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A relationship among the structure-factor magnitudes for *P*1.

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From the definition of the structure factor,

$$F_{\mathbf{h}} = \sum_{j=1}^{N} f_{j\mathbf{h}} \exp\left(-2\pi i \mathbf{h}.\mathbf{r}_j\right), \tag{1}$$

it is possible to show that relationships exist among the magnitudes of the structure factors (Hauptman & Karle, 1950). In this note a simple statistical relationship among the magnitudes of the structure factors is derived for space group $P1$ which is valid for the case that the crystal contains N identical point atoms per unit cell. Strictly speaking our formula holds rigorously only for the case that no two interatomic vectors coincide. However, it has approximate validity if the overlap of Patterson peaks is small.

In space group $P1$ the normalized structure factor $E_{\mathbf{h}}$ is defined by means of

$$E_{\mathbf{h}} = F_{\mathbf{h}} \Big/ \left(\sum_{j=1}^{N} f_{j\mathbf{h}}^2\right)^{\frac{1}{2}}, \tag{2}$$

which becomes, for the case of N identical point atoms (with atomic number Z) per unit cell,

$$E_{\mathbf{h}} = F_{\mathbf{h}}/Z\sqrt{N}\,. \tag{3}$$

Equation (1) then implies

$$E_{\mathbf{h}} = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} \exp\left(-2\pi i \mathbf{h}.\mathbf{r}_j\right), \tag{4}$$

$$|E_{\mathbf{h}}|^2 - 1 = E_{\mathbf{h}} E_{-\mathbf{h}} - 1 = \frac{1}{N} \sum_{\substack{j=1 \\ j \neq j'}}^{N} \exp\left[-2\pi i \mathbf{h}.(\mathbf{r}_j - \mathbf{r}_{j'})\right], \tag{5}$$

$$(|E_{\mathbf{h}}|^2 - 1)(|E_{\mathbf{k}}|^2 - 1) = \frac{1}{N^2} \sum_{\substack{j=1 \\ j \neq j'}}^{N} \exp\left[-2\pi i (\mathbf{h}+\mathbf{k}).(\mathbf{r}_j - \mathbf{r}_{j'})\right] + R, \tag{6}$$

where

$$R = \frac{1}{N^2} \sum_{\substack{j=1 \\ j \neq j', l \neq l' \\ j, j' \neq l, l'}}^{N} \exp\left[-2\pi i \mathbf{h}.(\mathbf{r}_j - \mathbf{r}_{j'}) - 2\pi i k.(\mathbf{r}_l - \mathbf{r}_{l'})\right]. \tag{7}$$

In order to obtain a meaningful result from (6) we need to average both sides of (6) over all vectors $\mathbf{h}$, $\mathbf{k}$ subject to the restriction that $\mathbf{h}+\mathbf{k}$ is constant.

It is readily verified that the average value of R, as $\mathbf{h}$ and $\mathbf{k}$ range uniformly over all vectors in reciprocal space subject to the condition that $\mathbf{h}+\mathbf{k}$ is constant, vanishes. Hence (6) and (5) imply

$$|E_{\mathbf{h}+\mathbf{k}}|^2 - 1 = N\langle(|E_{\mathbf{h}}|^2 - 1)(|E_{\mathbf{k}}|^2 - 1)\rangle_{\mathbf{h}+\mathbf{k}}, \tag{8}$$

a formula which, in principle, enables one to compute the magnitude of any structure factor once the magnitudes of a sufficiently large number of structure factors are known. An extrapolation procedure for obtaining intensities outside the experimentally observable range is thus indicated. Whether the observable data are sufficiently extensive in any given case to justify the extrapolation may be judged by testing the formula for several fixed $\mathbf{h}+\mathbf{k}$ for which the $|E_{\mathbf{h}+\mathbf{k}}|^2$ are known.

It is interesting to note that if the joint distribution is used in the manner described in our Monograph (Hauptman & Karle, 1953) to obtain the average on the right side of (8), we find, after a lengthy computation,

$$|E_{\mathbf{h}+\mathbf{k}}|^2 - 1 \approx \frac{\sum_{1}^{N} f_{j\mathbf{h}}^2 \sum_{1}^{N} f_{j\mathbf{k}}^2 \sum_{1}^{N} f_{j\mathbf{h}+\mathbf{k}}^2}{\left(\sum_{1}^{N} f_{j\mathbf{h}} f_{j\mathbf{k}} f_{j\mathbf{h}+\mathbf{k}}\right)^2} \langle(|E_{\mathbf{h}}|^2 - 1)(|E_{\mathbf{k}}|^2 - 1)\rangle_{\mathbf{h}+\mathbf{k}}, \tag{9}$$

$$|E_{\mathbf{h}+\mathbf{k}}|^2 - 1 \approx \frac{\left(\sum_{1}^{N} Z_j^2\right)^3}{\left(\sum_{1}^{N} Z_j^3\right)^2} \langle(|E_{\mathbf{h}}|^2 - 1)(|E_{\mathbf{k}}|^2 - 1)\rangle_{\mathbf{h}+\mathbf{k}}, \tag{10}$$

where the symbol $\approx$ denotes probable equality. Evidently (10) reduces to (8) for the case of identical point atoms.

It is readily verified that (8) is valid also for space group $P222$ if attention is restricted to those structure factors which, as a consequence of the space-group symmetry, are not real. This suggests that it would be worth-while to investigate whether (8) has universal validity for all non-centrosymmetric space groups.

Equation (8) may be compared with the formula of Hughes (1953):

$$E_{\mathbf{h}+\mathbf{k}} = N^{\frac{1}{2}} \langle E_{\mathbf{h}} E_{\mathbf{k}} \rangle_{\mathbf{h}+\mathbf{k}}. \tag{11}$$

Bullough & Cruickshank (1955) have independently obtained formulas for space groups $P\bar{1}$ and $P2_1/a$ by methods similar to those described in this note (private communication).

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