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Ripple reduction in Fourier representations: the cube-diagonal synthesis for cadmium 'apatites'.

By A. J. C. Wilson, *Department of Physics, University of Birmingham, Birmingham B*15 *2TT, England*

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Abstract

A Fourier representation of the distribution of the halogen atoms along **c** of Cd analogues of apatite should show a reduction in ripples, paid for by poorer resolution in the Rayleigh sense, if the reflexions within a cube having its triad axis along **c** are used, rather than all those within the observable sphere in reciprocal space [Wilson (1979). *Acta Cryst.* A**35**, 122–130, §2.7.2]. Syntheses with the data of Wilson, Sudarsanan & Young [*Acta Cryst.* (1977), B**33**, 3142–3154] show the predicted effect. The variance of such distributions is discussed.

Introduction

Wilson, Sudarsanan & Young (1977) attempted to determine the distribution of the halogen atoms along the hexad axis of several Cd analogues of apatite by several methods. In particular (their Fig. 1), they gave the density distribution determined by Fourier syntheses based on the equivalent of six or seven 00*l* reflexions (*l* even up to 12 or 14) from a structure containing the halogen atoms only. They found that this line synthesis gave better resolution, in the Rayleigh (1879) sense, than was obtained by a line section through a three-dimensional synthesis based on all observed reflexions. Wilson (1979), in a general discussion of problems of resolution, pointed out that the Rayleigh criterion of resolution was not the only possible one, and that for some applications the ratio of the depth of the first trough to the height of the central maximum would be more appropriate. On this basis, the one-dimensional synthesis is not as good as a line section through the three-dimensional synthesis and, by analogy with certain results in particle-size broadening, neither should be as good as a line section through a three-dimensional synthesis based on all reflexions within a cube contained within the observable sphere of reflexions and with one of its triad axes pointing along the hexad axis of the crystal.

Cube-diagonal synthesis

The result given by such a section of the three-dimensional synthesis would depend to some extent on the orientation of the cube relative to the other axes of the crystal, and would show statistical fluctuations as the cube is rotated about its triad axis relative to the crystal. Such statistical effects can be avoided, at least partially, by using instead a one-dimensional synthesis whose coefficients are the values of $\Delta_0(**l)$ given in Tables 5–9 of Wilson, Sudarsanan & Young (1977), each weighted by the area intercepted by the cube from a plane perpendicular to the triad axis and passing through the point 00*l*. Mo radiation was used in the experiments quoted, but because of mechanical obstruction in the goniometer observations could not be made quite to the Mo limit; the effective radius of the limiting sphere was approximately equivalent to $l = 16$. The length of the triad axis of the cube was therefore taken as $l = 32$, and the relative areas of intersection corresponding to smaller values of *l* are given in Table 1. The relative density distributions of the halogen atoms for the five 'apatites' in question, based upon the data of Wilson, Sudarsanan & Young (1977) weighted with these values, are given in Fig. 1. On comparing this figure with the corresponding figure of the earlier paper it will be noticed that the ripples have almost entirely disappeared, and the appearance of the density distribution functions is humanly more acceptable. It must be kept in mind, however paradoxical it seems, that the representations in the earlier paper are closer, in the least-squares sense, to the true density distributions, although the peaks and troughs may be largely or entirely artifacts.

Variance of the Fourier representation

The functions plotted in Fig. 1 of this and of the earlier paper are relative probabilities of halogen-atom positions:

$$P(z) = S(z)/S(z_m), \tag{1}$$

Table 1. *Relative areas of cross section of a reciprocal-space cube intersected by planes perpendicular to* **c***

l	Relative area	*l*	Relative area
0	1·00000	8	0·37500
2	0·95312	10	0·21094
4	0·81250	12	0·09375
6	0·58594	14	0·02344

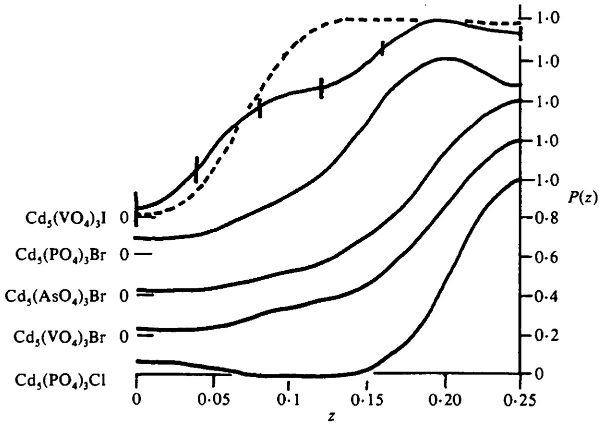

Fig. 1. Cube-diagonal syntheses for the probability distribution of halogen atoms along **c** of five Cd 'apatites'. The scale relates to $Cd_5(PO_4)_3Cl$; for clarity each of the other curves is displaced vertically by increments of 0·2. The ideal uniform distribution at the same resolution is shown for $Cd_5(VO_4)_3I$ (dashed line).

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where

$$S(z) = \sum_l A_l \cos 2\pi lz, \qquad (2)$$

z_m is the value of z for which $S(z)$ attains its maximum value, and A_l is the lth Fourier coefficient. [In the present application A_l is either $\Delta_0(^{**}l)$ itself or $\Delta_0(^{**}l)$ multiplied by the relative areas of cross section given in Table 1.] For two of the 'apatites' z_m is about 0·20, and for the other three it is 0·25. One has, after differentiation and some reduction:

$$\frac{\partial P(z)}{\partial A_l} = S_m^{-1}[\cos 2\pi lz - P(z)\cos 2\pi lz_m], \qquad (3)$$

so that, to the usual approximation,

$$\sigma^2[P(z)] = S_m^{-2} \sum_l [\cos 2\pi lz - P(z)\cos 2\pi lz_m]^2 \sigma^2(A_l). \qquad (4)$$

The variance of $P(z)$ thus vanishes, as obviously it should, for $z = z_m$, and varies slowly but appreciably with z over the rest of the range. The error bars attached to the curve for $Cd_5(VO_4)_3$ in Fig. 1 correspond to $\pm 3\sigma$, the standard deviations of $\Delta_0(^{**}l)$ being taken from Table 1 of Wilson, Sudarsanan & Young (1977).

Discussion

Not surprisingly, the intuitive deduction about the behaviour of Fourier syntheses, based on analogy with results in particle-size broadening (Wilson, 1979, §2.7.2), is confirmed by calculation.

Wilson, Sudarsanan & Young (1977) compared their values of $\Delta_0(^{**}l)$ with those to be expected for a uniform distribution (square wave.). This function was chosen partly because of its simplicity, partly because other models (Gaussian, Cauchy, Laplacian) were excluded by the behaviour of the signs of $\Delta_0(^{**}l)$, and partly because the dip in the distribution functions for two 'apatites' at $z = 0·25$ was reminiscent of that given by a square wave represented by only its first few Fourier components. It is therefore of interest to calculate what a square wave would look like if synthesized from its first seven Fourier coefficients, seven being the maximum number available for any of the 'apatites' (even values of l up to 14). Such a curve is shown in Fig. 1 for a square wave with half-width δ approximately the expected value for $Cd_5(VO_4)_3I$. The 'observed' distribution for this substance lies below the square wave by much more than 3σ near $z = 0·12$, as would be expected from the weakness of the $\Delta_0(^{**}4)$ component, noted for four of the five substances in the earlier paper.

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On the occurrence of polytypism in cadmium sulphide thin films.

By S. PRASAD, B. K. TIWARI and O. N. SRIVASTAVA, *Department of Physics, Banaras Hindu University, Varanasi* 221005, *India*

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Abstract

Cadmium sulphide thin films have been found to exhibit the occurrence of polytypism. The polytypes are formed when amorphous cadmium sulphide thin films undergo an amorphous to crystalline transformation. The single-crystal regions correspond to different polytypes. Two types of polytypic modifications were found to occur most frequently. One of these, the low-temperature modification, had $a = 4·15$ and $c = 6·72$ Å and corresponded to the known crystallographic variant $2H$. The observed polytypes based on this phase were $4H$ ($a = 4·15$; $c = 13·44$ Å) and $6H$ ($a = 4·15$; $c = 20·16$ Å). In addition, a disordered long-period polytype has also been observed. The other common type found was a high-temperature modification with $a = 5·12$ and $c = 8·62$ Å. This new type has been designated as $2H_1$. The observed polytype based on this modification corresponded to $5H_1$ ($a = 5·12$; $c = 21·50$ Å).

Cadmium sulphide is an important electronic semiconductor (band gap 2·5 eV) and has recently been widely used in the fabrication of solar cells. Although it is isostructural with zinc sulphide, which exhibits a profuse preponderance of polytypes, until recently no polytype except $2H$ had been found to occur in cadmium sulphide (Baronnet, 1978). In view of the facts that the electronic band gap of the polytypic crystals varies with polytype periodicity (Knippenberg, 1963; Rao & Srivastava, 1978) and that for maximum efficiency of energy conversion in solar cells there is an optimum band gap of about 1·5 eV (Loferski, 1950), there is some justification in studies seeking to explore the possibility of occurrence of polytypism in cadmium sulphide. We have recently found that in sharp contrast to the known results on single crystals and polycrystalline structural variants (both in bulk and thin-film form) polytypes do form in their single-crystal regions as a consequence of amorphous CdS films transforming to the crystalline phase. Besides the known $2H$ and $3C$ phases several new polytypes such as $4H$, $6H$, $2H_1$ and $5H_1$ have been found to be formed in the present investigation. Here the subscript 1 denotes a new hexagonal phase whose lattice parameters are different from that of $2H$, and $5H_1$ is a polytype based on $2H_1$.

Amorphous CdS thin films were formed by depositing

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