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Method for Determining the Signs of the Structure Factors of Long-chain Compounds

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Crystals of certain molecules show periodicities within their unit cell, which can be described by a much smaller subcell. By means of a relation between the structure factors of the main cell and the subcell, the structure of the subcell can be determined and from this information the solution of the main-cell structure obtained.

Certain molecules, especially those of high molecular weight, often contain more or less developed structural periodicities within the molecule, e.g. the repeated zigzags of a hydrocarbon chain or of conjugated chains in carotenoids, or the less perfectly developed repeats in polypeptide chains of proteins. When such molecules form a crystal, each crystal unit cell (axes a_j) may contain one or more limited regions in which the distribution of electron density in space is periodic and can be described by a subcell (axes s_j) much smaller than the main cell. The volume occupied by such subcells is called the subcell region, and there may be several such in the crystal cell. For simplicity we shall assume at first one subcell region.

Let u be the vector from the origin of the main cell to the nearest corner of the subcell region, and r a basis vector for the subcell, then the equivalent positions in the subcell region are

$$x = u + t^j s_j + r,$$

where t^j represents three integers, enumerating the subcells in the subcell region, and the sum is to be taken over the doubly occurring index j $(=1, 2, 3)$. The periodicity in the subcell region requires that within it the electron density

$$\rho(x) = \rho(r).$$

The centre of the subcell region lies formally at the centre of gravity of the subcell origins, i.e. at

$$x_m = u + \tfrac{1}{2}\Sigma(N^j - 1)\, s_j,$$

where N^j, s_j are assumed to be the edges of the block-shaped subcell region.

The diffraction effect of the subcell region is naturally referred to axes S_j in reciprocal space, obtained from s_j by the usual reciprocal transformation.

The maxima of the Fourier transform of the subcell region lie at the points $H = H_j S_j$, where H_j are three integers, equivalent to the three Miller subcell indices. Owing to the finite volume of the subcell region each of these points will be surrounded by an oscillating function of the Laue type

$$L = \prod_j \frac{\sin \pi N^j H_j}{\sin \pi H_j}.$$

However, owing to the arrangement of the sublattice regions in an infinite main lattice, the function L must be multiplied by a modulating factor $\exp(2\pi i x_m h)$, where h is the order vector (equivalent to the Miller indices) of the main cell, of the diffraction by the crystal, with translations (a_i). The diffraction amplitude is then referred to the origin of the main cell, instead of the centre x_m of the subcell region.

As the contributions of different parts of the main cell to the structure factors are additive, we can write the following expression for the structure factor F_h of the main cell:

$$F_h = F_h^0 + \prod_j \frac{\sin \pi N^j H_j}{\sin \pi H_j} F_H \exp(2\pi i x_m h), \qquad (1)$$

where F_h^0 is the contribution from the atoms which are not included in the subcell region and F_H is the structure factor of the subcell. If there are more than one subcell region, further terms corresponding to them may be added. When the subcell regions are related by elements of symmetry, the resulting expression may be considerably simplified, depending on the particular space group.

The (large) crystal translations (a_i) can be expressed in terms of the (small) subcell translations (s_k) by a linear transformation

$$(a_i) = (g_i^k)\,(s_k),$$

and the relation between the diffraction orders h_k for the crystal cell and H_i for the subcell is then given by the same transformation matrix

$$(H_i) = (g_i^k)\,(h_k)$$

(see e.g. *Internationale Tabellen* ... (1935), vol. 1, p. 74).

When the number of non-sublattice atoms is small, their perturbations F_h^0 can be neglected to a first approximation, and since the value of L will be small except near the points of integral H, where it may assume large values, an enhancement of amplitude is to be expected for those orders h which follow from the inversion of the above transformation, i.e.

$$(h_i) = (g_i^k)^{-1}\,(H_k).$$

If in the diffraction effect of the crystal such regions

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of enhancement are discernible, it may be concluded that a sublattice is present.

It may then be possible to obtain first the shape of the subcell, and from the relation (1) the absolute values of the subcell structure factors. Using these values, the distribution of the electron density within the subcell may be solved. This is a comparatively easy task, since the subcell will, in general, be very simple and contain only a few atoms as compared with the main cell. The solution of this step gives the phases (or signs) of F_H. On substituting these back into (1), phases of the structure factors of the main cell are then obtained.

The method described above is similar to a certain extent to the method of a heavy atom. Where the F_h^0 are so small that only a few of the signs or phases of the calculated F_h are incorrect, a Fourier synthesis of the main cell, using observed magnitudes of F_h, but calculated signs or phases, reveals not only the sublattice atoms, but also the rest of the atoms not belonging to the sublattice.

Further refinements may then be obtained, using the standard methods of structure analysis.

The above method has been successfully applied to trilaurin, where the unit cell contains two subcell regions related by a centre of symmetry.

Reference

Internationale Tabellen zur Bestimmung von Kristallstrukturen (1935). Berlin: Bornträger.

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Barium Titanate Twinning at Low Temperatures

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The phase transitions of barium titanate ($BaTiO_3$) single crystals have been investigated by means of X-rays from room temperature to −160° C. Below the second transition at about 0° C., crystals which were single at room temperature became highly twinned. Likewise, a complicated twinning occurred below the third transition at approximately −90° C. The temperature variation of the axial parameters and of the unit-cell volume has been measured from X-ray diffraction photographs, and the symmetry and twinning arrangement of the low-temperature phases have been determined.

1. Introduction

The existence of three phase transitions in barium titanate ($BaTiO_3$) has been established by optical observations, by X-rays, and from measurements of the dielectric constant. The nature of the first transition at approximately 120° C. was described (Megaw, 1947) from X-ray photographs of sintered material. Above this temperature $BaTiO_3$ possesses the cubic symmetry of a typical perovskite-type structure. Below 120° C., the symmetry becomes tetragonal with the development of polar properties along the tetrad axis of the unit cell. The structural change was shown to be discontinuous by Harwood, Popper & Rushman (1947) and by Kay (1948); this was also confirmed by the author.

The existence of two further transitions, near 0° C. and −90° C. respectively, was first indicated by measurements of the dielectric constant (Wul, 1946; Roberts, 1947; Matthias & von Hippel, 1948; Merz, 1949). Optical observations on single crystals have shown that the symmetry changes from tetragonal to orthorhombic at the second transition (0° C.) and finally to trigonal below the third transition (Kay & Vousden, 1949; Forsbergh, 1949). Crystals of $BaTiO_3$ have been studied by the author by X-ray methods down to liquid-air temperatures; the present paper describes the results obtained, and amplifies the conclusions already set out briefly in an earlier note (Rhodes, 1949). The account presented here describes experimental results, and offers interpretations, which are in harmony with those published by Kay & Vousden and by Forsbergh.

2. Apparatus

To obtain X-ray photographs of single crystals at low temperatures the camera, shown diagrammatically in Fig. 1, was designed for use with the Unicam goniometer. It consisted essentially of a thermally lagged, brass pot of outside radius 3 cm. and height 18 cm., provided with a 0·5 cm. slot for the passage of the X-rays. The film was contained in a light-tight, thermally insulated envelope, which fitted smoothly to the camera walls. By sliding the film vertically, a series of fifteen exposures could be made at different temperatures without reloading.

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