possible solutions found. In addition, this search can be done with the strongest reflections only. In order to decrease CPU time for the packing search, the main-chain atoms alone may be used. Because the packing function is quite smooth, it can be calculated in a very coarse grid (5 Å or even larger). All this means that, even in a general case, the search can be done in an acceptable time.

The programs are written in Fortran and have no computer-specific features. Source and executable modules are available from the authors on request.

III. General notes

The presence of several independent molecules in the asymmetric unit is common and can be a source of problems for structure solution. The programs described here provide a tool for the solution of the translation problem for such cases.

The programs for the two-model search were developed before the fast algorithm for the calculation of the packing function and correlation-coefficient distributions was published (Stubbs & Huber, 1991) and, unfortunately, do not use it. However, available up-to-date hardware allows the use of the programs even for very large structures.

The accuracy of the result depends on the search step but also on rotation-function errors, differences between the search and real models *etc.* Therefore, decreasing the search step does not necessarily improve the solution. Refinement programs with a large convergence of radius for a rigid-body/rigid-groups model, like those of Brünger, Kuriyan & Karplus (1987), Urzhumtsev, Lunin & Vernoslova (1989) and Castellano, Oliva & Navaza (1992), can follow these search programs in order to improve the orientation and position of each model, which also allows the checking of several possible solutions to find the right one.

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References

Brünger, A. T., Kuriyan, J. & Karplus, M. (1987). *Science*, **235**, 458–460.
Castellano, E. E., Oliva, G. & Navaza, J. (1992). *J. Appl. Cryst.* **25**, 281–284.
Cohen, G. (1977). Personal communication.
Fitzgerald, P. M. D. (1991). *Crystallographic Computing* 5, edited by D. Moras, A. D. Podjarny & J.-C. Thierry, pp. 333–347. Oxford Univ. Press.
Fujinaga, M. & Read, R. J. (1987) *J. Appl. Cryst.* **20**, 517–521.
Harada, Y., Lifchitz, A., Berthou, J. & Jolles, P. (1981). *Acta Cryst* A**37**, 398–406.
Hendrickson, W. A. & Ward, K. B. (1976). *Acta Cryst* A**32**, 778–780.
Stubbs, M. T. & Huber, R. (1991). *Acta Cryst* A**47**, 521–526.
Urzhumtsev, A. G., Lunin, V. Yu. & Vernoslova, E. A. (1989). *J. Appl. Cryst.* **22**, 500–506.

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DIMS – a direct-method program for incommensurate modulated structures.*

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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 & Císařová (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 Fobs phi,

where *k*, *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 $P^{C2/m}_{1\ s}$ are input as

```
 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.
```

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

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

with

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

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):

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

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.*

$$\mathbf{F}(\hat{\mathbf{H}}) = (\theta/V)\Big[\sum_{\hat{\mathbf{H}}'} \mathbf{F}_m(\hat{\mathbf{H}}')\mathbf{F}_m(\hat{\mathbf{H}} - \hat{\mathbf{H}}') + 2\sum_{\hat{\mathbf{H}}'} \mathbf{F}_m(\hat{\mathbf{H}}')\mathbf{F}_s(\hat{\mathbf{H}} - \hat{\mathbf{H}}') + \sum_{\hat{\mathbf{H}}'} \mathbf{F}_s(\hat{\mathbf{H}}')\mathbf{F}_s(\hat{\mathbf{H}} - \hat{\mathbf{H}}')\Big], \qquad (4)$$

where the subscript m denotes main reflections and the subscript s denotes satellite reflections. If $\mathbf{F}(\hat{\mathbf{H}})$ 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

$$\mathbf{F}_s(\hat{\mathbf{H}}) = (\theta/V)\Big[2\sum_{\hat{\mathbf{H}}'} \mathbf{F}_m(\hat{\mathbf{H}}')\mathbf{F}_s(\hat{\mathbf{H}} - \hat{\mathbf{H}}') + \sum_{\hat{\mathbf{H}}'} \mathbf{F}_s(\hat{\mathbf{H}}')\mathbf{F}_s(\hat{\mathbf{H}} - \mathbf{H}')\Big]. \qquad (5)$$

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

$$\mathbf{F}_s(\hat{\mathbf{H}}) = 2(\theta/V)\sum_{\hat{\mathbf{H}}'}\mathbf{F}_m(\hat{\mathbf{H}}')\mathbf{F}_s(\hat{\mathbf{H}}-\hat{\mathbf{H}}'). \quad (6)$$

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

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

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: γ-Na_2CO_3

The structure was originally solved with X-ray diffraction data (van Aalst, den Hollander, Peterse & de Wolff, 1976). The superspace group is $P^{C2/m}_{1\,s}$ with three-dimensional unit-cell parameters $a = 8.904$, $b = 5.239$ and $c = 6.042$ Å and $\beta = 101.35°$ 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* $Bi_2Sr_2Ca_2Cu_3O_x$, *high-T_c superconducting phase*

The incommensurate modulation was studied with 0*klm* electron diffraction data (Mo, Cheng, Fan, Li, Sha, Zheng, Li & Zhao, 1992). The superspace group is $P^{Bbmb}_{1\bar{1}1}$ with three-dimensional unit-cell parameters $a = 5.49$, $b = 5.41$, $c = 37.1$ Å and $\alpha = \beta = \gamma = 90°$ 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.

References

AALST, W. VAN, DEN HOLLANDER, J., PETERSE, W. J. A. M. & DE WOLFF, P. M. (1976). *Acta Cryst.* B**32**, 47–58.

BLUNDELL, T. L., PITTS, J. E., TICKLE, I. L., WOOD, S. P. & WU, C. W. (1981). *Proc. Natl Acad. Sci. USA*, **78**, 4175–4179.

FAN, H. F., YAO, J. X., ZHENG, C. D., GU, Y. X. & QIAN, J. Z. (1991). *SAPI-91: a Computer Program for Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Institute of Physics, Chinese Academy of Sciences, Beijing, People's Republic of China.

FU, Z. Q., HUANG, D. X., LI, F. H., LI, J. Q., ZHAO, Z. X., CHENG, T. Z. & FAN, H. F. (1994). *Ultramicroscopy.* Submitted.

HAO, Q., LIU, Y. W. & FAN, H. F. (1987). *Acta Cryst.* A**43**, 820–824.

JANNER, A. & JANSSEN, T. (1977). *Phys. Rev. B*, **15**, 643–658.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

MO, Y. D., CHENG, T. Z., FAN, H. F., LI, J. Q., SHA, B. D., ZHENG, C. D., LI, F. H. & ZHAO, Z. X. (1992). *Supercond. Sci. Technol.* **5**, 69–72.

PACIOREK, W. A. (1991). In *Methods of Structural Analysis of Modulated Structures and Quasicrystals*, edited by J. M. PÉREZ-MATO, F. J. ZÚÑIGA & G. MADARIAGA, pp. 268–279. Singapore: World Scientific.

PETŘÍČEK, V., MALÝ, K. & CÍSAŘOVÁ, I. (1991). In *Methods of Structural Analysis of Modulated Structures and Quasicrystals*, edited by J. M. PÉREZ-MATO, F. J. ZÚÑIGA & G. MADARIAGA, pp. 262–267. Singapore: World Scientific.

SAYRE, D. (1952). *Acta Cryst.* **5**, 60–65.

SEQUEIRA, A. , YAKHMI, J. V., IYER, R. M., RAJAGOPAL, H. & SASTRY, P. V. P. S. S. (1990). *Physica (Utrecht)*, C**167**, 291–296.

WOLFF, P. M. DE (1974). *Acta Cryst.* A**30**, 777–785.

XIANG, S. B., FAN, H. F., WU, X. J., LI, F. H. & PAN, Q. (1990). *Acta Cryst.* A**46**, 929–934.

YAMAMOTO, A. (1991). *Methods of Structural Analysis of Modulated Structures and Quasicrystals*, edited by J. M. PÉREZ-MATO, F. J. ZÚÑIGA & G. MADARIAGA, pp. 249–261. Singapore: World Scientific.

YAO, J. X. (1983). *Acta Cryst.* A**39**, 35–37.

LABORATORY NOTES

The International Union of Crystallography can assume no responsibility for the accuracy of claims made.

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A rotating sample mounting device for a Guinier powder diffractometer.

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Abstract

The replacement of a sample mounting device for a Guinier powder diffractometer that allows translational movements of the sample by a rotating sample mounting device resulted in an improvement in the accuracy of line intensities with respect to texture and grain-size effects.

The accuracy of intensity data collected by powder methods suffers in many cases from texture and grain-size effects. It is well known (*cf.* de Wolff, Taylor & Parrish, 1959; Parrish & Huang, 1983) that movement of the sample improves the results. Thus, diffractometers of the Bragg–Brentano type (*e.g.* Siemens D5000 apparatus) allow rotation of the sample around an axis perpendicular to the sample surface. The Huber Guinier diffractometer, however, allows only transitional movements tangential to the focusing circle. Moving the sample results in more representative line profiles since a larger number of crystallites are used in the diffraction process. Preferred orientation of the grains in the powder sample is however not changed and texture effects cannot be avoided or diminished.

Improvements can be achieved also for Guinier techniques by rotating samples although it is not possible to avoid preferred orientations completely. The application of rotating sample holders for Guinier–Hägg cameras has been described (Wölfel, 1981; Ihringer, 1982).

For these reasons, the sample mounting device provided by the manufacturer (Fig. 1) was replaced by a rotating sample mounting device (Fig. 2) that allows rotations around an axis perpendicular to the sample surface. Instead of the rectangular sample on a Mylar foil (size 20 × 2.5 mm), a circular sample is used with a diameter of about 6 mm. The sample holder is fastened on the mounting device (60 mm diameter disc) that is ball-bearing mounted. The disc is driven by a motor with variable velocity. The speed should be selected such that at least one cycle of rotation is performed for each step in the step-scanning measurements. The result of changing the sample holder is shown in Figs. 3(*a*)–(*c*). Fig. 3(*a*) shows part of the diffraction pattern of $[In(C_6Cl_2O_4)_3(NH_4)_3]$ using the original sample mounting. The two strong lines seem to be nearly the same intensity. Fig. 3(*b*) shows the same part of the pattern with the rotating sample mounting device; the change of the