

Fellowship. A grant from the *Swedish Natural Science Research Council* to one of us (G. B.) is gratefully acknowledged.

The microanalyses were carried out at the Analytical Department of the Chemical Institute.

1. Julian, P. L., Cole, W., Diemer, G. and Schafer, J. B. *J. Am. Chem. Soc.* **71** (1949) 2058.
2. Wilds, A. L. *Org. Reactions* **2** (1944) 178.
3. Bellamy, L. J. *The Infrared Spectra of Complex Molecules*, Methuen, London 1958, p. 100.
4. Roberts, J. D. *Nuclear Magnetic Resonance*, McGraw-Hill, New York 1959, p. 49.
5. Julian, P. L. and Cole, W. *J. Am. Chem. Soc.* **57** (1935) 1609.
6. Cook, J. W. *J. Chem. Soc.* **1928** 2798.
7. *Ibid.* **1926** 2160.
8. Cannon, C. G. and Sutherland, G.B.B.M. *Spectrochim. Acta* **4** (1951) 373.

Received March 13, 1965.

An Integrated Set of Programmes for Crystallographic Calculations

SIXTEN ABRAHAMSSON, STIG ALEBY,
KÄRE LARSSON, BO NILSSON,
KJELL SELIN and ANDERS WESTERDAHL

Crystallography Group, Institute of Medical Biochemistry, University of Göteborg, Göteborg, Sweden

In connection with the installation at this institute of a digital computer for which no crystallographic programmes were available we have written a set of routines for X-ray structure analyses. The programmes are intended to be completely general and easy to use for the crystallographer. The input data are presented in the form of directives (e.g. Table 1) and are as free from punching conventions as possible. All parameters that do not change during a structure analysis are stored with the reflexion data on magnetic tape. Most programmes,

Table 1. Typical set of directives for Fourier summation.

TITLE	Trilaurin first trial;	
SPACE GROUP	2	
SECTIONS	Y	0,20:20
RANGES	X	0,30:30
	Z	0,30:60
DIFF		
SF	Tape 1	Block 75
SORTED	Tape 2	Block 15
RESULT	Tape 1	Block 105
START		

therefore, need a minimum of input parameters particularly if use is made of the fixed area in the core memory where other parameters common to several programmes (atomic coordinates etc.) are also stored. It is, for example, possible to calculate interatomic distances and angles after structure factor calculation without any parameter input. The programme system is designed to make it possible — if the structure allows — to perform a complete structure determination including refinement in one session at the computer. The programmes are therefore fully compatible with each other and their input from magnetic tape is controlled by a special monitor routine.

Machine. The programmes have been written for the D21 computer.* It is a binary, fixed-point, single address machine with a 24 bit word. The addition and multiplication times are 9.6 μ s and 35.6 μ s, respectively. An automatic interrupt system allows slow peripheral units to work at the same time as computations are performed by the central processor.

The programmes require a core memory of at least 16 384 words and four magnetic tape drives. Input is five or eight channel punched paper tape (500 ch/sec), whereas output can be obtained on both paper tape (150 ch/sec) and on a line printer (1000 lines/min). The programme system now handles three different paper tape codes but others are easily incorporated.

Fixed point operation is used in all programmes where high computing speed is essential as floating point arithmetic is not included in the hardware but as compiler subroutines. Great care has therefore been taken in scaling the data to ensure

* Manufactured by Svenska Aeroplan AB (Saab), Sweden.

sufficient accuracy. Sometimes double precision arithmetic has been used (*e.g.* in least-squares refinement).

The programmes have generally been written in DAC 1 Autocode,¹ a symbolic address language with standard routines for input, output and elementary mathematical functions. The purely arithmetical and logical parts of the resulting machine programmes are effectively machine coded.

Crystallographic programmes. Most routines necessary for a structure analysis have now been written. The system was first reported at the 6th International Crystallography Congress in 1963.² The different programmes are described in detail in a series of papers elsewhere.⁴⁻¹⁰ Only brief accounts of the programmes will be given here.

1 FILM. The programme controls the operation of an on-line photographic film scanner^{3,4} and processes the data from the film into X-ray reflexion coordinates and integrated intensities. A later version will also index the reflexions given approximate unit cell dimensions.

2 ABS. Corrects reflexion intensities for absorption effects using the Gauss' quadrature method to evaluate the integral.⁵ The equations of the bounding surfaces are used as input for defining the crystal shape.

3 DR. General data reduction routine for application of Lorentz and polarization factors to Weissenberg, oscillation and precession intensities.⁶ For each reflexion $\sin^2\theta$ and the form factor values for all atom kinds of the structure are calculated and stored on magnetic tape together with the indices and F' -values in a form required by the structure factor programme. Sharpened F^2 -values are stored on another tape for Patterson syntheses. Wilson statistics will soon be incorporated.

4 SFLS. A series of programmes have been written for structure factor and least-squares calculation.^{7,8} Symmetry is specified as in all other programmes by giving the space group number from the *International Tables for X-ray Crystallography*, Vol. I. Symmetries higher than tetragonal must be handled by using an appropriate sub-group. Special routines for this purpose can be prepared for each case. The full matrix is used in least-squares refinement. The maximum number of reflexions to be used in the refinement is 5120. In pure SF-calculations the number is practically unlimited. Up to 1022 parameters can be refined, but then the matrix operations become exceedingly time consuming as

the different matrices are stored on magnetic tape with relatively long access times. It is possible to perform any type of refinement and to put any crystallographically reasonable constraint on it as only those parameters are refined that are included in a special refine list. Provision to refine groups of atoms as rigid bodies will be added later.

5 FOURIER. The programme calculates threedimensional Fourier series with sections parallel to any unit cell surface. The smallest summation interval is 1/480 of the unit cell edge. Symmetries higher than orthorhombic are handled by transformation to lower symmetries (alternatively special routines available from the author⁹ may be used). The result from the summation is stored on magnetic tape. It can either be printed fully or in regions around peaks on transparent paper on an approximately correct scale for direct contouring. The series sum can also be scanned for peaks in the computer. A list of peak coordinates and peak heights is then produced together with a paper tape for direct input in the structure factor programme. The peaks can be plotted by an on-line X-Y recorder projected on to the unit cell surface parallel to which sections are calculated.

6 PATTSUP. The origin of the Patterson series (FOURIER magnetic tape output) is shifted to each position in a series of postulated atoms.⁶ A function, *e.g.* the Buerger minimum function, of the values found at each point in space by these shifts is then calculated. The result is stored on magnetic tape for use by the print and scan routines of the Fourier programme.

7 DA. Evaluates interatomic distances and angles.¹⁰ Symmetry routines up to and including tetragonal space groups are now included (same as in SFLS).

8 MOLAX. The programme¹⁰ finds the moment of least and greatest inertia and thus the best least-squares plane through a group of given atoms. The distances of these atoms to the plane are listed. If desired distances to other given atoms than those defining the plane are also calculated.

9 H. Coordinates of hydrogen atoms in XH, XH₂ and XH₃ groups are evaluated by the programme.¹⁰ A paper tape is punched for input into the structure factor programme. Alternatively the hydrogen coordinates are added to the standard parameter list in the core memory and

structure factors can be calculated directly without any further input of data.

CRAD. The monitor routine controls the input of the programmes from magnetic tape. A register block with information about all programmes, such as programme number and location in core and on tape, is inserted after each programme to reduce search time. When a programme has been executed control is transferred to the monitor specifying the number of the next programme to be read. This can also easily be performed manually from the console. The monitor also contains parts for quickly dumping on to magnetic tape and restoring the content of the core memory.

1. DAC 1 Programming System. Svenska Aeroplan AB, Linköping 1963.
2. Abrahamsson, S., Aleby, S. and Larsson, K. *Acta Cryst.* **16** (1963) A 172.
3. Abrahamsson, S. *Acta Cryst.* **16** (1963) A 147.
4. Abrahamsson, S. *To be published.*
5. Abrahamsson, S. and Westerdahl, A. *To be published.*
6. Abrahamsson, S. and Larsson, K. *Arkiv Kemi* **24** (1965) 383.
7. Abrahamsson, S. *Arkiv Kemi* **24** (1965) 389.
8. Aleby, S. *Arkiv Kemi* **24** (1965) 395.
9. Larsson, K. *Arkiv Kemi* **23** (1964) 17.
10. Abrahamsson, S., Nilsson, B. and Selin, K. *Arkiv Kemi* **24** (1965) 407.

Received March 17, 1965.

The Crystal Structure of Mo_3P

BERTIL SELLBERG and
STIG RUNDQVIST

*Institute of Chemistry, University of Uppsala,
Uppsala, Sweden*

On the basis of X-ray powder diffraction data Faller *et al.*¹ and Schönberg² reported that Mo_3P crystallizes with the Fe_3P -type structure. This result was recently questioned by Rundqvist and Lundström,³ who pointed out that the

structural evidence presented is not conclusive. In particular, the possibility that Mo_3P is isostructural with $\alpha\text{-V}_3\text{S}$ rather than with Fe_3P can hardly be ruled out by powder diffraction methods alone.

A single-crystal examination of Mo_3P has now been made. The results given below show that the Mo_3P structure does in fact belong to the $\alpha\text{-V}_3\text{S}$ type.

Polycrystalline samples of Mo_3P were prepared as described previously.³ It was possible to arc-melt these samples without excessive loss of phosphorus, and needle-shaped Mo_3P crystals were formed directly from the melts, presumably through a peritectic reaction. This observation is not in agreement with the results of Vogel and Horstmann,⁴ who reported the occurrence of an Mo-MoP eutectic. This eutectic may possibly be formed under metastable conditions.

Single-crystal diffraction data for Mo_3P were recorded in a Weissenberg camera with zirconium-filtered MoK radiation. The multiple film technique was used with thin iron foils interleaved between successive films, and the intensities were estimated visually. Numerical computations were made on the electronic computers BESK, FACIT EDB, and IBM 7090. In the calculations of structure factors, atomic scattering factors, including the real part of the dispersion correction, were interpolated from the values listed in Ref. 5. The unit cell dimensions were taken from Ref. 3.

The body-centred tetragonal symmetry reported earlier for Mo_3P was confirmed by the single-crystal data. It was further observed that the Laue symmetry is $4/mmm$ which immediately rules out the possibility that Mo_3P has the Fe_3P -type structure (Laue symmetry $4/m$).

At this stage of the structure analysis it appeared reasonable to assume that Mo_3P is iso-structural with $\alpha\text{-V}_3\text{S}$. According to Pedersen and Grønvold,⁶ the $\alpha\text{-V}_3\text{S}$ structure is based on space group $I4_2m$ with two sets of eight vanadium atoms in $8i$ positions, eight vanadium atoms in $8f$ and eight sulphur atoms in $8g$.

As a preliminary test of the validity of the structure proposal for Mo_3P , an electron density projection on (001) was calculated assuming the x parameters of corresponding atoms to be the same in Mo_3P and $\alpha\text{-V}_3\text{S}$. The resulting electron density map contained maxima with the expected positions and heights. After