

DIMS* – a direct-method program for incommensurate modulated structures. By FU ZHENG-QING and FAN HAI-FU,† *Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China*

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Abstract

A direct-method program, *DIMS* (direct methods for incommensurate modulated structures), has been written to solve the phase problem of incommensurate structures with one-dimensional modulation. The program uses conventional structure factors instead of normalized structure factors in the phase derivation. It derives phases for satellite reflections by making use of the known phases of main reflections, which can be calculated from the known basic structure or high-resolution electron-microscope images of the sample, or derived by a conventional structure-analysis method involving only main reflections. Two types of phase relationship are used in the program. The first type consists

of one main reflection and two satellites of the same order. This type of relationship is used to relate phases of satellites belonging to the same order with phases of main reflections. The second type of relationship consists of three satellites belonging to at least two different orders. This type of relationship is used to link satellites of different orders. X-ray as well as electron diffraction data from a dozen incommensurate modulated structures have been used to test the program. Two typical examples are described.

Introduction

Incommensurate modulated structures are an important category of crystal structures. They do not have three-dimensional periodicity but can be regarded as a three-dimensional hypersection of a higher-dimensional periodic structure (de Wolff, 1974; Janner & Janssen, 1977). A number of multidimensional least-squares programs, *REMOS*,

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JANA and *MSR* [see, respectively, Yamamoto (1991), Petříček, Malý & Čisářová (1991) and Paciorek (1991, and references therein)], have been written to solve and refine incommensurate modulated structures. However, it is known that least-squares methods are better for refinement than for the *ab initio* solution of crystal structures. It is preferable to have other *ab initio* methods, for which no preliminary assumption concerning the modulation is needed, for the solution of an incommensurate structure. A multidimensional direct method was proposed for this purpose (Hao, Lui & Fan, 1987). The method has been used successfully in the solution of a number of incommensurate modulated structures (Xiang, Fan, Wu, Li & Pan, 1990; Mo, Cheng, Fan, Li, Sha, Zheng, Li & Zhao, 1992; Fu *et al.*, 1994). In this paper, we describe the program *DIMS* (direct method for incommensurate modulated structures), which is based on the method of Hao, Lui & Fan (1987). *DIMS* is written in Fortran77 for the solution of incommensurate structures with one-dimensional modulation. It was originally used with a MicroVAXII minicomputer, but could easily be made to run on other computers. The direct-method phasing procedure for incommensurate modulated structures is divided into two stages. In the first stage, only phases of main reflections are developed, while, in the second stage, phases of satellite reflections are derived by making use of the known phases of main reflections obtained from the first stage. Because phases of main reflections can be derived easily by conventional structure-analysis methods in three-dimensional space, *DIMS* is dedicated to the derivation of phases for satellite reflections in four-dimensional space. The phasing procedure is, in fact, a phase-extension process, which extends phases from main reflections to satellites. Conventional structure factors are used instead of normalized structure factors throughout the process. As an improvement to the original method of Hao, Lui & Fan (1987), the use of phase relationships involving three satellite reflections is included in *DIMS*.

The diffraction data

DIMS accepts a set of symmetrically independent reflections. Each reflection is input as one record, in the format

$$h \ k \ l \ m \ F_{obs} \ \text{phi},$$

where h , k , l and m are the four integer indices of the reflection in four-dimensional reciprocal space, F_{obs} is the conventional observed structure-factor amplitude and phi is the phase of the structure factor. For main reflections, the phases are assumed to be known in advance and should be included in the input data. For satellite reflections, the phases are to be derived by the program and can be omitted in the input. If, however, the user supplies phases for satellite reflections in the input, these phases will not be used in the phasing process but will be used as the 'true' phases and compared with the direct-method phases to give an 'average phase error' for the direct-method results.

The symmetry information

Symmetry information other than that of three-dimensional lattice centring is expressed as symmetry generators and input to the program in free format. For example, symmetry

generators for the four-dimensional space group $P^{C2/m}_1$ are input as

$$\begin{array}{ccccc} 1 & 0 & 0 & 0 & 0.0 \\ 0 & 1 & 0 & 0 & 0.0 \\ 0 & 0 & 1 & 0 & 0.0 \\ 0 & 0 & 0 & 1 & 0.0 \\ -1 & 0 & 0 & 0 & 0.0 \\ 0 & -1 & 0 & 0 & 0.0 \\ 0 & 0 & -1 & 0 & 0.0 \\ 0 & 0 & 0 & -1 & 0.0 \\ 1 & 0 & 0 & 0 & 0.0 \\ 0 & -1 & 0 & 0 & 0.0 \\ 0 & 0 & 1 & 0 & 0.0 \\ 0 & 0 & 0 & 1 & 0.5 \end{array}$$

Phase extension from main reflections to satellites

According to de Wolff (1974) and Janner & Janssen (1977), for an incommensurate structure with a one-dimensional modulation, reflections can be indexed as $h \ k \ l \ m$ or, equivalently, $h_1 \ h_2 \ h_3 \ h_4$ in a four-dimensional space, where a reciprocal-lattice vector is expressed as

$$\hat{H} = h_1 \mathbf{b}_1 + h_2 \mathbf{b}_2 + h_3 \mathbf{b}_3 + h_4 \mathbf{b}_4 \quad (1)$$

with

$$\mathbf{b}_1 = \mathbf{a}^*; \quad \mathbf{b}_2 = \mathbf{b}^*; \quad \mathbf{b}_3 = \mathbf{c}^*; \quad \mathbf{b}_4 = \mathbf{q} + \mathbf{d}. \quad (2)$$

Here, \mathbf{a}^* , \mathbf{b}^* and \mathbf{c}^* are reciprocal-lattice vectors of the basic structure in conventional three-dimensional space, \mathbf{q} is the modulation wave vector and \mathbf{d} is a unit vector in the fourth dimension, which is perpendicular to \mathbf{a}^* , \mathbf{b}^* and \mathbf{c}^* . With this description, we have the Sayre equation (Sayre, 1952) in four-dimensional space (see Hao, Lui & Fan, 1987):

$$\mathbf{F}(\hat{H}) = (\theta/V) \sum_{\hat{H}'} \mathbf{F}(\hat{H}') \mathbf{F}(\hat{H} - \hat{H}'), \quad (3)$$

where θ is an atomic form factor and V is the unit-cell volume of the three-dimensional basic structure. The right-hand side of (3) can be split into three parts, *i.e.*

$$\begin{aligned} \mathbf{F}(\hat{H}) = (\theta/V) & \left[\sum_{\hat{H}'} \mathbf{F}_m(\hat{H}') \mathbf{F}_m(\hat{H} - \hat{H}') \right. \\ & + 2 \sum_{\hat{H}'} \mathbf{F}_m(\hat{H}') \mathbf{F}_s(\hat{H} - \hat{H}') \\ & \left. + \sum_{\hat{H}'} \mathbf{F}_s(\hat{H}') \mathbf{F}_s(\hat{H} - \hat{H}') \right], \quad (4) \end{aligned}$$

where the subscript m denotes main reflections and the subscript s denotes satellite reflections. If $\mathbf{F}(\hat{H})$ on the left-hand side of (4) corresponds to a satellite reflection, then the first summation on the right-hand side of (4) vanishes. Thus, we have

$$\begin{aligned} \mathbf{F}_s(\hat{H}) = (\theta/V) & \left[2 \sum_{\hat{H}'} \mathbf{F}_m(\hat{H}') \mathbf{F}_s(\hat{H} - \hat{H}') \right. \\ & \left. + \sum_{\hat{H}'} \mathbf{F}_s(\hat{H}') \mathbf{F}_s(\hat{H} - \hat{H}') \right]. \quad (5) \end{aligned}$$

Because terms in the second summation on the right-hand side of (5) will be, on average, much smaller than those in the first summation, (5) can be further simplified to give

$$F_s(\hat{H}) = 2(\theta/V) \sum_{\hat{H}'} F_m(\hat{H}') F_s(\hat{H} - \hat{H}') \quad (6)$$

Equation (6) is used in the program to derive phases of satellite reflections from the known phases of main reflections. However, for an incommensurate modulated structure having a three-dimensional basic structure, all main reflections will have their fourth index h_4 (or m) equal to zero. Consequently, all satellites related through (6) should be of the same order, *i.e.* they should have the same value of $|h_4|$. In cases where there exist second- or higher-order satellite reflections, (6) only allows one to obtain relative phases for satellites within the same order. A phase shift may exist between satellites belonging to two different orders. This problem is solved in the program by making use of (5), in which phase relationships involving three satellite reflections are included and are used to link phases of satellites belonging to different orders.

A random-starting-phase refinement procedure similar to that of Yao (1983) is used for phase extension. The correct solution is picked up by the combined figure of merit

$$\begin{aligned} \text{CFOM} = & w_1(M - M_{\min})/(M_{\max} - M_{\min}) \\ & + w_2[(\Psi_0)_{\max} - \Psi_0]/[(\Psi_0)_{\max} - (\Psi_0)_{\min}] \\ & + w_3(R_{\max} - R)/(R_{\max} - R_{\min}), \end{aligned} \quad (7)$$

where M , Ψ_0 and R are, respectively, the absolute, the psizero and the residual figures of merit defined in *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), but they are now calculated from $F(\mathbf{H})$ instead of the normalized structure factors $E(\mathbf{H})$. In this case, the absolute figure of merit M is less reliable. Therefore, the weight w_1 is usually set to zero while w_2 and w_3 are both set to 1.5.

Practical examples

A dozen incommensurate modulated structures have been used to test the program *DIMS*. All the testing structures are centrosymmetric or nearly centrosymmetric. Both the centrosymmetric space group and the corresponding non-centrosymmetric space group were tried for each structure. All the test calculations gave good resultant phases for satellite reflections. Two examples are shown below.

Example 1: $\gamma\text{-Na}_2\text{CO}_3$

The structure was originally solved with X-ray diffraction data (van Aalst, den Hollander, Peterse & de Wolff, 1976). The superspace group is $P_{111}^{C2/m}$ with three-dimensional unit-cell parameters $a = 8.904$, $b = 5.239$ and $c = 6.042$ Å and $\beta = 101.35^\circ$ and modulation wave vector $\mathbf{q} = 0.182\mathbf{a}^* + 0.3181\mathbf{c}^*$. The largest 300 main reflections, the largest 250 first-order satellite reflections and the largest 150 second-order satellite reflections were used in our test. Phases (signs) of main reflections were derived using the program *SAPI* (Fan, Yao, Zheng, Gu & Qian, 1991). Signs of satellite reflections were then derived by *DIMS* on the basis of the known signs of main reflections. The results were arranged in descending order of F_{obs} and compared with the final signs given by the original authors. It was found that the

signs of the top 163 first-order satellites and the top 134 second-order satellites were all correctly determined. Of the 250 largest first-order satellites, only eight had their signs wrongly determined and, of the 150 largest second-order satellites, only five had wrong signs. There is no doubt that, with resultant phases of such good quality, the incommensurate modulated structure could have been solved.

Example 2. Pb-doped $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$, high- T_c superconducting phase

The incommensurate modulation was studied with *Oklm* electron diffraction data (Mo, Cheng, Fan, Li, Sha, Zheng, Li & Zhao, 1992). The superspace group is P_{111}^{Bbmb} with three-dimensional unit-cell parameters $a = 5.49$, $b = 5.41$, $c = 37.1$ Å and $\alpha = \beta = \gamma = 90^\circ$ and modulation wave vector $\mathbf{q} = 0.117\mathbf{b}^*$. 42 main reflections and 70 first-order satellites were measured from the electron diffraction pattern taken with the incident beam parallel to the a axis. Phases (signs) of main reflections were calculated from the known average structure (Sequeira, Yakhmi, Iyer, Rajagopal & Sastry, 1990). Signs of satellite reflections were then derived by *DIMS* on the basis of the signs of main reflections. When the resultant signs are compared with those obtained after least-squares refinement by the original authors, it turns out that the signs of the 54 largest first-order satellites were all correctly determined. Of the total of 70 first-order satellites, only three resulted in wrong signs.

Discussion

It can be seen that the solution of the phase problem for the satellite reflections of incommensurate modulated structures with *DIMS* is a rather simple task. Because no preliminary assumption concerning the modulation is needed, the structure analysis of incommensurate modulated structures is put on an objective basis.

The use of conventional structure factors instead of normalized structure factors in a tangent-formula phase-extension procedure has been shown to be successful by Blundell, Pitts, Tickle, Wood & Wu (1981) in the phase extension of a small protein. Here, we have given examples of the phase extension from main reflections to satellites for incommensurate modulated structures. Replacement of normalized structure factors with conventional structure factors will weaken the reflections with large indices. As a result, phases derived for reflections with large indices will be less reliable. However, because most satellites are of the first and second orders and the essential features of incommensurate modulation can usually be well defined at relatively low resolution, the weakening of high-resolution reflections will have little effect on our results. On the other hand, with the weakening of high-resolution reflections, the truncation effect will be partially eliminated and the phase extension/refinement procedure may become more stable.

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