

## SHORT COMMUNICATION

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**Structure identification and the symmetry of oscillation photographs.** By S. MARDIX, *University of Rhode Island, Department of Electrical Engineering, Kingston, Rhode Island 02881, USA*

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### Abstract

It is demonstrated that non-symmetrical structures may give oscillation photographs with a symmetrical intensity distribution in respect to the zero layer line. The commonly utilized structure identification procedures ignoring this possibility are therefore inappropriate.

### Introduction

It is commonly accepted that a horizontal mirror line along the equator of a general oscillation photograph indicates a mirror plane perpendicular to the oscillation axis in the Laue group of the crystal (Ladd & Palmer, 1985). In dealing with close-packed structures it was correspondingly assumed (Ramsdell & Kohn, 1951; Verma & Krishna, 1966; Prager, 1974; Palosz & Przedmojski, 1980) that the observed zero layer line symmetry in an oscillation photograph indicates that the structure is either hexagonal, space group  $P6_3mc$ , or trigonal,  $P3m1$ , with a symmetric zigzag sequence (Ramsdell, 1947). The Zhdanov symbols (Zhdanov, 1945) of such sequences consist of an odd set of numbers repeated twice for structures of space group  $P6_3mc$ , e.g. (123123) and a symmetrical arrangement of numbers for space group  $P3m1$ , e.g. (1221), (123321) (Verma & Krishna, 1966).

### c-Axis oscillation photographs of close-packed structures

The structure factor for a crystal with a single type of atom is given by:

$$F_{hk.l} = f_a \sum_{n=1}^N \exp 2\pi i (hx_n + ky_n + lz_n)$$

where  $f_a$  is the atomic structure factor;  $N$  is the number of atoms in the unit cell;  $h, k, l$  are the Miller indices; and  $x_n, y_n, z_n$  are the coordinates of the  $n$ th atom. Applying the above expression to the close-packed structure using hexagonal axes, one obtains:

$$F_{hk.l} = f_a \Phi_{hk.l}$$

$$\Phi_{hk.l} = \sum_A \exp 2\pi i l Z_A / N + \sum_B \exp 2\pi i [l Z_B / N + (h-k)/3]$$

$$+ \sum_C \exp 2\pi i [l Z_C / N - (h-k)/3]$$

where  $Z_A/N, Z_B/N$  and  $Z_C/N$  are the  $z$  coordinates of atoms located at  $A, B$  or  $C$  sites, respectively. The symmetry of a  $c$ -axis oscillation photograph about the equator will depend

on the symmetry of  $|F_{hk.l}|$  only. This will still be correct for close-packed structures where the atoms are replaced by molecules for which  $f_m(hk.l) = f_m(hk.\bar{l})$  where  $f_m$  denotes the molecular structure factor replacing  $f_a$  in the expression for  $F_{hk.l}$ . Compounds of the type  $MX$ , for example, satisfy this condition. We shall restrict our discussion to the above cases.

The observed intensities are proportional to  $|F_{hk.l}|^\alpha$  where  $\alpha = 1$  for ideal crystals and  $1 < \alpha \leq 2$  for crystals deviating from the ideal case.

The absolute value of  $F_{hk.l}$  depends on the set of distances  $D_{pq} = Z_p - Z_q \text{ mod } N$  ( $p, q = A, B, C$ ), so that any interchange of atomic positions in a close-packed structure which does not change the set  $D_{pq}$  will not affect the intensity distribution; this is a special case of the condition for two structures to constitute a homometric pair (Patterson, 1944). It is easily seen that replacing each atom in a  $B$  site with one in a  $C$  site and *vice versa* will cause the values of  $|F_{hk.l}|$  and  $|F_{hk.\bar{l}}|$  to interchange, and if at the same time such an interchange of atomic positions will not change the set  $D_{pq}$  then  $|F_{hk.l}|$  must be equal to  $|F_{hk.\bar{l}}|$  resulting in a symmetric intensity distribution around the zero layer line of the corresponding oscillation photograph.

It is clear that a symmetric Zhdanov symbol of a  $P3m1$  structure will not change its  $D_{pq}$  set by a  $B$  and  $C$  interchange and therefore symmetry of the Zhdanov symbol is a sufficient condition for a symmetric oscillation photograph, as first stated by Ramsdell & Kohn (1951). However, it is by no means a necessary condition.

The condition  $\sum_{k=1}^{n/2} a_{2k-1} = \sum_{k=1}^{n/2} a_{2k}$  is a necessary condition (but not sufficient) for a structure, given by its Zhdanov symbol ( $a_1, a_2, \dots, a_n$ ) to give a symmetric oscillation photograph. Additional conditions are needed to constitute a set of sufficient conditions. All members of the family of close-packed structures, symmetric or non-symmetric, hexagonal or trigonal, which satisfy the above condition and the additional condition:  $a_k = 0 \text{ mod } 3$  ( $k = 1, \dots, n$ ) do not change their  $D_{pq}$  set by a  $B$  and  $C$  interchange and therefore will give a symmetric oscillation photograph. For example, the structures  $24T(9\ 6\ 3\ 6)$  and  $72T(27\ 15\ 3\ 9\ 6\ 12)$ , which are non-symmetrical trigonal structures, satisfy the given conditions and their intensity distribution is indeed symmetrical in respect to the equator of their oscillation photographs. However, the second condition is not necessary for a symmetric photograph: the set of trigonal non-symmetric structures with the Zhdanov symbol ( $a_1, a_2, \dots, a_{10}$ ) where  $a_1 = a_4 = a_6 = a_7 = m$ ;  $a_2 = a_3 = a_5 = a_8 = m +$

$3n$ ;  $a_9 = a_{10} = 2m + 3n$  ( $m, n = 1, 2, 3, \dots$ ) satisfies the necessary condition  $\sum_{k=1}^{n/2} a_{2k-1} = \sum_{k=1}^{n/2} a_{2k}$  but not the condition  $a_k = 0 \pmod{3}$ . Oscillation photographs of members of this set are symmetric in respect to their equator.

The simplest examples of such structures are:

$$\begin{array}{ll} 30T(1\ 4\ 4\ 1\ 4\ 1\ 1\ 4\ 5\ 5) & (m = 1, n = 1) \\ 42T(2\ 5\ 5\ 2\ 5\ 2\ 2\ 5\ 7\ 7) & (m = 2, n = 1) \\ 48T(1\ 7\ 7\ 1\ 7\ 1\ 1\ 7\ 8\ 8) & (m = 1, n = 2) \end{array}$$

Other groups of such structures were found, but the general character of trigonal structures with symmetric oscillation photographs is not yet clear.

#### Concluding remarks

In view of the evidence presented here it is clear that the common practice of discarding non-symmetric structures during the identification procedure of a  $P3m1$  structure with a symmetric oscillation photograph is inappropriate. While the given examples were restricted to close-packed structures

it is conceivable that similar effects may be found in other types of structures as well as in other space groups. The difficulties involved in the identification of structures with large unit cells, even with the aid of fast computers, can not be overstated and special features of the X-ray photographs are very helpful in simplifying the task. The knowledge of the necessary conditions for such features is therefore of great importance.

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## Book Reviews

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#### Molecular structure: chemical reactivity and biological activity. (IUCr Crystallographic Symposia No. 2).

Edited by J. J. STEZOWSKI, JIN-LING HUANG and M.-C. SHAO. Pp. xxvi+612. Oxford: International Union of Crystallography and Oxford University Press, 1988. Price £35.00.

This book reports the papers presented at an International Union of Crystallography Symposium which was held in Beijing, People's Republic of China, September 15–21, 1986. The symposium brought together structural scientists interested in the correlation of structural features to chemical or biochemical activity or to the physical properties of materials. The book contains a representation of the work presented in the symposium. The range of topics covered is impressive and encourages the reader to regard X-ray crystallographic results as a key to understanding molecules. However, the delay in the appearance of this book prevents it from being a useful source of primary structural information. Indeed, most of the papers seem to be summaries and compilations of the results of several previously published studies.

The useful features of the book are the focus on the use of structural information and the extensive scope of the studies included. These features make the book attractive as a summary of the field of molecular reactivity studies and useful as an introduction to the field. In addition, scientists working in the field can gain insight into new approaches for

structural analysis from the papers that cover different structural systems. The central focus on systematic consideration of structural properties and the import of such properties for reactivity makes the book a useful instructional tool. Many of the reports are instructive examples of novel approaches to structural correlation and to molecular design. The overview flavor of many of the papers included in the volume, and the convenient grouping of papers on similar subjects, allow the reader to reflect on the progress of a given subject area. For example, six papers on clathrates and cyclodextrins provide a perspective on the current understanding of the principles of molecular recognition, and the papers on the analysis of structure–drug–activity correlations are a eloquent tutorial on the methods of studying and of using structural results. The presentations covered in the book span most current areas of crystallography, including studies of enzymatic catalytic mechanisms, solid-state crystal chemistry, inorganic materials and molecules, drug activity, molecular recognition, development of direct methods, identification of predictive paradigms for structural trends, and structures of larger systems, like ribosomes and DNA.

The book suffers from poor proof-reading and editing. Many manuscripts were difficult to follow because there were no drawings of the molecules showing the atomic labeling even though the labeling was used extensively in the text. The typographical errors were mainly annoying; however, a misordering of pages in the introductory article obscured an otherwise fine report.

The book ends with a description of the determination of the penicillin structure by Dorothy Hodgkin and includes the electron density maps from that early work. This report is