approach by taking explicitly into account that, at some particular point in the analysis, the positions of a number of atoms in the test model are known to be correct. Such knowledge might either have come from an independent outside source (e.g. a heavy atom from a Patterson map, or a fragment located after a rotation–translation search) or be the result of earlier stages in the R_2-controlled analysis. This extra information is then added to the information contained in the set of observed E values. The operation is successful if it increases the resolving power S (1.3) of the R_2 criterion compared to $S(R_2)$ in which only the knowledge about E_o values is taken into account.

We can limit the discussion to the space group $P1$, since for $P\bar{1}$ the numerical values are different, but the general conclusions are the same. In our example the *observed* structure is a set of 100 equal atoms randomly placed in the cell, with a corresponding set of 1530 *observed* reflections. We compare the average value of R_2 (Table 1) and its spread (Table 2) for models $\{a + g,f;0\}$ *versus* $\{g,f;a\}$ and particularly $S(R_2)$ (Table 3) for situations going from $\{a,0;0\}$ to $\{a + g,0;0\}$ *versus* $\{0,0;a\}$ to $\{g,0;a\}$.

R_2 values for $\{g,f;a\}$ were calculated as outlined in § 3.1, those for $\{a + g,f;a\}$ from equations (3.12)–(3.13) given in part III. The numbers in Table 1 show, as was expected, only a very small dependence upon the introduction of a priori known atoms. Since the number of atoms treated statistically is smaller if a atoms known a priori are present, one expects, however, a decrease of $\sigma(R_2)$. Table 2 shows this indeed to be the case. Substitution of the appropriate values in (1.3) gives the resolving power, $S(R_2)$, of the R_2 criterion between two models. Table 3 demonstrates that the incorporation of a priori known atoms increases $S(R_2)$ considerably. Values of $S \geq 1$ indicate a perfect discrimination between models. The earlier (i.e after the addition of the smaller number of new

correct trial atoms) in the analysis $S(R_2) \geq 1$ is reached, the better an R_2 controlled determination lends itself to automation. It is therefore most important that the incorporation of a priori knowledge (Table 3) shifts the turning point $S(R_2) \geq 1$ towards lower a values.

Table 1. *Comparison of average R_2 values for some models with and without the knowledge of a priori correct atoms*

a	$\{0,10;a\}$	$\{a,10;0\}$	$\{10,0;a\}$	$\{a + 10,0;a\}$
10	0·83093	0·83062	0·80116	0·80058
20	0·75375	0·75019	0·70399	0·70027
30	0·66616	0·66951	0·59759	0·59980
40	0·57661	0·58874	0·48307	0·49932
50	0·49543	0·50804	0·38855	0·39895
60	0·42474	0·42753	0·29679	0·29877
70	0·35675	0·34730	0·20439	0·19887
80	0·28035	0·26741	0·10284	0·09927

Table 2. *Comparison of $\sigma(R_2)$ values for some models with and without the knowledge of a priori correct atoms*

a	$\{0,10;a\}$	$\{a,10;0\}$	$\{10,0;a\}$	$\{a + 10,0;a\}$
10	0·00549	0·00650	0·00626	0·00751
20	0·00709	0·00992	0·00764	0·01069
30	0·00832	0·01292	0·00841	0·01294
40	0·00932	0·01512	0·00871	0·01401
50	0·00982	0·01627	0·00843	0·01375
60	0·00991	0·01624	0·00774	0·01208
70	0·00997	0·01499	0·00656	0·00906
80	0·00972	0·01265	0·00422	0·00489

Table 3. *Comparison of the resolving power, $S(R_2)$, with and without using the knowledge of the a priori correct atoms*

a	S_1	S_2
10	0·84463	0·71475
20	1·12648	0·80753
30	1·36630	0·89847
40	1·62775	1·02306
50	1·95202	1·21136
60	2·41602	1·51578
70	3·07278	2·05737
80	4·24275	3·19514

$S_1 = (\langle R_2\{0,10;a\}\rangle - \langle R_2\{10,0;a\}\rangle)/3[\sigma(R_2\{0,10;a\}) + \sigma(R_2\{10,0;a\})]$.
$S_2 = (\langle R_2\{a,10;a\}\rangle - \langle R_2\{a + 10,0;a\}\rangle)/3[\sigma(R_2\{a,10;a\}) + \sigma(R_2\{a + 10,0;a\})]$.

APPENDIX A

The moments of (2.1.4) are written as

$$\langle E_c^\mu; E_a \rangle$$

$$= \frac{2\eta_c^2}{\eta_c^2 - \eta_a^2} \exp\left(-\frac{\eta_a^2 E_a^2}{\eta_c^2 - \eta_a^2}\right)$$

$$\times \int_0^\infty E_c^{\mu+1} \exp\left(-\frac{\eta_c^2 E_c^2}{\eta_c^2 - \eta_a^2}\right)$$

$$\times I_0\left(\frac{2\eta_c\eta_a E_c E_a}{\eta_c^2 - \eta_a^2}\right) dE_c. \qquad (A.1)$$

Using a generalization of Weber's first exponential integral (Bateman, 1953), we get

$$\int_0^\infty J_\nu(at) \exp(-p^2 t^2)\, t^{\mu-1}\, dt$$

$$= \frac{\Gamma(\tfrac{1}{2}\nu + \tfrac{1}{2}\mu)(\tfrac{1}{2}a/p)^\nu}{2p^\mu \Gamma(\nu+1)} {}_1F_1(\tfrac{1}{2}\nu + \tfrac{1}{2}\mu; \nu+1; -\frac{a^2}{4p^2}),$$

$$\mathrm{Re}(\nu + \mu) > 0,\ a \in C,\ \mathrm{Re}(p^2) > 0. \qquad (A.2)$$

This, together with the identity (Bateman, 1953)

$$I_\nu(z) = \exp(-i\tfrac{1}{2}\nu\pi) J_\nu[z \exp(i\pi/2)]$$

$$[-\pi < \arg(z) \leq \pi/2] \qquad (A.3)$$

and Kummer's first transformation (Bateman, 1953)

$$_1F_1(a; b; x) = e^x\, {}_1F_1(b - a; b; -x), \qquad (A.4)$$

we can write $(A.1)$ for the even moments, $\mu = 2n$, as

$$\langle E_c^{2n}; E_a \rangle$$

$$= n! \left(\frac{\eta_c^2 - \eta_a^2}{\eta_c^2}\right)^n {}_1F_1\left(-n; 1; -\frac{\eta_a^2 E_a^2}{\eta_c^2 - \eta_a^2}\right) \qquad (A.5)$$

with

$$_1F_1(a; b; x) = 1 + \frac{a}{b}\frac{x}{1!} + \frac{a(a+1)}{b(b+1)}\frac{x^2}{2!} + \cdots. \qquad (A.6)$$

Therefore, $(A.6)$ reduces, for a a negative integer, to a polynomial in E_a^2 of degree n.

APPENDIX B

The moments of (2.2.2) are written as

$$\langle E_c^\mu; E_a \rangle = \left(\frac{2\eta_c^2}{\pi(\eta_c^2 - \eta_a^2)}\right)^{1/2} \exp\left[-\frac{\eta_a^2 E_a^2}{2(\eta_c^2 - \eta_a^2)}\right],$$

$$\times \int_0^\infty E_c^\mu \exp\left[-\frac{\eta_c^2 E_c^2}{2(\eta_c^2 - \eta_a^2)}\right]$$

$$\times \cosh \frac{\eta_c\eta_a E_c E_a}{\eta_c^2 - \eta_a^2} dE_c. \qquad (B.1)$$

Using the identity (Bateman, 1953)

$$\cosh(z) = (\pi z/2)^{1/2} I_{-1/2}(z) \qquad (B.2)$$

and $(A.2)$–$(A.4)$, we find that $(B.1)$ becomes

$$\langle E_c^{2n}; E_a \rangle = 2^n \frac{\Gamma(n + \tfrac{1}{2})}{\Gamma(\tfrac{1}{2})} \left(\frac{\eta_c^2 - \eta_a^2}{\eta_c^2}\right)^n$$

$$\times {}_1F_1\left(-n; \tfrac{1}{2}; -\tfrac{1}{2}\frac{\eta_a^2 E_a^2}{\eta_c^2 - \eta_a^2}\right), \qquad (B.3)$$

since $-n$ is a negative integer $(B.3)$ reduces to a polynomial in E_a^2 of degree n.

APPENDIX C

The intensity distribution for correct added atoms, (3.1.2), is of the form

$$P(x,y,z) = ae^{-b} xe^{-cx^2} I_0(dx)I_0(gx). \qquad (C.1)$$

Thus,

$$\langle x^{2n}; y,z \rangle = ae^{-b} \int_0^\infty x^{2n+1} e^{-cx^2} I_0(dx)I_0(gx)\, dx. \qquad (C.2)$$

For $n = 0$ the result is easily found using the identity (Bateman, 1953)

$$\int_0^\infty xe^{-px^2} I_0(\varphi x)I_0(\xi x)\, dx = \frac{1}{2p} \exp\left(\frac{\varphi^2 + \xi^2}{4p}\right) I_0\left(\frac{\varphi\xi}{2p}\right). \qquad (C.3)$$

So

$$\langle x^0; y,z \rangle = \frac{ae^{-b}}{2c} \exp\left(\frac{d^2 + g^2}{4c}\right) I_0\left(\frac{dg}{2c}\right). \qquad (C.4)$$

To obtain the moments for $n \neq 0$, we use a theorem from the theory of Laplace transforms (Abramowitz & Stegun, 1972) which states that

$$\int_0^\infty t^n e^{-st} F(t)\, dt = (-1)^n f^{(n)}(s) \qquad (C.5)$$

with

$$f^{(n)}(s) = \frac{d^n f(s)}{ds^n}$$

$$f^{(0)}(s) = \int_0^\infty \exp(-st) F(t)\, dt. \qquad (C.6)$$

Replacing in $(C.2)$ cx^2 by t and introducing an extra variable s we get

$$\langle x^{2n}; y,z \rangle = \frac{a\, e^{-b}}{2c^{n+1}} \lim_{s \to 1} \int_0^\infty t^n \exp(-st)$$

$$\times I_0[d(t/c)^{1/2}] I_0[g(t/c)^{1/2}]\, dt. \qquad (C.7)$$

Equation (C.7) has now the form of (C.5) and thus after resubstitution of cx^2 for t we get

$$\langle x^{2n};y,z\rangle = \frac{ae^{-b}}{c^n} \lim_{s\to 1} \{(-1)^n$$

$$\times \frac{d^n}{ds^n} \int_0^\infty x \exp(-scx^2) I_0(dx) I_0(gx)\, dx\}.$$

(C.8)

Since this integral is now of the form of (C.3) one gets

$$\langle x^{2n};y,z\rangle = \frac{a\,e^{-b}}{2c^{n+1}}(-1)^n \lim_{s\to 1}\left\{\frac{d^n}{ds^n}\frac{1}{s}\right.$$

$$\left.\times \exp\left(\frac{d^2+g^2}{4cs}\right) I_0\left(\frac{dg}{2cs}\right)\right\}.$$

(C.9)

The only remaining task now is to perform the differentiation for those values of n needed for our purpose and to substitute the correct expressions for a, b, c, d and g. This gives us expressions (3.1.3).

APPENDIX D

The intensity distribution (3.2.1) for correct added atoms in the space group $P\bar{1}$ is of the form

$$P(x;y,z) = ae^{-b}\, e^{-cx^2} \cosh(dx) \cosh(gx). \quad (D.1)$$

Thus,

$$\langle x^{2n};y,z\rangle = ae^{-b}\int_0^\infty x^{2n} \exp(-cx^2)$$

$$\times \cosh(dx)\cosh(gx)\,dx. \quad (D.2)$$

Using the relation

$$\cosh(x) = (e^{+x}+e^{-x})/2 \quad (D.3)$$

and substituting

$$t = c^{1/2}x \pm \frac{d\pm g}{2c^{1/2}} \quad (D.4)$$

in the various integrals we get

$$\langle x^{2n};y,z\rangle$$

$$= \frac{a\,e^{-b}}{4c^{n+1/2}}\left\{\exp\left[\frac{(d+g)^2}{4c}\right]\right.$$

$$\times \left[\int_{-\frac{d+g}{2c^{1/2}}}^\infty \left(t+\frac{d+g}{2c^{1/2}}\right)^{2n} e^{-t^2}dt\right.$$

$$\left. + \int_{\frac{d+g}{2c^{1/2}}}^\infty \left(t-\frac{d+g}{2c^{1/2}}\right)^{2n} e^{-t^2}dt\right]$$

$$+ \exp\left[\frac{(d-g)^2}{4c}\right]\left[\int_{-\frac{d-g}{2c^{1/2}}}^\infty \left(t+\frac{d-g}{2c^{1/2}}\right)^{2n} e^{-t^2}dt\right.$$

$$\left.+ \int_{\frac{d-g}{2c^{1/2}}}^\infty \left(t-\frac{d-g}{2c^{1/2}}\right)^{2n} e^{-t^2}dt\right]\right\}.$$

(D.5)

Then, using the relation (Abramowitz & Stegun, 1972)

$$\frac{2}{\pi^{1/2}}\int_x^\infty \frac{(t-x)^n}{n!} e^{-t^2}dt = i^{2n}\,\mathrm{erfc}(x), \quad (D.6)$$

where

$$i^n\,\mathrm{erfc}(z) = \int_z^\infty i^{n-1}\,\mathrm{erfc}(t)\,dt, \; n=0,1,\ldots, \quad (D.7)$$

we get

$$\langle x^{2n};y,z\rangle$$

$$= \frac{\pi^{1/2}a(2n)!}{8c^{n+1/2}}e^{-b}\left\{\exp\left[\frac{(d+g)^2}{4c}\right]\left[i^{2n}\,\mathrm{erfc}\left(-\frac{d+g}{2c^{1/2}}\right)\right.\right.$$

$$\left.+ i^{2n}\,\mathrm{erfc}\left(\frac{d+g}{2c^{1/2}}\right)\right] + \exp\left[\frac{(d-g)^2}{4c}\right]$$

$$\left.\times\left[i^{2n}\,\mathrm{erfc}\left(-\frac{d-g}{2c^{1/2}}\right) + i^{2n}\mathrm{erfc}\left(\frac{d-g}{2c^{1/2}}\right)\right]\right\}.$$

(D.8)

With the help of the recursion relations (Abramowitz & Stegun, 1972)

$$i^n\,\mathrm{erfc}(z) = -\frac{z}{n} i^{n-1}\,\mathrm{erfc}(z) + \frac{1}{2n} i^{n-2}\,\mathrm{erfc}(z),$$

$$n = 1,2,3,\ldots \quad (D.9)$$

and the identities

$$i^{-1}\,\mathrm{erfc}(z) = \frac{z}{\pi^{1/2}}e^{-z^2}$$

$$i^0\,\mathrm{erfc}(z) = \mathrm{erfc}(z), \quad (D.10)$$

we can write (D.8) in terms of exponentials and error functions. After some algebraic manipulations and substitution of the correct expressions for a,b,c,d and g we get (3.2.2).

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New ZnS Polytypes of the Family 18L

BY S. SALIBA* AND S. MARDIX

Department of Electrical Engineering, University of Rhode Island, Kingston, RI 02881, USA

Abstract

ZnS crystals having wide polytypic regions were grown in sublimation. Twelve new polytypes of the family 18L were identified in one specimen. X-ray 10.l oscillation photographs are presented, the observed and calculated intensities are compared. A modified expression for intensity computations of rhombohedral polytypes is described.

Introduction

ZnS crystals grown by sublimation of a large number of adjacent regions stacked along their common c axis. Most of these regions are faulted 2H structures. A small number of specimens contain uniform polytypic regions, most of them less than 100 μm wide (along their c axis), wider regions are rare and regions of 500 μm are extremely rare (Alexander, Kalman, Mardix & Steinberger, 1970).

Experimental

The polytypes reported here were found in a platelet (specimen 17-1) grown by the static sublimation method (Pátek, 1961) with strict stabilization of temperature (±0·02 K) and pressure (±100 Pa) during growth. A peculiar characteristic of the crystals is the abundance of specimens with wide uniform polytypic regions: tens of specimens were found in each growth batch containing polytypic regions of 500 μm and wider.

* In partial fulfilment of requirements for the BS degree.

Cu Kα radiation was used to take the 10.l row lines 10° c-axis oscillation photographs of the polytypes. These are presented in Fig. 1. A list of all currently identified ZnS polytypes of the family 18L is given in Table 1. Observed and calculated intensities of the 10.l reflections of the new polytypes are compared in Table 2. The calculated intensities are proportional to $|F|^2$, where F is the structure factor: they include the Lorentz and polarization factors and are normalized to give the strongest intensity as 100·000.

The method of identification used is the 'elimination method' reported previously (Mardix, Kalman & Steinberger, 1970).

The structure factor of rhombohedral polytypes

The expression for the structure factor of a ZnS polytype commonly used in computations is given by (Mardix, Kalman & Steinberger, 1970):

$$|F_{hk.l}|^2 = f^2|\varphi_{hk.l}|^2$$

where

$$f^2 = f_{Zn}^2 + f_S^2 + 2f_{Zn}\,f_S \cos\frac{3\pi l}{2n}.$$

f_{Zn} and f_S are the atomic scattering factors of Zn and S, respectively, n is the number of layers in the unit cell. For $h - k = 1$ mod 3:

$$|\varphi_{hk.l}|^2 = \left[\sum_{z=1}^{n} \cos 2\pi\left(\frac{lz}{n} + \frac{\alpha_z}{3}\right)\right]^2$$
$$+ \left[\sum_{z=1}^{n} \sin 2\pi\left(\frac{lz}{n} + \frac{\alpha_z}{3}\right)\right]^2.$$