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The Probability Distribution of X-ray Intensities. VIII. A Note on the Compensation for Excess Average Intensity

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Symmetry elements producing absences (centring, glide planes, screw axes) produce simultaneously groups of reflexions with average intensity equal to an integral multiple of the average intensity of all reflexions. The additional intensity in these groups is just compensated by the intensity missing in the absences. Symmetry elements not producing absences (except centres) are also characterized by groups of reflexions with an average intensity equal to a multiple of the general average, but the method of compensation is not so obvious. Because of the finite size of atoms, symmetry elements of the latter type are surrounded by a volume that cannot be occupied by the centres of atoms in general positions, and the shape transform of this volume modulates the average intensity distribution in reciprocal space. For a mirror plane in a unit cell of moderate size most of the compensation for the high intensity in the zero layer line takes place in the two or three adjacent layer lines.

The average intensity of the *hkl* reflexions from a crystal is equal to Σ, the sum of the squares of the atomic scattering factors (Wilson, 1942). Symmetry elements producing absences (centring, glide planes, screw axes) produce at the same time groups of reflexions with an average intensity equal to an integral multiple of Σ. The fraction of reflexions absent and the integral multiple are related in such a way that the average intensity remains equal to Σ, and thus in calculating averages for such purposes as putting relative intensity estimates on an absolute scale no difficulty arises. All reflexions are included with their observed intensity, whether zero or enhanced, and the compensation for the enhanced intensity is obvious. Certain symmetry elements not producing absences cause equivalent atoms to coincide in pairs or larger groups in a plane (or line) projection, and so produce a zone (or row) in reciprocal space for which the average intensity of reflexions is again an integral multiple of Σ (Wilson, 1950). There are, however, no accompanying absences, and it is not clear whether, in forming the average intensity over all reflexions, such enhanced intensities should be included at their observed value, or whether they should be divided by the enhancement factor. If a sufficient number of reflexions is measured, of course, it makes little difference, as the reflexions included in the zone (or row) form only a small fraction of the total, but when comparatively few reflexions are observed (poorly crystalline materials or materials with rather small unit cells) the average intensity calculated by the two procedures may differ appreciably. Which procedure is the more correct depends on whether the additional intensity in the zone (or row) is compensated by an infinitesimal general weakening of all other reflexions or whether the compensation takes place in a more restricted region in reciprocal space. The second of these possibilities appears to be correct, as the argument below shows for the particular example of a mirror plane. At any rate when the paucity of reflexions arises from the small size of the unit cell the correct procedure would appear to be to include all reflexions with their observed intensity, and not to weight the intensities by dividing by the enhancement factor. A weighting based on the different volumes of reciprocal space contributing to different layer lines would still be appropriate.

Suppose that the crystal contains a mirror plane perpendicular to **c**. Every atom at x, y, z is repeated also at $x, y, \bar{z}$, but, because of the finite size of the atoms, there is a minimum value of z, equal to half the interatomic distance. This will vary with the chemical nature of the atom, but for obtaining an approximate idea of the effect it will be sufficient to assume that it is the same for all atoms. In a crystal with no symmetry the atoms can be regarded as distributed more or less randomly over the entire unit cell, but in a crystal with a mirror plane the random distribution of atoms is confined to a range of z reaching from α to $\frac{1}{2}-\alpha$, where α is the average atomic radius expressed as a fraction of **c**. There is thus a layer 2α thick containing no atomic centres around each mirror plane. Obviously α must be less than $\frac{1}{2}$, and statistical ideas will be applicable only if it is considerably less. The structure factor is

$$F = \sum_{i}^{N} f_i \exp\left[2\pi i(hx_i+ky_i+lz_i)\right] \qquad (1)$$

$$= 2\sum_{i}^{\frac{1}{2}N} f_i \exp\left[2\pi i(hx_i+ky_i)\right] \cos 2\pi l z_i\,, \qquad (2)$$

and the intensity is

$$I = 4\sum_{i,j}^{\frac{1}{2}N} f_i f_j \exp\left[2\pi i\{h(x_i-x_j)+k(y_i-y_j)\}\right] \times \cos 2\pi l z_i \cos 2\pi l z_j \quad (3)$$

$$= 4\sum_{i}^{\frac{1}{2}N} f_i^2 \cos^2 2\pi l z_i + 4\sum_{i\neq j}^{\frac{1}{2}N} f_i f_j \exp\left[2\pi i\{h(x_i-x_j)+k(y_i-y_j)\}\right] \times \cos 2\pi l z_i \cos 2\pi l z_j \,. \quad (4)$$

In equation (4) the terms in the first summation are all positive, but those in the second summation can take on positive and negative values, both real and complex. On averaging over a range of values of h and k, therefore, the second summation will give approximately zero, so that the mean value of the intensity is

$$\langle I\rangle_{hk} = 4\sum_{i}^{\frac{1}{2}N} f_i^2 \cos^2 2\pi l z_i \,. \quad (5)$$

On the assumption that z is uniformly distributed over the range α to $\frac{1}{2}-\alpha$ the average intensity for a given value of l will be

$$\langle I\rangle_{hkz} = 4\sum_{i}^{\frac{1}{2}N} f_i^2 \times \frac{1}{\frac{1}{2}-2\alpha}\int_{\alpha}^{\frac{1}{2}-\alpha} \cos^2 2\pi l z\, dz = \frac{4\Sigma}{1-4\alpha}\left[\frac{\pi l z + \frac{1}{4}\sin 4\pi l z}{2\pi l}\right]_{\alpha}^{\frac{1}{2}-\alpha}, \quad (6)$$

which becomes, after a little rearrangement,

$$\langle I\rangle = \Sigma + \frac{\Sigma}{1-4\alpha}\cdot\frac{\sin 2\pi l(1-2\alpha)-\sin 4\pi l\alpha}{2\pi l}. \quad (7)$$

For $l=0$ this reduces to

$$\langle I\rangle = 2\Sigma\,, \quad (8)$$

so that the mean intensity of the $hk0$ reflexions is not altered. For $l\neq 0$, however, the mean intensity becomes

$$\langle I\rangle = \left[1-\frac{\sin 4\pi l\alpha}{\pi l(1-4\alpha)}\right]\Sigma\,, \quad (9)$$

which is appreciably less than Σ for l less than about $1/4\alpha$. For a cell of moderate size, a reasonable value of α would be about one-tenth, and the main compensation for the excess intensity in the zero layer would come in the first and second layers. For any particular structure, of course, α could be estimated for the actual atoms and probable bond type.

The total diminution of mean intensity of the non-zero layers, including those with negative l, is

$$\Delta \equiv 2\Sigma\sum_{l=1}^{\infty}\frac{\sin 4\pi l\alpha}{\pi l(1-4\alpha)}\,. \quad (10)$$

This series is well-known:

$$\sum_{n=1}^{\infty}\frac{\sin n\varphi}{n} = \tfrac{1}{2}(\pi-\varphi)\,, \quad (11)$$

so that

$$\Delta = 2\Sigma\cdot\frac{1}{\pi(1-4\alpha)}\cdot\tfrac{1}{2}(\pi-4\pi\alpha) = \Sigma\,. \quad (12)$$

The loss in average intensity for the higher-order layer lines thus just compensates for the extra intensity in the zero layer. The series in equation (10) is an oscillating one, but only the first 'loop', for $l<1/4\alpha$, is of great importance.

It would be easy to use the idea of inaccessible volume to make similar calculations for other symmetry elements, such as rotation axes and centres, and to allow for atoms in special conditions if necessary. The question of where the compensation for excess intensity comes is of some importance not only in putting relative intensity estimates on an absolute scale but also in testing for the presence of symmetry elements. The problem first suggested itself to me in conversations with Dr J. W. Jeffery and Dr D. Rogers on the former subject.

References

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