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Application and comparison of different tests on twinning by merohedry

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Abstract

Three different tests on twinning by merohedry from the literature have been applied to single-crystal data sets of five different inorganic crystal structures. Although the three test procedures differ significantly with regard to their efficiency, in both detecting the existence of twinning and estimating the volume fractions of the twin individuals, they represent useful tools in the early stages of a structure analysis and should be applied routinely in the preliminary stage of a structure determination whenever a twinning by merohedry is possible.

1. Introduction

The presence of twinning by merohedry in a crystal is one of the more serious problems one can encounter in the course of a single-crystal structure analysis. This is mainly due to the fact that the classical preliminary investigations such as camera techniques and polarization microscopy are not feasible for this type of twinning. In principle, a twinning by merohedry could be detected by means of X-ray diffraction topography (Klapper, 1996) or transmission electron microscopy (Nord, 1992). However, these methods are not necessarily available for crystallographers doing single-crystal structure analysis and require special conditions to be fulfilled concerning the sample dimensions or sample stability, respectively.

According to Catti & Ferraris (1976) two different types of twins by merohedry have to be distinguished:

Type 1: The twin operation belongs to the Laue group, but not to the point group of the crystal.

Type 2: The twin operation belongs to the point group of the translation lattice (holohedry), but not to the point group of the crystal.

With regard to the influence of the twinning on the success of a structure determination and refinement these two different types of twins by merohedry represent different pitfalls. Twins of type 1 cannot occur with centrosymmetric space groups and can always be described as inversion twins. As long as Bijvoet differences can be neglected, the diffraction data from such a twin are identical with the intensity data of a single crystal. As the diffraction behaviour of twin type 2 is considerably more dangerous, the discussion will focus particularly on this type. In the case of a twin consisting of only two individuals, the measurable twin intensities J_1 and J_2 are the weighted sums of the *a priori* unknown intensities $I_1 = |F^o(\mathbf{h_1})|^2$ and $I_2 = |F^o(\mathbf{h_2})|^2$ of two overlapping reflections $\mathbf{h_1} = (h_1k_1l_1)$ and $\mathbf{h_2} = (h_2k_2l_2)$ superimposed by the twinning law.

$$J_1 = \alpha I_1 + (1 - \alpha)I_2 \tag{1}$$

$$J_2 = \alpha I_2 + (1 - \alpha)I_1 \tag{2}$$

These equations have been discussed by Britton (1972), and α and $(1 - \alpha)$ correspond to the volume fractions of the two twin domains. As the two superimposed reflections are not equivalent by Laue symmetry, the data set is systematically falsified. For the worst case, $\alpha = 0.50$, an enhanced diffraction symmetry equal to the lattice symmetry is simulated. Generally, the evaluation of the resulting diffraction pattern of the twin can be attributed to one of 55 space-group types (Koch, 1995). Only in four cases ($P4_2/n$; $I4_1/a$; $Pa\bar{3}$; $Ia\bar{3}$) can the twinning be detected from discrepancies between the apparent Laue symmetry and the extinction rules.

Recently, Herbst-Irmer & Sheldrick (1998) listed typical warning signs that are indicative of possible twinning. According to their experience the use of the mean value $\langle|E^2 - 1|\rangle$, for example, might be helpful in deciding on the possible existence of twinning. They observed that this parameter, which is calculated by many data reduction and structure solution programs, is in many cases much lower than the expected value of 0.736 for non-centrosymmetric crystals when the data set is subject to twinning by merohedry. However, for the non-centrosymmetric data set TRINEP ($\langle|E^2 - 1|\rangle = 0.782$) of the present investigation this single number was not a diagnostic feature (see also Table 1).

In the literature different test methods have been proposed to detect a twinning by merohedry in the preliminary stages of a structure analysis. They are based on the evaluation of statistical test parameters which can be calculated directly from the reduced data set. Additionally, the tests allow an estimation of the twinning parameter α. In the present paper the procedures proposed by Britton (1972), Rees (1980) and

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Table 1. *Selected crystallographic data for the five twinned compounds*

Structure code	Space group	Formula unit; Z	Unique reflections	V (Å^3)
TRINEP[(a)]	$P6_1$	$NaAlSiO_4$; 24	2748	2145.3
DODECA[(b)]	$I4_1/a$	$17SiO_2.C_4H_8O$; 4	1176	3648.1
NAHEX[(c)]	$P\bar{3}c$	$Na_7Mn_5F_{13}(PO_4)_3(H_2O)_3$; 4	2018	2230.7
LAOZ[(d)]	$P\bar{3}m$	La_2O_3; 1	501	82.2
COMPLEX[(e)]	$Fd3$	$[Cr(NH_3)_6][Ni(H_2O)_6]Cl_5.\frac{1}{2}NH_4Cl$; 16	1065	8539.7

References: (*a*) Kahlenberg & Böhm (1998); (*b*) Knorr & Depmeier (1997); (*c*) Stief *et al.* (1998); (*d*) Bärnighausen (1985); (*e*) Moron *et al.* (1990).

Yeates (1988) were compared using five different data sets of twinned inorganic compounds. These three approaches are now briefly summarized.

1.1. *Test after Britton (1972)*

For every pair of twin-related reflections $(h_1k_1l_1)$ and $(h_2k_2l_2)$ in the data set the ratio $k = J_1/(J_1 + J_2)$ can be calculated. According to Britton, $W(k)$, the relative frequency distribution of the ratio k, can be evaluated to detect the presence of twinning.

In contradistinction to the case of an untwinned crystal, where all possible values of k in the interval $0 \leq k \leq 1$ can occur with a certain probability, the values of $W(k) \neq 0$ for a twinned data set are restricted to a region $k_1 \leq k \leq k_2$ symmetrical to $k = 0.5$. The values k_1 and k_2 of the discontinuities correspond to the volume fractions α and $1 - \alpha$.

1.2. *Test after Rees (1980)*

Rees investigated the influence of a twinning by merohedry on the well known $N(z)$ distribution. This method is an extension of earlier studies made by Stanley (1972).

Two sets of theoretically derived curves for $N_{\bar{1}}(z,\alpha)$ and $N_1(z,\alpha)$ were calculated for centrosymmetric and non-centrosymmetric crystals, respectively. They can be compared with the observed cumulative distribution function of the normalized intensities. In contrast to the approach proposed by Britton, this test does not require knowledge of the twinning law superimposing the reciprocal lattices. Furthermore, the method can also be evaluated for $\alpha = 0.5$, where the Britton test fails. However, the test implies that the Wilson statistic can be applied for the calculation of the intensity distributions of the untwinned reflections.

1.3. *Test after Yeates (1988)*

Yeates (1988) defined a variable $H = (J_1 - J_2)/(J_1 + J_2)$, where J_1 and J_2 are the intensities of reflections related by the twinning operation. Assuming that the intensities for the untwinned reflections are independent of each other, the theoretical cumulative intensity distribution of H, $S(H)$, can be derived for centrosymmetric and non-centrosymmetric crystals.

$$S_{\bar{1}}(H) = (1/\pi)\mathrm{acos}[H/(2\alpha - 1)] \quad (3)$$

$$S_1(H) = \tfrac{1}{2}\{1 + [H/(1 - 2\alpha)]\} \quad (4)$$

The distribution of the parameter H can be directly calculated from the observed intensity data and compared with the predicted distributions for different values of α, in order to test if twinning is present. In contrast to the Rees test no normalization is required prior to analysis and the theoretical distributions can be expressed by analytical functions for the centrosymmetric and the non-centrosymmetric case, respectively. Furthermore, the value of α for the twin fraction can be estimated from the average of the absolute value of H, $\langle|H|\rangle$, or the average of the square of H, $\langle H^2\rangle$, according to

$$\alpha = \tfrac{1}{2}[1 - \langle|H|\rangle(\pi/2)] \quad (5)$$

$$\alpha = \tfrac{1}{2}[1 - (2\langle H^2\rangle)^{1/2}] \quad (6)$$

for centrosymmetric and

$$\alpha = \tfrac{1}{2}(1 - 2\langle|H|\rangle) \quad (7)$$

$$\alpha = \tfrac{1}{2}[1 - (3\langle H^2\rangle)^{1/2}] \quad (8)$$

for non-centrosymmetric structures. However, the test fails for $\alpha = 0.50$.

2. Experimental

The three test procedures have been applied to five twinned inorganic crystal structures covering hexagonal, tetragonal, trigonal and cubic symmetry and a wide range of structural complexities. Selected crystallographic data for the structures are given in Table 1. In the case of the acentric structure the number of unique reflections corresponds to those under the Laue symmetry rather than those under the crystal class, *i.e.* Friedel opposites were averaged.

For the data sets of NAHEX and LAOZ a face-indexing absorption correction was applied. The calculation of the observed $N(z)$ distributions was accomplished using the program *SIR*92 (Altomare *et al.*, 1992). Reflections, which are unaffected by twinning, were

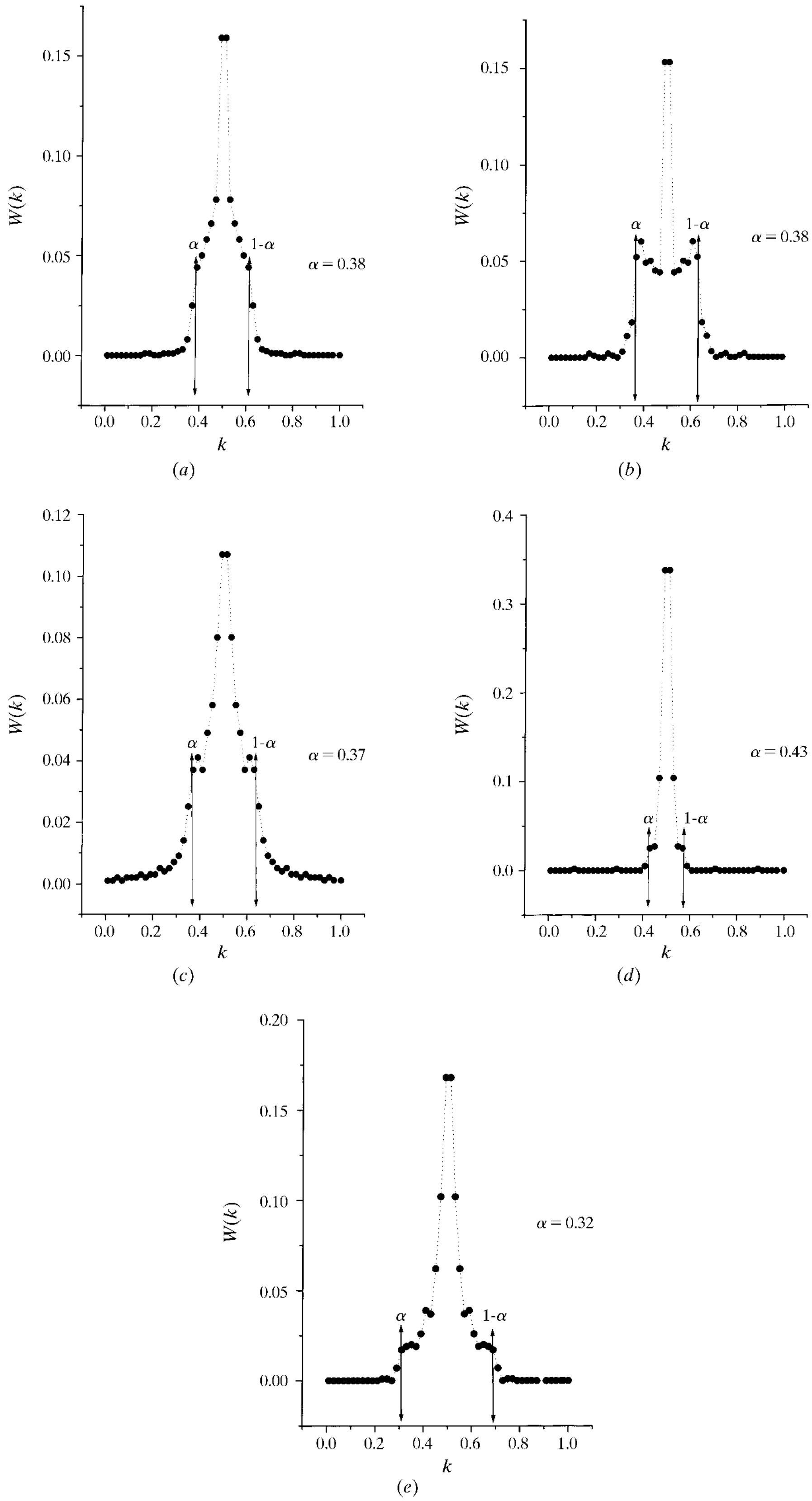


Fig. 1. Britton plots for (*a*) TRINEP, (*b*) DODECA, (*c*) NAHEX, (*d*) LAOZ and (*e*) COMPLEX.

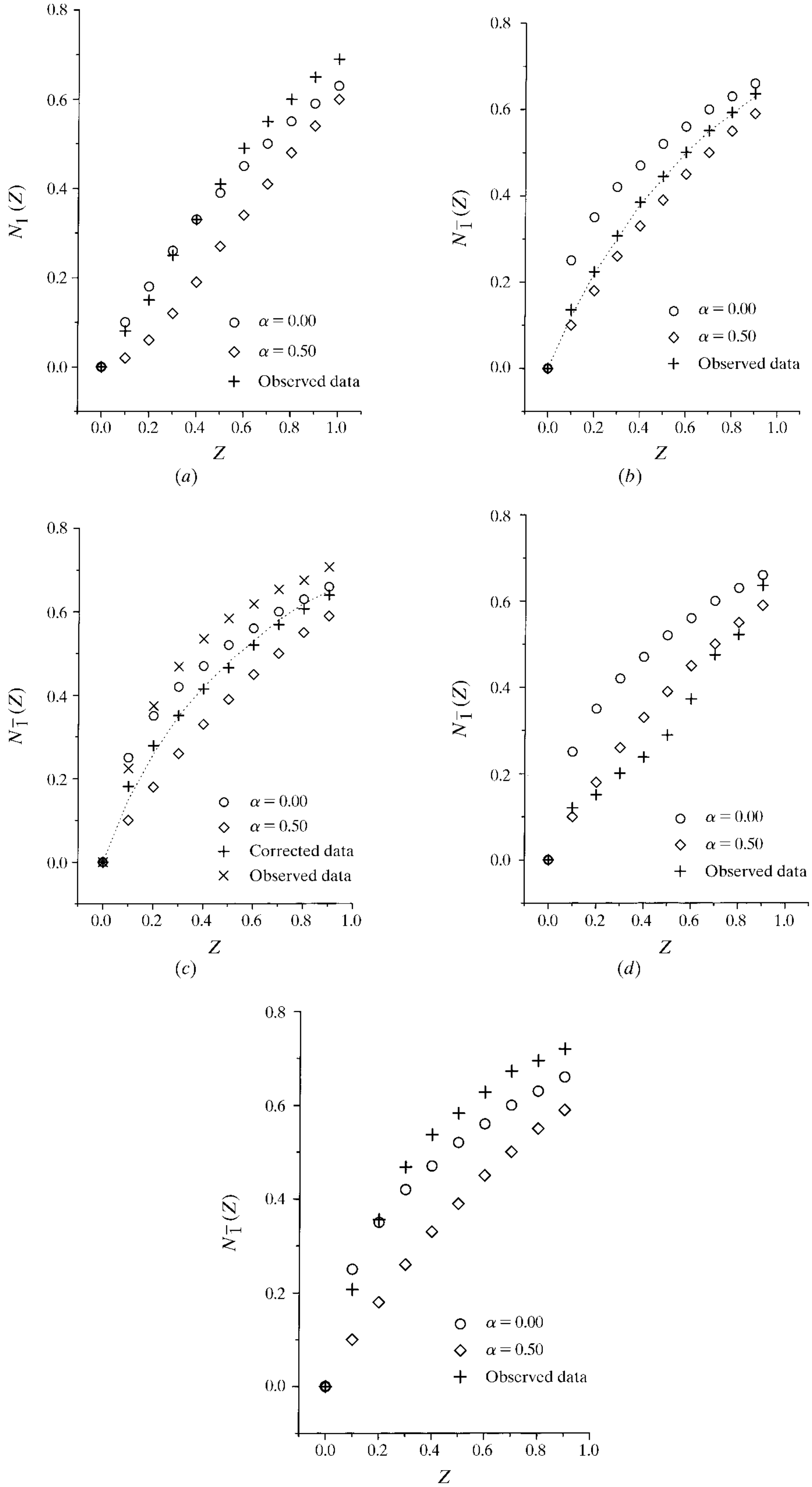
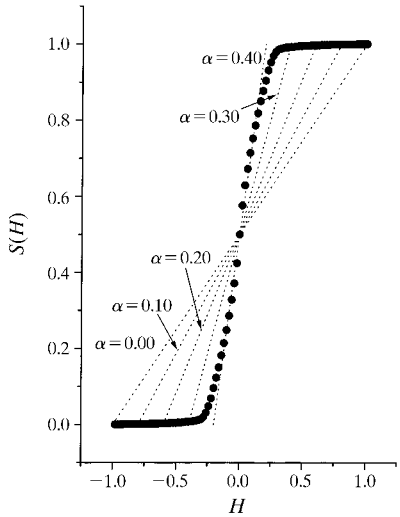
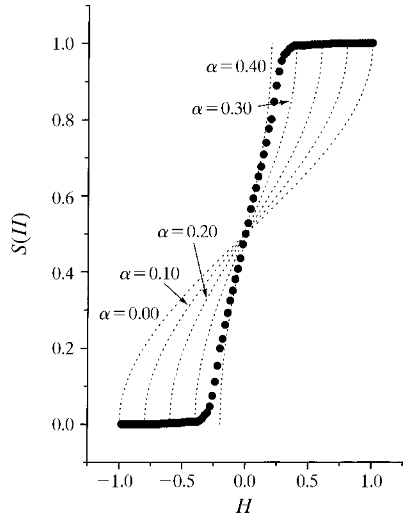


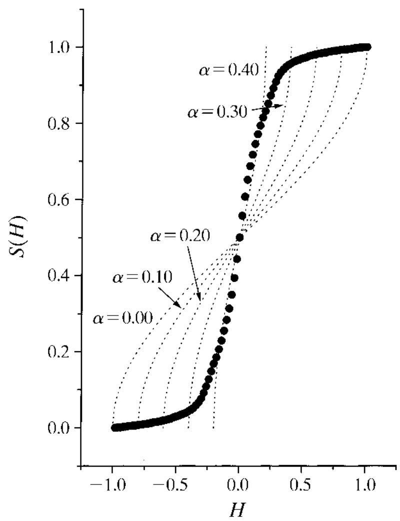
Fig. 2. Rees plots for (*a*) TRINEP, (*b*) DODECA, (*c*) NAHEX, (*d*) LAOZ and (*e*) COMPLEX.



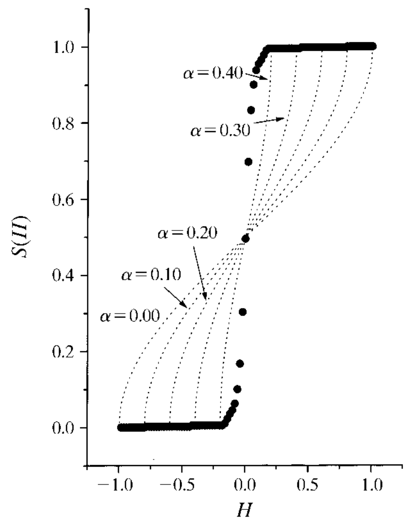
(a)



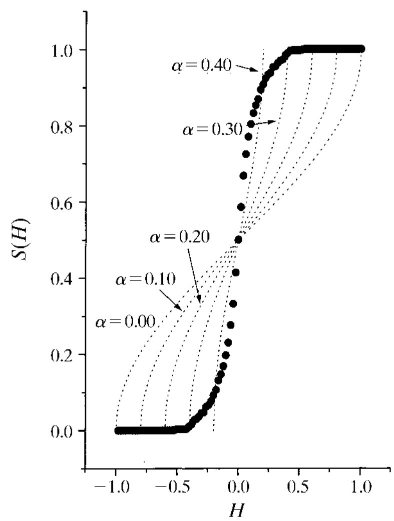
(b)



(c)



(d)



(e)

Fig. 3. Yeates plots for (*a*) TRINEP, (*b*) DODECA, (*c*) NAHEX, (*d*) LAOZ and (*e*) COMPLEX.

Table 2. *Twin operations and twin parameters for the five twinned compounds*

Structure code	Twin operation	Refined α parameter	α parameter from Britton test	α parameter from Yeates test
TRINEP	$m_{[210]}$	0.372 (1)	0.38	0.38/0.36
DODECA	$m_{[010]}$	0.37 (1)	0.38	0.37/0.36
NAHEX	$2_{[001]}$	0.363 (3)	0.36	0.36/0.33
LAOZ	$m_{[210]}$	0.462 (3)	0.45	0.47/0.44
COMPLEX	$m_{[110]}$	0.313 (5)	0.32	0.39/0.37

excluded from the normalization procedure. The distributions for the tests of Britton and Yeates were obtained with the program *TWIN*2.0 (Kahlenberg, 1997) assuming the twin operations given in Table 2. The value for the refined twinning parameter α in this table corresponds to the result of the structure refinements using the program *SHELXL*93 (Sheldrick, 1993).

3. Results and discussion

The analysis from the results of the Britton test showed that twinning by merohedry could be detected in all five cases. Figs. 1(*a*)–(*e*) show the graphical representations of the $W(k)$ distributions. The discontinuities are not equally well pronounced for all selected examples. However, a distinct step is clearly visible in all five distributions. Even for the LAOZ data set with a twinning parameter close to 0.50 the identification of twinning was possible. The volume ratio α estimated from the values of k corresponding to the discontinuities are marked with arrows and compiled in Table 2. They are in excellent agreement with the data obtained from the structure refinements.

The $N(z)$ distributions for the five test data sets are given in Figs. 2(*a*)–(*e*). For DODECA (Fig. 2*b*) the points are significantly different from the distribution expected for an untwinned centrosymmetric crystal (α = 0.00). They are very close to the theoretical curve for α = 0.20, indicating that twinning is present. Nevertheless, this value is considerably lower compared with the result of the structure refinement listed in Table 1. The result for NAHEX is a good example for the influence of pseudo-translational symmetry on the $N(z)$ statistic. The data marked with an 'x' sign correspond to the usual normalization process (Fig. 2*c*). During the normalization a pseudo-translational symmetry concerning the reflection class with $l = 2n$ was detected, which was accounted for in a second calculation. This second data set is marked with a '+'. The points indicate a twinning with $\alpha = 0.10$. However, this value is much lower than the result of $\alpha = 0.36$ from the refinements. In the case of LAOZ the $N(z)$ distribution showed remarkable deviations from the theoretical curves of the Rees test (Fig. 2*d*). The main reason for this deviation is the breakdown of the Wilson statistic for a structure with only three atoms in the asymmetric unit. The assumption of equiprobability for all atomic positions is no longer valid and therefore the Rees test fails. The $N(z)$ distributions for TRINEP and COMPLEX (Figs. 2*a* and 2*e*) could not be evaluated either with regard to the question if twinning is present.

The $S(H)$ curves of the Yeates test are given in Figs. 3(*a*)–(*e*). The comparison between the observed and theoretical cumulative intensity distributions shows clearly that twinning is present in all data sets. The estimated volume fractions α were calculated from both $\langle|H|\rangle$ and $\langle H^2\rangle$ and the results are listed in Table 2. For the first four examples the volume fractions are in good agreement with the refined values. The estimation based on $\langle|H|\rangle$ seems to be slightly more reliable. For COMPLEX the quality of the estimation of α is significantly worse. The results are approximately 18% and 14% higher than the corresponding refined result.

Naturally, a set of only five different twinned data sets cannot be considered as representative. However, the comparison of the three tests reveals that the procedure proposed by Britton gives the most reliable results for inorganic crystal structures, where the twinning element is in most cases a pseudo-symmetry element even in the untwinned crystal. As a consequence of the resulting rational dependencies between the atomic coordinates the intensities of the overlapping reflections are not independent of each other and the $N(z)$ test becomes unreliable. This disadvantage may be less pronounced for organic substances. Although there was a significant deviation in the determination of α in the case of COMPLEX, the Yeates method can be considered as nearly equal to the Britton test with regard to both detecting twinning by merohedry and estimating the volume fraction α. In summary one can say that the tests of Britton and Yeates should be applied routinely in the preliminary stage of a structure determination whenever a twinning by merohedry is possible.

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