THE
BRITISH RUBBER PRODUCERS'
RESEARCH ASSOCIATION

Publication No. 61

THE STRUCTURE OF POLYISOPRENES.

I. THE CRYSTAL STRUCTURE OF GERANYLAMINE HYDROCHLORIDE.

By G. A. JEFFREY.

Reprinted without change of pagination from the
Proceedings of the Royal Society, A, *volume* 183, 1945

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I. The crystal structure of geranylamine hydrochloride

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By G. A. Jeffrey

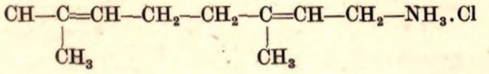
(*Communicated by W. N. Haworth, F.R.S.—Received* 25 *May* 1944)

An X-ray analysis employing three-dimensional Fourier syntheses has established the crystal structure and molecular dimensions of the di-isoprene derivative, geranylamine hydrochloride. The molecules, which have a *trans* configuration and are therefore analogous to gutta-percha, lie parallel and end to end in pairs within an ionic framework where each nitrogen atom is equidistant from four chlorine neighbours. The two isoprene units are planar and have normal interatomic distances, but are linked by a C-C bond markedly shorter than a normal single bond. This unusual bond feature is accompanied by a coplanar arrangement with the adjacent carbon bonds.

Introduction

The difficulty of crystal structure determination of complex organic molecules is to some degree offset by the extent of the diffraction data. With the polyisoprenes much of this information is obscured both by the diffuse nature of the fibre diagrams and by ambiguities arising from imperfect crystallite orientation. The resulting lack of precision is well illustrated by the example of rubber, where attempts at direct analysis have led to considerable disagreement even in the preliminary description of the unit cell (Lotmar & Meyer 1936; Sauter 1937; Morss 1938; Misch & Van der Wyk 1940). The detailed structures for rubber and β-gutta-percha recently proposed by Bunn (1942) are subject to the same limitations and cannot be regarded as necessarily final solutions, particularly as they entail surprisingly large valency distortions of a type hitherto unparalleled.

With the object of determining indirectly the interatomic dimensions in these polymers attention has been directed to simpler analogues. Following the study of a mono-isoprene compound by Cox & Jeffrey (1942), derivatives of geraniol were considered since they possess a di-isoprene system akin to the repeating units in the long-chain polymers. Although many of these compounds are unsuitable for X-ray methods, the hydrochloride of geranylamine (1) afforded the requisite crystals for intensity measurements, and their favourable space group together with the presence of a comparatively heavy chlorine atom has made possible the complete and accurate analysis of the structure:



$$\mathrm{CH{-}\underset{\underset{CH_3}{|}}{C}{=}CH{-}CH_2{-}CH_2{-}\underset{\underset{CH_3}{|}}{C}{=}CH{-}CH_2{-}NH_3.Cl}$$

(1)

Experimental

Four molecules of $C_{10}H_{18}NH_2 . HCl$ are associated by the space-group symmetry $P2_1/c$ in a unit cell of dimensions $a = 22{\cdot}68\,A$, $b = 5{\cdot}94\,A$, $c = 8{\cdot}98\,A$, $\beta = 98{\cdot}8°$. A complete description of the structure excluding the hydrogen atoms therefore requires the determination of 36 atomic parameters. For this purpose, all plane reflexions within the range of Cu K_α radiation were recorded on oscillation photographs about the principal axes, and their relative intensities were estimated by eye with the aid of calibration charts. As it is important that these values should be absolute, they were related to selected intensities transmitted through a thin crystal slab and measured by photometric comparison with a standard rock-salt (400) reflexion recorded on the same film. All photographs were taken three or more times with different exposures, using aluminium screens of known absorption to bring strong spots within the range of linear X-ray density.

From the experimental measurements the structure amplitudes of 1060 planes were calculated by the usual formulae, and were used first in the summation of a three-dimensional F^2 (Patterson) Fourier synthesis.

The arrangement of the chlorine atoms

The positions of the chlorine atoms were derived directly from the Patterson synthesis by virtue of the outstanding Cl-Cl vector peaks, two at co-ordinates (0·107, 0·50, 0·162) and (0·107, 0·50, 0·662) and a third of double height at (0·00, 0·00, 0·50). These peaks must arise from atoms at either (0·053, 0·25, 0·081) or (0·053, 0·25, 0·331) in conjunction with atoms symmetrically related. The former was ultimately shown to be correct, but both possibilities had to be considered since no distinction can be made between the centre of symmetry and the screw axis for atoms on the glide planes.

The Patterson synthesis, having symmetry planes at $y = 0$ and $\frac{1}{2}$, cannot reveal any small departure in the y parameter from 0·250. This was assumed to be exact for the approximate structure, and during the successive refinements no evidence to the contrary was observed. Further confirmation was available at the conclusion of the analysis from the comparison of the agreement between observed and calculated structure amplitudes for planes with l odd, where the chlorines make zero contribution, and those with l even:

$$\frac{\Sigma\,|\,F_{\text{obs.}}\,|-|\,F_{\text{calc.}}\,|}{\Sigma\,|\,F_{\text{obs.}}\,|}\quad 17{\cdot}0 \text{ and } 17{\cdot}8\,\% \text{ respectively.}$$

As shown in figures 4 and 5 these halogen atoms lie in sheets close to the (100) planes enclosing the organic molecules in pairs between them.

DETERMINATION OF THE APPROXIMATE STRUCTURE

The general orientation of the molecules was apparent from the length of the a axis; and from the weak odd layer lines on the c axis photographs it was clear that other atoms besides the halogens must lie on or near the glide planes. Further information was derived from the Patterson synthesis which was computed over sections parallel to (010) at intervals of y sufficiently close to reveal all prominent peaks. Six such peaks of height corresponding to Cl-N and Cl-C distances indicated positions for N, C_1, and C_2 in which the nitrogen was equidistant from four chlorine atoms and the interatomic distances and valency angles were approximately normal. This was the only arrangement compatible with the vector maps. Beyond this stage, however, these became much more complicated and further direct interpretation was not possible. For the remaining eight atoms trial and error methods were adopted and the Patterson synthesis was useful only in restricting the number of possibilities to be considered.

A model based on normal interatomic dimensions was used, first to ascertain arrangements which would satisfy the principal structure factors of the ($h0l$) zone, and then for further trials with general planes. Owing to the wide range of free rotation about each single bond, a large number of configurations was tried and rejected before arriving at a set of co-ordinates which, when refined by Fourier F synthesis, resulted in a marked improvement in the agreement between the observed and calculated structure factors. These and all subsequent syntheses were of the three-dimensional type, since projections were of little value even on the most favourable (010) plane.

THE FOURIER F SYNTHESIS

Starting from the approximate structure, the atomic co-ordinates were refined by the method of successive Fourier syntheses. The summations were evaluated from all the available data using Beevers and Lipson's strips over sections and along lines at values of x, y and z appropriate to the maximum of each atom peak. After

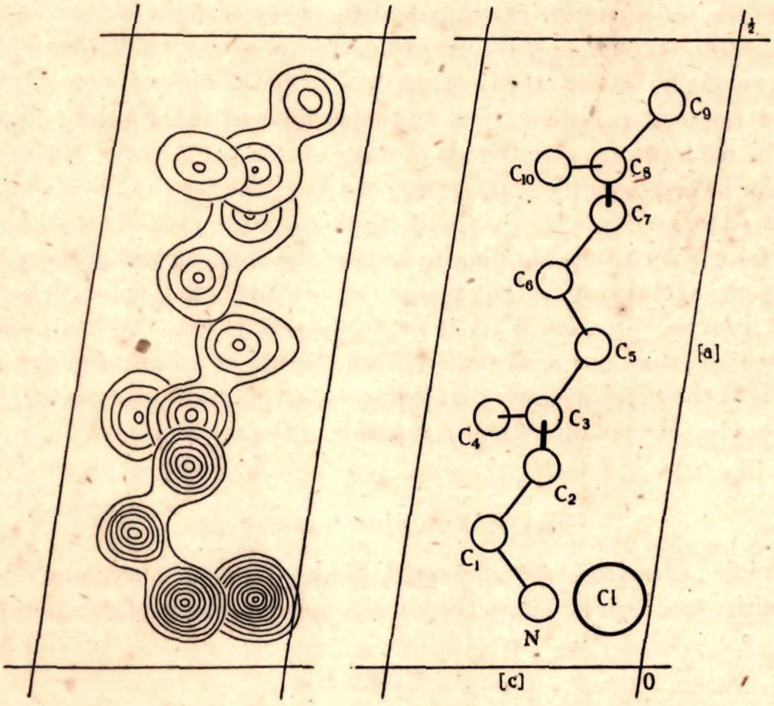


Figure 1. Projection of the molecule and Fourier sections on (010).

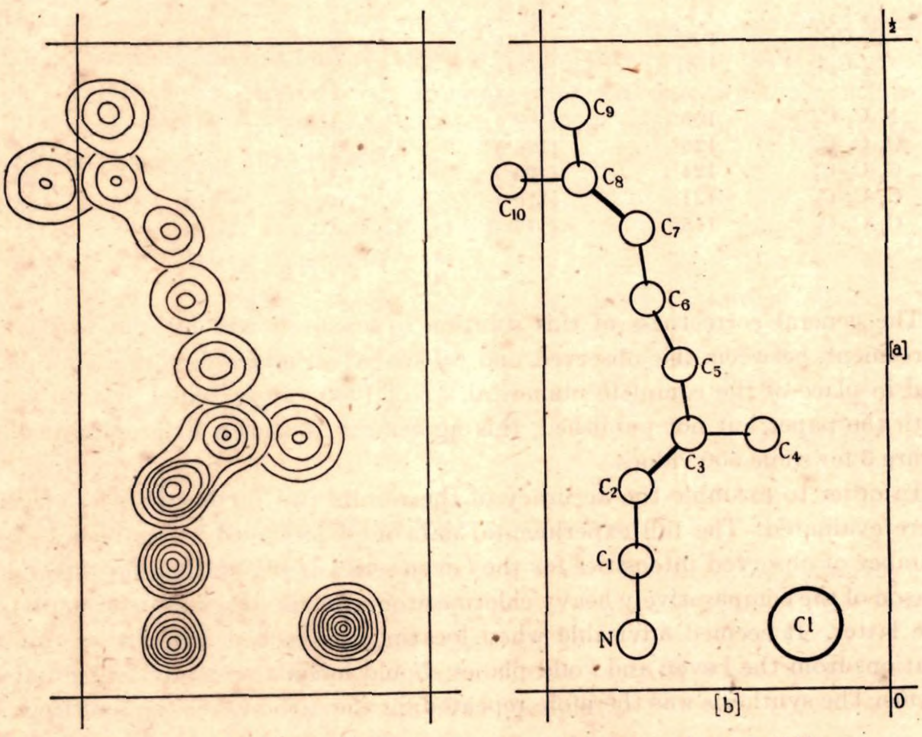


Figure 2. Projection of the molecule and Fourier sections on (001).

the fifth series, the structure-factor calculations revealed no further sign changes, and the electron maps from this final summation are shown in figures 1 and 2. For the purpose of illustration, the electron density peaks for one molecule have been taken from the sectional summations and superimposed on the *b* and *c* planes respectively. The contours are at intervals of one electron per A^3, with the exception of the chlorine atom where the scale is two electrons. The zero and first contours have been omitted for clarity in the diagrams. These maps show clearly that the peaks are different for carbon atoms at opposite ends of the molecule and although approximately equal in total volume they become progressively flatter for each atom along the chain from the nitrogen. While it cannot be certain that this has a real physical significance and does not arise merely from the use of a finite Fourier series, the magnitude of the effect suggests that it may be attributed to a variation in thermal motion between the polar and non-polar ends of the molecule.

THE FINAL ATOMIC PARAMETERS

The atomic parameters were measured directly from the maximum of each peak in the Fourier synthesis and gave the interatomic dimensions shown in table 1.

TABLE 1

N-C_1	1·49 A	(1·48)	C_5-C_6	1·44 A	(1·45)
C_1-C_2	1·54	(1·53)	C_6-C_7	1·51	(1·52)
C_2-C_3	1·31	(1·32)	C_7-C_8	1·31	(1·32)
C_3-C_4	1·53	(1·53)	C_8-C_9	1·53	(1·55)
C_3-C_5	1·51	(1·54)	C_8-C_{10}	1·54	(1·53)
N-C_1-C_2	109°	(109°)	C_3-C_5-C_6	115°	(112°)
C_1-C_2-C_3	126°	(126°)	C_5-C_6-C_7	112°	(112°)
C_2-C_3-C_4	124°	(124°)	C_6-C_7-C_8	129°	(129°)
C_2-C_3-C_5	121°	(119°)	C_7-C_8-C_9	124°	(123°)
C_4-C_3-C_5	115°	(117°)	C_7-C_8-C_{10}	121°	(121°)
			C_9-C_8-C_{10}	115°	(116°)

The general correctness of this solution is substantiated by the satisfactory agreement between the observed and calculated structure factors for all planes, and in place of the complete numerical list of 1060 values, which was submitted with the paper but not published, this agreement is shown diagrammatically in figure 3 for some 500 values.

In order to examine the accuracy of the results two further Fourier syntheses were evaluated. The full experimental data used previously contained a greater number of observed intensities for the *l* even series of planes than for the *l* odd by reason of the comparatively heavy chlorine atom contributing to the former but not the latter. It seemed advisable when locating the carbon atoms that the summations from the *l* even and *l* odd planes should include an equivalent number of terms. The synthesis was therefore repeated for the carbon skeleton omitting those

F values (*c.* 350) where the difference between F_{observed} and F_{chlorine} was less than 1·5 per molecule, this value being the minimum observable when F_{chlorine} was zero. The new atomic positions showed a mean shift of 0·02 A from those previously derived. The corresponding interatomic distances are given in parenthesis in table 1.

As an alternative method of balancing the l even and l odd terms, the F values were calculated for all planes of spacing greater than 0·9 A whose intensities were too small to be observed. These amounted to some 300 values which when included in the synthesis also resulted in shifts in the parameters of the order of 0·02 A and, as might be expected, considerably sharpened the electron peaks. The double bond lengths became 1·34 A, the C_5-C_6 bond 1·46 A, and the other bonds remained the same within 0·01 A. The progressive broadening of the contour intervals for each atom along the molecule was still clearly apparent, although the additional terms increased the maximum electron density of the peaks other than those at $y = \frac{1}{4}$ and $\frac{3}{4}$ by about $\frac{1}{2}$ electron/A^3.

Both these Fourier syntheses were an improvement on the original as regards the shape of the electron contours, particularly those of C_5 where the elongation of the peak in the c axis direction was completely removed. The changes in peak positions were of the same order as those between the penultimate and final successive Fourier syntheses, and the bond lengths and valency angles showed no variations beyond the limits of experimental errors which are estimated at ± 0·04 A and ± 4°.

Although the atom peaks were least sharp in the synthesis using the smaller number of F values, these atomic parameters (table 2) are considered to be the most reliable since they were derived solely from experimental data with the exclusion, for the organic part of the molecule, of such values as might impose a systematic error on the positions of the maxima.

TABLE 2

	x	y	z		x	y	z
Cl	0·053	0·250	0·080	C_5	0·253	0·625	0·182
N	0·049	0·750	0·216	C_6	0·304	0·700	0·287
C_1	0·103	0·750	0·333	C_7	0·357	0·746	0·207
C_2	0·158	0·751	0·255	C_8	0·394	0·916	0·212
C_3	0·198	0·593	0·264	C_9	0·447	0·918	0·118
C_4	0·198	0·379	0·358	C_{10}	0·392	1·120	0·315

THE STEREOCHEMISTRY OF THE MOLECULE

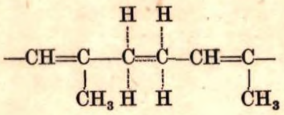
Within experimental error the two isoprene units are identical, the parameters of C_1-C_5 being more certain than C_6-C_{10} owing to the flattening of the Fourier peaks described above. They possess normal bond lengths (C═C 1·34 A, C—C 1·54 A) and the disposition of valencies about the double bonds is planar. Their angles appear to be distorted by about 5° from the theoretical 120° with the result that


150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
F_{hkl}
F. calc.
F. obs.
110
100
90
80
70
60
50
40
30
20
10
60
50
40
30
20
10

FIGURE 3

C_1-C_2 is not exactly parallel to C_3-C_5, nor C_6-C_7 to C_8-C_9. This variation, although small and very near the margin of error, may be real and characteristic of the unsymmetrical arrangement of the groups about the double bond.

The bond C_5-C_6 linking the isoprene units is shorter than that associated with a normal C-C bond by an amount two or three times the probable experimental error. Furthermore the distribution of the adjoining C_3-C_5 and C_6-C_7 is planar. These features, reminiscent of those found in conjugated molecules, seem inexplicable in terms of the usual theory of mesomerism. As reported by Bateman & Jeffrey (1943), the amine hydrochloride group does not appear to be directly responsible and the hybrid character may result from a hyperconjugation process in which the α-methylenic C-H electrons become partially localized in the central bond:



$$-CH{=}\underset{CH_3}{\underset{|}{C}}-\overset{H}{\overset{\vdots}{\underset{H}{\underset{\vdots}{C}}}}{=}\overset{H}{\overset{\vdots}{\underset{H}{\underset{\vdots}{C}}}}-CH{=}\underset{CH_3}{\underset{|}{C}}-$$

Evidence as to what extent this can be regarded as a general property of the polyisoprene system must await the examination of compounds with a similar structural modification.

Other stereochemical features of importance in the geranylamine structure concern the angular position of the C_5-C_6 bond relative to the two isoprene planes. Free rotation about the bond C_3-C_5 will be influenced by repulsion of the CH_2 group by the CH and CH_3. If the CH_2 group lies in the plane of the isoprene ($C_1 \ldots C_5$), then the approach between one or other pair of these atoms would be of the order of $2\cdot8$ A; a distance which in the absence of any special bonding between the hydrogen atoms provides an appreciable energy barrier. In the observed structure the C_5-C_6 bond is oriented at 80° to the isoprene plane and the steric repulsions balance at almost equal distances (C_6-C_2 $3\cdot28$ A, C_6-C_4 $3\cdot24$ A). In contrast, since there is no methyl addendum to C_7, the rotation about C_6-C_7 relative to the other isoprene plane is influenced solely by the approach of the CH_2 to the $CH_{3(10)}$. Over a large angular range, this repulsion will be ineffectual and the factors determining the observed angle of 45° between the C_5-C_6 bond and the $C_6 \ldots C_{10}$ plane must arise mainly from the packing of adjacent molecules in the crystal lattice, and probably from the relation between the terminal $C(CH_3)_2$ groups in particular. Whereas this latter steric effect is specific to the particular intermolecular arrangement, the former depends upon intramolecular forces and, since it will apply to any molecule with the same configuration, has an important bearing on the stereochemistry of the long-chain polymers.

THE INTERMOLECULAR ARRANGEMENT

The packing of the molecules in the crystal lattice is illustrated in figures 4 and 5. The hydrocarbon chains lie parallel with the molecules end to end in pairs. Each nitrogen is associated with four chlorine atoms at nearly equal distances.

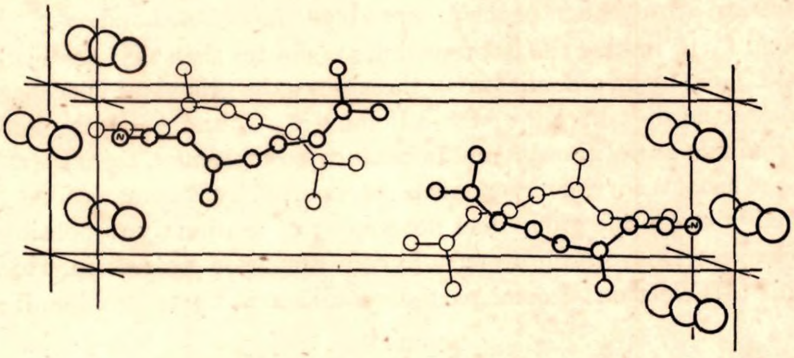


FIGURE 4. The structure of geranylamine hydrochloride.

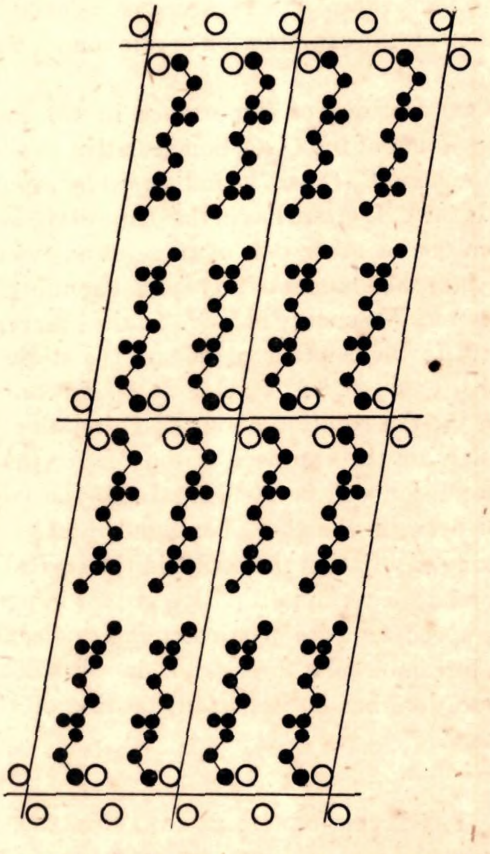


FIGURE 5. Projection of the structure on (010).

All other distances between atoms in adjacent molecules conform to Van der Waal's forces and are greater than 3·75 A with the exception of 3·60 A between centrosymmetrically related C_9 atoms.

TABLE 3

N-Cl_1	3·24 A	N-Cl_3	3·24 A
N-Cl_2	3·17	N-Cl_4	3·24

ACKNOWLEDGEMENTS

I am grateful to Professor Sir Lawrence Bragg and Dr E. G. Cox for advice and criticism and to Professor W. N. Haworth for facilities granted at Birmingham University for the earlier part of the work. Thanks are also given to Dr D. A. Sutton for preparation of the geranylamine hydrochloride.

The above work has been carried out as part of a programme of fundamental research undertaken by the Board of the British Rubber Producers' Research Association.

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For the tables of calculated and observed structure factors see pages 398–404.

Calculated and observed structure factors

hkl	$F_{\text{calc.}}$	$F_{\text{obs.}}$	*hkl*	$F_{\text{calc.}}$	$F_{\text{obs.}}$	*hkl*	$F_{\text{calc.}}$	$F_{\text{obs.}}$
100	48	48	$\bar{1}02$	26	27	$\bar{1}04$	5	<8
200	17	16	$\bar{2}02$	51	47	$\bar{2}04$	9	13
300	30	41	$\bar{3}02$	59	60	$\bar{3}04$	29	25
400	−25	33	$\bar{4}02$	87	106	$\bar{4}04$	18	16
500	45	50	$\bar{5}02$	54	76	$\bar{5}04$	39	38
600	−46	56	$\bar{6}02$	24	26	$\bar{6}04$	42	42
700	−55	76	$\bar{7}02$	32	41	$\bar{7}04$	43	45
800	−73	82	$\bar{8}02$	10	19	$\bar{8}04$	24	6
900	−71	74	$\bar{9}02$	53	78	$\bar{9}04$	−38	54
1000	−41	53	$\overline{10}02$	−35	42	$\overline{10}04$	6	6
1100	−32	25	$\overline{11}02$	−64	88	$\overline{11}04$	4	<8
1200	−42	47	$\overline{12}02$	−31	28	$\overline{12}04$	−12	13
1300	−17	16	$\overline{13}02$	−43	49	$\overline{13}04$	−14	13
1400	−18	18	$\overline{14}02$	−16	13	$\overline{14}04$	−13	12
1500	9	<8	$\overline{15}02$	−20	24	$\overline{15}04$	−25	18
1600	21	32	$\overline{16}02$	−8	7	$\overline{16}04$	−24	19
1700	14	15	$\overline{17}02$	−4	4	$\overline{17}04$	−14	12
1800	23	24	$\overline{18}02$	14	18	$\overline{18}04$	−17	14
1900	22	27	$\overline{19}02$	6	<8	1904	−1	<8
2000	41	47	$\overline{20}02$	−3	<8	2004	−1	5
2100	10	10	$\overline{21}02$	16	16	2104	6	7
2200	0	<8	$\overline{22}02$	12	13	2204	8	10
2300	3	<8	$\overline{23}02$	7	4	2304	10	10
2400	−8	7	$\overline{24}02$	13	10	2404	7	9
			$\overline{25}02$	4	<8	2504	6	8
002	−111	130						
102	19	10				006	−27	23
202	62	89	004	−1	<8	106	−34	27
302	−47	54	104	−26	16	206	−26	16
402	−18	27	204	−60	60	306	−18	18
502	−108	109	304	−33	25	406	−12	12
602	−49	66	404	−38	28	506	−4	10
702	−44	34	504	−16	<8	606	−8	13
802	−42	47	604	−4	12	706	12	12
902	−33	39	704	−15	13	806	22	18
1002	−15	<8	804	1	<8	906	17	14
1102	28	38	904	11	12	1006	23	18
1202	14	32	1004	9	<8	1106	18	16
1302	26	31	1104	−1	<8	1206	12	9
1402	29	34	1204	28	9	1306	5	<8
1502	27	34	1304	25	20	1406	5	<8
1602	23	21	1404	14	12	1506	−1	<8
1702	21	21	1504	13	8	1606	−1	<8
1802	13	9	1604	3	<8			
1902	1	<8	1704	5	<8	$\bar{1}06$	−23	14
2002	−13	12	1804	−2	<8	$\bar{2}06$	−18	14
2102	2	<8	1904	−2	<8	$\bar{3}06$	−5	<8
2202	3	<8	2004	−3	<8	$\bar{4}06$	0	<8
2302	−10	<8	2104	−9	<8	$\bar{5}06$	3	<8
2402	−5	10	2204	−10	8	$\bar{6}06$	20	15
2502	−14	11	2304	−5	6	$\bar{7}06$	12	12

CALCULATED AND OBSERVED STRUCTURE FACTORS

hkl	$F_{\text{calc.}}$	$F_{\text{obs.}}$	*hkl*	$F_{\text{calc.}}$	$F_{\text{obs.}}$	*hkl*	$F_{\text{calc.}}$	$F_{\text{obs.}}$
$\bar{8}06$	34	39	410	−21	18	$\overline{11}11$	4	<8
$\bar{9}06$	42	48	510	−56	39	$\overline{12}11$	−20	22
$\overline{10}06$	26	22	610	−65	62	$\overline{13}11$	2	<8
$\overline{11}06$	23	21	710	−26	25	$\overline{14}11$	11	12
$\overline{12}06$	15	10	810	−20	9	$\overline{15}11$	−1	<8
$\overline{13}06$	5	6	910	7	14	$\overline{16}11$	3	<8
$\overline{14}06$	−22	22	1010	6	11	$\overline{17}11$	15	14
$\overline{15}06$	−7	14	1110	10	11	$\overline{18}11$	7	8
$\overline{16}06$	−11	17	1210	33	33			
$\overline{17}06$	−14	16	1310	31	33	012	−18	13
$\overline{18}06$	−15	15	1410	40	43	112	−146	140
$\overline{19}06$	−17	16	1510	18	15	212	−79	84
$\overline{20}06$	−8	8	1610	6	<8	312	−59	60
$\overline{21}06$	−5	<8	1710	11	18	412	−47	43
$\overline{22}06$	−2	<8	1810	5	7	512	14	20
$\overline{23}06$	2	<8	1910	−15	16	612	−17	17
$\overline{24}06$	0	<8	2010	1	<8	712	−17	20
			2110	0	<8	812	11	<8
008	−12	6	2210	−12	12	912	14	9
108	3	5	2310	−8	8	1012	15	<8
208	−1	<8	2410	−8	8	1112	40	37
308	4	5				1212	29	29
408	10	8	011	18	21	1312	20	19
508	17	14	111	15	22	1412	11	11
608	24	16	211	49	50	1512	16	15
708	9	8	311	−80	80	1612	−7	9
808	4	12	411	8	<8	1712	−10	<8
908	13	12	511	10	15	1812	−15	<8
1008	2	<8	611	11	18	1912	−24	14
1108	6	12	711	16	16	2012	−7	8
			811	−33	41	2112	−8	9
$\bar{1}08$	−16	9	911	1	<8	2212	−9	<8
$\bar{2}08$	−17	12	1011	4	7	2312	−4	<8
$\bar{3}08$	−37	28	1111	4	<8	2412	−3	<8
$\bar{4}08$	−16	18	1211	4	<8	2512	4	<8
$\bar{5}08$	−10	<8	1311	−3	<8			
$\bar{6}08$	−7	<8	1411	−7	7	$\bar{1}12$	7	8
$\bar{7}08$	3	<8	1511	2	<8	$\bar{2}12$	5	<8
$\bar{8}08$	−4	<8	1611	0	<8	$\bar{3}12$	17	25
$\bar{9}08$	9	<8	1711	10	10	$\bar{4}12$	51	64
$\overline{10}08$	10	<8	1811	−4	<8	$\bar{5}12$	70	76
$\overline{11}08$	16	14	1911	−8	7	$\bar{6}12$	49	55
$\overline{12}08$	6	<8				$\bar{7}12$	55	59
$\overline{13}08$	10	10	$\bar{1}11$	−31	29	$\bar{8}12$	62	62
$\overline{14}08$	18	15	$\bar{2}11$	−44	46	$\bar{9}12$	37	32
$\overline{15}08$	8	8	$\bar{3}11$	51	58	$\overline{10}12$	11	11
$\overline{16}08$	2	<8	$\bar{4}11$	−3	<8	$\overline{11}12$	6	5
$\overline{17}08$	1	<8	$\bar{5}11$	5	<8	$\overline{12}12$	3	12
$\overline{18}08$	−1	<8	$\bar{6}11$	−4	5	$\overline{13}12$	−13	18
			$\bar{7}11$	−22	20	$\overline{14}12$	−15	17
110	60	75	$\bar{8}11$	0	<8	$\overline{15}12$	−16	20
210	−26	23	$\bar{9}11$	17	21	$\overline{16}12$	−33	33
310	−20	12	$\overline{10}11$	−3	<8	$\overline{17}12$	−30	33

CALCULATED AND OBSERVED STRUCTURE FACTORS

hkl	$F_{\text{calc.}}$	$F_{\text{obs.}}$
$\overline{18}12$	-29	34
$\overline{19}12$	-30	30
$\overline{20}12$	-1	<8
$\overline{21}12$	3	4
$\overline{22}12$	2	6
$\overline{23}12$	7	9
$\overline{24}12$	7	12
$\overline{25}12$	11	13
013	-14	11
113	-6	<8
213	-9	8
313	18	17
413	7	8
513	-17	18
613	4	9
713	-10	8
813	22	20
913	-4	<8
1013	-8	12
$\overline{1}13$	10	10
$\overline{2}13$	5	5
$\overline{3}13$	4	8
$\overline{4}13$	-3	<8
$\overline{5}13$	0	<8
$\overline{6}13$	-14	15
$\overline{7}13$	12	17
$\overline{8}13$	9	13
$\overline{9}13$	-8	11
$\overline{10}13$	-8	8
$\overline{11}13$	-5	6
$\overline{12}13$	18	17
$\overline{13}13$	4	<8
$\overline{14}13$	-1	<8
$\overline{15}13$	-5	6
$\overline{16}13$	-1	<8
$\overline{17}13$	7	9
014	-53	55
114	-2	4
214	-16	12
314	-20	17
414	7	<8
514	-7	<8
614	47	43
714	52	59
814	33	36
914	38	36
1014	31	26
1114	16	13
1214	1	<8
1314	0	<8
1414	-10	10
1514	-18	14
1614	-16	14
1714	-15	14
1814	-15	12
1914	-12	9
$\overline{1}14$	-63	72
$\overline{2}14$	-56	74
$\overline{3}14$	-48	56
$\overline{4}14$	-24	24
$\overline{5}14$	-31	24
$\overline{6}14$	-13	12
$\overline{7}14$	8	<8
$\overline{8}14$	2	<8
$\overline{9}14$	46	53
$\overline{10}14$	53	67
$\overline{11}14$	35	43
$\overline{12}14$	34	43
$\overline{13}14$	31	33
$\overline{14}14$	18	11
$\overline{15}14$	-7	9
$\overline{16}14$	-5	8
$\overline{17}14$	-13	14
$\overline{18}14$	-13	13
$\overline{19}14$	-9	11
$\overline{20}14$	-21	21
$\overline{21}14$	-16	16
$\overline{22}14$	-10	10
$\overline{23}14$	-6	<8
015	-5	<8
115	4	<8
215	-3	<8
315	4	<8
415	-7	<8
515	1	<8
615	0	<8
715	-1	<8
815	-3	<8
$\overline{1}15$	2	<8
$\overline{2}15$	1	<8
$\overline{3}15$	-3	<8
$\overline{4}15$	-3	<8
$\overline{5}15$	-2	<8
$\overline{6}15$	12	8
$\overline{7}15$	-9	8
$\overline{8}15$	0	<8
$\overline{9}15$	-2	<8
$\overline{10}15$	5	8
016	2	<8
116	-1	<8
216	18	15
316	30	24
416	27	25
516	29	21
616	8	<8
716	3	<8
816	14	<8
916	3	<8
1016	-6	6
1116	-7	6
1216	-5	6
1316	-13	9
1416	-13	10
1516	-11	11
1616	-12	8
$\overline{1}16$	-6	<8
$\overline{2}16$	-14	<8
$\overline{3}16$	-17	17
$\overline{4}16$	-40	31
$\overline{5}16$	-28	26
$\overline{6}16$	-22	18
$\overline{7}16$	-8	<8
$\overline{8}16$	-10	<8
$\overline{9}16$	-8	<8
$\overline{10}16$	-5	<8
$\overline{11}16$	10	<8
$\overline{12}16$	13	8
$\overline{13}16$	10	8
$\overline{14}16$	16	16
$\overline{15}16$	20	17
$\overline{16}16$	14	10
$\overline{17}16$	9	8
$\overline{18}16$	4	<8
$\overline{19}16$	-2	<8
$\overline{20}16$	-4	<8
$\overline{21}16$	-3	<8
$\overline{22}16$	-5	<8
$\overline{23}16$	-5	7
$\overline{24}16$	-11	8
018	8	8
118	11	9
218	10	8
318	13	9
418	9	7
518	6	7
618	8	7
718	6	6

CALCULATED AND OBSERVED STRUCTURE FACTORS

hkl	$F_{\text{calc.}}$	$F_{\text{obs.}}$
$\bar{1}18$	8	<8
$\bar{2}18$	5	<8
$\bar{3}18$	−9	<8
$\bar{4}18$	2	<8
$\bar{5}18$	−9	<8
$\bar{6}18$	−10	8
$\bar{7}18$	−16	14
$\bar{8}18$	−24	17
$\bar{9}18$	−12	9
$\overline{10}18$	−3	<8
$\overline{11}18$	−5	<8
$\overline{12}18$	2	<8
$\overline{13}18$	8	9
$\overline{14}18$	9	9
$\overline{15}18$	9	10
$\overline{16}18$	7	<8
$\overline{17}18$	10	9
$\overline{18}18$	2	<8
020	−110	103
120	−92	97
220	−40	43
320	−47	34
420	8	8
520	33	32
620	4	10
720	36	34
820	39	39
920	47	49
1020	47	50
1120	32	32
1220	20	20
1320	12	8
1420	0	<8
1520	8	8
1620	−9	9
1720	−25	26
1820	−19	24
1920	−28	30
021	−15	17
121	−10	14
221	5	<8
321	8	<8
421	−13	8
521	4	<8
621	−6	9
721	−4	8
821	−3	<8
921	3	<8
1021	−4	9
1121	3	<8
1221	6	<8
1321	−2	<8
1421	8	8
1521	−2	<8
1621	−2	<8
1721	2	<8
1821	7	<8
1921	−1	<8
2021	−4	<8
2121	2	<8
$\bar{1}21$	−4	<8
$\bar{2}21$	33	35
$\bar{3}21$	−34	37
$\bar{4}21$	−8	<8
$\bar{5}21$	4	8
$\bar{6}21$	12	13
$\bar{7}21$	4	8
$\bar{8}21$	−13	13
$\bar{9}21$	5	<8
$\overline{10}21$	−2	<8
$\overline{11}21$	0	<8
$\overline{12}21$	0	<8
$\overline{13}21$	1	<8
$\overline{14}21$	−2	<8
$\overline{15}21$	1	<8
$\overline{16}21$	−8	11
022	11	15
122	−7	11
222	0	<8
322	21	25
422	24	21
522	24	30
622	70	64
722	44	46
822	29	27
922	24	16
1022	−5	9
1122	−6	12
1222	−12	16
1322	−20	21
1422	−23	25
1522	−29	29
1622	−22	20
1722	−10	7
1822	−8	<8
1922	0	<8
2022	5	<8
$\bar{1}22$	−16	7
$\bar{2}22$	−36	27
$\bar{3}22$	−35	37
$\bar{4}22$	−63	61
$\bar{5}22$	−45	45
$\bar{6}22$	−30	32
$\bar{7}22$	−14	15
$\bar{8}22$	−8	<8
$\bar{9}22$	8	<8
$\overline{10}22$	13	12
$\overline{11}22$	33	30
$\overline{12}22$	32	32
$\overline{13}22$	34	35
$\overline{14}22$	34	32
$\overline{15}22$	0	<8
$\overline{16}22$	7	<8
$\overline{17}22$	1	<8
$\overline{18}22$	−6	<8
$\overline{19}22$	−2	<8
$\overline{20}22$	−6	6
$\overline{21}22$	−10	9
$\overline{22}22$	−10	8
$\overline{23}22$	−7	9
023	19	17
123	3	<8
223	8	<8
323	−31	25
423	10	8
523	9	13
623	4	10
723	2	<8
823	−16	11
923	11	11
$\bar{1}23$	−2	<8
$\bar{2}23$	−32	29
$\bar{3}23$	10	<8
$\bar{4}23$	8	8
$\bar{5}23$	0	<8
$\bar{6}23$	0	<8
$\bar{7}23$	−5	<8
$\bar{8}23$	−3	<8
$\bar{9}23$	1	<8
$\overline{10}23$	0	<8
$\overline{11}23$	14	15
$\overline{12}23$	−15	13
$\overline{13}23$	−4	<8
$\overline{14}23$	5	<8
$\overline{15}23$	1	<8
$\overline{16}23$	8	8
$\overline{17}23$	−13	12
024	2	<8
124	27	18
224	33	29
324	29	25

CALCULATED AND OBSERVED STRUCTURE FACTORS

hkl	$F_{\text{calc.}}$	$F_{\text{obs.}}$
424	32	25
524	24	16
624	1	<8
724	1	<8
824	7	<8
924	−10	<8
1024	1	<8
1124	−9	8
1224	−23	13
1324	−17	11
1424	−15	9
1524	−14	8
1624	−4	<8
1724	−4	<8
1824	0	<8
1924	2	<8
$\bar{1}24$	1	<8
$\bar{2}24$	−15	16
$\bar{3}24$	−21	22
$\bar{4}24$	−28	20
$\bar{5}24$	−32	26
$\bar{6}24$	−29	24
$\bar{7}24$	−31	26
$\bar{8}24$	−19	10
$\bar{9}24$	0	<8
$\overline{10}24$	7	9
$\overline{11}24$	−5	<8
$\overline{12}24$	15	15
$\overline{13}24$	4	<8
$\overline{14}24$	9	<8
$\overline{15}24$	27	21
$\overline{16}24$	18	15
$\overline{17}24$	15	12
$\overline{18}24$	10	8
$\overline{19}24$	3	<8
$\overline{20}24$	3	<8
$\overline{21}24$	−3	<8
$\overline{22}24$	−7	9
$\overline{23}24$	−7	8
$\overline{24}24$	−9	9
$\overline{25}24$	−8	8
025	−7	7
125	0	<8
225	−4	<8
325	12	8
425	−5	<8
525	−12	8
625	2	<8
725	5	6
825	12	8
$\bar{1}25$	−8	8
$\bar{2}25$	4	<8
$\bar{3}25$	7	<8
$\bar{4}25$	−4	<8
$\bar{5}25$	0	<8
$\bar{6}25$	−16	9
$\bar{7}25$	5	<8
$\bar{8}25$	7	<8
$\bar{9}25$	3	<8
$\overline{10}25$	−2	<8
$\overline{11}25$	−18	9
$\overline{12}25$	−14	11
026	24	19
126	26	20
226	21	17
326	21	14
426	10	10
526	7	7
626	4	<8
726	−7	<8
826	−20	14
926	−22	17
1026	−23	21
1126	−21	17
1226	2	<8
1326	−7	<8
$\bar{1}26$	19	17
$\bar{2}26$	14	12
$\bar{3}26$	4	<8
$\bar{4}26$	2	<8
$\bar{5}26$	−6	6
$\bar{6}26$	−14	13
$\bar{7}26$	−19	16
$\bar{8}26$	−20	24
$\bar{9}26$	−38	32
$\overline{10}26$	−28	28
$\overline{11}26$	−16	17
$\overline{12}26$	−16	8
$\overline{13}26$	5	8
$\overline{14}26$	8	11
$\overline{15}26$	8	9
$\overline{16}26$	10	9
$\overline{17}26$	13	12
$\overline{18}26$	12	13
$\overline{19}26$	12	12
$\overline{20}26$	6	7
028	10	8
128	2	<8
228	−2	<8
328	−6	6
428	−9	7
528	−12	9
628	−12	12
728	−11	9
$\bar{1}28$	12	8
$\bar{2}28$	18	13
$\bar{3}28$	21	15
$\bar{4}28$	18	13
$\bar{5}28$	9	8
$\bar{6}28$	8	7
$\bar{7}28$	−1	<8
$\bar{8}28$	−10	17
$\bar{9}28$	6	8
$\overline{10}28$	−6	<8
$\overline{11}28$	−8	8
$\overline{12}28$	−8	8
$\overline{13}28$	−13	11
$\overline{14}28$	−10	9
$\overline{15}28$	−6	<8
$\overline{16}28$	−4	<8
$\overline{17}28$	−2	<8
$\overline{18}28$	−4	<8
130	1	<8
230	11	8
330	18	10
430	15	15
530	45	37
630	30	21
730	17	11
830	10	8
930	4	<8
1030	−4	<8
1130	−16	15
1230	−18	18
1330	−21	18
1430	−25	23
1530	−25	20
1630	−2	<8
031	−3	<8
131	−14	13
231	−3	<8
331	13	9
531	−4	<8
431	−3	<8
631	−2	<8
731	−4	<8
831	9	11
931	2	<8
1031	−4	<8
1131	0	<8
1231	−1	<8
$\bar{1}31$	8	<8
$\bar{2}31$	5	<8

CALCULATED AND OBSERVED STRUCTURE FACTORS

hkl	$F_{\text{calc.}}$	$F_{\text{obs.}}$
$\bar{3}31$	14	12
$\bar{4}31$	−3	<6
$\bar{5}31$	−4	<6
$\bar{6}31$	−2	<6
$\bar{7}31$	5	7
$\bar{8}31$	6	5
$\bar{9}31$	−4	<8
$\overline{10}31$	−3	<8
$\overline{11}31$	0	<8
$\overline{12}31$	7	<8
$\overline{13}31$	2	<8
$\overline{14}31$	−2	<8
$\overline{15}31$	−2	<8
032	54	48
132	38	31
232	39	31
332	38	32
432	36	34
532	10	10
632	−9	8
732	9	8
832	−11	8
932	−11	8
1032	−17	16
1132	−26	23
1232	−25	21
1332	−18	17
1432	−12	8
1532	−2	<8
1632	−7	<8
1732	−4	<8
1832	7	<8
1932	6	<8
$\bar{1}32$	9	15
$\bar{2}32$	7	<8
$\bar{3}32$	−24	31
$\bar{4}32$	−31	39
$\bar{5}32$	−13	15
$\bar{6}32$	−37	34
$\bar{7}32$	−38	42
$\bar{8}32$	−37	39
$\bar{9}32$	−26	31
$\overline{10}32$	−10	8
$\overline{11}32$	−4	<8
$\overline{12}32$	−4	<8
$\overline{13}32$	11	8
$\overline{14}32$	−13	12
$\overline{15}32$	16	8
$\overline{16}32$	28	26
$\overline{17}32$	16	14
$\overline{18}32$	21	23
$\overline{19}32$	10	19
$\overline{20}32$	10	9
$\overline{21}32$	0	<8
034	17	17
134	25	20
234	21	13
334	0	<8
434	−7	7
534	−14	7
634	−4	<8
734	−38	29
834	−34	34
934	−29	29
1034	−28	16
1134	2	<8
1234	−6	<8
1334	−3	<8
1434	4	<8
1534	6	<8
1634	13	11
1734	15	10
1834	8	6
$\bar{1}34$	33	28
$\bar{2}34$	30	28
$\bar{3}34$	30	35
$\bar{4}34$	27	30
$\bar{5}34$	11	13
$\bar{6}34$	1	<8
$\bar{7}34$	−6	7
$\bar{8}34$	−16	14
$\bar{9}34$	−8	14
$\overline{10}34$	−39	39
$\overline{11}34$	−36	42
$\overline{12}34$	−29	30
$\overline{13}34$	−26	20
$\overline{14}34$	9	<8
$\overline{15}34$	4	<8
$\overline{16}34$	−2	<8
$\overline{17}34$	7	9
$\overline{18}34$	8	9
$\overline{19}34$	13	13
$\overline{20}34$	9	9
$\overline{21}34$	7	<8
036	1	<8
136	−6	6
236	−16	11
336	−18	13
436	−16	14
536	−20	12
636	−15	<8
736	−5	<8
836	−3	<8
$\bar{1}36$	8	8
$\bar{2}36$	11	9
$\bar{3}36$	15	13
$\bar{4}36$	21	13
$\bar{5}36$	22	11
$\bar{6}36$	19	12
$\bar{7}36$	5	8
$\bar{8}36$	1	<8
$\bar{9}36$	1	<8
$\overline{10}36$	−5	<8
$\overline{11}36$	4	<8
$\overline{12}36$	−5	<8
$\overline{13}36$	−10	8
$\overline{14}36$	−16	10
$\overline{15}36$	−15	10
$\overline{16}36$	−5	<8
038	−3	<8
138	−4	<8
$\bar{1}38$	−2	<8
$\bar{2}38$	2	<8
$\bar{3}38$	−2	<8
$\bar{4}38$	4	<8
$\bar{5}38$	8	8
$\bar{6}38$	10	8
$\bar{7}38$	3	<8
$\bar{8}38$	12	8
$\bar{9}38$	13	10
$\overline{10}38$	5	10
$\overline{11}38$	3	8
040	29	23
140	39	30
240	31	27
340	22	15
440	−4	<8
540	19	14
640	−1	<8
740	−17	9
840	−20	16
940	−22	17
1040	−33	34
1140	−21	22
1240	−13	18
1340	−6	8
042	9	8
142	−2	<8
242	−6	10
342	−13	9
442	−9	8
542	−10	13
642	−44	36
742	−28	28

CALCULATED AND OBSERVED STRUCTURE FACTORS

hkl	$F_{\text{calc.}}$	$F_{\text{obs.}}$
842	−16	14
942	−10	8
1042	3	<8
1142	−3	<8
1242	6	<8
$\bar{1}42$	14	9
$\bar{2}42$	18	14
$\bar{3}42$	23	20
$\bar{4}42$	27	24
$\bar{5}42$	26	24
$\bar{6}42$	18	16
$\bar{7}42$	10	8
$\bar{8}42$	3	<8
$\bar{9}42$	−10	8
$\overline{10}42$	−8	8
$\overline{11}42$	−13	10
$\overline{12}42$	−19	13
044	−2	<8
144	−14	9
244	−23	14
344	−17	16
444	−22	14
544	−17	8
644	2	<8
744	−1	<8
844	−4	<8
944	2	<8
1044	0	<8
$\bar{1}44$	−2	<8
$\bar{2}44$	8	7
$\bar{3}44$	7	9
$\bar{4}44$	18	15
$\bar{5}44$	25	16
$\bar{6}44$	16	14
$\bar{7}44$	13	8
$\bar{8}44$	6	8
$\bar{9}44$	6	8
$\overline{10}44$	−2	<8
$\overline{11}44$	−4	<8
$\overline{12}44$	−7	8
046	−8	12
146	−13	11
246	−10	8
$\bar{1}46$	−13	11
$\bar{2}46$	−9	9
$\bar{3}46$	−9	7
$\bar{4}46$	0	<8
$\bar{5}46$	7	<8
$\bar{6}46$	5	<8
$\bar{7}46$	8	14
$\bar{8}46$	10	16

hkl	$F_{\text{calc.}}$	$F_{\text{obs.}}$
041	5	<8
141	−5	<8
241	0	<8
341	9	9
441	−6	<8
541	−1	<8
$\bar{1}41$	−8	<8
$\bar{2}41$	4	<8
$\bar{3}41$	0	<8
$\bar{4}41$	2	<8
150	4	<8
250	−10	8
350	−7	8
450	−20	14
550	−23	14
650	−13	9
750	−9	8
850	−7	8
950	−4	<8
1050	1	<8
1150	8	<8
052	−18	18
152	−28	23
252	−18	19
352	−20	15
452	−14	11
552	−3	<8
652	−4	<8
752	1	<8
852	3	<8
$\bar{1}52$	−8	<8
$\bar{2}52$	−2	<8
$\bar{3}52$	8	8
$\bar{4}52$	7	8
$\bar{5}52$	8	9
$\bar{6}52$	20	15
$\bar{7}52$	18	17
$\bar{8}52$	16	16
$\bar{9}52$	11	11
$\overline{10}52$	2	<8
$\overline{11}52$	6	<8
054	−11	8
154	−8	8
254	−9	8
354	−5	<8
454	4	<8
554	1	<8
654	8	<8
754	15	10

hkl	$F_{\text{calc.}}$	$F_{\text{obs.}}$
854	16	14
954	14	12
1054	10	20
$\bar{1}54$	−15	12
$\bar{2}54$	−18	16
$\bar{3}54$	−16	15
$\bar{4}54$	−11	9
$\bar{5}54$	−5	<8
$\bar{6}54$	−6	<8
$\bar{7}54$	4	<8
$\bar{8}54$	4	<8
$\bar{9}54$	8	<8
060	−22	20
160	−11	14
260	−11	10
360	−5	6
460	3	<8
560	−3	<8
660	4	<8
760	8	9
860	11	11
960	10	13
1060	9	11
062	4	<8
162	−1	<8
262	−4	<8
362	6	<8
462	0	<8
562	13	9
662	13	9
762	8	8
$\bar{1}62$	−7	<8
$\bar{2}62$	−7	<8
$\bar{3}62$	−13	10
$\bar{4}62$	−14	11
$\bar{5}62$	−7	7
064	−1	<8
164	2	<8
264	12	8
364	4	<8
464	5	<8
$\bar{1}64$	−2	<8
$\bar{2}64$	−3	<8
$\bar{3}64$	−3	<8
$\bar{4}64$	−1	<8
$\bar{5}64$	−11	8
$\bar{6}64$	−7	6
$\bar{7}64$	−4	<8