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The weighting of intensities for statistical surveys. By E. STANLEY,* *Division of Physics, National Research Council, Ottawa, Canada*

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Introduction

The space groups $P1$ and $P\bar{1}$ each give reflexion intensities distributed according to single distribution functions. All other space groups give limited groups of reflexions whose intensities can be described by one or other of the two distribution functions of Wilson (1949) unless additional symmetries of the type described by Lipson & Woolfson (1952) and by Rogers & Wilson (1953) are present. In general the only group of reflexions whose intensities can be described by a single distribution function is one in which the reflexions are the successive orders from the same set of planes (i.e. a row in reciprocal space passing through the origin). All the more general groups, zones or complete arrays, are likely to contain sub-groups which are described by different distributions because the value of the mean intensity or the distribution type, or both, are different from those appropriate to the remainder of the group.

The 'mean' intensity of a group

In general the mean intensity of a group of reflexions has no unique meaning. In any homogeneous group of reflexions S/Σ is the same throughout and, provided proper account is taken of systematic absences, $\langle I\rangle$ is equal to S (Rogers, 1950), where $S = n\Sigma$, n is a small integer depending on the symmetry elements causing the effective superposition of atoms for particular groups of reflexions, and $\Sigma = \sum f^2$. Instead of calculating the mean intensity, the preferred procedure is to determine

$$\Sigma_{\text{obs.}} = \sum \frac{1}{n} I_n / \Sigma N_n = \frac{1}{N} \sum \frac{1}{n} I_n \,, \qquad (1)$$

where N_n is the number of reflexions of intensities I_n for which $S/\Sigma = n$. The group may contain sub-groups of different distribution types but this is of no consequence since both are distributed about the same mean value.

In the application of the method of Wilson (1942) for the determination of the absolute scale and the temperature coefficient, $\log(\Sigma_{\text{obs.}}/\Sigma)$ should be plotted against $\sin^2\theta/\lambda^2$. Kartha (1953) proposed that the value of the absolute scale be determined by comparing $V\int_V \varrho^2 dV$ and $\sum_{-\infty}^{+\infty} I(hkl)$. To apply this method correctly the integrals should be evaluated for each group of reflexions or $N\Sigma_{\text{obs.}}$ should be used instead of $\sum I$.

If the space group is not completely known when the absolute scale and temperature coefficient are to be determined, all reflexions for which S/Σ is in doubt must be omitted from the survey. When the space group has been completely determined all the reflexions can be included.

The number of reflexions in rows, zones and arrays in an isometric lattice included within a sphere of radius $|\mathbf{s}|$ are roughly in the ratio of $|\mathbf{s}|:\frac{1}{2}\pi|\mathbf{s}|^2:\frac{2}{3}\pi|\mathbf{s}|^3$. Unless the intensities are properly weighted, the graph of $\log(\langle I\rangle/\Sigma)$ against $\sin^2\theta/\lambda^2$ will be curved and will lead to errors in the temperature coefficient and in the factor for conversion to the absolute scale, quite apart from biasing the values of $\langle I\rangle$ to higher values. A wrong temperature coefficient will impart an error systematic in $\sin\theta$ to the intensities, the effect of which on the statistical tests has been considered by Rogers, Stanley & Wilson (to be published). In space groups of low symmetry the number of reflexions with values of S/Σ different from unity is likely to be small and their effect correspondingly small. But in the space group $P6/mmm$, for example, there are, in reciprocal space, one row with $S/\Sigma = 12$, six rows with $S/\Sigma = 4$ and seven zones with $S/\Sigma = 2$. In any lattice with a finite number of reflexions, failure to weight the intensities of the special groups of reflexions would profoundly affect the shape of the graph of $\log(\langle I\rangle/\Sigma)$ against $\sin^2\theta/\lambda^2$.

The statistical tests for symmetry elements

In the tests of Wilson (1949, 1951), Howells, Phillips & Rogers (1950) and Rogers (1950) for the identification of non-translatory symmetry elements, particular groups of reflexions are assigned to one of two theoretical distributions (Wilson, 1949), which, in the form given by Howells *et al.* (1950), are

$$(1)P(z)dz = \exp(-z)dz \qquad (2)$$

and

$$(\bar{1})P(z)dz = (2\pi z)^{-\frac{1}{2}} \exp(-\tfrac{1}{2}z)dz \,, \qquad (3)$$

where $z = I/\Sigma$.

A reasonable agreement between the observed and theoretical distributions is to be expected only if the groups of reflexions treated are homogeneous in distribution type and in S. Those groups of reflexions whose distribution type is known must be excluded from any survey and the remainder weighted by Σ/S if known or omitted if S/Σ is not known. For example, in distinguishing between $P2$, Pm and $P2/m$, after Rogers (1950), the [010] zone, which always is homogeneous in distribution type and in S, although the value of S/Σ is not known, is first examined. If the distribution of the intensities is acentric, $(1)P(z)$, the space group is Pm. If centric, $(\bar{1})P(z)$, the space group is either $P2$ or $P2/m$ and the $h0l$ reflexions will have $S/\Sigma = 1$ or 2 and the $0k0$ reflexions will have $S/\Sigma = 2$. Any other zone or the whole array of intensities can now be examined, omitting all $h0l$ reflexions and either omitting the $0k0$ reflexions or weighting their intensities by $\frac{1}{2}$. The tables of Rogers (1950) give the distribution types and values of S/Σ for all special groups of reflexion in all space groups and indicate those zones and rows whose intensities should be omitted from the survey in any particular instance and the way in which the remainder should be weighted.

Failure to use only legitimate groups of reflexions with properly weighted intensities is unlikely to lead to serious errors in space groups of low symmetry, but for $P6/mmm$ (referred to above) an approximately isometric lattice of

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1000 reflexions contains only about 150 general reflexions with $S/\Sigma = 1$ and the unweighted intensities would have a specific variance (Wilson, 1951) of intrinsic value 3·6. The salt $NaK_5Cl_2(S_2O_6)_2$ had alternative space groups *P4nc* or *P4/mnc* (Stanley, 1953). The $N(z)$ distributions (Howells *et al.*, 1950) for the [100] zone with and without proper weighting of the intensities are shown in Fig. 1.

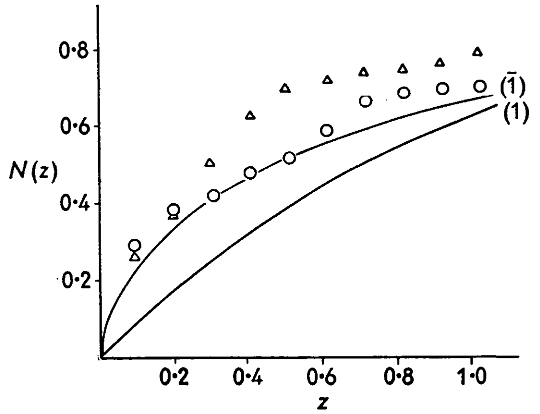

Fig. 1. $N(z)$ distribution for reflexions in the [100] zone of $NaK_5Cl_2(S_2O_6)_2$. Triangles: unweighted intensity data; circles: properly weighted intensity data.

The values of the specific variance with and without proper weighting were 2·14 and 2·34.

Since the distribution of intensities in a group of reflexions heterogeneous in S/Σ is a function of $|\mathbf{s}|$, failure properly to weight the intensities may result in wrong conclusions concerning pseudo-symmetry.

In the method of multipliers (Rogers, 1950) the values of S and Σ are compared and it is necessary that the correct weighting procedure be observed in the determination of the value of Σ(obs.).

Conclusion

The distribution functions of Wilson (1949) apply to the intensities in any group of reflexions for which the value of S/Σ is the same for all reflexions and which is homogeneous in distribution type. In the determination of the temperature coefficient and the factor for conversion to the absolute scale all reflexions should be weighted by Σ/S or omitted if this quantity is not known. Groups of intensities used for the statistical tests for symmetry elements must be homogeneous in distribution type and in S/Σ or made so by weighting by Σ/S.

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The application of an X-ray method to the study of lattice bending.

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The limit of resolution of many of the X-ray techniques employed in the study of the mechanism of sub-boundary formation is such that much of the evidence obtained, such as the background darkening between separated X-ray diffraction spots, may be interpreted as arising either from a continuously bent lattice or from sub-grains that are too small to be resolved and whose orientations cover the range between the resolved X-ray spots (Beck, 1954). The high resolving power of the double-crystal diffractometer, together with the Berg–Barrett technique of X-ray microscopy, gives detailed information which enables one to eliminate the possibility of lattice bending.

The rocking curve obtained using Cu $K\alpha$ radiation reflected in the first order from the cleavage planes of calcite mates mounted as the A and B crystals of the diffractometer had a half-width of 14 seconds of arc. The half-width of the first crystal is therefore $14/\sqrt{2} \approx 10$ seconds of arc. Crystal B was then rotated to the $(1, +1)$ position and the slit system was adjusted until most of the α_2 component of the rocking curve was suppressed (Intrater & Weissmann, 1954). The axis of rotation coincides with what in the experiment is the specimen surface, and the angular rotation is so small that the area of the specimen irradiated can be considered to be fixed.

A rocking curve of the test specimen mounted in the $(n, -n)$ position is obtained and is then retraced in discrete steps with an image of the reflecting area recorded at each setting. The small area of specimen irradiated will register, on a film placed close to and parallel to the reflecting planes, an image that consists of reflection from all regions accessible to the beam whose orientations are identical within the 10 seconds of arc non-parallelism of the monochromatized beam; misoriented neighbors will reflect to adjacent regions on the film but will do so at different specimen settings (Intrater & Weissmann, 1954).

Consider a specimen containing a random distribution of relatively perfect unresolvable small domains whose overall misorientation is 40 seconds of arc. The peak of the Gaussian rocking curve and the densest image are recorded for that specimen orientation in which the