Acta Cryst. (1977). A**33**, 649–654

Photographic Neutron Diffraction Study of L-Histidine.HCl.H_2O by the Modified Laue Method

BY DIETMAR HOHLWEIN*

Institut Laue-Langevin, 156X Centre de Tri, 38042–Grenoble Cédex, France

(*Received 2 November* 1976; *accepted 14 December* 1976)

Film-recorded neutron intensities from modified Laue measurements (a convergent-beam technique) were evaluated quantitatively and a crystal structure was refined. About 4000 reflexions were collected on 60 films in altogether 30 hours exposure of a 0·3 mm^3 crystal of L-histidine.HCl.H_2O, space group $P2_12_12_1$ with $a=15·36$, $b=8·92$ and $c=6·88$ Å. The corrections necessary for this technique are described. The structure factors were derived from the optical densities scanned by an automatic microdensitometer and processed by computer programs. Refinement on 741 symmetry-independent reflexions yielded $R(F^2)=0·121$. The parameters obtained are compared with those from conventional four-circle work. The mean differences in the positional parameters are 0·009 Å for C, O and Cl and 0·022 Å for H. For the anisotropic temperature factors U_{ij} differences of 0·0054 and 0·0105 $Å^2$ for heavy atoms and hydrogens respectively were observed between the results of the two techniques. A hydrogen atom misplaced in earlier X-ray work was located from film data collected in only 15 hours.

Introduction

The modified Laue technique was proposed by Maier-Leibnitz (1967) to speed up data collection in neutron single-crystal work. In this method many reflexions are diffracting simultaneously. Registration can be achieved by a counter system with many individual adjustable detectors (Klar, 1973) or by a photographic film sandwiched between two converter foils (Thomas, 1972*a*). First quantitative film measurements on a KCl crystal were reported previously (Hohlwein, 1975*a*). We present here the structure refinement from data systematically collected on 60 films, scanned by an automatic microdensitometer and processed by computer programs. The results are compared with the structure determined from data measured on a conventional four-circle diffractometer (Fuess, Hohlwein & Mason, 1977 – FHM).

The measurements were done at the instrument D12 (Hohlwein, 1975*a*) installed at the end of a thermal-neutron guide of the Grenoble high flux reactor to ensure a low background of γ-rays and fast neutrons. Two monochromators (one above the other) reflect neutrons to the two sides of the guide. One beam is produced by a curved copper monochromator (Hohlwein, 1975*b*) for modified Laue measurements while the other is reflected by a flat graphite monochromator for 'classical' film methods like Weissenberg and precession techniques (Hohlwein & Joswig, 1976).

The modified Laue technique

With the modified Laue technique, as with the conventional Laue method, a stationary crystal gives rise to many simultaneous reflexions which are integrated by the incoming wavelength band. In the modified Laue technique this band is very restricted ($\Delta\lambda/\lambda\sim5\%$) and has a dominant angular part. It is produced by a cylindrical bent monochromator at a thermal-neutron guide. Then the disadvantage of the normal Laue technique for structure-factor determination, namely that the different orders of a reflexion are diffracting in the same direction, is avoided. The dominance of the angular part allows a comparison with the oscillation technique where the convergence of the incoming beam is replaced by the oscillation movement. In the modified Laue photograph of Fig. 1 one can clearly see the layer lines as in an oscillation photograph. In the modified Laue technique the wavelength varies with the incoming beam direction which gives rise to a very different situation on the two sides of the beam, known as the focusing and antifocusing sides as shown in Fig. 2 for reciprocal space. In comparison with the oscillation technique the 'active' volume is contracted on the focusing side and expanded on the other side. Therefore a special Lorentz factor has to be applied. The reflexions can be collected systematically by turning the crystal a few degrees (equal to the convergence angle of the incoming beam) around a vertical axis after each exposure. There will be a blind region near the vertical axis as well as a limited $\sin\theta/\lambda$ range for recordable reflexions in this direction. A second orientation is therefore needed for a complete set of data for a given wavelength.

Data collection and reduction

A cylindrically bent copper monochromator (Hohlwein, 1975*b*) with radius of curvature 2·7 m, placed 65 cm from the sample, was used to focus a beam of wavelength $\lambda=1·46\pm0·04$ Å. The convergence angle was

---

* Present address: Institut für Kristallographie der Universität, 74-Tubingen, Charlottenstrasse 33, Federal Republic of Germany.

3° and the reflecting planes (200) were inclined at 5° to the surface.

A crystal of 0·7 × 0·7 × 0·6 mm was mounted with its *b* axis vertical and parallel to the axis of a turntable. A section of 90° was swept in steps of 3° on 30 films. The procedure was repeated with the *a* axis vertical. The exposure time of each film was 30 min. We therefore recorded about 4000 reflexions on 60 films in a total of 30 hours; 741 of these reflexions were symmetry-independent. The films were pressed between two converter foils consisting of a mixture of ^{6}LiF and ZnS (Thomas, 1972*b*) in a vertical cylindrical camera of radius 31 mm. Fig. 1 shows a typical photograph.

The optical densities of the films were measured by an Optronix drum scanner and transferred on magnetic tape by the 'Service de Microdensitometrie' (University Paris-Sud, Orsay). The scanning area was 11 × 15 cm and the size of one measuring point 100 × 100 μm. Therefore one film gives $1{\cdot}65 \times 10^6$ optical densities ($\log I_0/I$) in the range of 0 to 3 digitized from 0 to 255.

In order to derive the structure factors from the optical densities one has to correct for the non-linear calibration curve, the intensity distribution in the wavelength band, the Lorentz factor, the pathway in the converter screen, the absorption and the scale factor between different films.

The calibration curve gives the neutron intensities as a function of the optical densities, Fig. 3. Because of the Schwarzschild effect the optical density is a function of time and intensity (for more details see Hohlwein, 1975*a*). We measured therefore the optical densities which are produced by attenuated monochromatic neutron beams of 4 mm diameter in a constant time. The intensities of the attenuated beams were determined by a ^{3}He counter. The calibration curves for different time intervals were put on the same scale so that it was valid for modified Laue photographs where all reflexions have identical exposure times, Fig. 3.

In the modified Laue technique each reflexion is mainly integrated by one wavelength (which is a function of the incident angle) of the incoming band. The intensity distribution as a function of the incident angle can be measured by an ω scan of a reflexion situated near the focusing position, Fig. 4. The integrated intensity of each individual reflexion was corrected for this inhomogeneity according to the wavelength which was diffracted.

The Lorentz factor is

$$L = \cos\omega / [\sin^2\theta \cos(\nu \pm \omega)]$$

with θ the Bragg angle, ω the angle between the primary beam and the projection of the reciprocal lattice vector onto the horizontal plane. The angle ν is defined in Fig. 2 and the sign of ω is positive for the antifocusing and negative for the focusing side. The formula can be transformed to the expression derived by Klar (1973).

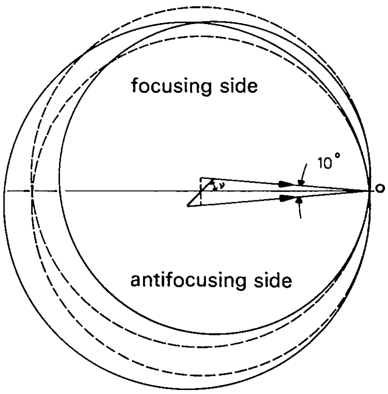


Fig. 2. Limiting Ewald spheres for 10° oscillation technique (---) and the modified Laue technique for 10° (for clarity) convergence (——); *O* = origin of the reciprocal space.

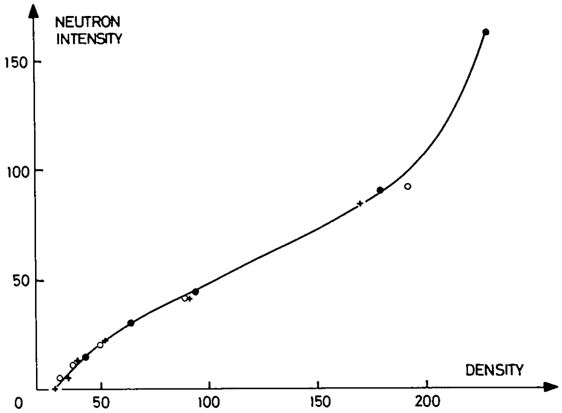


Fig. 3. Neutron intensity as a function of the optical density for constant exposure times of 5 min (+, ●) and 2 min. The densitometer range 0–255 corresponds to conventional optical densities 0·0–3·0.

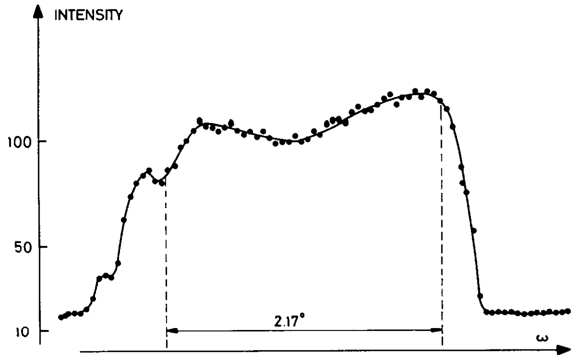


Fig. 4. Intensity distribution of the incoming wavelength band, measured with a ω scan of the 002 reflexion on the focusing side. The range of 2·14° in ω corresponds to an incoming convergent beam of 3°.

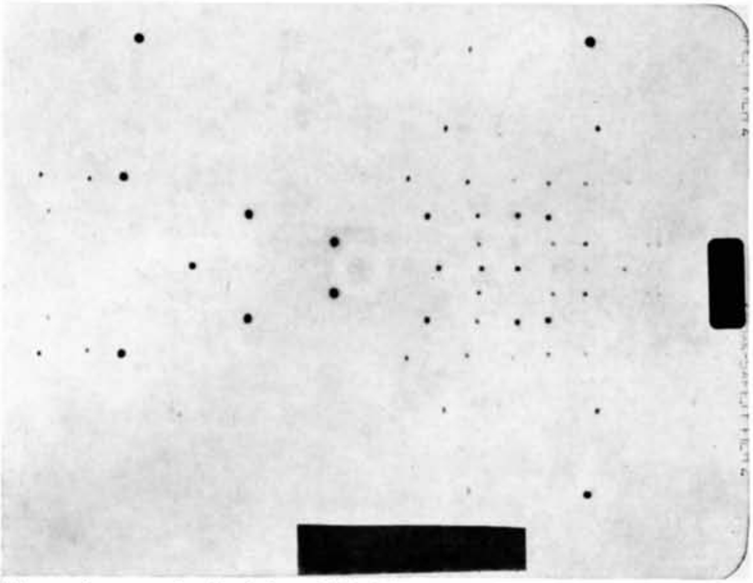


Fig. 1. Modified Laue photograph of a 0·3 mm^3 histidine crystal; exposure time 30 min, *b* axis vertical.

The efficiency of neutron detection by the converter–film system depends on the incident angle of the diffracted beam on the film, Fig. 5. This can be explained by the longer pathway in the converter foil if the beam does not impinge vertically. We corrected for this effect.

The absorption coefficient μ was determined by transmission measurements with a narrow attenuated neutron beam. The value found was $\mu = 2{\cdot}88$ cm^{-1}. The absorption program *ORABS* (Wehe, Busing & Levy, 1962) adapted for the modified Laue method (Hohlwein & Klar, 1976) was used to calculate the transmission factors for the measured reflexions. The values were between 0·82 and 0·86. Therefore no correction for absorption was applied.

The Kodak Regulix films used in this work were developed under carefully controlled conditions (temperature, time, bath movement) to avoid the determination of scale factors between the films.

The corrections described for calibration curve, Lorentz factor and intensity distribution of the wavelength band were done automatically by a set of Fortran programs which treat the densitometer data on the magnetic tapes. This program package consists of indexing (reflexion positioning), centring and integration parts and was specially written for this purpose. The integration field in the peak area was chosen to be square, 1·2 × 1·2 mm, and the background was determined in four rectangular stripes around the peak area.

Crystal data are given in Table 1.

Table 1. *Crystal data*

$a = 15{\cdot}36$ Å
$b = 8{\cdot}92$
$c = 6{\cdot}88$
$V = 942{\cdot}6$ Å^3
$\lambda = 1{\cdot}46 \pm 0{\cdot}4$ Å

$C_6O_2N_3H_9.HCl.H_2O$
Space group $P2_12_12_1$
$Z = 4$
$\mu = 2{\cdot}04$ cm^{-1} (calculated)
$\mu = 2{\cdot}88$ cm^{-1} measured for $\lambda = 1{\cdot}5$ Å

Structure refinement

The structure factors of 1800 reflexions were derived from the first set of 30 films (*b* vertical). Over-exposed and half-recorded reflexions (film edge) were eliminated, together with some evidently (in comparing symmetry-equivalent reflexions) partially integrated reflexions on the focusing side. Fig. 2 shows that the volume between the limiting Ewald spheres on the focusing side is very small so that partial integration can easily appear. From the remaining 1633 structure factors we averaged the symmetry equivalents and determined their standard deviation σ_{exp}. We found a linear relationship $\sigma_{\text{exp}} = 3 + 0{\cdot}1\text{F}^2$ used in the least-squares refinement. The 385 symmetry-independent reflexions showed clearly on a difference Fourier map that a hydrogen atom of the water molecule was misplaced in the X-ray structure determination (Donohue & Caron, 1964).

For the second 30 films (*a* vertical) we evaluated only the intensities on the antifocusing side: (2177 reflexions). Then we determined the standard deviation σ_{exp} as before by averaging symmetry-equivalent reflexions but not including those which differed more than 20% on the same film: $\sigma_{\text{exp}} = 3 + 0{\cdot}07\text{F}^2$. We thus obtained 585 independent structure factors.

The data of the two film packs were refined independently to determine a scale factor. We then averaged the symmetry-equivalent reflexions of the two sets and obtained 741 independent structure factors.

The refinement was carried out with the program *ORXFLS*3 (Busing *et al.*, 1971). The starting parameters were the atomic positions given by Donohue & Caron (1964) together with isotropic temperature factors. The erroneous *x* parameter of one hydrogen atom, mentioned above, was corrected. The quantity minimized in the refinement was $\sum_i w_i(F_{io}^2 - F_{ic}^2)$ with the weights $w_i = 1/\sigma_{\text{exp}}(F^2)$, with σ_{exp} defined above. The refinement was carried out with anisotropic temperature factors (241 parameters) and yielded $R(F^2) = 0{\cdot}121$ and $S = [\Sigma(\Delta F^2/\sigma_{\text{exp}})^2/(m-n)]^{1/2} = 1{\cdot}02$ after four cycles. Unit weights gave $R(F^2) = 0{\cdot}111$. The final parameters from the refinement with the experimental weighting scheme are given in Table 2.

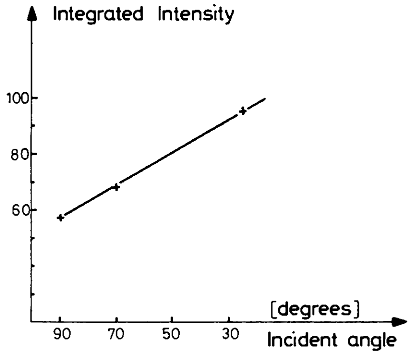


Fig. 5. Increased efficiency of the converter–film system for non-vertical (90°) incident beams.

Comparison with results from a four-circle diffractometer

The structure was independently refined from 1483 symmetry-independent reflexions collected on the conventional four-circle diffractometer D8 at the ILL high flux reactor (FHM, 1977). The crystal used (crystal II in FHM) had a volume about 10 times larger than the crystal used for the photographic study. The conventional $R(F^2)$ was 0·036. Table 2 shows the final parameters with their standard deviation (*b*) together with the parameters derived from the modified Laue measurements (*c*) and those of the X-ray structure determination (*a*) (Donohue & Caron, 1964). To compare the parameters on a statistical basis we made normal and half-normal probability plots (Abraham &

Table 2. *Fractional coordinates* (× 10^4) *and temperature parameters* (× 10^4)

(*a*) X-ray structure determination (Donohue & Caron, 1964);
(*b*) neutron structure determination (FHM);
(*c*) modified Laue measurements.

		x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	(*a*)	3645 (5)	1939 (8)	5044 (11)	36 (3)	53 (8)	114 (18)	5 (9)	16 (12)	23 (21)
	(*b*)	3643 (1)	1934 (1)	5064 (2)	22 (1)	53 (1)	75 (2)	1(1)	4 (1)	3 (1)
	(*c*)	3638 (7)	1937 (9)	5058 (9)	26 (5)	23 (9)	66 (12)	0 (7)	3 (7)	10 (8)
C(2)	(*a*)	4020 (5)	1169 (9)	3240 (12)	20 (3)	63 (8)	150 (17)	10 (8)	−9 (12)	−13 (22)
	(*b*)	4013 (1)	1163 (1)	3236 (2)	17 (1)	45 (1)	80 (2)	5 (1)	3 (1)	−1 (1)
	(*c*)	4009 (6)	1155 (9)	3243 (9)	14 (5)	23 (9)	71 (12)	4 (7)	6 (5)	2 (8)
C(3)	(*a*)	4513 (4)	2237 (9)	1900 (11)	20 (3)	76 (9)	155 (17)	9 (9)	22 (11)	−20 (24)
	(*b*)	4510 (1)	2240 (1)	1888 (2)	19 (1)	54 (1)	100 (2)	3 (1)	9 (1)	2 (1)
	(*c*)	4512 (7)	2236 (11)	1863 (9)	20 (6)	65 (12)	66 (14)	13 (8)	9 (6)	12 (10)
C(4)	(*a*)	4016 (5)	3625 (8)	1321 (11)	23 (3)	45 (8)	125 (16)	−21 (8)	13 (12)	−17 (19)
	(*b*)	4012 (1)	3613 (1)	1311 (2)	20 (1)	43 (1)	73 (2)	−2 (1)	5 (1)	−3 (1)
	(*c*)	4006 (6)	3606 (8)	1285 (8)	6 (4)	34 (9)	72 (11)	1 (6)	12 (5)	4 (9)
C(5)	(*a*)	3414 (6)	5251 (10)	9337 (14)	29 (4)	97 (11)	187 (22)	−12 (10)	−19 (14)	28 (26)
	(*b*)	3403 (1)	5253 (2)	9329 (2)	32 (1)	72 (2)	127 (3)	−2 (1)	−11 (1)	27 (2)
	(*c*)	3400 (8)	5263 (11)	9316 (11)	45 (8)	55 (11)	122 (18)	12 (8)	12 (7)	22 (12)
C(6)	(*a*)	3680 (5)	4766 (9)	2392 (13)	26 (3)	74 (9)	187 (19)	−7 (9)	14 (15)	23 (26)
	(*b*)	3678 (1)	4758 (1)	2403 (2)	28 (1)	47 (1)	93 (2)	1 (1)	6 (1)	−8 (1)
	(*c*)	3690 (7)	4757 (10)	2404 (9)	21 (6)	53 (10)	80 (14)	7 (7)	9 (5)	7 (10)
N(1)	(*a*)	3305 (4)	384 (7)	2173 (10)	22 (3)	60 (7)	148 (14)	2 (8)	9 (11)	−34 (17)
	(*b*)	3306 (1)	374 (1)	2176 (1)	23 (1)	51 (1)	102 (2)	−1 (1)	−1 (1)	−11 (1)
	(*c*)	3307 (6)	384 (8)	2181 (9)	34 (3)	48 (8)	86 (13)	0 (6)	6 (6)	28 (9)
N(2)	(*a*)	3836 (5)	3964 (8)	9397 (9)	33 (3)	95 (9)	100 (13)	−21 (9)	13 (11)	−10 (20)
	(*b*)	3833 (1)	3962 (1)	9394 (1)	29 (1)	65 (1)	77 (2)	−5 (1)	1 (1)	3 (1)
	(*c*)	3816 (5)	3970 (7)	9398 (7)	41 (5)	59 (8)	56 (10)	−5 (6)	2 (4)	5 (7)
N(3)	(*a*)	3301 (5)	5734 (7)	1123 (12)	35 (3)	54 (7)	213 (17)	−2 (9)	4 (14)	20 (20)
	(*b*)	3301 (1)	5754 (1)	1130 (2)	31 (1)	49 (1)	151 (2)	4 (1)	3 (1)	9 (1)
	(*c*)	3303 (6)	5761 (8)	1116 (8)	41 (5)	57 (9)	118 (11)	9 (7)	12 (5)	12 (8)
O(1)	(*a*)	2857 (3)	1836 (6)	5413 (9)	26 (2)	96 (7)	171 (12)	6 (7)	32 (10)	−34 (19)
	(*b*)	2854 (1)	1840 (2)	5398 (2)	23 (1)	78 (2)	137 (3)	1 (1)	18 (1)	−23 (2)
	(*c*)	2862 (8)	1845 (13)	5401 (11)	20 (6)	84 (15)	102 (15)	2 (10)	11 (6)	1 (13)
O(2)	(*a*)	4204 (4)	2628 (7)	6055 (9)	35 (3)	147 (10)	136 (12)	−26 (10)	0 (9)	−77 (20)
	(*b*)	4202 (1)	2635 (2)	6061 (2)	32 (1)	132 (3)	97 (3)	−18 (1)	3 (1)	39 (2)
	(*c*)	4187 (8)	2613 (16)	6066 (11)	20 (6)	161 (20)	92 (10)	13 (10)	4 (6)	28 (17)
O(3)	(*a*)	802 (4)	1001 (9)	4083 (10)	36 (3)	187 (12)	208 (17)	29 (11)	3 (11)	112 (26)
	(*b*)	813 (1)	989 (3)	4103 (3)	33 (1)	182 (4)	175 (5)	19 (1)	8 (2)	89 (4)
	(*c*)	832 (11)	977 (19)	4064 (17)	22 (9)	200 (28)	185 (25)	24 (14)	30 (10)	104 (23)
Cl	(*a*)	1758 (1)	2276 (2)	299 (3)	34 (1)	69 (2)	126 (4)	16 (2)	−5 (3)	4 (5)
	(*b*)	1757 (1)	2275 (1)	306 (1)	32 (1)	62 (1)	98 (2)	7 (1)	2 (1)	1 (1)
	(*c*)	1760 (5)	2275 (7)	297 (6)	43 (4)	66 (8)	70 (9)	3 (6)	1 (4)	5 (7)
H(C2)	(*a*)	4460	390	3690						
	(*b*)	4473 (2)	293 (3)	3732 (4)	31 (1)	81 (3)	181 (6)	15 (2)	−8 (2)	19 (4)
	(*c*)	4494 (16)	307 (20)	3762 (19)	54 (15)	57 (21)	114 (26)	24 (17)	−18 (14)	11 (23)
H(C3)	(*a*)	4720	1630	750						
	(*b*)	4710 (2)	1638 (3)	573 (5)	55 (2)	101 (4)	162 (6)	17 (2)	43 (3)	−7 (4)
	(*c*)	4727 (16)	1616 (22)	581 (24)	31 (12)	102 (28)	201 (39)	3 (17)	21 (15)	13 (29)
H(C3)	(*a*)	5060	2510	2680						
	(*b*)	5107 (2)	2569 (4)	2645 (5)	24 (1)	120 (4)	258 (8)	−5 (2)	−12 (3)	33 (5)
	(*c*)	5128 (15)	2570 (23)	2638 (24)	12 (11)	113 (28)	213 (35)	7 (15)	9 (14)	10 (28)
H(C5)	(*a*)	3210	5750	8090						
	(*b*)	3194 (3)	5826 (4)	8012 (5)	62 (2)	141 (5)	196 (7)	11 (3)	32 (3)	65 (5)
	(*c*)	3169 (18)	5858 (23)	8054 (28)	71 (18)	113 (30)	195 (39)	42 (22)	11 (19)	27 (31)
H(C6)	(*a*)	3700	4850	3840						
	(*b*)	3682 (3)	4960 (4)	3945 (4)	63 (2)	117 (4)	111 (5)	14 (2)	4 (3)	−31 (4)
	(*c*)	3662 (18)	4967 (20)	3967 (20)	75 (20)	80 (27)	89 (27)	9 (18)	6 (14)	3 (21)
H(N1)	(*a*)	2800	1120	1870						
	(*b*)	2808 (2)	1083 (3)	1724 (5)	31 (1)	95 (3)	201 (7)	3 (2)	−17 (2)	−8 (4)
	(*c*)	2810 (18)	1055 (27)	1697 (23)	45 (16)	104 (30)	143 (34)	10 (20)	24 (15)	11 (28)
H(N1)	(*a*)	3500	0	870						
	(*b*)	3558 (2)	−177 (3)	956 (4)	40 (1)	97 (3)	133 (5)	4 (2)	4 (2)	−38 (4)
	(*c*)	3548 (14)	−178 (21)	942 (18)	35 (14)	115 (25)	77 (24)	7 (15)	0 (11)	−80 (23)
H′(N1)	(*a*)	3050	−450	2960						
	(*b*)	3046 (2)	−443 (3)	3070 (5)	40 (1)	103 (4)	193 (7)	−20 (2)	6 (3)	7 (4)
	(*c*)	3082 (14)	−421 (25)	3081 (24)	26 (13)	132 (30)	132 (29)	12 (17)	15 (13)	18 (28)
H(N2)	(*a*)	4020	3330	8210						
	(*b*)	3975 (2)	3326 (3)	8114 (4)	45 (1)	110 (4)	107 (5)	−9 (2)	4 (2)	−3 (4)
	(*c*)	3988 (14)	3313 (21)	8157 (16)	52 (12)	131 (30)	31 (22)	−16 (16)	23 (12)	43 (20)

Table 2 (*cont.*).

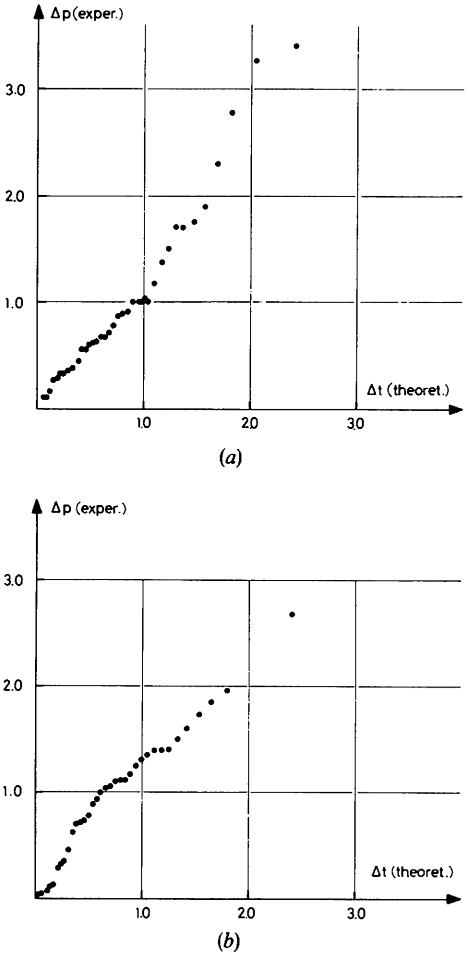
		x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
H(N3)	(*a*)	2990	6700	1500						
	(*b*)	2965 (2)	6716 (3)	1453 (6)	47 (1)	79 (3)	312 (10)	18 (2)	22 (3)	−2 (5)
	(*c*)	2932 (18)	6671 (23)	1411 (31)	22 (14)	45 (24)	288 (47)	4 (16)	14 (16)	9 (27)
H(O3)	(*a*)	1110	1420	2970						
	(*b*)	1113 (2)	1311 (5	2933 (6)	47 (2)	180 (5)	193 (7)	12 (3)	19 (3)	52 (6)
	(*c*)	1127 (19)	1309 (28)	2929 (30)	62 (18)	149 (34)	176 (38)	19 (23)	7 (21)	33 (32)
H(O3)	(*a*)	2230	1470	4060						
	(*b*)	270 (2)	1500 (4)	4112 (5)	38 (1)	165 (5)	193 (7)	11 (2)	−1 (3)	22 (5)
	(*c*)	237 (19)	1535 (28)	4082 (27)	51 (14)	187 (40)	194 (37)	46 (23)	47 (18)	70 (32)

Keve, 1971; Hamilton, 1974) of the film and diffractometer data. This is a check for the right standard deviations and for the absence of systematic deviations.

In constructing the plot the (absolute) differences between the parameters Δp_i, which are defined as

$$\Delta p_i = [p_i(\mathrm{D12}) - p_i(\mathrm{D8})]/[\sigma_i^2(\mathrm{D12}) + \sigma_i^2(\mathrm{D8})]^{1/2}$$

with p_i the compared parameters and σ_i their standard deviations, are arranged in order of increasing magnitude and plotted against the expected values Δt_i (small samples) for a (half)-normal distribution.



(*a*)

(*b*)

Fig. 6. Half-normal probability plots of the positional parameters compared with the results of the four-circle diffractometer D8 for heavy atoms (*a*) and hydrogens (*b*).

The half-normal probability plots for the positional parameters of the heavy atoms and the hydrogen atoms are shown in Fig. 6(*a*,*b*). The standard deviations are approximately correct (unit slope of a straight line). The mean value of the deviations between the D8 and D12 parameters is 0·009 Å for the heavy atoms and 0·022 Å for the hydrogen atoms.

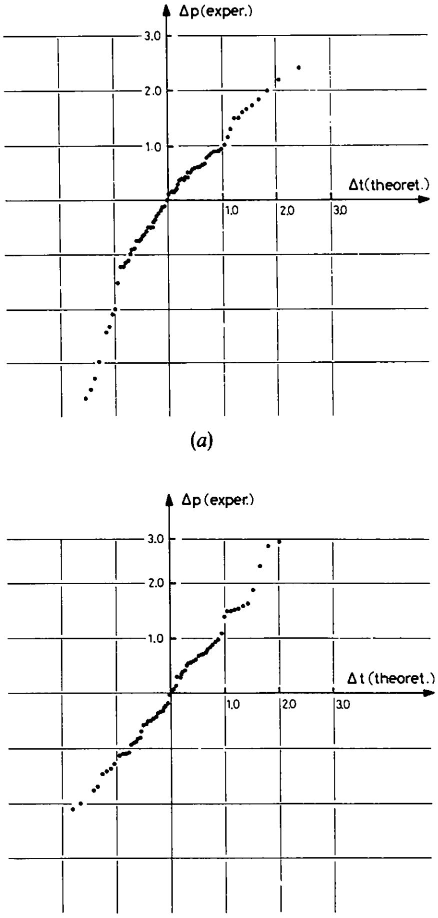
Normal probability plots were made for the temperature factors, Fig. 7(*a*,*b*). The plot for the heavy atoms suggests some systematic differences. Table 2 shows that the β_{33} values of the film results are nearly always about 1σ lower than the corresponding diffractometer data. The mean value of the deviations relative to the D8 measurements is 0·0054 Å^2 for the mean-square displacements [U_{ij} in $\exp\{-2\pi^2(U_{11}h^2a^{*2}+\ldots)\}$] of the heavy atoms and 0·0105 Å^2 for the hydrogens.

To have an estimate of the time gained in data collection compared with an automatic four-circle diffractometer we measured 350 reflexions with the same crystal at the D8 instrument. If the diffractometer works at its maximum speed of about 250 reflexions a day the standard deviations of the intensities (only counting statistics) are almost equal to those of the film measurements, namely about 7%. Thus the film measurements are about three times faster if one compares only the collection of symmetry-independent reflexions. The neutron flux at the sample was 2×10^7 n cm^{-2} s^{-1} for the D8 instrument situated near the reactor core and 1×10^7 for the D12 apparatus at the end of a thermal-neutron guide. Lower symmetry and larger cell dimensions of the crystal increase the gain factor of the D12 instrument.

Conclusions

This was the first structure refinement with neutron film data. We used a new diffraction method – the modified Laue technique.

The standard deviations of the refined parameters are almost equal to those of the heavy-atom parameters in the X-ray structure refinement made with Weissenberg film data (Donohue & Caron, 1964). The correctness of the derived standard deviations is proved by a direct comparison with a precise structure determination on a conventional four-circle diffractometer (FHM, 1977).



(a)

(b)

Fig. 7. Normal probability plots for the temperature factors β_{ij} of the heavy atoms (*a*) and hydrogens (*b*).

The method is of considerable advantage in all cases where only small crystals are available. The gain in data collection time is most important for large unit cells or for series of measurements with only small structural changes (phase transitions, chemical composition, magnetic ordering).

The author is indebted to his colleagues Dr B. Klar and Dr H. Fuess for many helpful discussions and suggestions. The support of the technical and computer staff of the ILL and especially the technical assistance of Mr Berneron is gratefully acknowledged.

References

Abrahams, S. C. & Keve, E. T. (1971). *Acta Cryst.* A**27**, 157–165.

Busing, W. R., Martin, K. O., Levy, H. A., Ellison, R. D., Hamilton, W. C., Ibers, J. A., Johnson, C. K. & Thiessen, W. E. (1971). *ORXFLS*3, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Donohue, J. & Caron, A. (1964). *Acta Cryst.* **17**, 1178–1180.

Fuess, H., Hohlwein, D. & Mason, S. A. (1977). *Acta Cryst.* B**33**, 654–659.

Hamilton, W. C. (1974). *International Tables for X-ray Crystallography*, Vol. IV. Birmingham: Kynoch Press.

Hohlwein, D. (1975*a*). *Proc. Neutron Diffraction Conf. Petten*, Report 234, pp. 410–429, Reactor Centrum, Nederland.

Hohlwein, D. (1975*b*). *J. Appl. Cryst.* **8**, 465–468.

Hohlwein, D. & Joswig, W. (1976). *J. Appl. Cryst.* **9**, 130–133.

Hohlwein, D. & Klar, B. (1976). *Absorption Correction for the Modified Laue Method*, Report 76H42S, Institut Laue–Langevin, Grenoble, France.

Klar, B. (1973). Thesis, Saarbrücken.

Maier-Leibnitz, H. (1967). *Ann. Acad. Sci. Fenn.* **AVI**, 267.

Thomas, P. (1972*a*). *J. Appl. Cryst.* **5**, 83–88.

Thomas, P. (1972*b*). *J. Appl. Cryst.* **5**, 373–374.

Wehe, D. J., Busing, W. R., Levy, H. A. (1962). *ORABS*: a *Fortran Program for Calculating Single Crystal Absorption Corrections*, Report ORNL-TM229, Oak Ridge National Laboratory, Oak Ridge, Tennessee.