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The Determination of Pseudosymmetric Structures

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A method is described for the determination of pseudosymmetric structures with a 'superstructure', i.e. structures where the atoms are only slightly displaced from positions corresponding to a higher symmetry structure in such a way that additional reflexions result. The advantages of the method are its directness, and its avoidance of the problem of the thermal vibrations.

Introduction

The detailed determination of pseudosymmetric structures is of considerable interest, not only because of the relation between the small atomic displacements in these structures and their crystal chemistry (e.g. see Megaw, 1952), but because of the anomalous dielectric properties of a number of them, and in particular of those which are ferroelectric. Up to the present, however, only two such pseudosymmetric structures have been solved in detail: (*a*) that of KH_2PO_4 by careful refinement of Fourier syntheses (Frazer & Pepinsky, 1953), and (*b*) that of $BaTiO_3$ by the solution of structure-factor equations (Evans, 1951). Both methods required the very accurate measurement of the intensities of a large number of high-order reflexions, and the introduction of anisotropic temperature factors.

The use of high-order data was essential in the above two examples because the atomic displacements appreciably affect only these intensities. The structure determination is therefore extremely difficult, both because of the lack of accurate knowledge of the atomic scattering factors for large values of $\sin\theta/\lambda$ and because of the large effect which thermal vibrations have on the intensities. Another difficulty is that in these structures there is a strong probability of two different displacement configurations giving nearly the same intensities (e.g. see Evans, 1952).

These difficulties can be avoided, however, in pseudosymmetric structures which possess a 'superstructure'. In these structures, the displacements result in *additional* reflexions. These reflexions are very weak at low angles, and have intensities directly related to the displacements. The object of this paper is to show how they can be used to determine the structure.

The method described has already been applied to the special case of $NaNbO_3$ (Vousden, 1951), and it is thought that it should be of general interest. It may be remarked that it is very difficult to apply Fourier methods to these structures, for in general we have no circumstantial evidence to suggest trial values of the displacements, and thus no reliable way of giving signs to the superstructure reflexions.*

Definitions

A pseudosymmetric structure may be conveniently defined as one in which the atoms are only slightly displaced from positions corresponding to a higher symmetry structure, subsequently termed the ideal structure, in such a way that no additional symmetry elements are thereby introduced. These displacements are of the order of one-tenth of the interatomic distances, i.e. 0·05–0·2 Å. Perhaps the best known examples are to be found in substances which have a pseudo-perovskite structure (e.g. see Wood, 1951).

The pseudosymmetric structure may be regarded as a slight distortion of the ideal structure. This distortion will in general result in a change in cell dimensions, which is appropriate to the loss of symmetry involved. The change will be quite small, say less than 5 %, if the number of formula units in the unit cells of the two structures is the same, but, if the unit cell of the pseudosymmetric structure contains more formula units than does the ideal structure, its dimensions will then be near to integral multiples of those of the original unit cell. In this latter case the distortion may be referred to as a superstructure, and the structural unit in the pseudosymmetric structure corresponding to the contents of the primitive cell of the ideal structure may be termed a subcell. A superstructure will clearly give rise to additional reflexions which will be very weak at low angles.

Method

Our object is to derive a set of linear equations which express the superstructure intensities in terms of the atomic displacements. The constants in these equations will depend only on the atomic scattering factors and the atomic positions in the ideal structure.

The structure factor $F(hkl)$ of the hkl reflexion of the ideal structure may be written,

$$F(hkl) = \sum_{i=1}^{N} f_i \cos 2\pi \boldsymbol{\sigma} \cdot \boldsymbol{\varrho}_i , \qquad (1)$$

* Existing sign-determining methods appear to break down for weak reflexions.

where f_i is the scattering factor of the ith atom, $\boldsymbol{\sigma}$ is the vector in reciprocal space from the origin to the point hkl, and $\boldsymbol{\varrho}_i$ is the vector in real space from the origin to the ith atom. It is assumed that the ideal structure has a centre of symmetry, a situation which will be the case in at least the great majority of these structures, but which will not in general be true of the pseudosymmetric structure.

In the pseudosymmetric structure let the displacement of the ith atom in the pqrth subcell be represented by the vector $\boldsymbol{\delta}_i^{pqr}$. The pseudosymmetric unit cell is taken to have dimensions approximately $p_0q_0r_0$ times those of the original unit cell, $p_0q_0r_0$ being integers.

We then have

$$F(hkl) = \frac{1}{p_0q_0r_0} \sum_{i=1}^{N} \sum_{pqr=1}^{p_0q_0r_0} f_i \times \{\cos 2\pi\boldsymbol{\sigma}.(\boldsymbol{\varrho}_i+\mathbf{s}^{pqr}+\boldsymbol{\delta}_i^{pqr})+i\sin 2\pi\boldsymbol{\sigma}.(\boldsymbol{\varrho}_i+\mathbf{s}^{pqr}+\boldsymbol{\delta}_i^{pqr})\}, \quad (2)$$

where $\mathbf{s}^{pqr}$ is a vector from the origin of the unit cell to that of the pqrth subcell. $F(hkl)$ can now be non-zero for fractional values of hkl, the corresponding reflexions being those of the superstructure.

The moduli $|F(hkl)|^2$ may be written

$$|F(hkl)|^2 = \frac{1}{(p_0q_0r_0)^2} \sum_{ij=1}^{N^2} \sum_{\substack{pqr \\ p'q'r'\}=1}}^{p_0q_0r_0} f_if_j \times \cos 2\pi\boldsymbol{\sigma}.(\boldsymbol{\varrho}_i-\boldsymbol{\varrho}_j+\mathbf{s}^{pqr}-\mathbf{s}^{p'q'r'}+\boldsymbol{\delta}_i^{pqr}-\boldsymbol{\delta}_j^{p'q'r'}). \quad (3)$$

Remembering that (1) is zero for the superstructure reflexions, then, as long as $\boldsymbol{\sigma}.\boldsymbol{\delta} \ll 1$, we have for these reflexions

$$|F(hkl)|^2 = \frac{2\pi}{(p_0q_0r_0)^2} \sum_{ij=1}^{N^2} \sum_{pqr=1}^{p_0q_0r_0} f_if_j\boldsymbol{\sigma}.(\boldsymbol{\delta}_i^{pqr}-\boldsymbol{\delta}_j^{p'q'r'}) \times \sin 2\pi\boldsymbol{\sigma}.(\boldsymbol{\varrho}_i-\boldsymbol{\varrho}_j+\mathbf{s}^{pqr}-\mathbf{s}^{p'q'r'}). \quad (4)$$

Writing

$$\alpha_{mn} = \frac{2\pi}{(p_0q_0r_0)^2} f_if_j \sin 2\pi\boldsymbol{\sigma}.(\boldsymbol{\varrho}_i-\boldsymbol{\varrho}_j+\mathbf{s}^{pqr}-\mathbf{s}^{p'q'r'}),$$

so that

$$\boldsymbol{\delta}_i^{pqr} = \boldsymbol{\delta}_m \quad \text{and} \quad \boldsymbol{\delta}_j^{p'q'r'} = \boldsymbol{\delta}_n,$$

we have

$$|F(hkl)|^2 = \sum_{m,n=1}^{N^2} \alpha_{mn}[h(_x\delta_m-{}_x\delta_n)+k(_y\delta_m-{}_y\delta_n)+l(_z\delta_m-{}_z\delta_n)], \quad (5)$$

the summations being over all the atoms in the unit cell.

The expressions (5) for different hkl form a set of linear simultaneous equations with independent coefficients. Since the α_{mn} are accurately known from the ideal structure these may be solved for the $\boldsymbol{\delta}$'s provided that there are enough reflexions for which the approximation $\boldsymbol{\sigma}.\boldsymbol{\delta} \ll 1$ is valid. If we allow an error of 10 % in the $|F(hkl)|^2$, and displacements of 0·1 Å, then we may use reflexions up to $\sin\theta/\lambda = 0{\cdot}5$. The number of superstructure reflexions within this range can be readily shown, by considering typical values, to be of the order of five times the number of parameters, and this ratio is approximately independent of the cell volume and symmetry. Hence there will always be enough reflexions, so that the limiting factor is the number of equations it is practicable to solve. The permissible number of unknowns may be up to three times this number, since the displacements can be separated into three sets by considering the $h00$ etc. type reflexions alone.

In special circumstances additional simplifications may be made. For example, some or all of the atoms may be in special positions in the ideal structure, so that many of the sine terms in (5) are the same. If in addition some of the displacements are equal or zero, then equalities or absences of corresponding reflexion classes will result which may be readily interpreted. Moreover, the displacement of any especially heavy atoms may always be determined from the moderately-high-angle superstructure reflexions, for such atoms will provide the predominant contribution to these reflexions (see Vousden, 1951).

Conclusions

The above method should enable approximate values of the displacements to be calculated in at least a moderately complex pseudosymmetric structure which has a superstructure. The correction for thermal vibration is negligible since only moderately low-order reflexions are used. Moreover, since it is a direct and not a trial-and-error method, the results obtained should be well founded, and any possible ambiguities in the structure may be readily detected.

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