1956, 1957, 1958) may then be employed to determine more accurately the values of all the phases.

We note finally that complex crystal structures, in particular protein structures, often satisfy (at least approximately) the present hypothesis II, as well even as our earlier hypothesis (1966). We therefore anticipate that the methods described here and in the earlier paper may eventually find application in the elucidation of such structures.

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The Influence of Intensity Errors on the Higher-Moment Test for Centrosymmetry*

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The sensitivity of the higher-moment test for detection of centrosymmetry to errors in the intensity data is examined. The errors considered are (1) random errors proportional to I, (2) systematic errors of the type $I_o = k\Sigma\,[1-\exp(-I/k\Sigma)]$, (3) errors associated with the non-observance of very weak reflexions, and (4) errors systematic in $\sin\theta$. Mathematical expressions are obtained in a compact form for $\langle z^n\rangle$ including the effect of errors in all the cases except (4). Tables of $\langle z^n\rangle$ with errors are given. It is found that it would not be profitable to use moments of very high order such as $\langle z^4\rangle$ or $\langle z^5\rangle$ but that the higher-moment test is relatively safe for crystals whose weighted reciprocal lattice contains a large percentage of very weak reflexions.

Introduction

Various statistical criteria based on the statistical distribution of X-ray intensities have been used to distinguish between centrosymmetric and non-centrosymmetric crystals (or projections). Deviations from Wilson's (1949) distributions occur for various reasons such as the presence of a few dominating atoms, pseudo-symmetry, *etc.*, and the distributions of intensities in these special cases have been considered by various authors. The distributions obtained in practical cases may also deviate from Wilson's distributions (even in the absence of the above mentioned disturbing features which are structural in nature) because of the use of inaccurate intensity data, *i.e.* intensity data with errors of observation. Rogers, Stanley & Wilson (1955, hereafter referred to as R–S–W) have considered the effect of errors of various kinds in the original intensity data on the statistical criteria such as the cumulative distribution function $N(z)$, the test-ratio ϱ of Wilson, and the specific variance, v, with the aim of finding a rough upper limit for the discrepancy that can be allowed in practical cases where intensities with the errors of observation are involved. This enables one to avoid correlating such deviations (*i.e.* the statistical anomalies arising from the use of inaccurate intensity data) with structural peculiarities. In the present paper we shall study the effect of errors in the intensity data on the higher-moment test which has been proposed by Foster & Hargreaves (1963*a*,*b*) and independently by Srinivasan & Subramanian (1964). The additional advantage of the higher-moment test over other statistical criteria is that the exact theoretical values of the higher moments can be obtained under very general conditions (Foster & Hargreaves, 1963*a*,*b*). We shall however consider here only the equal-atom-random-position case as has been done by R–S–W since this would suffice to show the influence of intensity errors on the higher-moment test.

A second aim of the present investigation is to study the sensitivity of the various higher moments to the errors of intensity data; such a study may therefore provide some guidance regarding the choice of a particular higher moment as optimum in practical cases.

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As in R–S–W, we shall consider mainly four kinds of error in the intensity data, *viz.* (1) random errors proportional to the intensity, (2) systematic errors in I of the form $I_o = k\,\Sigma\,[1-\exp(-I/k\,\Sigma)]$, (3) errors associated with the non-observance of very weak reflexions, and (4) errors systematic as a function of $s\,(=\sin\theta/\lambda)$.

The notation in this paper closely follows that of R–S–W and the relevant quantities may be defined as follows:

I = true (error-free) value of the intensity of a reflexion $\mathbf{H}\,(=hkl)$

I_o = observed value of the intensity of the reflexion $\mathbf{H}$

$z = I/\langle I\rangle$ = true value of the normalized intensity of the reflexion $\mathbf{H}$

$z_o = I_o/\langle I_o\rangle$ = observed value of the normalized intensity of a reflexion $\mathbf{H}$

$$\langle I\rangle = \Sigma$$

$$g_1 = \langle I_o\rangle/\langle I\rangle \quad (1)$$

and

$$z_o = I_o z/(I g_1)\,. \quad (2)$$

We shall presently obtain the values of $\langle z_o^n\rangle$ in the presence of each one of these errors.

The influence of random errors on the higher-moment test

We shall assume that the error in the intensity is proportional to I. That is

$$I_o = I(1+\Delta) \quad (3)$$

where Δ is normally distributed with $\langle\Delta\rangle=0$ and $\langle\Delta^2\rangle=\sigma_\Delta^2$. That is

$$P(\Delta)=(2\pi\sigma_\Delta^2)^{-\frac{1}{2}}\exp(-\Delta^2/2\sigma_\Delta^2)\,. \quad (4)$$

From (3) we have

$$\langle I_o^n\rangle = \langle I^n(1+\Delta)^n\rangle\,. \quad (5)$$

Since I and Δ have no correlation (see R–S–W) we can write (5) as

$$\langle I_o^n\rangle = \langle I^n\rangle\langle(1+\Delta)^n\rangle\,, \quad (6)$$

which gives for $n=1$, in the light of $\langle\Delta\rangle=0$, that $\langle I_o\rangle=\langle I\rangle$ as would be required. Equation (6) can therefore be written

$$\langle z_0^n\rangle = \langle z^n\rangle\langle(1+\Delta)^n\rangle\,,$$

which, on application of the binomial theorem, becomes

$$\langle z_o^n\rangle = \langle z^n\rangle\left\langle\sum_{j=0}^{n}\binom{n}{j}\Delta^j\right\rangle = \langle z^n\rangle\left[\sum_{j=0}^{n}\binom{n}{j}\langle\Delta^j\rangle\right]\,, \quad (7)$$

where $\binom{n}{j}$ is the binomial coefficient defined by

$$\binom{n}{j} = \frac{n!}{j!(n-j)!}\,. \quad (8)$$

From (4) we obtain

$$\langle\Delta^j\rangle = (2\pi\sigma_\Delta^2)^{-\frac{1}{2}}\int_{-\infty}^{\infty}\Delta^j\exp(-\Delta^2/2\sigma_\Delta^2)\,\mathrm{d}\Delta = \begin{cases}\pi^{-\frac{1}{2}}(2\sigma_\Delta^2)^{j/2}\,\Gamma\left(\frac{j+1}{2}\right) & \text{if } j=\text{even}\,.\\ 0 \text{ if } j=\text{odd}\,.\end{cases} \quad (9)$$

From (7) and (9) we have

$$\langle z_o^n\rangle = \langle z^n\rangle\left[\sum_{j=0}^{n}{}'\binom{n}{j}\frac{(2\sigma_\Delta^2)^{j/2}}{\sqrt{\pi}}\,\Gamma\left(\frac{j+1}{2}\right)\right]\,. \quad (10)$$

where the prime on the summation symbol denotes that terms for which j is odd take the value zero. For simplicity we write (10) as

$$\langle z_0^n\rangle = \omega_n\langle z^n\rangle\,, \quad (11)$$

where

$$\omega_n = \sum_{j=0}^{n}{}'\binom{n}{j}\frac{(2\sigma_\Delta^2)^{j/2}}{\sqrt{\pi}}\,\Gamma\left(\frac{j+1}{2}\right)\,. \quad (12)$$

It is clear that ω_n represents the fraction by which $\langle z_o^n\rangle$ exceeds $\langle z^n\rangle$. When $\sigma_\Delta\to 0$, $\omega_n\to 1$ so that $\langle z_o^n\rangle\to\langle z^n\rangle$ as required. The expressions of ω_n for $n=2$, 3, 4 and 5 are given below:

$$\omega_2 = 1+\sigma_\Delta^2 \quad (13a)$$

$$\omega_3 = 1+3\sigma_\Delta^2 \quad (13b)$$

$$\omega_4 = 1+6\sigma_\Delta^2+3\sigma_\Delta^4 \quad (13c)$$

$$\omega_5 = 1+10\sigma_\Delta^2+15\sigma_\Delta^4\,. \quad (13d)$$

The values of the higher moments $\langle z_o^n\rangle$ for $n=2$, 3, 4 and 5 are given in Table 1 for various values of σ_Δ *viz.* $\sigma_\Delta=0$, 0·1, 0·2, ..., 0·7 for both centrosymmetric and non-centrosymmetric crystals. A study of this table reveals the following:

Table 1. *Values of the higher moments of the normalized intensity as a function of* σ_Δ

C = Centrosymmetric crystal
A = Non-centrosymmetric crystal
Subscript n to A or C denotes the nth moment

σ_Δ	A_2	C_2	A_3	C_3	A_4	C_4	A_5	C_5
0·0	2·00	3·00	6·00	15·00	24·00	105·0	120·0	945
0·1	2·02	3·03	6·18	15·45	25·45	111·3	132·2	1041
0·2	2·08	3·12	6·72	16·80	29·88	130·7	170·9	1346
0·3	2·18	3·27	7·62	19·05	37·54	164·3	242·6	1910
0·4	2·32	3·48	8·88	22·20	48·88	213·9	358·1	2820
0·5	2·50	3·75	10·50	26·25	64·50	282·2	532·5	4193
0·6	2·72	4·08	12·48	31·20	85·17	372·6	785·3	6184
0·7	2·98	4·47	14·82	37·05	111·85	489·3	1140·2	8987

(i) For a given σ_Δ the percentage error in $\langle z_o^n \rangle$ increases as n increases. For example, when $\sigma_\Delta = 0{\cdot}2$, the percentage errors in $\langle z_o^n \rangle$ are respectively 4%, 12%, 24% and 42% for $n=2$, 3, 4 and 5. Thus, in practical cases it seems better to confine ourselves to the second or third moments of z.

(ii) For a given n, as σ_Δ increases, the percentage error in $\langle z_o^n \rangle$ increases as required.

(iii) Even when σ_Δ is as high as 0·3, a non-centrosymmetric crystal cannot be mistaken for a centrosymmetric crystal. Ambiguities and wrong assignments may arise when $\sigma_\Delta > 0{\cdot}3$.

The influence of systematic errors on the higher-moment test

We shall consider the systematic error in the intensity as a function of intensity as given by the relation (see R–S–W)

$$I_o = k\,\Sigma\,[1-\exp(-I/k\,\Sigma)]\,. \tag{14}$$

It is clear that as $k \to \infty$, $I_o \to I$. Following R–S–W, we write

$$z' = I_o/\langle I \rangle = g_1 z_o = k[1-\exp(-z/k)]\,, \tag{15}$$

where $0 \le z' \le k$. We shall first consider the non-centrosymmetric crystal.

Non-centrosymmetric crystal

It has been shown that z' is distributed in accordance with (see R–S–W):

$$P(z') = (1-z'/k)^{k-1},\ 0 \le z' \le k\,. \tag{16}$$

Since $\langle z_o \rangle = 1$, it is clear that

$$\langle z' \rangle = \langle g_1 z_o \rangle = g_1 = k/(k+1) \tag{17}$$

as obtained in R–S–W. From (15) and (16) we obtain

$$\langle z_0^n \rangle = \frac{1}{g_1^n}\langle z'^n \rangle = \frac{1}{g_1^n}\int_0^k z'^n\left(1-\frac{z'}{k}\right)^{k-1} dz'\,. \tag{18}$$

Making the substitution $x = z'/k$, (18) can be shown to be

$$\langle z_0^n \rangle = k(k+1)^n B(n+1,k)\,. \tag{19}$$

where we have used (17). Since we have [see equation (4), p. 31 of Rainville, 1960]

$$\Gamma(n) = \lim_{k\to\infty} k^n B(n,k)\,.$$

We obtain from (19):

$$\lim_{k\to\infty}\langle z_o^n \rangle = \lim_{k\to\infty}\frac{k(k+1)^n}{k^{n+1}}\,\Gamma(n+1) = \Gamma(n+1) = \langle z^n \rangle$$

as required. Equation (19) can be written

$$\langle z_0^n \rangle = \alpha_n(1)\,\langle z^n \rangle\,, \tag{20}$$

where

$$\alpha_n(1) = \frac{k(k+1)\,\Gamma(k)}{\Gamma(n+k+1)}\,. \tag{21}$$

The expressions of $\alpha_n(1)$ for $n=2$, 3, 4 and 5 are given below:

$$\alpha_2(1) = \frac{k+1}{k+2} \tag{22a}$$

$$\alpha_3(1) = \frac{(k+1)^2}{(k+2)(k+3)} \tag{22b}$$

$$\alpha_4(1) = \frac{(k+1)^3}{(k+2)(k+3)(k+4)} \tag{22c}$$

$$\alpha_5(1) = \frac{(k+1)^4}{(k+2)(k+3)(k+4)(k+5)}\,. \tag{22d}$$

Centrosymmetric crystal

It has been shown (see R–S–W) that z' is distributed in accordance with:

$$P(z') = \frac{(1-z'/k)^{k/2-1}}{[2\pi k\,\log_e(1-z'/k)^{-1}]^{\frac{1}{2}}}\,,\ 0 \le z' \le k \tag{23}$$

and that

$$g_1 = \langle z' \rangle = k[1-\{k/(k+2)\}^{\frac{1}{2}}]\,. \tag{24}$$

The nth moment of z_o is given by

$$\langle z_0^n \rangle = \frac{1}{g_1^n}\langle z'^n \rangle = \frac{1}{g_1^n}\int_0^k \frac{z'^n(1-z'/k)^{k/2-1}dz'}{[2\pi k\,\log_e(1-z'/k)^{-1}]^{\frac{1}{2}}}\,,$$

which on substitution, $1-(z'/k) = \exp(-p^2)$, simplifies to

$$\langle z_o^n \rangle = \left(\frac{k}{g_1}\right)^n \sqrt{\frac{2k}{\pi}}\int_0^\infty [1-\exp(-p^2)]^n \exp(-kp^2/2)dp\,. \tag{25}$$

Using the binomial theorem, (25) can be written

$$\langle z_0^n \rangle = \left(\frac{k}{g_1}\right)^n \left(\frac{2k}{\pi}\right)^{\frac{1}{2}} \sum_{j=0}^{n} \binom{n}{j}(-1)^j \int_0^\infty \exp[-p^2(j+\tfrac{1}{2}k)]dp$$

$$= \frac{k^{n+\frac{1}{2}}}{g_1^n}\sum_{j=0}^{n}\binom{n}{j}(-1)^j\frac{1}{\sqrt{2j+k}}\,. \tag{26}$$

It is possible to show that

$$\lim_{k\to\infty}\langle z_o^n \rangle = \langle z^n \rangle \tag{27}$$

as would be required (see Appendix). The expressions for $\langle z_0^n \rangle$ for $n=2$, 3, 4, and 5 can be written

$$\langle z_0^2 \rangle = (k/g_1)^2\sqrt{k}\,(c_0-2c_1+c_2) \tag{28a}$$

$$\langle z_0^3 \rangle = (k/g_1)^3\sqrt{k}\,(c_0-3c_1+3c_2-c_3) \tag{28b}$$

$$\langle z_0^4 \rangle = (k/g_1)^4\sqrt{k}\,(c_0-4c_1+6c_2-4c_3+c_4) \tag{28c}$$

$$\langle z_0^5 \rangle = (k/g_1)^5\sqrt{k}\,(c_0-5c_1+10c_2-10c_3+5c_4-c_5) \tag{28d}$$

where we have used the simplifying notation $c_j = (2j+k)^{-\frac{1}{2}}$. The values of $\langle z_0^n \rangle$ for $n=2$, 3, 4 and 5 for the centrosymmetric and non-centrosymmetric crystals are given in Table 2 for $k=\infty$, 20, 15, 10, 5, 2 and 1. A study of this table reveals the following:

(i) For a given k, as n increases, the percentage error in $\langle z_o^n \rangle$ increases. It therefore seems better to confine the higher moment test to $n=2$ or 3.

(ii) A non-centrosymmetric crystal can never be mistaken for a centrosymmetric crystal if this type of error alone is present. However, when k is small (say $k \simeq 5$) there is a possibility that a centrosymmetric crystal will be mistaken for a non-centrosymmetric crystal.

(iii) The region of wrong assignment or ambiguities is confined to the values of $k \lesssim 15$.

The influence of unobserved reflexions on the higher-moment test

Let I_t be the threshold value of the intensity that can be measured. That is, the relation between I_o and I is expressed as

$$I_o = \begin{cases} I & \text{for} \quad I \geq I_t \\ 0 & \text{for} \quad I < I_t \,. \end{cases} \tag{29}$$

We shall write

$$z_t = I_t / \langle \mathrm{I} \rangle = I_t / \Sigma \,. \tag{30}$$

Non-centrosymmetric crystal

From (29) it is clear that I_o is distributed in accordance with

$$\mathrm{P}(I_o) = \begin{cases} \dfrac{1}{\Sigma} \exp(-I_o/\Sigma) & \text{for} \quad I \geq I_t \\ 0 & \text{for} \quad I < I_t \,. \end{cases} \tag{31}$$

The nth moment of I_o is therefore given by

$$\langle I_o^n \rangle = \frac{1}{\Sigma} \int_{I_t}^{\infty} I_o^n \exp(-I_o/\Sigma) dI_o \,. \tag{32}$$

Making the substitution $I_o/\Sigma = x$ in (32), we obtain

$$\begin{aligned} \langle I_o^n \rangle &= \Sigma^n \int_{z_t}^{\infty} x^n \exp(-x) dx \\ &= \Sigma^n [\Gamma(n+1) - \gamma(n+1, z_t)] \,, \end{aligned} \tag{33}$$

from which we obtain, by putting $n=1$,

$$g_1 = \langle I_o \rangle / \Sigma = 1 - \gamma(2, z_t) = (1 + z_t) \exp(-z_t) \,, \tag{34}$$

in agreement with the earlier result (R–S–W). The nth moment of z_o is given by

$$\begin{aligned} \langle z_o^n \rangle &= \langle I_o^n \rangle / \langle I_o \rangle^n = \langle I_o^n \rangle / (g_1 \Sigma)^n \\ &= \frac{1}{g_1^n} [\Gamma(n+1) - \gamma(n+1, z_t)] \,, \end{aligned} \tag{35}$$

where we have used (33) and (34). Since $\langle z^n \rangle = \Gamma(n+1)$, (35) can be written

$$\langle z_o^n \rangle = \beta_n(1) \langle z^n \rangle \,, \tag{36}$$

where

$$\beta_n(1) = \frac{1}{g_1^n} [1 - \frac{1}{\Gamma(n+1)} \gamma(n+1, z_t)] \,. \tag{37}$$

The expressions for $\beta_n(1)$ for $n = 2$, 3, 4 and 5 are:

$$\beta_2(1) = \frac{\exp(z_t)}{(1+z_t)^2} [1 + z_t + \tfrac{1}{2} z_t^2] \tag{38a}$$

$$\beta_3(1) = \frac{\exp(2z_t)}{(1+z_t)^3} [1 + z_t + \tfrac{1}{2} z_t^2 + \tfrac{1}{6} z_t^3] \tag{38b}$$

$$\beta_4(1) = \frac{\exp(3z_t)}{(1+z_t)^4} [1 + z_t + \tfrac{1}{2} z_t^2 + \tfrac{1}{6} z_t^3 + \tfrac{1}{24} z_t^4] \tag{38c}$$

$$\beta_5(1) = \frac{\exp(4z_t)}{(1+z_t)^5} [1 + z_t + \tfrac{1}{2} z_t^2 + \tfrac{1}{6} z_t^3 + \tfrac{1}{24} z_t^4 + \tfrac{1}{120} z_t^5] \,, \tag{38d}$$

where we have used the recurrence relation (Jahnke–Emde–Losch, 1960, p. 14):

$$\gamma(n+1, x) = n\gamma(n, x) - x^n \exp(-x) \tag{39}$$

and the relation

$$\gamma(1, x) = \int_0^x \exp(-x) dx = 1 - \exp(-x) \,.$$

It is clear that as $z_t \to 0$, $\beta_n(1) \to 1$, so that $\langle z_o^n \rangle \to \langle z^n \rangle$ as required.

Centrosymmetric crystal

From (29) the probability density function of I_o can be written in the form

$$P(I_o) = \begin{cases} (2\pi \, \Sigma \, I_o)^{-\frac{1}{2}} \exp(-I_o/2\,\Sigma) & \text{for} \quad I \geq I_t \\ 0 & \text{for} \quad I < I_t \,, \end{cases} \tag{40}$$

so that the nth moment of I_o will be

$$\langle I_o^n \rangle = \frac{1}{\sqrt{2\pi \Sigma}} \int_{I_t}^{\infty} I_o^{n-1/2} \exp(-I_o/2\,\Sigma) dI_o \,. \tag{41}$$

Making the substitution $I_o/2\,\Sigma = x$ in (41) we obtain

$$\begin{aligned} \langle I_o^n \rangle &= \frac{(2\,\Sigma)^n}{\sqrt{\pi}} \int_{z_t/2}^{\infty} x^{n-\frac{1}{2}} \exp(-x) dx \\ &= \frac{(2\,\Sigma)^n}{\sqrt{\pi}} [\Gamma(n+\tfrac{1}{2}) - \gamma(n+\tfrac{1}{2}, \tfrac{1}{2} z_t)] \,. \end{aligned} \tag{42}$$

Table 2. *Values of the higher moments of the normalized intensity as a function of k*

C = Centrosymmetric crystal A = Non-centrosymmetric crystal

Subscript n to A or C denotes the nth moment

k	A_2	C_2	A_3	C_3	A_4	C_4	A_5	C_5
∞	2·000	3·000	6·000	15·00	24·00	105·0	120·0	945
20	1·909	2·725	5·229	11·09	18·30	—	76·87	—
15	1·882	2·675	5·020	10·77	16·91	57·29	67·63	425
10	1·833	2·552	4·654	9·36	14·63	40·56	53·62	170
5	1·714	2·297	3·857	7·13	10·29	25·99	30·86	104
2	1·500	1·902	2·700	4·41	5·40	11·26	11·57	31
1	1·333	1·637	2·000	3·07	3·20	6·12	5·33	13

Putting $n=1$ in (42) and using the relation (Erdelyi, 1954, p.295):

$$\gamma(\tfrac{1}{2},x^2)=\sqrt{\pi}\,\mathrm{erf}\,(x) \quad (43)$$

we obtain

$$g_1=\langle I_o\rangle/\Sigma=1-\mathrm{erf}\,(\sqrt{z_t/2})+\left(\frac{2}{\pi}z_t\right)^{\frac{1}{2}}\exp\,(-z_t/2)\,, \quad (44)$$

which agrees with that obtained by R–S–W. The nth moment of z_o can be obtained from (42) as

$$\langle z_o^n\rangle=\langle I_o^n\rangle/(g_1\Sigma)^n = \frac{1}{g_1^n}\frac{2^n}{\sqrt{\pi}}[\Gamma(n+\tfrac{1}{2})-\gamma(n+\tfrac{1}{2},\tfrac{1}{2}z_t)]\,. \quad (45)$$

Since $\langle z^n\rangle=(2^n/\sqrt{\pi})\Gamma(n+\frac{1}{2})$, (45) can be written

$$\langle z_o^n\rangle=\beta_n(\bar{1})\,\langle z^n\rangle\,, \quad (46)$$

where

$$\beta_n(\bar{1})=\frac{1}{g_1^n}\left[1-\frac{1}{\Gamma(n+\frac{1}{2})}\gamma(n+\tfrac{1}{2},\tfrac{1}{2}z_t)\right]. \quad (47)$$

The expressions for $\beta_n(\bar{1})$ for $n=2$, 3, 4 and 5 are:

$$\beta_2(\bar{1})=\frac{1}{g_1^2}\left[1-\mathrm{erf}\,(\sqrt{z_{t/2}})+\left(\frac{2}{\pi}z_t\right)^{\frac{1}{2}}(1+\tfrac{1}{3}z_t)\exp\,(-z_{t/2})\right] \quad (48a)$$

$$\beta_3(\bar{1})=\frac{1}{g_1^3}\left[1-\mathrm{erf}\,(\sqrt{z_{t/2}})+\left(\frac{2}{\pi}z_t\right)^{\frac{1}{2}}(1+\tfrac{1}{3}z_t+\tfrac{1}{15}z_t^2)\exp\,(-z_{t/2})\right] \quad (48b)$$

$$\beta_4(\bar{1})=\frac{1}{g_1^4}\left[1-\mathrm{erf}\,(\sqrt{z_{t/2}})+\left(\frac{2}{\pi}z_t\right)^{\frac{1}{2}}(1+\tfrac{1}{3}z_t+\tfrac{1}{15}z_t^2+\tfrac{1}{105}z_t^3)\times\exp\,(-z_{t/2})\right] \quad (48c)$$

$$\beta_5(\bar{1})=\frac{1}{g_1^5}\left[1-\mathrm{erf}\,(\sqrt{z_{t/2}})+\left(\frac{2}{\pi}z_t\right)^{\frac{1}{2}}(1+\tfrac{1}{3}z_t+\tfrac{1}{15}z_t^2+\tfrac{1}{105}z_t^3+\tfrac{1}{945}z_t^4)\exp(-z_{t/2})\right] \quad (48d)$$

where we have used (39), (43) and (47). It is clear that as $z_t\to 0, \beta_n(\bar{1})\to 1$ so that $\langle z_o^n\rangle\to\langle z^n\rangle$ as required.

The values of $\langle z_o^n\rangle$ for $n=2$, 3, 4 and 5 are given in Table 3 both for centrosymmetric and non-centrosymmetric crystals for the values of $z_t=0$, 0·1, 0·2, ... 0·5. A study of Table 3 reveals the following:

(i) For a given z_t the percentage error in $\langle z_o^n\rangle$ increases as n increases. However, the percentage increase is small compared with the deviations caused by random errors or systematic errors.

(ii) For a given n, as z_t increases the percentage error in $\langle z_o^n\rangle$ increases, but slowly compared with the other kinds of error.

(iii) When $n=2$ or 3 no ambiguities may arise even when $z_t\simeq 0{\cdot}4$. Thus, compared with other statistical criteria (see R–S–W), the higher-moment test seems to be the best for crystals whose weighted reciprocal lattice contains a large percentage of weak reflexions. For example, the presence of even 40% of unobserved reflexions in centrosymmetric crystals and 30% in non-centrosymmetric crystals does not appreciably affect the higher-moment test.

The influence of errors systematic as a function of $s(\sin\theta/\lambda)$ on the higher-moment test

An important source of error of this kind would arise from the error in determining the local average intensity $\langle I\rangle_{\mathrm{det}}$ from the course of the $\langle I\rangle$ curve (which we assume as that obtained from a set of accurately estimated intensities). Following R–S–W we may write

$$\langle I\rangle_{\mathrm{det}}=\langle I\rangle[1+\varepsilon(s)]$$

where $\varepsilon(s)$ is a function of s and will be never large compared with unity in practical cases. Thus

$$z_{\mathrm{det}}=z/[1+\varepsilon(s)]\,.$$

The value of $\langle z_{\mathrm{det}}^n\rangle$ will actually be determined by the distribution of $\varepsilon(s)$, which is difficult to calculate. However, it is clear that $\langle z_{\mathrm{det}}^n\rangle$ will be $>$ or $<\langle z^n\rangle$, depending on the distribution of ε. It is however to be expected that the errors in the $\langle I\rangle$-curve are more serious for the $\langle z^n\rangle$ test than for other statistical tests. For example, an underestimation of the value of $\langle I\rangle_{\mathrm{det}}$ for even a few reflexions for which $z>1$ will cause a large increase in the value of the higher order moments. In a similar way, an overestimation of $\langle I\rangle_{\mathrm{det}}$ for a few reflexions for which $z\gg 1$ would decrease the value of $\langle z^n\rangle$ considerably. The seriousness of this sort of error increases as n increases in value and hence

Table 3. *Values of the higher moments of the normalized intensity as a function of z_t*

C = Centrosymmetric crystal; A = Non-centrosymmetric crystal
Subscript n to A or C denotes the nth moment

z_t	A_2	C_2	A_3	C_3	A_4	C_4	A_5	C_5
0·0	2·000	3·000	6·000	15·00	24·00	105·0	120·0	945
0·1	2·019	3·049	6·085	15·37	24·45	108·5	122·9	984
0·2	2·070	3·136	6·326	16·06	25·76	115·0	131·1	1058
0·3	2·149	3·247	6·715	16·95	27·90	123·6	144·8	1159
0·4	2·253	3·378	7·254	18·04	30·94	134·4	164·9	1286
0·5	2·381	3·525	7·953	19·32	35·02	147·3	192·5	1442

it is necessary to confine the value of n to $n=2$ or 3, and also it is necessary to compute $\langle I\rangle$ for each reflexion accurately from an accurate $\langle I\rangle$ curve.

Conclusion

The above studies indicate that it may not be useful to conduct higher-moment tests with moments of very high order. It would be profitable, in order to avoid wrong assignments or ambiguities, to use only $\langle z^2\rangle$ and $\langle z^3\rangle$ in practical cases. The presence of both the random and systematic errors of the 'extinction' type in a given case produce deviations which are opposed and thus tend to cancel. As has been pointed out earlier (R–S–W) the error in obtaining $\langle I\rangle$ is an adverse type and hence care must be taken in the evaluation of $\langle I\rangle$ for each reflexion from an accurate curve of $\langle I\rangle$ *versus* s. Unobserved reflexions do not produce any serious deviations in the case of higher moments. Thus, the higher-moment test is better suited to crystals which contain a large percentage (as high as 40%) of unobserved reflexions.

APPENDIX

When the value of k is large we can write equation (26) in the form

$$I=\lim_{k\to\infty}\langle z_o^n\rangle=\lim_{k\to\infty}\frac{k^{n+\frac{1}{2}}}{g_1^n}\sum_{j=0}^{n}\binom{n}{j}\frac{(-1)^j}{(2j+k)^{\frac{1}{2}}}\,. \quad (A\text{-}1)$$

Since $g_1\to 1$ as $k\to\infty$, $(A$–1) can be written

$$I=\lim_{k\to\infty}k^n\sum_{j=0}^{n}\binom{n}{j}(-1)^j\left(1+\frac{2j}{k}\right)^{-\frac{1}{2}}$$

$$=\lim_{k\to\infty}k^n\sum_{j=0}^{n}\binom{n}{j}(-1)^j \times\left[\sum_{i=0}^{\infty}\frac{r(r-1)\dots(r-i+1)}{i!}\left(\frac{2j}{k}\right)^i\right], \quad (A\text{–}2)$$

where we have used the binomial theorem and also the notation $r=(-\frac{1}{2})$. We can split the summation over i into two summations and rewrite $(A$–2) as

$$I=\lim_{k\to\infty}\sum_{j=0}^{n}\binom{n}{j}(-1)^j \times\left[\sum_{i=0}^{n}\frac{r(r-1)\dots(r-i+1)}{i!}(2j)^i k^{n-i}\right] \quad (A\text{–}3)$$

since the second summation which involves powers of $(1/k)$ vanishes. We can rewrite $(A$–3) as

$$I=\lim_{k\to\infty}\sum_{i=0}^{n}\frac{r(r-1)\dots(r-i+1)}{i!} \times 2^i k^{n-i}\sum_{j=0}^{n}\binom{n}{j}j^i(-1)^j\,. \quad (A\text{–}4)$$

Using equation (12·17) in p. 63 of Feller (1960), it can be shown that

$$\sum_{j=0}^{n}\binom{n}{j}j^i(-1)^j =(-1)^n\sum_{j=0}^{n}\binom{n}{j}j^i(-1)^{n-j}=n!\,\delta(i-n)\,. \quad (A\text{–}5)$$

From $(A$–4) and $(A$–5) we obtain

$$I=\lim_{k\to\infty}\sum_{i=0}^{n}\frac{r(r-1)\dots(r-i+1)}{i!} \times 2^i k^{n-i}(-1)^n n!\,\delta(i-n)$$

$$=(-1)^n 2^n r(r-1)\dots(r-n+1)$$

$$=1\cdot3\cdot5\dots(2n-1)\,, \quad (A\text{–}6)$$

since r was used to stand for $(-\frac{1}{2})$. We can write $(A$–6) as

$$I=\frac{(2n-1)!}{2\cdot4\cdot6\dots(2n-2)}=\frac{(2n-1)!}{2^{n-1}(n-1)!} =\frac{\Gamma(2n)}{2^{n-1}\Gamma(n)}=\frac{2^n}{\sqrt{\pi}}\Gamma(n+\tfrac{1}{2})\,, \quad (A\text{–}7)$$

where we have used the duplication formula for gamma function (Sneddon, 1961). The right hand side of $(A$–7) is nothing but $\langle z^n\rangle$ so that

$$I=\langle z^n\rangle \quad (A\text{–}8)$$

as required.

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