Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

Acta Cryst. (1973). **A29**, 89

The effect of the second derivatives of $|F_c|$ in the least-squares refinement of crystal structures.

By P. L. Orioli and A. Vacca, *Istituto di Chimica Generale e Laboratorio C. N. R., 39 via J. Nardi, Florence, Italy*

(*Received* 5 *August* 1972; *accepted* 14 *August* 1972)

The inclusion of second derivatives of $|F_c|$ in the least-squares refinement of crystal structures is discussed. By using a test case it is shown that convergence is reached in fewer cycles than with usual methods, although the total computing time is about the same. Standard deviations of parameters are a better approximation to the true values.

In the usual derivation of the normal equations in the least-squares refinement of crystal structures (*e.g.* Stout & Jensen, 1968) second derivatives of $|F_c|$ are neglected and the equations are written:

$$\mathbf{Ax}=\mathbf{v}$$

with

$$a_{ij}=\sum_r w_r \frac{\partial|F_c|_r}{\partial p_i}\frac{\partial|F_c|_r}{\partial p_j}$$

$$x_j=\Delta p_j$$

$$v_i=\sum_r w_r \Delta F_r \frac{\partial|F_c|_r}{\partial p_i}\,.$$

If one includes second derivatives, the a_{ij} terms become (Cruickshank, 1952; Waser, 1963):

$$a_{ij}=\sum_r w_r\left(\frac{\partial|F_c|_r}{\partial p_i}\cdot\frac{\partial|F_c|_r}{\partial p_j}-\frac{\partial^2|F_c|_r}{\partial p_i\partial p_j}\cdot\Delta F_r\right).$$

In the least-squares minimization of non-linear functions in numerical analysis the two expressions for the a_{ij} terms correspond respectively to the Newton–Gauss (NG) and the Newton–Raphson (NR) methods. The NG method is based on the assumption that the observable quantities are a linear function of the parameters, the second derivatives being therefore zero. In crystal-structure analysis, with a highly non-linear dependence of the structure factor upon the parameters, it is reasonable to expect that the NR expression would be a better approximation than the NG one, particularly far from the minimum where the ΔF's are not negligible.

Unfortunately the general expression for $\partial^2|F_c|/\partial p_i\partial p_j$ is rather unwieldy. With $|F_c|=(A^2+B^2)^{1/2}$ we have:

$$\frac{\partial^2|F_c|}{\partial p_i\partial p_j}=|F_c|^{-1/2}\left(-\frac{\partial|F_c|}{\partial p_i}\cdot\frac{\partial|F_c|}{\partial p_j}+\frac{\partial A}{\partial p_i}\cdot\frac{\partial A}{\partial p_j}+\frac{A\partial^2 A}{\partial p_i\partial p_j}+\frac{\partial B}{\partial p_i}\cdot\frac{\partial B}{\partial p_j}+\frac{B\partial^2 B}{\partial p_i\partial p_j}\right)$$

and its evaluation would require considerable effort.

However, in the case of a centric structure the expression simply reduces to the evaluation of the term $\partial^2 A/\partial p_i\partial p_j$, which gives non-zero contribution to the **A** matrix only for blocks about the diagonal involving correlations among parameters of the same atom (4×4 or 9×9 blocks according to whether the refinement is isotropic or anisotropic). Furthermore it should be pointed out that with careful programming, the evaluation of $\partial^2 A/\partial p_i\partial p_j$ does not require much additional computing time. It is interesting to note that in the case of refinement of F_o^2, the terms containing the second derivatives are non-zero everywhere in the matrix of the normal equations, even in the centric case.

A Fortran program, which is essentially a modification of *ORFLS* (Busing, Martin & Levy, 1962) to include second derivatives, has been written for an IBM 1130 computer and tested on the structure of β-fumaric acid (Bednowitz & Post, 1966). β-Fumaric acid was a logical choice because it is a centric structure and there are only four atoms to vary, not including hydrogens, which allowed the problem to be tackled by full-matrix least squares on a small capacity machine. With isotropic temperature factors and without the hydrogen contribution, the minimum was at an R index of 16·6% (weighted $R=16{\cdot}2\%$). The atomic parameters at the minimum are reported in Table 1. Random shifts, as increasing multiples of the standard deviations, were ap-

Table 1. *Atomic parameters and standard deviations for β-fumaric acid* ($R=16{\cdot}6\%$)

		Coordinates	e.s.d. ($\times10^5$) NG	NR
C(1)	x	0·40566	245	256
	y	0·37909	170	169
	z	0·39874	212	218
	B (Å^2)	2·80		
C(2)	x	0·45440	221	230
	y	0·21830	156	155
	z	0·44995	189	195
	B (Å^2)	2·27		
O(1)	x	0·27125	179	188
	y	−0·00475	127	124
	z	0·25647	154	159
	B (Å^2)	3·45		
O(2)	x	0·68347	183	194
	y	0·32398	129	128
	z	0·70222	158	164
	B (Å^2)	3·38		

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.

We would like to thank Dr A. Sabatini for helpful discussions and Professor L. Sacconi for his interest.

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.

By S. A. WILSON and M. J. COOPER, *Materials Physics Division, A.E.R.E. Harwell, Berkshire, England*

(*Received* 10 *July* 1972; *accepted* 11 *August* 1972)

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