Note that, as follows from § 2, the values $\{\partial\rho_j/\partial q_{j\alpha}\}_\alpha$ and $\{\sum_\beta l_{j\beta}(\partial^2\rho_j/\partial q_{j\alpha}\,\partial q_{j\beta})\}_\alpha$ can be computed as fast as the values $\rho_j(\mathbf{r}, \mathbf{q}_j)$.

Similarly, passing from the direction $(\mathbf{L}, \boldsymbol{\omega})$ in the variables $(\mathbf{Q}, \boldsymbol{\chi})$ to the direction $\boldsymbol{\Omega}$ in the variables $\mathbf{X}$, we have by (42) the following equation:

$$\Omega_{k\beta} = \sum_{j,\alpha} \{L_{j\alpha}[\partial q_{j\alpha}(\boldsymbol{\chi})/\partial\chi_{k\beta}] + Q_{j\alpha} \sum_{i,\gamma} \omega_{i\gamma}[\partial^2 q_{j\alpha}(\boldsymbol{\chi})/\partial\chi_{k\beta}\,\partial\chi_{i\gamma}]\}. \quad (51)$$

It should be emphasized that, in contrast to Agarwal (1981), Dodson (1981) and Hendrickson & Konnert (1980), who have made approximations for the matrix $H = \nabla^2_{qq} R(\mathbf{q})$, we obtain by (43)–(51) an absolutely accurate product $\nabla^2_{\chi\chi} R\boldsymbol{\omega}$ without further assumptions for the elements of the matrix $\nabla^2 R$.

3.4. *Résumé*

Thus, we have shown that for any method of describing an atomic model by generalized parameters and for every minimized function $R(\boldsymbol{\chi})$ an algorithm may be obtained that allows $R(\boldsymbol{\chi})$ and the derivative in the direction $\partial R(\boldsymbol{\chi})/\partial\boldsymbol{\omega}$ as well as all the components of the vectors $\nabla_\chi R$ and $\nabla^2_{\chi\chi} R\boldsymbol{\omega}$ to be computed in four times the time needed to calculate the value of $R(\boldsymbol{\chi})$. Given the model and refinement criteria, we must only specify the transforms

$$\boldsymbol{\chi} \rightarrow \mathbf{q}(\boldsymbol{\chi}) \quad \text{and} \quad \{f_s^R, f_s^I\} \rightarrow R.$$

It should be noted that the criteria expressed by atomic parameters (criterion R_S) can be estimated in a similar way, but the procedure in this case is greatly simplified: once the values of $\mathbf{q}$ have been determined, the criterion can be calculated without the transform $\mathbf{q} \rightarrow \boldsymbol{\rho} \rightarrow (\mathbf{f}^R, \mathbf{f}^I)$.

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Distribution Fitting Methods for Centrosymmetric Structures*

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Abstract

Tests of the distribution fitting methods for centrosymmetric structures show that these methods can be used successfully for the search of a correct solution in direct methods. To get good resolving power, different types of seminvariants ($\sum_1$, triplets, quartets) should be used, as is done in other methods.

1. Introduction

The power of direct methods for solving the phase problem is dependent on the information about the structure that is contained in the structure invariants

* This research was carried out when the first author was a visiting scientist at the University of Amsterdam.

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and seminvariants. In general the information content of an invariant or seminvariant is expressed as a probability distribution based on a finite number of normalized structure-factor magnitudes $|E|$. Contemporary methods concentrate their attention on the optimal use of the most reliably determined seminvariants.* The distribution fitting methods described by Hašek (1984*a*, *b*, *c*, *d*) take full benefit of the structure information contained in less reliably determined seminvariants, thus allowing the use of information on the whole profile of the distribution functions of the seminvariants. These methods search for a correct set of phases according to the best fit between the trial and the true distribution of seminvariants.† The true distribution, being unknown until the structure is solved, is estimated either purely from theory or as a semiempirical distribution, the parameters of which are determined using a number of known structures. The trial distribution is the distribution, which follows from a set of trial phases, obtained from a practical direct-method procedure.

From a theoretical point of view, these methods should give better results than figures of merit (FOM) based on 'one-point' comparison of the characteristics of the distributions. However, a number of problems are met when trying to use these methods in practice. Most of them are solved by a compromise between several requirements (*e.g.* theoretical estimate of the true distribution, number of seminvariants used and their sampling).

In this paper, the discriminating power of the distribution fitting method is tested on several centrosymmetric structures. Seminvariants were calculated with the program *SIMPEL*. No attempt was made to optimize their sampling using an analysis of the graph of phase relations (Hašek, Huml, Schagen & Schenk, 1983). In the discussion of results, the following three types of seminvariants were treated separately: (1) one-phase structure seminvariants determined from the first phasing shell ($\sum_1$ relation); (2) three-phase structure invariants (triplets) determined from the three $|E|$ values involved; (3) four-phase structure invariants (quartets) determined from the four main terms and three cross terms. Finally, the global coefficients based on all $\sum_1$, triplet and quartet relations are discussed.

2. Method

Two different measures of the fit between the trial and theoretical probability distributions of seminvariants are used in this paper, *viz* the χ^2 test and the Kolmogorov test.

The χ^2 test for centric seminvariants is defined by Hašek (1984*b*). Since it is convenient to use different parameters for different types of seminvariants, the test is first used separately for individual types of seminvariants. The coefficient K_k for the kth type of seminvariant is calculated using

$$K_k = \sum_j w_{jk}(Q_{+jk}^{\text{trial}} - Q_{+jk}^{\text{theor}})^2, \qquad (1)$$

where Q_{+jk}^{trial} is the relative frequency of positive sign in the set of seminvariants belonging to the kth type and the jth region for the trial set of signs of structure factors tested and Q_{+jk}^{theor} is its theoretical estimate.

A correct choice of the weighting scheme is important to ensure optimal properties for the method. The best results were obtained with a modified weighting scheme compared with the theoretical one, given by Hašek (1984*b*, equation 18):

$$w_{jk} = [x_{jk}(1 - x_{jk})/N_{jk} + q^2]^{-1}, \qquad (2)$$

where

$$x_{jk} = \min[1 - c, \max(c, Q_{+jk}^{\text{theor}})]. \qquad (3)$$

The constants c and q are related to the expected reliability of the estimate of the distribution.

For increasing numbers of seminvariants in a single region one obtains more precise estimates of the trial distributions and the corresponding weight is then determined only by the coefficient q, which represents the remaining uncertainty in the estimate of both distributions to be compared:

$$\lim_{N_{jk} \to \infty} w_{jk} = q^{-2}. \qquad (4)$$

In regions with $Q_{+jk}^{\text{theor}} \to 1$ or $Q_{+jk}^{\text{theor}} \to 0$, where the weighting scheme given by Hašek (1984*b*) does not depend on the sampling size, the weight (2) reduces to

$$w_{jk} = [c(1 - c)/N_{jk} + q^2]^{-2}, \qquad (5)$$

i.e. w_{jk} decreases with the decreasing number of seminvariants N_{jk} in a single region. These properties are important for the χ^2 test based on the usual choice of most reliable triplets and quartets using fixed regions, because of large differences in the numbers of seminvariants in the regions. The tests presented here were made with $q = c = 0{\cdot}1$. However, no systematic attempt has been made to optimize coefficients q and c.*

The coefficient K (for all seminvariant types) is calculated simply as a weighted sum of coefficients K_k,

$$K = \sum_k a_k K_k, \qquad (6)$$

* Throughout this paper the term seminvariant is used as shorthand notation for structure invariants and structure seminvariants (Hašek, 1984*a*).

† The notions true, theoretical, empirical and trial distributions and *a priori* structure information are explained by Hašek (1984*b*).

* Analogous results were obtained with the weighting scheme (2), where $x_{jk} = Q_{+jk}^{\text{theor}} - c(Q_{+jk}^{\text{theor}} - 0{\cdot}5)$.

where weights a_k are used to equalize the influence of the different degrees of freedom* for different seminvariant types on the resulting values of the χ^2 test.

The application of the Kolmogorov test has been described by Hašek (1984*d*, equations 6-8). For centric seminvariants the Kolmogorov test reduces to a rejection of all the solutions having a difference

$$D_{jk} = |N_{+jk}^{\text{theor}} - N_{+jk}^{\text{trial}}| \tag{7}$$

greater than the critical value D_{jk}^{crit} (Table 1 in Hašek, 1984*c*) for every region and every seminvariant type.

The measure of the fit is given by the maximal ratio

$$\text{RATIO} = D_{jk}^{\max}/D_{jk}^{\text{crit}}, \tag{8}$$

where $D_{jk}^{\max}$ is the maximal difference between the cumulative distributions of seminvariants and D_{jk}^{crit} is the critical value at the significance level $\alpha = 0{\cdot}01$. The lower the RATIO the larger the chance that the solution is true.†

The program *CENTRO*, used for the calculation of the χ^2 and Kolmogorov tests for centrosymmetric structures, was used with program system *SIMPEL*82 (Schenk, 1983). $\sum_1$ relationships, triplets and quartets have been calculated by the program *TRIQUA*. Trial signs are used in different forms: either as symbolic signs (output from symbolic addition procedure *SYMBAD*), or as signs of structure factors refined by the tangent formula (program *TANREF*), or as 'true' signs after refinement of the structure.

When the symbolic addition is used, some reflexions are assigned several different symbolic signs, which for some trial solutions result in both indications + and −. Then the sign with the highest sum of weights of contributing triplets is accepted; however, if

$$(W_+ - W_-)/(W_+ + W_-) < \text{LIM}_1,$$

$$\text{or} \qquad \max(W_+, W_-) < \text{LIM}_2, \tag{9}$$

the indication is uncertain and the sign remains undetermined. The symbol W_+ (W_-) denotes the sum of weights of triplets indicating the positive (negative) sign of the reflexion. LIM_1, LIM_2 are limits set by the user.

The distribution fitting methods can be employed with any type of seminvariant; here, the tests have been performed for one-phase structure seminvariants, and for the structure-invariant triplets and quartets. A generator for random numbers was used for selecting a random sample of seminvariants when the number of seminvariants in the input file was larger than 3000. Limits for the weights of seminvariants defining the regions can be fixed either in advance (fixed regions) or can be calculated in subroutine *REGION* so that every region contains approximately the same number of seminvariants.

2.1. *Number of variables*

The application of the distribution fitting method is more complicated when the number of variables in both distribution functions used in the test is greater, because the number of regions and also the required number of seminvariants rise steeply with the dimension of the space in which the distributions are applied. As a consequence, a reduction of dimensionality leads to a reduction in computing time. However, this also diminishes the discriminating power of the method.

The theoretical probability distribution $P(\psi, R_1 \ldots, R_m)$ is usually expressed as a function of $(m+1)$ variables (*i.e.* of m phasing magnitudes and of the seminvariant value). Under general conditions it is possible to use new 'generalized coordinates', $y_1 = y_1(R_1, \ldots, R_m), \ldots, y_m = y_m(R_1, \ldots, R_m)$, such that the probability function mainly depends on $r < m$ generalized coordinates. Then, from the point of view of the distribution fitting methods, little structure information is lost if the corresponding marginal distribution is used:

$$P(\psi, y_1, \ldots, y_r) = (1/V) \times \int \ldots \int P(\psi, y_1, \ldots, y_r, y_{r+1}, \ldots, y_m)\, \mathrm{d}y_{r+1} \ldots \mathrm{d}y_m. \tag{10}$$

The other possibility is to use the respective conditional probability distribution

$$P(\psi, y_1, \ldots, y_r | y_{r+1}, \ldots, y_m), \tag{11}$$

where coordinates $y_{r+1}, \ldots, y_m$ may be fixed, *e.g.* at the average values of these generalized coordinates. Generally, the reduction of the number of variables may lead to the partial loss of discriminating ability of the method caused simply by the fact that the distributions are not described in sufficient detail.

In this paper we use the simplest procedure valid for any seminvariant type by taking the distribution of seminvariants as a function of a single generalized coordinate P^{theor} [*i.e.* equations (18) for one-phase seminvariants, (19) for triplets and (20) for quartets]. The ideal fit between the theoretical and trial distributions is evaluated according to the deviations of the chart of Q^{trial} against Q^{theor} from the plane $Q^{\text{trial}} = Q^{\text{theor}}$ for acentric seminvariants or from the straight line $Q_+^{\text{trial}} = Q_+^{\text{theor}}$ for centric seminvariants (Fig. 1).* The efficiency of the distribution fitting methods would be higher if the distributions were described in more dimensions, particularly in the case of quartets. However, no attempt has been made here to test

* Number of regions minus one.

† The value of D_{jk}^{crit} depends on the number of seminvariants in the respective regions.

* For the difference between P^{theor} and Q^{theor} see Hašek (1984*b*).

experimentally the influence of an increase in the number of variables on the discriminating power of these methods.

2.2. *Criteria*

The following criteria are used in this paper for a comparison of the efficiency of the methods:

1. *sequence number* of the correct solution in the ordered list of tested figures of merit, SEQNO;

2. *selectivity* of the method, defined as the ratio of the number of trial solutions NREJ that have been rejected by the criterion used to the total number of trial solutions NTOT. The selectivity SEL = NREJ/NTOT is written as an unreduced fraction (*e.g.* 2/64);

3. *maximal relative difference*, MAXD = $100(K_h - K_c)/K_h$, where K_c is the coefficient (1) for the correct set of phases and K_h is the highest (*i.e.* the worst) coefficient (1);

4. *minimal relative difference*, MIND = $100(K_2 - K_c)/K_h$, where K_2 is the lowest coefficient (1) among the wrong solutions.

The figures of merit are considered to be more efficient if they systematically give lower SEQNO and SEL. If these measures give identical results, the better procedure is determined according to the higher value of the maximal relative difference MAXD. Higher values of MIND imply a higher discriminating power.

The efficiency of the distribution fitting method is influenced mainly by the following three parameters:

number of regions in which the theoretical and trial distributions are compared;

average number of seminvariants per region. This parameter is closely related to the statistical error in the trial distribution;

percentage of directly tested phases, PERC = 100 × NINCL/NREF, where NINCL is the number of phases included in at least one of the seminvariants used, NREF is the total number of reflexions used.

It is expected that the importance of PERC increases for structures with low internal consistency within the set of reliable seminvariants used in the calculation of trial sets of phases. The results of the distribution fitting methods are compared in Tables 3, 4, 6 with the following figures of merit (Schenk, 1983) based on $\sum_1$ relationships, Harker-Kasper relationships, the $\sum_2$ consistency relationship (Schenk, 1971*b*) and positive and negative quartets, respectively:

$$\mathrm{FOM}_1 = \sum w_H (P_+ - 0{\cdot}5), \tag{12a}$$

$$\mathrm{FOM}_2 = \sum w_{H+K} w_{H-K} |E_H^2 E_{H+K} E_{H-K}| \times (2|E_K|^2 + |E_{2H}|^2 - 2), \tag{13a}$$

$$\mathrm{FOM}_3 = \sum w_K w_{H-K} w_L w_{H-L} \times f(|E_H|, |E_K|, |E_{H-K}|, |E_L|, |E_{H-L}|), \tag{14a}$$

$$\mathrm{FOM}_4 = \sum w_H w_K w_L w_{-H-K-L} |E_H E_K E_L E_{-H-K-L}| \times \{1 + (|E_{H+K}| + |E_{L+H}| + |E_{K+L}|)/N^{1/2}\} \tag{15a}$$

$$\mathrm{FOM}_5 = \sum w_H w_K w_L w_{-H-K-L} |E_H E_K E_L E_{-H-K-L} \times (|E_{L+H}|^2 + |E_{K+L}|^2 + \ldots + |E_{K+H}|^2 - 2), \tag{16a}$$

where w_H is equal to the trial sign of E_H multiplied by a weight reflecting the reliability of this sign. All the figures of merit are given by their relative values in Tables 3, 4, 6:

$$S1 = 100 \times \mathrm{FOM}_1/\mathrm{FOM}_1^{\max}, \tag{12b}$$

$$\mathrm{HK} = 100 \times \mathrm{FOM}_2/\mathrm{FOM}_2^{\max}, \tag{13b}$$

$$Q = 100 \times \mathrm{FOM}_3/\mathrm{FOM}_3^{\max}, \tag{14b}$$

$$\mathrm{PQ} = 100 \times \mathrm{FOM}_4/\mathrm{FOM}_4^{\max}, \tag{15b}$$

$$\mathrm{NQ} = 100 \times \mathrm{FOM}_5/\mathrm{FOM}_5^{\max}. \tag{16b}$$

Combined figures of merit (Schenk, 1983; Main *et al.*, 1980) are defined by

$$\mathrm{CFOM} = \sum k_i \times \mathrm{FOM}_i / \sum k_i, \tag{17}$$

where k_i are weighting coefficients. The combined figure of merit CFOM used in Table 8 is defined by (17), where the summation runs over all FOM's defined by (12*b*)-(16*b*), with all coefficients $k_i = 1$.

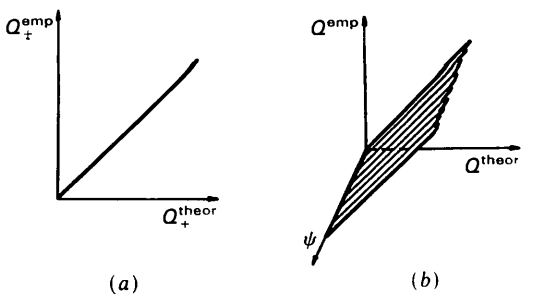

Fig. 1. Ideal fitting between the theoretical and empircal distributions corresponding to the linear dependence of Q^{emp} on Q^{theor}, when the generalized coordinate is chosen to be Q^{theor}: (*a*) centric seminvariants; (*b*) acentric seminvariants.

3. Results

All structures used for testing are listed in Table 1. The numbers of sets of trial signs generated automatically in the course of the symbolic addition (*SIMPEL*82) are given in the first column of Table 2. The second column shows the numbers of the highest $|E|$ values used for the calculation of triplets and quartets. Cross terms were looked for among all the measured reflexions. Column 4 contains the numbers of triplets with $|E_H E_K E_{-H-K}|/N^{1/2} > E3_{\min}$. Unlike the triplets, whose numbers were approximately the same for all the tested structures, the numbers of quartets with

Table 1. *Structures used for testing*

N is the total number of non-H atoms in the unit cell.

	N	Z	Space group	Formula	R	References
MARIN	30	2	$P\bar{1}$	$C_8H_7Cl_3N_4$	0·034	(*a*)
WILLES	40	2	$P\bar{1}$	$C_{17}H_{23}NO_2$	0·067	(*b*)
BORAAN	58	2	$P\bar{1}$	$C_{28}H_{25}B$	0·057	(*c*)
ONONIE	72	4	$P2_1/n$	$C_{14}H_{22}N_2O_2$	0·044	(*d*)
BIBIME	100	4	$P2_1/c$	$C_{25}H_{16}$	0·060	(*e*)
DIAM	120	8	$P4_2/n$	$C_{14}H_{20}O$	0·090	(*f*)

References: (*a*) Tinant, Germain, Declercq & Van Meerssche (1979); (*b*) de Jong, Dik-Edixhoven & Schenk (1973); (*c*) Finocchiaro *et al.* (1980); (*d*) Schenk (1971*a*); (*e*) Schenk (1972); (*f*) Rogers & Kennard (1980).

$|E_HE_KE_LE_{-H-K-L}|/N > E4_{\min}$ differ almost by two orders of magnitude (columns 6–9). No calculation of quartets has been made for the structure DIAM.

3.1. $\sum_1$ *relation*

The probability of the positive sign of a one-phase structure seminvariant was determined using the relationship

$$P_+ = \tfrac{1}{2}+\tfrac{1}{2}\tanh\left[N^{-1/2}\sum_K E_H(|E_K|^2-1) \times\exp(2\pi iKt_s)\right], \quad (18)$$

where the summation runs over all reciprocal vectors K for which

$$K(I-R_s)=H.$$

I is the unit matrix, R_s is a rotational matrix and t_s the corresponding translation vector of the space group in question. The value P_{+jk}^{theor} in every region was computed for the average argument of tanh taken for all seminvariants in this region (Hašek, 1984*b*, equation 11*c*).

Measurements of the efficiency of the method for six structures are given in Table 3. Calculations were made for fixed regions with limits corresponding to the theoretical probabilities 1·0, 0·8, 0·6, 0·5, 0·4, 0·2, 0·0. For MARIN and BIBIME two symbolic signs and for WILLES one were not included in any one-phase seminvariant thus giving groups of undistinguished trial sets. Comparison of columns SEQNO and PERC confirms that the efficiency of the χ^2 test for the $\sum_1$ relation is correlated with the percentage of directly tested phases. It implies higher efficiency of the test for space groups of higher order. The Kolmogorov test (columns 5, 6) has very poor selectivity. With the exception of DIAM, all differences between the trial and theoretical distributions are tolerated for almost all trial sets of phases. In agreement with our expectation, the $\sum_1$ criterion (12), given in the two latter columns, has properties that resemble the χ^2 test (compare SEQNO's in columns 1 and 7).

3.2. *Triplet relationships*

The theoretical probability of the positive sign of a triplet is calculated using the hyperbolic tangent formula (Cochran & Woolfson, 1955):

$$P_+ = \tfrac{1}{2}+\tfrac{1}{2}\tanh(N^{-1/2}|E_HE_KE_{-H-K}|). \quad (19)$$

The results of the χ^2 test based on triplets are summarized in Table 4. With this criterion alone, good results were obtained for structures crystallizing in non-triclinic space groups, and the Kolmogorov test also does very well. Only MARIN showed a surprisingly large number of positive triplets for the correct set of signs, among 3600 triplets [where about 300 negative triplets are expected according to (19)] only 25 negative triplets were actually observed.

The distribution fitting method based on triplet relationship (19) and $\sum_2$ FOM Q (Schenk, 1971*b*) seems to be roughly of equal quality (see Table 4).

Unlike $\sum_1$ relationships, triplet relationships give a sufficient number of triplets to test directly all structure-factor phases (PERC in column 4 are ~100%). Therefore, some freedom remains to specify the limits of the regions and to choose the numbers of triplets in the regions. Table 5 shows how the discriminating power of the χ^2 and Kolmogorov tests decreases with decreasing number of randomly selected triplets for fixed limits of the regions. It seems that the number of triplets in any region must not fall under 100 to preserve the efficiency of the test.

Since the triplet relationships usually form the basis of the calculation of the trial sets of phases, it is probable that all trial distributions of triplets fit the theoretical distribution rather well. As a result only poor resolving power of the test can be expected when the estimate of the 'true distribution' is largely in error, as in the case of MARIN. Therefore, to increase the efficiency of this test more attention should be devoted to deriving an exact expression for the distribution of triplets taking into account the preliminary knowledge on the arrangement of atoms in the crystal.

3.3. *Quartet relationships*

Four different relationships for the theoretical probability of a positive sign of quartets based on seven magnitudes $|E_H|, |E_K|, |E_L|, |E_{-H-K-L}|, |E_{H+K}|, |E_{H+L}|, |E_{K+L}|$ were tested (Schenk, 1973; Hauptman & Green, 1976; Giacovazzo, 1977, 1980, equations 8.49–50). For our sampling of quartets (see Table 2), the best fit was obtained for the last formula:

$$P^+ = \tfrac{1}{2}+\tfrac{1}{2}\tanh[N^{-1}|E_HE_KE_LE_{-H-K-L}| \times(|E_{H+K}|^2+|E_{H+L}|^2+|E_{K+L}|^2-2)]. \quad (20)$$

If any of the cross magnitudes was outside the measurement sphere, its $|E|$ value was set to 1.

Formula (20) was used here in all tests for the calculation of the theoretical probability of a positive

Table 2. *Characteristics of source data for all tested structures*

	Number of trial sets	Number of reflections	Number of $\sum_1$ relationships	Number of triplets	$E3_{min}$	Number of quartets with at least n cross terms				$E4_{min}$
						0	1	2	3	
MARIN	128	300	30	3533	0·7	5200	5198	4818	1267	1·1
WILLES	32	300	27	3076	0·6	19038	18807	15218	3347	1·0
BORAAN	64	400	61	5575	0·6	33131	33129	30940	8001	1·0
ONONIE	8	500	65	5233	0·7	7387	7285	5864	303	0·6
BIBIME	64	350	37	3358	0·6	497	478	336	31	0·7
DIAM	4	300	81	3988	0·6	—	—	—	—	—

Table 3. *Test of figures of merit based on $\sum_1$ relationship*

	χ^2 test for $\sum_1$				Kolmogorov test for $\sum_1$		$\sum_1$ criterion (12)	
	SEQNO	MAXD	MIND	PERC (%)	SELECT	RATIO	SEQNO	*S*1
MARIN	19	96	−4	10	1/128	0·3	58	51
WILLES	6	96	−3	9	0/32	0·2	4	72
BORAAN	3	94	−4	15	2/64	0·4	3	79
ONONIE	2	70	−6	13	0/8	0·4	1	66
BIBIME	8	82	−4	11	7/64	0·5	14	77
DIAM	1	69	15	27	2/4	0·7	2	50

Table 4. *Test of distribution fitting methods based on triplets and the Q criterion*

	χ^2 test for triplets				Kolmogorov test		*Q* criterion (14)	
	SEQNO	MAXD	MIND	PERC (%)	SELECT	RATIO	SEQNO	*Q*
MARIN	127	6	−89	100	16/128	1·4*	7	95
WILLES	6	98	−2	100	4/32	0·2	12	59
BORAAN	7	94	−3	100	4/64	0·7	13	86
ONONIE	1	93	15	99·4	7/8	0·8	1	76
BIBIME	1	98	7	100	62/64	0·6	1	81
DIAM	2	93	−2	100	2/4	0·9	—	—

* The correct set of phases was rejected by the Kolmogorov test.

sign for quartets for any number of cross terms. Because of the small number of quartets with all three cross terms known (Table 2), the efficiency of the method was better when additional quartets with at least two known cross terms were used. The results of the χ^2 and Kolmogorov tests for this case are given in Table 6. In comparison with the results obtained using $\sum_1$ and triplet relationships, the distribution fitting method based on quartets give much better results. For MARIN, ONONIE and BIBIME the best fit of both distributions actually corresponds to the correct solution. However, only small differences exist between the most probable sets (MIND = 1%) for MARIN. For WILLES and BORAAN, the correct solution corresponds to the second-best fit between the distributions of quartets (MIND = −1, −2% respectively).

Table 5. *Increase in the discriminating power of the distribution fitting method with increasing number of seminvariants used for the test*

(ONONIE, random choice from the set of 5233 triplets, fixed regions, $E3_{min} = 0·7$.)

Average number of triplets in region	190	175	150	70	20	4
SEQNO	1	1	1	1	2	5
MAXD	99	94	96	90	79	28
MIND	16	18	22	25	−2*	−17*
PERC	99·6	99·6	99·6	93·0	58·4	21·2
SELECT	7/8	7/8	7/8	1/8	0/8	0/8
RATIO	0·8	0·7	0·7	0·5	0·3	0·3

* Negative values indicate that the correct solution does not have the lowest coefficient *K*.

3.4. *Global coefficient of the fit*

Because a simultaneous use of one-phase seminvariants, triplets and quartets substantially increases the amount of *a priori* structure information used, the combination of the three coefficients K_k in (6) and also the combination of the individual FOM in the combined figure of merit CFOM(17) result in a practically unique solution (Table 7). Good properties of the combined figures of merit (Schenk, 1983; Main *et al.*, 1980) require a proper choice of the weighting coefficients k_i in (17). Analogously, the global coefficient K is sensitive to the choice of the correction terms c, k in the weighting scheme (2) used

Table 6. *Test of figures of merit based on quartets*

Approximately 3000 quartets were used for the distribution fitting method (χ^2 and Kolmogorov tests)

	χ^2 test (1)				Kolomogorov test (7)		HK criterion (13)		PQ criterion (15)		NQ criterion (16)	
	SEQNO	MAXD	MIND	PERC	SELECT	RATIO	SEQNO	HK	SEQNO	PQ	SEQNO	NQ
MARIN	1	98	1	95	16/128	0·4	2	69	3	96	1	100
WILLES	2	78	−2	98	14/32	0·9	1	74	11	88	1	93
BORAAN	2	93	−1	96	60/64	1·5	6	66	4	93	1	92
ONONIE	1	96	25	89	7/8	1·0	—	—	1	99	3	75
BIBIME	1	95	8	41	63/64	0·8	62	38	1	87	19	66

Table 7. *Test of combined figures of merit CFOM* (17) *and K* (6)

	Coefficient K (6)			Combined FOM (17)	
	SEQNO	MAXD	MIND	SEQNO	CFOM
MARIN	1	97	1	1	82
WILLES	1	88	1	1	77
BORAAN	1	87	1	1	83
ONONIE	1	95	22	1	79
BIBIME	1	96	14	1	70
DIAM	1	95	2	1	59

for the calculation of the coefficients K_k of the individual seminvariant types. These constants, showing the reliability of the theoretical estimate of the true distribution, should be determined from experiments with a larger number of structures.

4. Discussion

In agreement with Schenk (1980), it is found that the combined FOM is superior to the individual FOM's, of which different ones occasionally are the best. However, their weighted sums CFOM(17) or K(6) determine the correct solution with great reliability (Table 7).

When standard calculation of seminvariants is used, most seminvariants can be found in regions with highest P_+^{theor}. If boundaries of the regions are chosen such that each region contains the same number of seminvariants (the same expected error in the determination of empirical distribution), the distributions of triplets and quartets would be described in detail in parts with reliably positive seminvariants. This would lead to disappearance of the influence of parts containing a small number of seminvariants determined with lower reliability. On the other hand, equidistant limits of regions cause most of the seminvariants to concentrate in one or two regions. This, however, devalues the gain ensuing from the great number of seminvariants used, as there is no sense in reducing the random error in the estimate of the trial distribution below one quarter of the expected error of the true distribution.

In this paper, problems due to the non-uniform occurrence of seminvariants of different weight have been solved by a compromise: the boundaries of the regions were empirically fixed so as partly to suppress effects from both equidistantly fixed boundaries and boundaries calculated to make the same number of seminvariants fall into each region. It was observed that an inadequate choice of regions may decrease the selectivity of the method.

Arguments discussed in this paper lead us to the conclusion that more attention should be devoted to obtaining better estimates of the true distributions of seminvariants and a better sampling of seminvariants for the calculation of the trial distributions. Also, it indicates how the method should be developed.

1. Purely theoretical distributions of seminvariants should be replaced by semiempirically derived distributions depending on the unique character of the structure under study and, for every distribution type, the optimal number of dimensions for calculation of the empirical distribution should be determined.

2. A method of generation of seminvariants should be developed such that the seminvariants form a reliably connected graph in every region (Hašek, Huml, Schagen & Schenk, 1983).

In conclusion, it can be stated that distribution fitting methods can be successfully used as figures of merit.

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Characterization of Lattice Imperfections by the Multi-Beam-Imaging Method in High-Voltage Electron Microscopy

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Abstract

It is the purpose of this paper to introduce and discuss the multi-beam-imaging (MBI) method for studying lattice imperfections in high-voltage electron microscopy. The image contrast is compared with the theoretical contrast based on the many-beam dynamical theory of electron diffraction; the effect of absorption is included in the calculation. It is shown that the nature of imperfections can be studied from only one image taken by the MBI method instead of the bright- and dark-field images that are generally used. Further, the images of a thick crystal taken by the MBI method become much brighter than the ordinary bright-field and dark-field images. Finally, the technique is applied to the characterization of stacking faults and screw dislocations in thick regions observed in the 1 MeV electron microscope.

1. Introduction

There has been considerable interest in using high-resolution electron microscopy to study the structure of imperfections in crystals such as grain boundaries, coherent twin boundaries, edge and screw dislocations, intrinsic and extrinsic stacking faults, stacking-fault tetrahedra, GP zone and impurity atoms. (See also the review by Hashimoto & Takai, 1983.) These observations are mostly confined to the relatively thin crystals of about a few hundred ångströms in thickness. Since the properties of bulk materials are determined by the total contained imperfections, it is preferable to study such imperfections in specimens with bulk properties. However, as shown theoretically and experimentally for MgO (Hashimoto, Endoh, Takai, Ajika, Tomita, Kuwabara & Hiraga, 1983; Endoh & Hashimoto, 1984*a*, *b*), the atomic structure images from thick crystals cannot be obtained even though high-voltage microscopes capable of high resolution are used. It was shown that the atomic-structure image at 1 MeV of an MgO crystal with contrast higher than say 20% can only be obtained if the crystal is less than 3000 Å thick and thus it is rather difficult to observe the atomic structure image of bulk specimens using the high-resolution technique. Therefore, in order to study the lattice imperfections in thick crystals the conventional bright-field and dark-field imaging methods (Howie & Whelan, 1961; Hashimoto, Howie & Whelan, 1960, 1962), the weak-beam dark-field imaging method (Cockayne, Ray & Whelan, 1969) and the bright-field imaging method using a higher-order reflection (Osiecki & Thomas, 1971; Beseg, Jones & Smallman, 1971) are most frequently employed in the study of dislocation images in thick crystals.

At high voltage (>300 kV), the Bragg angles of scattered waves become small and in particular those of low-order reflections become almost the same as the optimum aperture angle for obtaining the atom resolution image, it thus seems appropriate to investigate the use of both primary and Bragg-reflected waves within an aperture instead of using a small aperture to take respective bright-field or dark-field images. Even though the waves of low-order Bragg reflections are included in the imaging, many higher-order Bragg reflections that are excited at a high

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