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A Statistical Treatment of Superlattice Relexions

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By considering the ratio of the intensities of weak superlattice reflexions to those of ordinary reflexions, averaged over limited ranges of Bragg angle, an estimate has been obtained for the r.m.s. magnitude of the atomic displacements from the pseudo-structure which give rise to the weak reflexions.

Introduction

In X-ray photographs it is often observed that certain classes of reflexion are systematically much weaker than the remainder. This phenomenon is ascribed to the existence in the crystal of pseudo-symmetry and the crystal can be considered as having, to a first approximation, the smaller cell and simpler structure found by neglecting the weak reflexions. The exact structure may then be obtained by distorting the approximate structure to give the extra reflexions observed. The latter process is generally difficult and time-consuming in proportion to the value of the information obtained, but it is nevertheless useful to know roughly how near a pseudo-structure is to the true structure.

A method for estimating the r.m.s. displacement necessary to give rise to extra reflexions of a given relative intensity has been developed, based on the ratio of the mean intensities of super-lattice and ordinary reflexions over the same ranges of Bragg angle.

Pseudo-halving of *c* dimension

Consider a particular case, frequently encountered, in which odd-order layer lines when the crystal is rotated about the *c* axis are very weak. This implies that the true unit cell is divided by the plane $z = \frac{1}{2}$ into two very similar parts. The differences between the parts could be of two types:

(*a*) Difference in atomic contents, i.e. more electrons in one half than in the other; for example, a mixed Mg/Ca salt might have the same structure in each half cell but have Mg and Ca ions occurring in alternate half cells. This type of difference can be recognised from the constancy of the ratio of the mean intensity of superlattice reflexions to the mean intensity of other reflexions for all ranges of θ. Assuming unitary scattering curves, the ratio will be roughly $(N_1-N_2)^2/(N_1+N_2)^2$, where N_1 and N_2 are the numbers of electrons in the two halves.

(*b*) Differences in atomic positions. This case is treated in some detail below.

The two classes are not mutually exclusive and (*a*) will generally imply (*b*) to a slight extent.

Effect of distortions

Let $\mathbf{H}$ represent the reciprocal-lattice vector $(h\mathbf{a}^*+k\mathbf{b}^*+l\mathbf{c}^*)$ and $\mathbf{r}_j$ the position vector $(x\mathbf{a}+y\mathbf{b}+z\mathbf{c})$ of the jth atom in the full cell. Suppose first the two halves of the cell are identical; that is, take the pseudo-structure. Corresponding to each atom at $\mathbf{r}_j$ there will be an identical atom at $\mathbf{r}_j+\frac{1}{2}\mathbf{c}$. The structure amplitude for those reflexions for which $l = 2n$ is given by $F_H = \sum_j f_j \exp{[2\pi i(\mathbf{H}.\mathbf{r}_j)]}$, the summation being carried over the atoms in both half-cells. For reflexions with $l \neq 2n$, $F_H = 0$. If now the atoms are given a set of small displacements $\mathbf{r}$, then

$$F_H+\delta F_H = \sum_j f_j \exp{[2\pi i(\mathbf{H}.\mathbf{r}_j)]} \exp{[2\pi i(\mathbf{H}.\delta\mathbf{r}_j)]}.$$

When the components making up F_H are represented on an Argand diagram in the usual way, it can be seen that the effect of introducing the small displacements is to rotate the jth vector through an angle $2\pi(\mathbf{H}.\delta\mathbf{r}_j)$. It is apparent, also, that the mean intensity of a group of reflexions for which $l = 2n$ is unaltered by slight changes in atomic coordinates.

On making the displacements, reflexions with $l \neq 2n$, which were previously extinguished because vectors occurred in mutually cancelling pairs, will appear with small amplitudes, since members of pairs of vectors will be rotated out of coincidence leaving small resultants. The contribution of each vector will be $f_j\delta\theta = 2f_j\mathbf{H}.\delta\mathbf{r}_j$, and these contributions will have the same angular distributions (except for a rotation of 90°) as large reflexions with the same value of $\mathbf{H}$, that is, with the same Bragg angle. Therefore, individual amplitudes bear the same relationship to the resultant amplitudes in the two cases, and hence the ratio of the mean intensity of a group of ordinary reflexions to that of a group of superlattice reflexions averaged over the same small range of θ values is $1/4\pi^2(\mathbf{H}.\delta\mathbf{r}_j)^2 = R$.

$(\mathbf{H}.\delta\mathbf{r}_j)^2 = \mathbf{H}^2.(\delta\mathbf{r}_j)^2.\cos^2\varphi$, where φ is the angle between $\mathbf{H}$ and $\delta\mathbf{r}_j$. Unless there is evidence to the contrary, all directions for $\mathbf{H}$ and $\delta\mathbf{r}_j$ may be assumed to be equally probable. The mean value of $\cos^2\theta$ is therefore $\frac{1}{2}$; the r.m.s. value of $\mathbf{H}$ is d^* and the r.m.s.

value of $\delta\mathbf{r}_j$ is δr, the quantity which it is required to estimate. Hence $R = 1/(d^*\delta r)^2 2\pi^2$ or Rd^{*2} = constant $= 1/2\pi^2\delta r^2$.

Example of pseudo-halving

For the trigonal crystals of β-$Ca_3(PO_4)_2$ reflexions with l odd are weak, and the ratio R (mean intensity of reflexions with l even divided by mean intensity of reflexions with l odd) was found to vary with d^* as follows:

d^* (Å^{-1})	R	Rd^{*2}
0·26–0·39	30	3·2
0·39–0·52	7·3	1·5
0·52–0·65	10·1	3·4
0·65–0·78	6·6	3·4
0·78–0·91	6·8	4·8
0·91–1·04	4·8	4·5
1·04–1·17	5·1	6·2

R is thus seen to follow very approximately the expected law, Rd^{*2} having the value of about 5. This gives 0·1 Å for the r.m.s. displacement from the pseudo-structure. This conclusion can be checked in the following way.

Quantitative check

Booth (1945) has shown that there is a relationship between the reliability index $R_2 = \Sigma(|F_o|-|F_c|)^2 \div \Sigma F_o^2$ and the r.m.s. error of the atomic coordinates.

Compare two structures: (*a*) the real structure of β-$Ca_3(PO_4)_2$, and (*b*) a hypothetical structure so constructed as to give perfect agreement with those observed reflexions which have l even and to give zero amplitude for all reflexions with l odd. Then the observed amplitudes of β-$Ca_3(PO_4)_2$ can be inserted into the above expression for R_2 as F_o and the same amplitudes for reflexions with l even also serve as F_c. When l is odd F_c will be zero. This gives

$$R_2 = \frac{\sum\limits_{l\text{ even}} (|F_o|-|F_c|)^2 + \sum\limits_{l\text{ odd}} (|F_o|-|F_c|)^2}{\sum\limits_{\text{all } l} F_o^2}$$

$$= \sum_{\text{odd } l} F_o^2 \Big/ \sum_{\text{all } l} F_o^2 = 0{\cdot}17\ .$$

Booth's table gives for this value of R_2 the r.m.s. displacement of 0·09 Å, which will be that error which, when applied to all coordinates in the pseudo-structure, will produce an R_2 value of 0·17.

Conclusion

The agreement obtained is better than would be expected considering the variations in Rd^{*2} actually found. 0·1 Å is quite a large r.m.s. displacement and a trial of the method on a structure with perhaps 0·01 Å displacements would afford a more critical test. The method, or its variants to suit special cases, is, however, considered as a possible supplement to Booth's methods of estimating residual displacements.

The work described forms part of a thesis approved by the University of London for the Ph.D. degree.

Reference

Booth, A. D. (1945), *Phil. Mag.* (7), **36**, 609.

Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.

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Morphologie und Struktur des Reddingits, $P_2O_5 . 3FeO . 3H_2O$.

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Für die Untersuchung standen einige gut ausgebildete Reddingitkristalle von Hagendorf (Pfälzer Wald) zur Verfügung. Morphologisches Achsenverhältnis:

$a/b = 0{,}864 \pm 0{,}001,\ c/b = 0{,}945 \pm 0{,}001;$

(0,863:1:0,942 nach Steinmetz (1926) und Steinmetz & Laubmann (1920)).

Die morphologische Diskussion des Formsystems lieferte folgende Rangordnung: (010), (001), (100), (101), (111), (120), (212), (221), (012), (113), (322), (211), (011), (112), (301), (223), (121), (232), (201), (102), (103), (332).

Nach Donnay & Harker (1937) wurde auf Grund des morphologischen Aspektes die Raumgruppe $Pcmb$-D_{2h}^{11} ermittelt (vergl. auch Kleber (im Druck); Fig. 1).

Die Strukturbestimmung wurde mit Hilfe von Drehkristall- und Weissenberg-Aufnahmen durchgeführt (Co $K\alpha$, Cu $K\alpha$). Gitterkonstanten: