Table 2. *Comparison between the NG and NR refinement methods**

	R_w (run 1)		R_w (run 2)		R_w (run 3)		R_w (run 4)	
Cycle	NG	NR	NG	NR	NG	NR	NG	NR
1	28·0 %	28·0 %	48·6 %	48·6 %	55·8 %	55·8 %	51·5 %	51·5 %
2	18·9	18·6	34·5	28·0	45·4	39·9	45·7	44·5
3	16·3	16·2	23·7	16·8	35·1	28·4	41·9	40·2
4	16·2	16·2	16·4	16·2	27·7	21·9	39·8	39·1
5	16·2		16·2	16·2	22·4	16·4	38·9	38·6
6			16·2		16·6	16·2	38·6	38·4
7					16·2	16·2	38·4	38·3
8					16·2		38·4	false
9					16·2		38·3	minimum
							false	
							minimum	

* Mean atomic displacements were: 0·10, 0·24, 0·36 and 0·37 Å respectively for runs 1, 2, 3, and 4.

plied to the atomic coordinates using a random-number generator program. With the temperature factors fixed at their values at the minimum, the twelve atomic coordinates and an overall scale factor were refined in subsequent cycles. Refinement was halted when all the parameter shifts were less than 10^{-4}. Unit weights were used in all the calculations.

From the results reported in Table 2 it can be seen that the inclusion of second derivatives allows convergence to be attained in fewer cycles than with the usual NG technique and this is more evident the further one starts from the minimum. However, the computing time per cycle was 4·56 and 3·42 min for the NR and the NG method respectively. There is no evidence that one of the two methods can converge from further away from the minimum than the other one.

Standard deviations on atomic coordinates, calculated from the diagonal terms of the inverse matrix, are slightly different in the two cases (Table 1). Of course, standard deviations calculated with the inclusion of second derivatives are a better approximation to the true values.

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References

BEDNOWITZ, A. L. & POST, B. (1966). *Acta Cryst.* **21**, 566–571.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*, Report ORNL-TM-305 Oak Ridge National Laboratory, Oak Ridge, Tennessee.

CRUICKSHANK, D. W. (1952). *Acta Cryst.* **5**, 511–518.

STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*. New York: MacMillan.

WASER, J. (1963). *Acta Cryst.* **16**, 1091–1094.

Acta Cryst. (1973). A**29**, 90

White radiation neutron-diffraction techniques.

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In a recent paper Hubbard, Quicksall & Jacobson [*Acta Cryst.* (1972). A**28**, 236–245] describe a highly efficient white-radiation neutron-diffraction technique. The present note discusses some of the problems which arise from the use of such techniques in the light of recent measurements at Harwell and emphasizes that, because of these problems, structure determination using white-beam techniques is less reliable than that possible using conventional monochromatic beam techniques.

In a recent paper Hubbard, Quicksall & Jacobson (1972) describe a highly efficient neutron-diffraction technique using a white-radiation beam incident on the sample. They state that this technique dramatically increases both counting precision and data collecting rates over conventional monochromatic beam techniques. However, the usefulness of the technique depends on the reliability with which the data can be interpreted and thus on the accuracy with which systematic effects can be accounted for, particularly as these are likely to be a more serious problem when measurements extend over an appreciable range of wavelength. The purpose of this note is to comment on the use of such techniques in the light of white-radiation neutron-diffraction measurements made at Harwell specifically to study the importance of these problems.

Data-collection rates are much higher for white-radiation techniques because of the increased intensity available from the spectrum of wavelengths present in the beam, the inherent integration of the intensity of a Bragg reflexion over a range of wavelength and the possibility of simultaneous measurement of a large number of reflexions. A given precision in the Bragg-intensity measurements can thus be achieved much more rapidly than with conventional monochromatic beam techniques. However, the fact that many of the measurements consist of a summation of the intensity over a number of orders of the fundamental Bragg reflexion

reduces the reliability with which the structural parameters can be determined. Furthermore, the usefulness of the technique also depends on the satisfactory solution of a number of problems, such as the description of the incident white-beam spectrum in terms of intensity as a function of wavelength, the ability to specify the wavelength dependence of certain systematic effects such as absorption, extinction and thermal diffuse scattering and the ability of the method of analysis to overcome problems arising from correlation between parameters. Our own extensive measurements over the past few years indicate that these prolems are such that structure determination using white-beam techniques is inherently less reliable than that possible using conventional monochromatic-beam techniques.

In order to investigate these basic problems we collected a total of 601 Bragg-intensity measurements from a single crystal of KCl, involving reflexions for neutrons with wavelengths in the range 0·5 to 6·25 Å. Analysis of these white-radiation measurements indicated that the spectrum from the DIDO reactor deviates significantly from a Maxwellian and that the Zachariasen (1967) theory of extinction is not generally satisfactory for neutron-diffraction measurements of this type. The latter problem was overcome by using the modified extinction theory given by Cooper & Rouse (1970) which includes the appropriate angular dependence of the extinction on intensity. With this modified extinction theory and a Maxwellian spectrum we were able to obtain an R value for intensity of about 6%. Use of a more appropriate spectrum would reduce this value somewhat. The fact that systematic effects are relatively less serious for conventional monochromatic-beam techniques is borne out by recent conventional measurements on a single crystal of KCl which have given R values for intensity of less than 1% (Cooper & Rouse, 1972).

The variation of the refined parameters as a function of the spectrum parameter ($P3$), found by Hubbard, Quicksall & Jacobson (1972) in their Table 1 appears to indicate that in their case also there are systematic deviations in the spectrum from a Maxwellian.

Both white-beam and monochromatic-beam measurements on KCl have shown that the basic extinction parameters, r and g (see Cooper & Rouse, 1970), are not well defined individually, even over the wavelength range involved in the white beam case. Similar conclusions have been reached from conventional single crystal measurements on ZnS and ZnTe (Cooper, Rouse & Fuess, 1972). It is therefore difficult, in the white-beam case, to determine the most appropriate model for the extinction. Furthermore, there is also virtually no experimental verification for the wavelength dependence of extinction effects as predicted by these theories.

Further white-beam measurements have been made on single crystals of K_2NaCrF_6 (El Pasolite), urea and hexamethylene tetramine. These have also shown that thermal diffuse scattering and absorption can be serious problems when measurements extend over a large range of wavelength. Although R values for intensity of the order of 10% have been obtained in each case, it is clear that there are still systematic effects to be accounted for and that some further improvement is possible. However, conventional least-squares refinement programs do not appear to be very suitable for this type of data and an existing program (see Cooper, 1970) which uses a search algorithm procedure (Powell, 1965) is being extended for use in this work.

We are hopeful that the problems discussed above can be accounted for adequately in the model used to provide theoretical intensity values. However, it is clear that the magnitude of these problems is such that the reliability of structure determination using white-beam techniques is considerably less than that possible using conventional monochromatic-beam techniques.

Full details of the measurements referred to above will be published when our analysis has been completed.

References

COOPER, M. J. (1970). *Acta Cryst.* A**26**, 208–214.

COOPER, M. J. & ROUSE, K. D. (1970). *Acta Cryst.* A**26**, 214–223.

COOPER, M. J. & ROUSE, K. D. (1972). To be published.

COOPER, M. J., ROUSE, K. D. & FUESS, H. (1972). *Acta Cryst.* A**29**, 49–56.

HUBBARD, C. R., QUICKSALL, C. O. & JACOBSON, R. A. (1972). *Acta Cryst.* A**28**, 236–245.

POWELL, M. J. D. (1965). *Comput. J.* **7**, 303–305.

ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1973) A**29**, 91.

An Algol program for crystal-structure illustrations on a digital plotter using a small computer.

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An Algol program for drawing ordinary or stereoscopic-pair views of a crystal on a digital plotter is described. The program is suitable for use on a small computer and plots clinographic projections of ball-and-stick or space-filling models.

Introduction

The object of the program is to produce on a digital plotter normal or stereoscopic-pair views of a crystal unit cell from any angle.

The basis of calculation differs from that used in previous programs of this nature (Johnson, 1965; Cole & Adamson, 1969) in that clinographic projections on crystallographic planes are plotted rather than perspective views from a point specified by polar coordinates. This gives con-