

X 23/8

235



✓
Keli
22-9-95

TH-815

VERIFIED
1981
INL...
✓

66114
19.65

VERIFIED
INL... *[Signature]* ...

The Crystal Structures of β -Alanine
and some of its metal complexes

VERIFIED
1983
INL... *[Signature]* ...

I take this opportunity to express my
of gratitude to Dr. A.M.Pant for his able
during the course of this work. I am thankful to
Thesis submitted for the Degree
Dr. A.B.Biswas for his of interest in this work. I

would also like to thank my husband Dr. S.S.Jose for
Doctor of Philosophy
my valuable suggestions in connection with the thesis
in the
University of Poona, National Chemical

Laboratory, for permission to submit this work in the

04:548-73
JOS

by

Parimala Jose, M.Sc., B.T.

VERIFIED
1977
INL... *[Signature]* ...

Physical Chemistry Division
National Chemical Laboratory
Poona (India)

1964

66114
19.65
[Signature]

A C K N O W L E D G E M E N T S

I take this opportunity to express my deep sense of gratitude to Dr. L.M.Pant for his able guidance during the course of this work. I am thankful to Dr. A.B.Biswas for his keen interest in this work. I would also like to thank my husband Dr. C.I.Jose for many valuable suggestions in connection with the thesis

I am grateful to the Director, National Chemical Laboratory, for permission to submit this work in the form of a thesis

Poona
1964

Parimala Jose

CONTENTS

<u>CHAPTER</u>	<u>Page</u>
Abstract	iv
List of Diagrams	vii
I Introduction	1
II Experimental details of β -Alanine	6
Measurement of Intensities	8
Correction for spot extension	8
Scale Factor and Temperature Factor	12
Determination of Space Group	15
III Patterson Projections, Harker Sections and Trial Structure of β -Alanine	17
Trial Structure	26
IV Refinement of Atomic parameters of β -Alanine	31
Structure Factor Formulae	32
The (001) electron density projection	33
The (100) electron density projection	36
Refinement of atomic co-ordinates by the method of least squares	36
Refinement of x, y and z parameters using general reflexions	43

IV (Continued)	
Estimation of Standard Deviations	46
V Results and Discussion of β -Alanine	
Structure	48
Molecular Structure	49
Crystal Structure	52
VI The Structures of Nickel and Cobalt complexes	56
A. Experimental details	
Nickel β -Alanine dihydrate	
Scale Factor and Temperature factor	59
Correction for dispersion	60
Cobalt β -Alanine dihydrate	61
B. Patterson projections of Nickel β -Alanine	65
Refinement of Nickel β -Alanine dihydrate structure	65
(001) electron density projection	66
Refinement of atomic parameters by difference syntheses	67
Refinement of thermal parameters	72
(001) difference electron density projection	74
(100) electron density projection	78
(100) difference electron density projection	78
Refinement of thermal parameters for the (100) projection	79

VI (Continued)		
	Refinement of (010) projection	82
	C. Refinement of Cobalt β -Alanine dihydrate structure	85
VII	Results and Discussion of the Nickel and Cobalt β -Alanine complexes	90
	Results	91
	Discussion	
	Molecular Structure	93
	Crystal Structure	95
	APPENDIX : Observed and Calculated Structure Factors	101
	I β -Alanine	102
	II Nickel β -Alanine	109
	III Cobalt β -Alanine	115
	REFERENCES	121

A B S T R A C T

In the present studies the crystal and molecular structures of β -Alanine and its Nickel and Cobalt complexes have been determined by X-ray diffraction.

β -Alanine, molecular formula $\text{NH}_2\text{CH}_2\text{CH}_2\text{COOH}$ crystallises in the orthorhombic system with 8 molecules in a unit cell. The unit cell dimensions are

$$a = 9.865\text{\AA}, \quad b = 13.81\text{\AA} \quad \text{and} \quad c = 6.07\text{\AA}$$

The systematic absences establish the space group as Pbc_a. The trial structure was fixed from the three Harker lines $P(\frac{1}{2}0)$, $P(\frac{1}{2}0w)$ and $P(0v\frac{1}{2})$. The structure was refined by a few cycles of difference Fourier syntheses followed by a few cycles of least square refinements of (001) and (100) projections and finally by a least squares refinement using all the general reflexions.

The bond lengths and bond angles within the β -Alanine molecule are close to the expected values. The molecular configuration of β -Alanine in its complexes with Nickel and Cobalt and in the free state is the same, namely, the gauche form.

The amino nitrogen forms three strong hydrogen bonds to carboxylic oxygens in three different adjacent molecules. These bonds are nearly tetrahedrally disposed

with respect to the C-N bond. The nearly tetrahedral arrangement of the hydrogen bonds around nitrogen implies that β -Alanine molecules in the crystal exist in the zwitterion form. The N-H...O hydrogen bonds tie the molecules into infinite double layers parallel to (010) plane. The neighbouring double layers are linked by Van der Waal's bonds.

The complexes of Nickel and Cobalt with β -Alanine crystallise as dihydrates in the triclinic system and are isomorphous. The unit cell dimensions are

Nickel β -Alanine dihydrate, $\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{COO})_2 \cdot 2\text{H}_2\text{O}$

$a = 8.48$	$b = 6.77$	$c = 4.93\text{\AA}$
$\alpha = 103.0^\circ$	$\beta = 95.2^\circ$	$\gamma = 102.3^\circ$

Cobalt β -Alanine dihydrate, $\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{COO})_2 \cdot 2\text{H}_2\text{O}$

$a = 8.54$	$b = 6.79$	$c = 4.96\text{\AA}$
$\alpha = 103.3^\circ$	$\beta = 95.8^\circ$	$\gamma = 101.3^\circ$

The space group is $P\bar{1}$ and there is one molecule per unit cell.

The structure of Nickel β -Alanine dihydrate was determined from the three Patterson projections. The refinement was done for all the three projections by repeated difference syntheses. Individual isotropic temperature factors for all atoms were obtained by the least squares method during the final stages of refinement.

Refinement of the atomic co-ordinates of Cobalt β -Alanine was started from the final atomic co-ordinates

of the Nickel complex. Refinement of the structure was done by ($F_o - F_c$) syntheses and using individual temperature factors for each atom.

In these structures the metal ion is surrounded by two carboxylic oxygen atoms, two nitrogens (one from each β -alanine molecule) and two water molecules. They form a slightly distorted octahedron around the metal. The chelation of the amino acid molecules to the metal is of the trans form and the metal ion takes part in the formation of a six membered ring in both the structures.

Nickel and cobalt β -Alanine dihydrate units are held by N-H...O and O-H...O hydrogen bonds in a stable layer structure parallel to (100) plane. Larger thermal vibration amplitudes normal to the layers of molecules are indicated by the contours around nickel and the oxygen atoms in the difference map and also by the temperature factors for the three zones. The stacking of the layers normal to (100) plane is governed by Van der Waal's bonds.

LIST OF DIAGRAMS

		<u>Facing</u> <u>page No.</u>
Fig. II-1	Wilson's graphs for scale factors and temperature factors	13
Fig. II-2	Wilson's graphs for scale factors and temperature factors	15
Fig. III-1	Schematic diagram of the von Eller Photosommateur	20
Fig. III-2	(001) Patterson projection of β -Alanine	21
Fig. III-3	(100) Patterson projection of β -Alanine	21
Fig. III-4	Symmetry elements for the space group Pbc _a	23
Fig. III-5	The Harker Section $P(uv\frac{1}{2})$	24
Fig. III-6	The Harker Section $P(u\frac{1}{2}w)$	24
Fig. III-7	The Harker Section $P(\frac{1}{2}vw)$	24
Fig. III-8	$P(ov\frac{1}{2})$ Harker line	26
Fig. III-9	Line Fourier Synthesis $\rho(o\gamma o)$	26
Fig. III-10	$P(u\frac{1}{2}o)$ Harker line	28
Fig. III-11	Showing two orientations of β -Alanine molecule	29
Fig. III-12	$P(\frac{1}{2}ow)$ Harker line	29
Fig. IV-1	(001) electron density projection of β -Alanine	34
Fig. IV-2	(100) electron density projection of β -Alanine	36
Fig. V-1	Bond lengths and bond angles in β -Alanine	48
Fig. V-2	β -Alanine structure projected on (001)	52

		Facing Page no.
Fig. V-3	β -Alanine structure projected on (100)	52
Fig. VI-1	Wilson's graphs for scale factors and temperature factors (Nickel β -Alanine. $2H_2O$)	59
Fig. VI-2	Wilson's graphs for scale factors and temperature factors (Cobalt β -Alanine. $2H_2O$)	63
Fig. VI-3	Sharpened (001) Patterson projection of Nickel β -Alanine dihydrate	65
Fig. VI-4	Sharpened (100) Patterson projection of Nickel β -Alanine. $2H_2O$	65
Fig. VI-5	(001) electron density projection showing bond lengths and bond angles in Nickel β -Alanine	66
Fig. VI-6	(001) difference electron density projection	74
Fig. VI-7	(100) electron density projection	78
Fig. VI-8	(100) difference electron density projection	80
Fig. VII-1	Bond lengths and bond angles in Cobalt β -Alanine	90
Fig. VII-2	Structure projected on (001)	95
Fig. VII-3	Structure projected on (100)	95

CHAPTER - I

INTRODUCTION

The discovery by Laue, Friedrich and Knipping that a crystal could behave as a three dimensional diffraction grating led to the use of X-rays for studying the internal structure of crystals. The diffraction spots in X-ray photographs were explained by W.L.Bragg as arising due to the reflexion of X-rays by various sets of crystal planes. The first crystals to be analysed by him were those of alkali halides.

W.H.Bragg (1915) suggested that since a crystal is periodic in three dimensions it can be represented by a Fourier Series in which the coefficient of any term will be proportional to the structure amplitude to which it corresponds. This suggested the possibility of determining the crystal structures by summing up the Fourier series using experimentally observed structure amplitudes. However, the series cannot be summed directly, since experimentally, only the amplitudes of the various reflexions can be determined and not their phases. The usual method of obtaining the phases is by trial and error. In this process, a trial structure which seems likely is assumed and for the assumed positions of the atoms the structure amplitudes and hence the theoretical

intensities are calculated. These are then compared to the observed ones. A close correlation of the calculated and observed structure amplitudes would show the correctness of the assumption.

The two dimensional Fourier Series took form in 1925. This represents the projection of a structure on to a plane thus reducing considerably the work involved in summing a triple Fourier series. The first two dimensional Fourier were the three principal plane projections of diopside (Bragg, 1929b). In the next few years the two dimensional Fourier Series played an important role in adding geometrical precision to the molecules of organic chemistry. Two dimensional Fourier projections demand a large number of measurements since all the reflexions around a zone are needed upto a maximum $\sin \theta$ value which decides the resolution of the Fourier map. Weissenberg (1924) introduced the moving film method of recording the reflexions on diffraction photographs. and Bernal (1927) put forward a simplified method of interpreting ^{rotation} these photographs based on Ewald's concept of the reciprocal lattice.

A.L.Patterson in 1934, developed a method of obtaining information about interatomic distances in crystals by using a Fourier series whose coefficients are the observed intensities (corrected for certain geometrical factors). The result is a map, not of the atomic positions,

but showing the superposition of all the interatomic vectors in the crystal. The 'Patterson' was the first of a series of discoveries about the ways Fourier Series can be manipulated for the purposes of X-ray analysis.

Harker (1936) pointed out that much useful information about the atomic coordinates is concentrated in certain planes of the three dimensional Patterson function. The use of the symmetry of the crystal leads to these plane sections.

The early structural work which formed the basis of the study of organic crystals was on diamond and graphite. These structures proved to be the prototypes for the atomic arrangements present in aliphatic and aromatic compounds respectively. Based on these structures the arrangement and general orientation of the molecules in the naphthalene and anthracene crystals (Bragg 1921, 1922) were correctly deduced. Long chain compounds which, with the structure of diamond provided the essential basis to the understanding of the structures of aliphatic compounds, were studied by Muller and Shearer and others. The outstanding example of a complete structure determination at that time was hexamethyl benzene by K. Lonsdale (1928, 1929).

With the development of the Fourier Series and simplified computational methods Robertson (1933) completely determined the structures of naphthalene and anthracene and a large number of other molecules. A

land mark was the determination of Phthalocyanine structure (Robertson and Woodward 1937) with 60 parameters, made possible by the substitution of a heavy atom in the centre of the group. Accurate determination of bond lengths was now possible and ^{led to} their interpretation in terms of the nature of chemical bond.

From 1939 onwards a systematic survey of related compounds in the field of amino acids and simple peptides was carried out mainly in the Pasadena School. These results form the basis of helical models of protein structure proposed by Pauling (1951).

In recent years the attention of the crystallographers has been focussed on the elucidation of highly complex structures on the one hand and more accurate refinements of relatively simple structures on the other. Among the complex structures could be cited those of Penicillin by Crowfoot, Bunn and others (1952), Vitamin B₁₂ (Hodgkin et al, 1957) and the proteins myoglobin and haemoglobin. An example of the second is the elaborate refinement and the interpretation of results in terms of thermal vibration of atoms carried out on anthracene and naphthalene by Cruickshank (1956, 1957).

Amino acids are an important class of compounds having a dipolar structure and are constituents of biological materials. The α -amino acids have been extensively studied as they are related to proteins. The β -amino acids, however, have received little attention.

β -Alanine (β -Amino propionic acid) is the simplest amino acid with the amino group on the β -Carbon atom. It is found free in nature and is a constituent of Pantothenic acid and coenzyme A.

In the present work the crystal and molecular structures of β -Alanine and its Nickel and Cobalt complexes have been determined. The structures of the complexes were investigated in order to get some idea of the molecular geometry of β -Alanine, as an earlier attempt to solve its structure by trial and error and direct methods was not successful. In combination with Harker synthesis, however, the structure of the free amino acid has been solved.

CHAPTER - II

EXPERIMENTAL

β -Alanine crystals were grown from aqueous solution of a sample of B.D.H. Laboratory reagent as colourless plates parallel to (100) face. The preliminary Laue photographs showed that the crystals belong to the orthorhombic system. The axis normal to the plate was found to be the longest axis; to obtain diffraction photographs along the other two axes the crystals were cut into suitable sizes. Accurate setting of the crystal was done by the method of double oscillation (Davies, 1950).

Preliminary values of unit cell dimensions were obtained from rotation photographs taken with CuK_α radiation. Accurate determination of axial lengths was carried out from high angle spots in equatorial Weissenberg photographs taken around the a and c axes.

The reflexions used were

10, 0, 0; 12, 1, 0; 12, 2, 0 and 12, 5, 0 for the a axis
0, 16, 0; 2, 17, 0 and 4, 17, 0 for the b axis
and 006, 027, 047, 087 for the c axis.

The approximate values of a , b and c obtained from 10, 0, 0 and 0, 16, 0 and 006 respectively were used to calculate a , b and c from the hko , okl reflexions by means of the expressions

$$a = \frac{\lambda}{2} \sqrt{h^2 + \frac{a^2}{b^2} k^2} \operatorname{cosec} \theta$$

$$b = \frac{\lambda}{2} \sqrt{k^2 + \frac{b^2}{a^2} h^2} \operatorname{cosec} \theta$$

and

$$c = \frac{\lambda}{2} \sqrt{l^2 + \frac{c^2}{b^2} k^2} \operatorname{cosec} \theta$$

where θ is the Bragg angle.

The mean values obtained from the above reflexions are $a = 9.865 \text{ \AA}$, $b = 13.81 \text{ \AA}$ and $c = 6.07 \text{ \AA}$.

The unit cell dimensions reported by McCrone and KRc. Jr. (1950) are $a = 9.86 \text{ \AA}$, $b = 13.81 \text{ \AA}$ and $c = 6.09 \text{ \AA}$.

Density was measured by flotation in a mixture of Ethylene dichloride and Ethylene dibromide at 24°C . The observed value is 1.423 g/c.c. while that calculated for 8 units of $\text{NH}_2\text{CH}_2\text{CH}_2\text{COOH}$ per cell is 1.431 g.cm^{-3} . The observed density (pycnometer) reported by McCrone and KRc. Jr. is 1.412 g/c.c. The crystals show cleavage parallel to (010).

The linear absorption coefficient of β -Alanine for CuK_α radiation, given by the expression

$$\mu = \rho \frac{\sum n \mu_a}{M}$$

where ρ is the density, μ_g the gram atomic absorption coefficient and M the molecular weight, was found to be 11.5 cm^{-1} . The optimum thickness $t = \frac{2}{\mu}$ was 0.174 cm. The dimensions of the crystals used to collect the three dimensional intensity data were 0.3 mm along a axis, 0.5 mm along b axis and 0.6 mm along c axis.

Three dimensional intensity data were obtained from equi-inclination Weissenberg photographs taken with CuK_{α} radiation for all layer lines having inclination angle of less than 30° and using the multiple film technique. With the crystal rotated around c axis data were collected for 5 layers including the zero layer and with the crystal rotated around a axis for seven layers including the zero layer. Short exposure ($1\frac{1}{2}$ hr.) Weissenberg photographs were taken to estimate the intensities of strong reflexions. 247 independent reflexions were observed out of the possible 917 within the CuK_{α} limiting sphere. The intensities were estimated separately for the two sets of data visually, by comparison with intensity scales prepared with the same crystals using a pack of three films.

Correction for spot extension in upper level Weissenberg photographs

Intensities of the spots on higher layer Weissenberg photographs were estimated from the extended spots only and corrected for the effect of spot extension (Phillips, 1954). In these photographs, corresponding reflexions are

extended on one side and contracted on the other, the degree of distortion varying from reflexion to reflexion.

The variation in spot area arises from the divergence of the X-ray beam incident on the crystal. Small elements of length in the crystal (by supposition that the crystal is divided into small elements of length) receive X-rays at angles of incidence which depend on their position in the crystal. All do not reflect at the same instant but they are brought into the reflecting position as the crystal is rotated and in fact the spots on the upper level photographs grow from one end. During the time taken to complete a reflexion in this way the film has moved a distance depending on the camera constants. The reflexion spots on the film are therefore, contracted or extended according as whether the film motion is in the same direction as the spot growth or in the opposite direction.

The fractional increase in the area of an extended reflexion spot is given by $W = \frac{A+\Delta A}{A}$ where A is the area of reflexion recorded without camera translation, (Phillips, 1956). When the distortions are small and $\frac{A+\Delta A}{A}$ is less than about 1.5, the correct intensity I can be calculated from the visually estimated intensities of extended ^{and contracted spots} spots by the relation

$$I = \frac{2I_E I_C}{I_E + I_C} \dots \dots \dots \text{II.1}$$

where I_E and I_C are the intensities of extended and

contracted spots respectively.

When the variation in the area is large the correct intensity is best obtained from the extended spots only by the expression

$$I = WI_E \dots \dots \dots \text{II.2}$$

Intensities of $1kl$ reflexions were estimated from both the contracted and extended spots as the extension was small and the relation II.1 was used to obtain the correct intensity. For the other layers intensities were estimated from the extended spots only and correction obtained from curves of constant W in reciprocal space given by Phillips (1956) was applied.

Lorentz and polarisation factors.

The relative intensity I , on an oscillation or Weissenberg photograph is given by

$$I \propto \frac{1 + \cos^2 2\theta}{\sin 2\theta} PAF^2 \dots \dots \dots \text{II.3}$$

where I is the integrated intensity, θ , the Bragg angle, F , the structure amplitude, A , the absorption factor. P is a factor that depends on the angle of inclination of the reflecting planes to the axis of rotation of the crystal, and $\frac{1 + \cos^2 2\theta}{\sin 2\theta}$ represents the Lorentz-polarisation (L_p) factor.
and becomes unity for zero layer photographs

The term $\frac{1 + \cos^2 2\theta}{2}$ is the polarisation factor which takes into account the partial polarisation of the reflected beam. This holds only if the incident beam is unpolarised which is generally true for the characteristic emission from an X-ray tube.

The Lorentz factor $\frac{1}{\sin 2\theta}$ expresses for rotating crystal photographs, the relative time any crystal plane spends within the narrow angular range over which the reflexion occurs. In terms of the reciprocal lattice each reciprocal lattice ^{point} has a finite size and as the reciprocal lattice rotates through the sphere of reflexion each point spends a finite time passing through the surface of the sphere. This factor varies with the distance of the reciprocal lattice point from the origin which in turn is related to the angle of reflexion. If ν is the angle which the line traced out by a reciprocal lattice point makes with the normal to the surface of the sphere of reflexion at the point where the reciprocal lattice point passes through the sphere, the ^{product of} Lorentz factor ^{and P, defined overleaf} $LP = \sec \nu$

In terms of the cylindrical co-ordinates ξ, ζ of the reciprocal lattice point

$$LP = (\xi \cos \theta)^{-1} \quad \dots \quad \text{II.4}$$

for equi-inclination Weissenberg setting.

For zero layer lines $\zeta = 0$ and $\xi = 2 \sin \theta$ ^{and P is unity so that} and the expression II.4 reduces to

$$L = (\sin 2\theta)^{-1}$$

Since the polarisation and Lorentz factors are both functions of θ they are combined in the form

$$\frac{\xi \cos \theta}{1 + \cos^2 2\theta}$$

Lp factor corrections were obtained from curves of constant $\frac{\xi \cos \theta}{1 + \cos^2 2\theta}$ in reciprocal space. (Cochran, 1948).

For the higher layer reflexions the height ξ of the layer was also taken into account.

The intensities (after correction for Lp factor) from different photographs were brought to the same scale by comparing the intensities of common reflexions.

Temperature factor and scale factor

The relative intensities were put on an absolute scale and the overall temperature factor B was determined by Wilson's (1942) statistical method. The reflexions were divided into groups lying between certain values of $\sin^2 \theta$. The mean value of the observed intensities $\langle I \rangle$ ($= \frac{\sum I}{n}$ where $\sum I$ denotes the sum of intensities in a certain range and n, the number of reflexions in that range) was evaluated over each range. The constant C which makes the average equal to $\sum f_n^2$ i.e. $C = \frac{\sum f_n^2}{\langle I \rangle}$ was found. $\sum f_n^2$ is the sum of scattering factors of atoms (at rest), the summation being done over all the atoms in the unit cell. McWeeny's (1951) values of scattering factors were used. $\log_e C$ was plotted against the mean value of $\frac{\sin^2 \theta}{\lambda^2}$ for each range: The slope of the line drawn through the plotted points gives the value of 2B. The intercept at $\sin \theta = 0$ gives the value of $\log_e C_0$ and

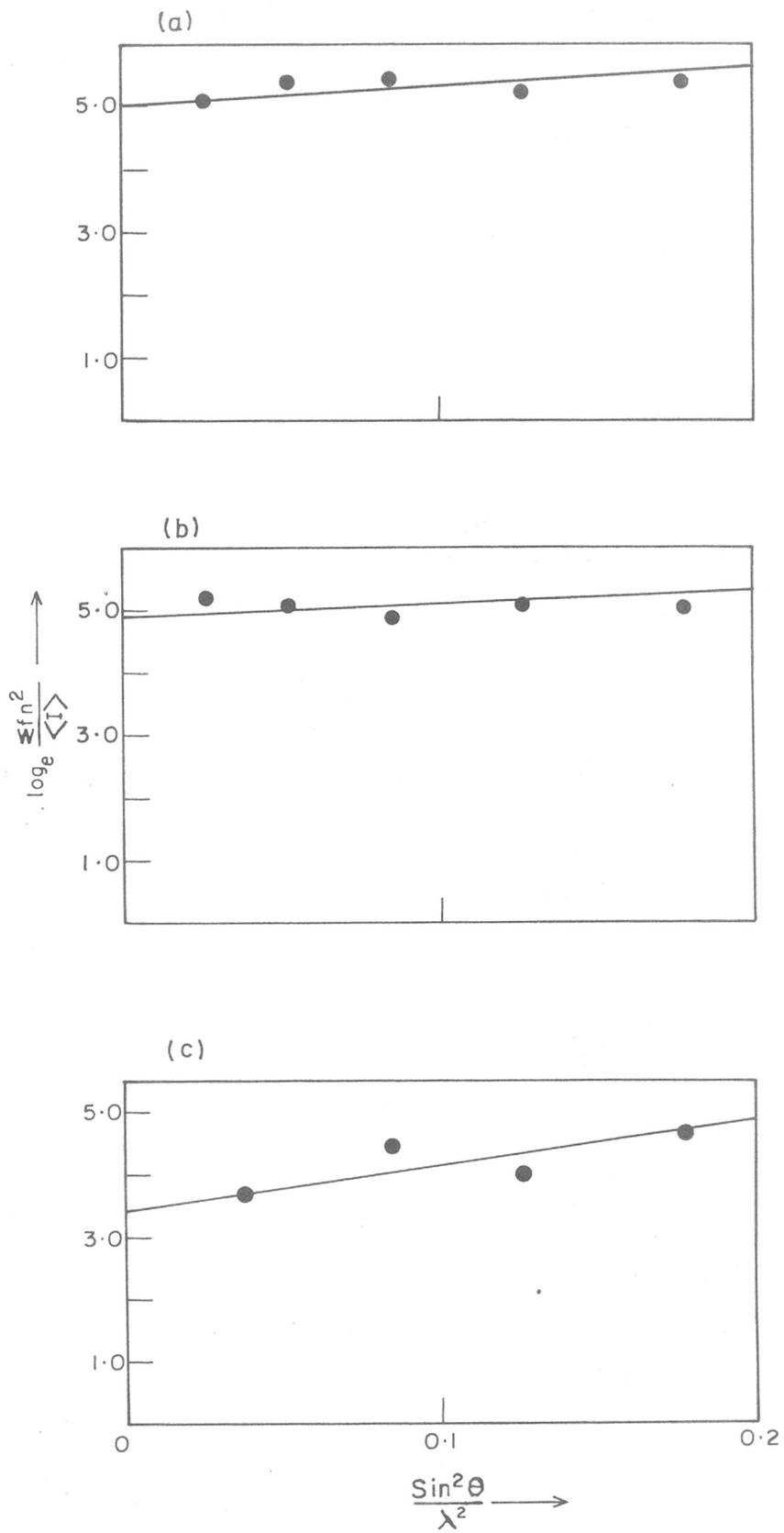


FIG. II-1 Wilson's graphs for scale factors and temp-factors.
 (a) hkl reflexions (b) okl reflexions (c) hko reflexions

hence C_0 , the scale factor.

The graphs of $\log_e C$ against $\frac{\sin^2 \theta}{\lambda^2}$ for hko, hk1, hk2 and okl reflexions are shown in figures II-1 and fig. II.2 and the corresponding data are given in table II.1

T A B L E II.1

Determination of temperature factor and scale factor of the hko reflexions

$\sin \theta$	$\frac{\sin^2 \theta}{\lambda^2}$	$\sum f_n^2$	$\langle I \rangle$	$C = \frac{\sum f_n^2}{\langle I \rangle}$	$\log_e C$
0.2-0.4	0.038	420.9	11.0	37.95	3.636
0.4-0.5	0.085	223.9	2.64	84.80	4.440
0.5-0.6	0.127	162.2	3.29	49.33	3.899
0.6-0.7	0.178	116.4	1.09	106.6	4.670

From the graph, scale factor = 5.6 (for 4 molecules in half unit cell);

$$2B = 6.8 \text{ \AA}^2$$

- - -

Determination of scale factor and temperature factor for hk1 reflexions

$\sin \theta$	$\frac{\sin^2 \theta}{\lambda^2}$	$\sum f_n^2$	$\langle I \rangle$	$C = \frac{\sum f_n^2}{\langle I \rangle}$	$\log_e C$
0.2-0.3	0.026	1331.2	8.118	164.0	5.100
0.3-0.4	0.052	882.4	4.00	220.6	5.396
0.4-0.5	0.085	447.8	1.909	234.6	5.458
0.5-0.6	0.127	324.4	1.717	188.9	5.241
0.6-0.7	0.178	232.8	1.053	221.1	5.399

From the graph, $2B = 3.6 \text{ \AA}^2$; scale factor, 12.2

Determination of scale factor and temperature factor
for okl reflexions

Sin θ	$\frac{\text{Sin}^2\theta}{\lambda^2}$	Σf_n^2	$\langle I \rangle$	$C = \frac{\Sigma f_n^2}{\langle I \rangle}$	$\log_e C$
0.2-0.3	0.026	1331.2	7.33	181.6	5.2017
0.3-0.4	0.052	882.4	5.23	168.8	5.1288
0.4-0.5	0.085	447.8	3.275	136.8	4.9186
0.5-0.6	0.127	324.4	1.954	166.0	5.1120
0.6-0.7	0.178	232.8	1.50	155.2	5.0448

From the graph $2B = 1.8\text{\AA}^2$; scale factor = 11.6

Scale factor and temperature factor for hk2
reflexions

sin θ	$\frac{\text{sin}^2\theta}{\lambda^2}$	Σf_n^2	$\langle I \rangle$	$C = \frac{\Sigma f_n^2}{\langle I \rangle}$	$\log_e C$
0.3-0.4	0.052	882.4	3.27	269.9	5.598
0.4-0.5	0.085	447.8	2.469	181.3	5.200
0.5-0.6	0.127	324.4	1.172	276.8	5.623
0.6-0.7	0.178	232.8	0.633	367.8	5.908

From the graph $2B = 3.2\text{\AA}^2$; scale factor = 13.5

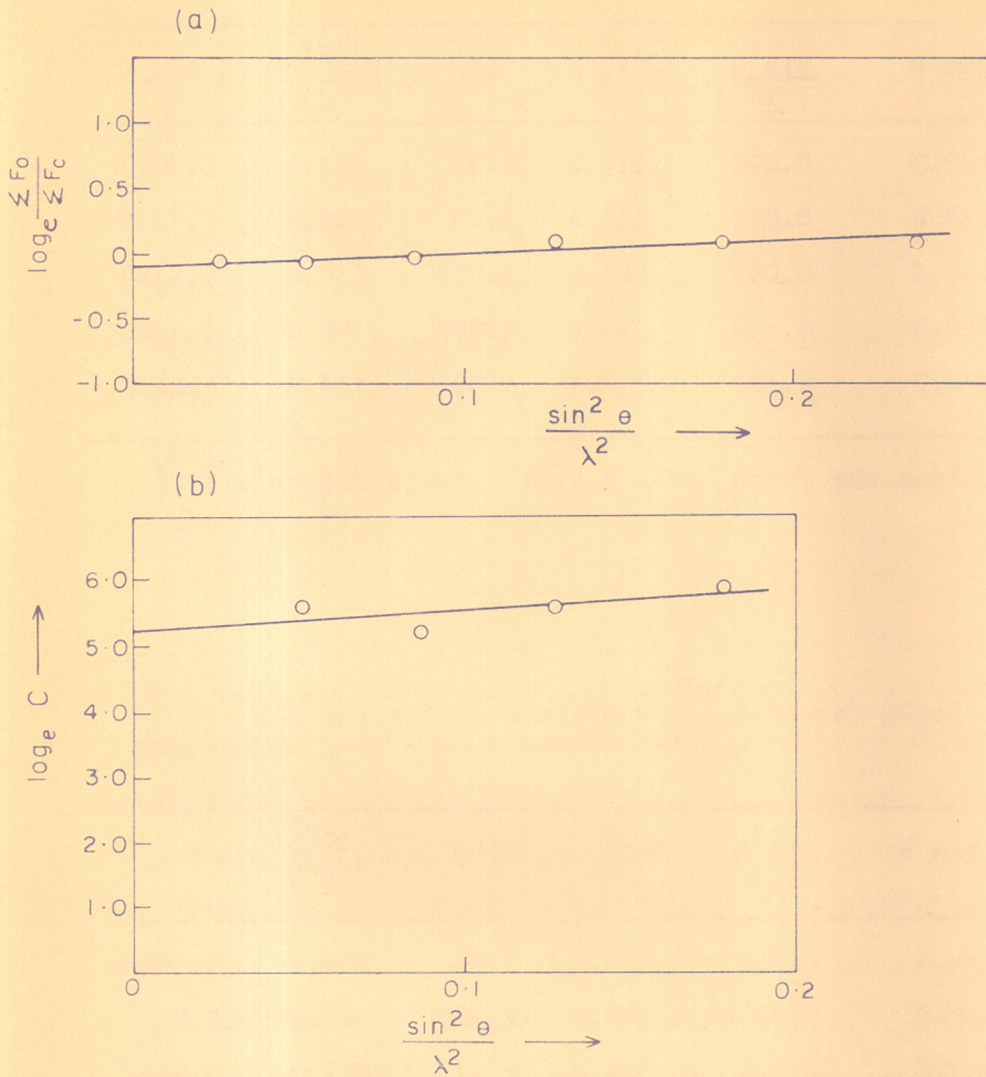


FIG. II-2. Wilson's graphs for scale factors and temperature factors

(a) hko reflexions using F_o and F_c ~~reflexions~~. (b) hk2 reflexions.

Scale factor and temperature factor for hko
reflexions using F_o and F_c

$\sin \theta$	$\frac{\sin^2 \theta}{\lambda^2}$	ΣF_o	ΣF_c	$C = \frac{\Sigma F_o}{\Sigma F_c}$	$\log_e C$
0.2-0.3	0.026	263	276	0.953	-0.0472
0.3-0.4	0.052	207	222	0.933	-0.0694
0.4-0.5	0.085	177	182	0.973	-0.0274
0.5-0.6	0.127	164	150	1.093	0.0891
0.6-0.7	0.178	168	157	1.07	0.0677
0.7-0.8	0.237	13	12	1.083	0.0799

From the graph $\Delta B = -1.0 \text{ \AA}^2$; Scale factor = 1.1

For the remaining reflexions (hk3, hk4 etc.) a temperature factor of 1.2 \AA^2 was used. The temperature factor for hko reflexions was revised during the later stages of refinement using observed and calculated structure factors by Wilson's method. The Wilson's graph is shown in figure II.2. The revised B value was 2.4 \AA^2 . At each stage of refinement the observed structure factors were scaled by a factor given by $\frac{\Sigma F_c}{\Sigma F_o}$

Determination of space group

The systematic absences determined from the zero layer and higher layer Weissenberg photographs were the following:

- hkl - No systematic absences
- hoo - absent for h odd

oko - absent for k odd
ool - absent for l odd
hko - absent for h odd
okl - absent for k odd
hol - absent for l odd.

These systematic absences established the space group as Pbcu.

CHAPTER - III

Patterson projections, Harker Sections and Preliminary Structure Determination of β -Alanine.

The vector representation of crystal structure was put forward by A.L.Patterson (1934) to overcome the difficulty of the lack of knowledge of relative phases of structure factors in summing up the Fourier Series of electron density.

A function $P(uvw)$ was defined by

$$P(uvw) = \int_0^1 \int_0^1 \int_0^1 \rho(xyz) \rho(x+u, y+v, z+w) dx dy dz \quad \text{III.1}$$

where $\rho(xyz)$ and $\rho(x+u, y+v, z+w)$ are the electron densities at (x,y,z) and $(x+u, y+v, z+w)$ respectively; x, y, z and $x+u, y+v, z+w$ are fractional coordinates and V is the volume of the unit cell. If the two functions $\rho(xyz)$ and $\rho(x+u, y+v, z+w)$ are expanded in terms of the corresponding Fourier series

$$\rho(xyz) = \frac{1}{V} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} F(hkl) \exp\{-2\pi i(hx+ky+lz)\}$$

and

$$\rho(x+u, y+v, z+w) = \frac{1}{V} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} F(h'k'l') \exp\{-2\pi i(h'x+k'y+l'z)\} \\ \times \exp\{-2\pi i(k'u+l'v+l'w)\}$$

and integration effected in (III.1), then

$$P(uvw) = \frac{1}{V} \sum \sum \sum_{-\infty}^{\infty} |F(hkl)|^2 \exp \{-2\pi i(hu+kv+lw)\} \quad \text{III.2}$$

Collecting together the coefficients in pairs hkl and $\bar{h}\bar{k}\bar{l}$ in the equation III.2,

$$\begin{aligned} P(uvw) &= \frac{1}{2V} \sum \sum \sum |F(hkl)|^2 \exp \{-2\pi i(hu+kv+lw)\} \\ &\quad + |F(\bar{h}\bar{k}\bar{l})|^2 \exp \{2\pi i(hu+kv+lw)\} \\ &= \frac{1}{V} \sum \sum \sum |F(hkl)|^2 \left[\exp \{-2\pi i(hu+kv+lw)\} \right. \\ &\quad \left. + \exp \{2\pi i(hu+kv+lw)\} \right] \end{aligned}$$

since

$$|F(hkl)|^2 = |F(\bar{h}\bar{k}\bar{l})|^2$$

Therefore

$$P(uvw) = \frac{1}{V} \sum \sum \sum_{-\infty}^{\infty} |F(hkl)|^2 \cos 2\pi(hu+kv+lw) \quad \text{III.3}$$

The product of the electron densities in the expression (III.1) is in general zero unless u , v and w represent vector distances between two atoms. The Patterson summation will be finite only for values of u , v , w that represent vectors joining two atoms. The Patterson map has a large peak at the origin due to the overlap of several maxima, each maximum appearing owing to the interaction of any atom of the unit cell with itself. The other peaks in the Patterson map occur at distances from the origin equal to the vector distances between different pairs of atoms in the crystal.

The two dimensional Patterson Series can be used to solve a structure fairly directly when the crystal contains a relatively small number of heavy atoms in the unit cell along with lighter atoms. The Patterson peaks due to the heavy atoms then stand out against a background of overlapping smaller peaks and give immediately the coordinates of these atoms. The remaining atoms can then be located by direct Fourier methods. However, when the crystal consists of atoms of nearly the same atomic number, the Patterson peaks are broad due to the overlapping of many maxima of nearly equal height and as such their interpretation becomes very difficult.

The Patterson function in a two dimensional projection is given by

$$P(uvo) = \frac{1}{A} \sum \sum |F(hko)|^2 \cos 2\pi(hu+kv) \quad \text{III.4}$$

where A is the area of the projection.

In the case of β -Alanine the two Patterson projections $P(uvo)$ and $P(ovw)$ were obtained from the hko and okl intensities with the help of von Eller photosommateur.

Von Eller Photosommateur

The computation of electron densities and Patterson functions is excessively laborious in three dimensions and sufficiently lengthy even in two dimensions. Since

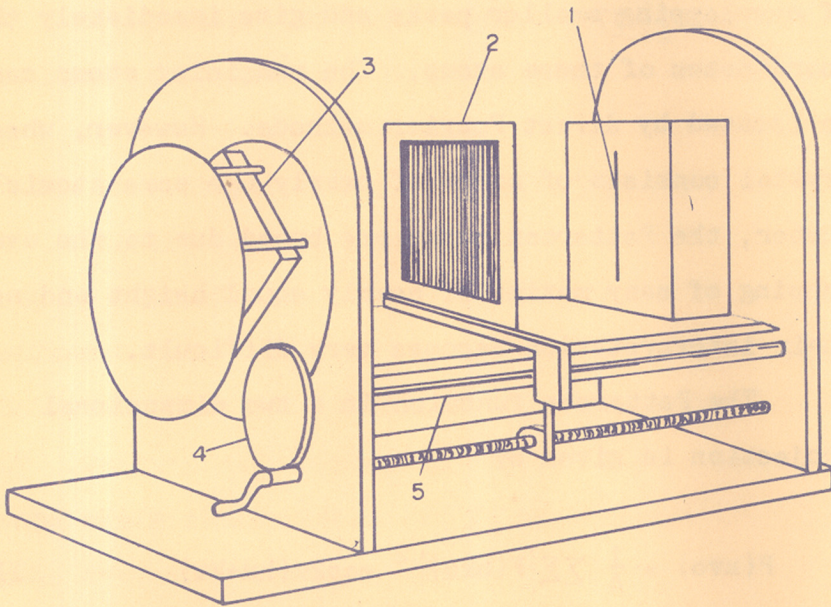


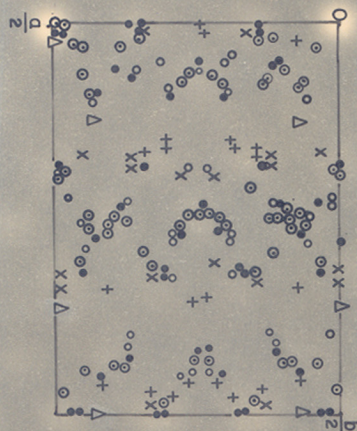
Fig. III - 1. Schematic diagram of von Eller Photosommateur

the process of Fourier summation is essentially the adding of sets of fringes, W.L.Bragg (1929a), suggested that for two dimensions the process could be carried out photographically by projecting these fringes on to a photographic plate with an exposure proportional to the Fourier coefficients modulus of structure factors in the case of electron density maps and squares of modulus of structure factors in the case of Patterson maps. Huggins (1944) improved the technique by using sets of masks on a 35 mm. film on the basis of a square unit cell. von Eller (1955) designed an elegant modification of the Bragg-Huggins technique. In the Eller photosommateur schematically drawn in fig.III-1, the slit source of light (1) is parallel to the fringes on the grating (2). The shadow of the fringes on the photographic plate (3) consists of a wave of dark and bright regions. The wave length of the wave can be adjusted by moving the grating towards or away from the source of light. When the cross wires on the rotating circle coincide with the origin of the reciprocal lattice pasted on the rotating circle, the grating touches the slit source of light. When the intersection of the crosswires is moved to, say, 100 reciprocal lattice point through a distance x , the grating moves away from the slit source by a distance kx (proportional to x) and the wave length of the fringes on the photographic plate is related to x by

$$\frac{\lambda}{n} = \frac{D}{kx}$$



Fig. III-2 (001) Patterson projection



- C-C peak
- C-N peak
- ⊙ C-O peak
- + N-O peak
- △ N-N peak
- X O-O peak

Fig. III-3 (100) Patterson projection

where n is the wavelength of fringes on the grating and D is the distance between the source of light and the photographic plate. As k , n and D are constants $\Delta \propto \frac{1}{x}$. $\frac{1}{x}$, x on the reciprocal lattice is equal to $\frac{\lambda}{d}$ where λ is the wave length of x rays and d is the spacing of 100 planes. This means $\Delta \propto \frac{1}{d}$. To obtain the correct slopes of fringes corresponding to the different combinations of h and k the different reciprocal lattice points are brought into coincidence with the cross wires. The required value of $|F(hko)|^2$ or $|F(hko)|$ as the case may be, is obtained by varying the exposure time. The phases of the structure factors can be altered by the lateral movement of the grating by means of a knob (4). When all the reflexions are exposed under these conditions the result is an optical summation of the Fourier Series.

The two Patterson projections of β -alanine ^{are shown in} figures III.2 and III.3. A suitable trial structure could not be postulated from these projections. However from the final structure (described in chapter IV) the various peaks could be identified in $P(uvo)$. The structure projected along c axis was plotted on the same scale as that of $P(uvo)$. The Patterson peaks arising from the various inter-atomic interactions were plotted on a tracing paper for a quarter of the unit cell. From figure III-2 the similarity between observed and calculated Patterson maps can be seen.

The determination of a suitable trial structure of β -Alanine was done from the Harker lines $P(u\frac{1}{2}0)$, $P(ov\frac{1}{2})$

and $P(\frac{1}{2}0w)$ and with the help of line Fourier Syntheses.

Harker Sections and Harker lines

The complete evaluation of the three dimensional Patterson distribution $P(uvw)$ requires excessive labour but Harker (1936) pointed out that in crystals with certain symmetry elements information about atomic coordinates may sometimes be obtained from certain lines and planes. An example of this is found in a crystal having c-glide plane of symmetry perpendicular to b axis. Taking the origin on the glide plane, the equivalent points related by this glide have co-ordinates x, y, z and $x, \bar{y}, \frac{1}{2}+z$. The peaks in the $P(uvw)$ distribution corresponding to the distance between these two atoms have coordinates $\pm (0, 2y, -\frac{1}{2})$. The peaks corresponding to atoms related by the c glide plane thus all lie on the line $P(0, v, \frac{1}{2})$ of the Patterson map.

For the line $u=0, w=\frac{1}{2}$ the Patterson function $P(uvw)$ reduces to

$$\begin{aligned}
 P(0, v, \frac{1}{2}) &= \sum_{-w}^{\infty} \sum_{-u}^{\infty} |F(hkl)|^2 \cos 2\pi(kv + \frac{1}{2}) \\
 &= \sum_k \left\{ \sum_l (-1)^l |F(hkl)|^2 \right\} \cos 2\pi kv \quad \dots \quad \text{III.5}
 \end{aligned}$$

The line $P(0v\frac{1}{2})$ known as Harker Line can be computed easily with the observed intensities $|F(hkl)|^2$. The peaks in the $P(0v\frac{1}{2})$ give the y coordinates of the atoms. Similarly expressions can be derived for other symmetry elements like 2 fold screw axes, mirror planes etc.

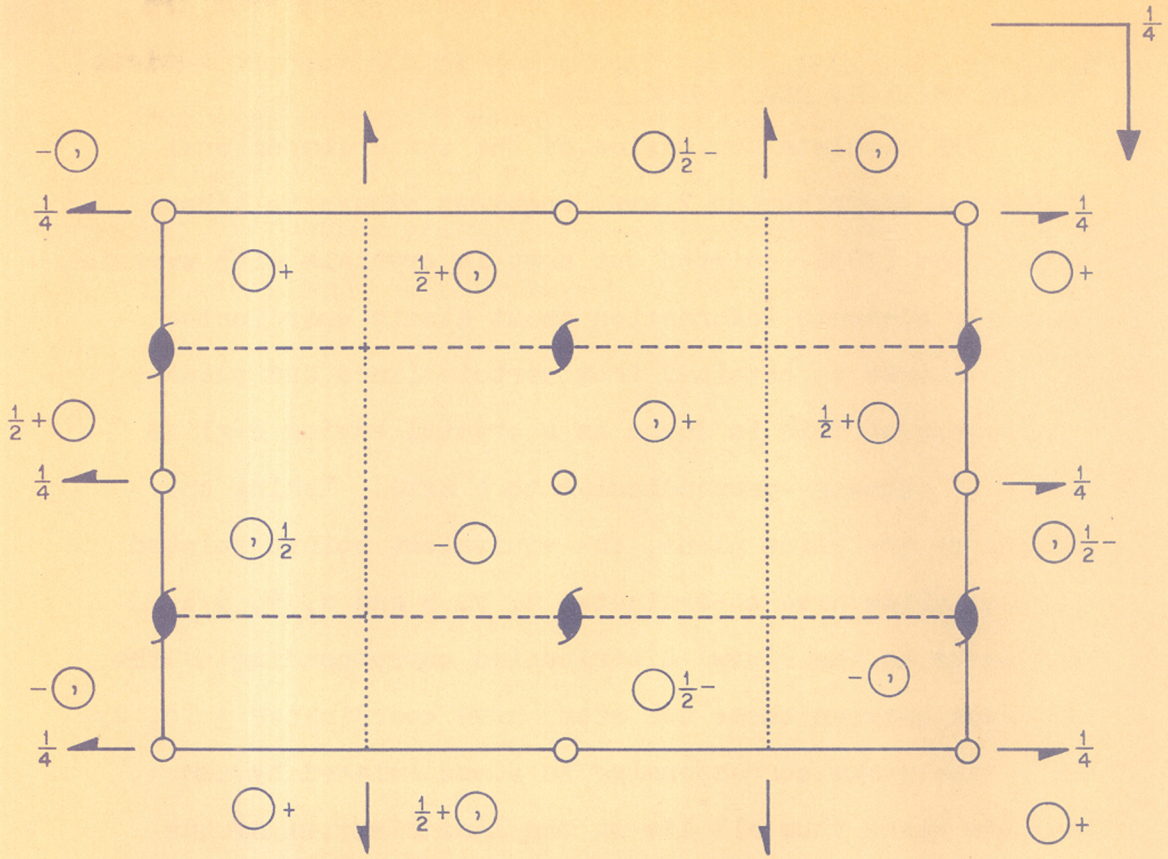


FIG. III-4. Symmetry elements for the space group $Pbc1$ and the equivalent positions.

The symmetry elements for the space group Pbc₂a are drawn in Fig.III-4. The plane group in all the projections is pgm. There are eight molecules of β-Alanine in a unit cell and the space group Pbc₂a has 8 equivalent points. The asymmetric unit therefore consists of one molecule. Taking the origin at the centre of symmetry, the coordinates of the equivalent ~~points~~^{positions} are

$$x, y, z; \frac{1}{2}+x, \frac{1}{2}-y, \bar{z}; \bar{x}, \frac{1}{2}+y, \frac{1}{2}-z; \frac{1}{2}-x, \bar{y}, \frac{1}{2}+z.$$

$$\bar{x}, \bar{y}, \bar{z}, \frac{1}{2}-x, \frac{1}{2}+y, z; x, \frac{1}{2}-y, \frac{1}{2}+z; \frac{1}{2}+x, y, \frac{1}{2}-z.$$

The three glide planes are situated at $(\frac{1}{4}yz)$, $(x\frac{1}{4}z)$ and $(xy\frac{1}{4})$ and the three 2_1 screw axes at $(x\frac{1}{4}o)$, $(o\bar{y}\frac{1}{4})$ and $(\frac{1}{4}oz)$ respectively.

The Patterson function P(uvw) will have peaks at $(-2x, \frac{1}{2}, \frac{1}{2}-2z)$ due to the interaction between atoms at (xyz) and $(\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z)$ related by 2_1 screw axis parallel to b. A section through the three dimensional Patterson function in the plane $y = \frac{1}{2}$ is given by

$$P(u\frac{1}{2}w) = \frac{1}{V} \sum_{h=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} \left\{ \sum_{k=-\infty}^{\infty} (-1)^k |F(hkl)|^2 \right\} \cos 2\pi(hu+lw) \quad \text{III.6}$$

Such a section is called the Harker Section.

Similarly Harker sections in the planes $x=\frac{1}{2}$ and $z=\frac{1}{2}$ are given by the expressions

$$P(\frac{1}{2}vw) = \frac{1}{V} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} \left\{ \sum_{h=-\infty}^{\infty} (-1)^h |F(hkl)|^2 \right\} \cos 2\pi(kv+lw) \quad \text{III.7}$$

$$P(uv\frac{1}{2}) = \frac{1}{V} \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \left\{ \sum_{l=-\infty}^{\infty} (-1)^l |F(hkl)|^2 \right\} \cos 2\pi(hu+kv) \quad \text{III.8}$$

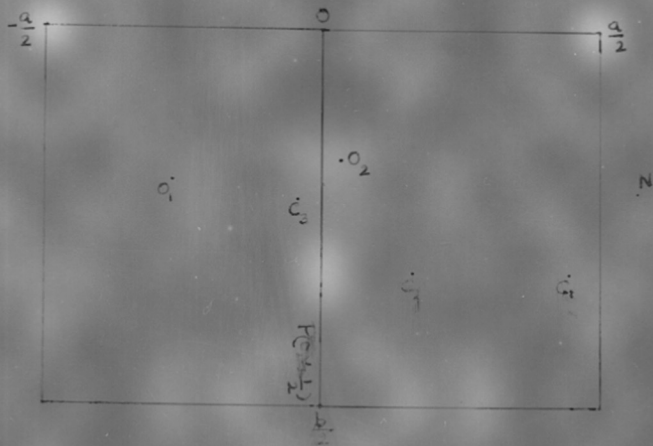


Fig. III-5 The Harker Section $P(u \ v \ \frac{1}{2})$

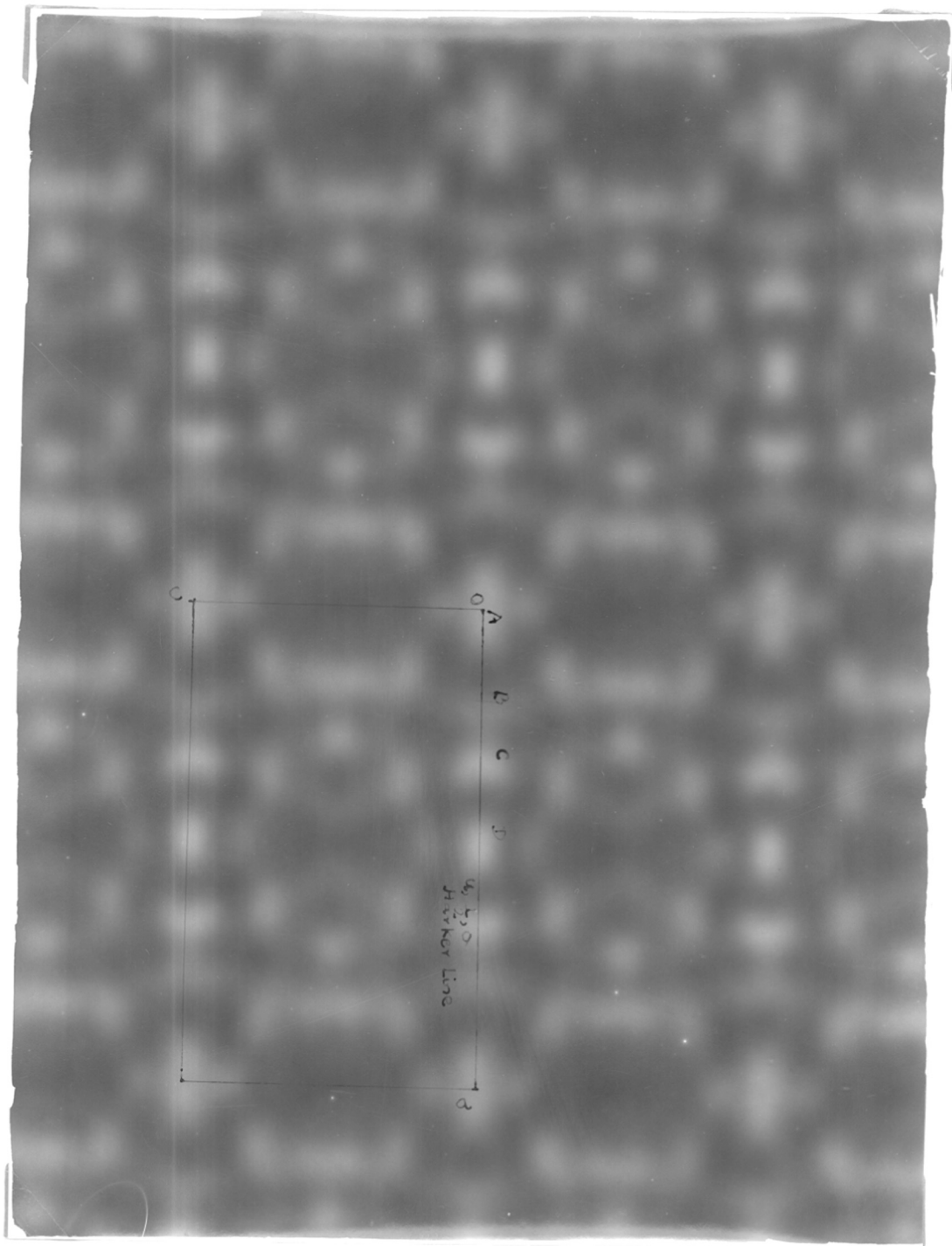


Fig. III-6 The Harker Section $P(u_{1/2}w)$

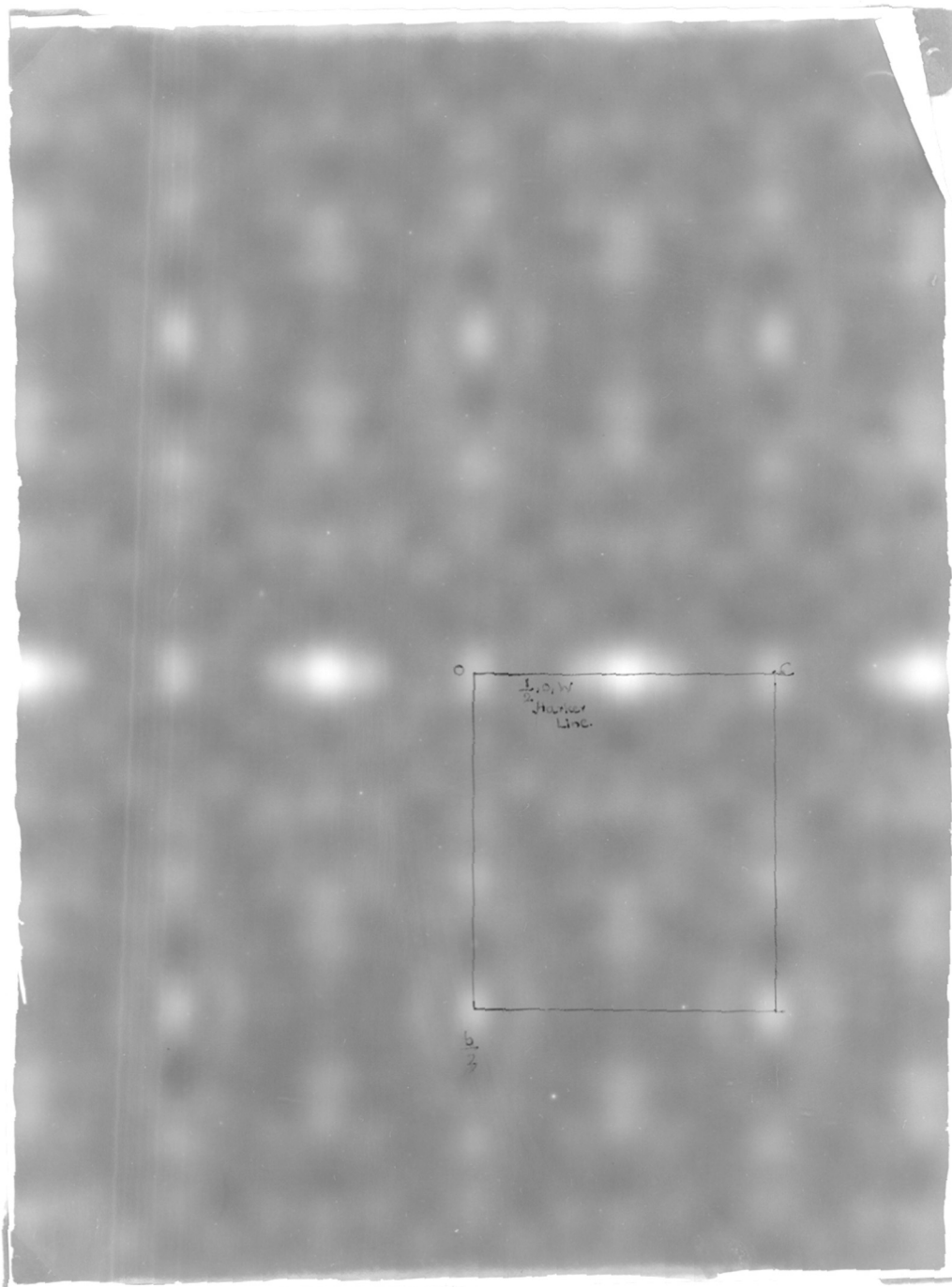


Fig. III-7 The Harker Section $P(\frac{1}{2}vw)$

To obtain the Harker Sections given by equations III.6, III.7 and III.8 all the observed hkl intensities were used, giving half weight to hko, okl, and hol intensities and quarter weight to those of hoo, oko, and ool reflexions. The weighting was done to account for the summation over h, k and l from $-\infty$ to $+\infty$. In every case the observed intensities were summed over one index contained within flower brackets in the equations III.6, III.7 and III.8. These were then arranged in tabular form to sum over the other two indices. The reciprocal lattices drawn for the three projections were used for optical summation of the three sections. The summation of the Harker Section was then carried out by the photo-sommateur using $\sum (-1)^h |F(hkl)|^2$, $\sum (-1)^k |F(hkl)|^2$ and $\sum (-1)^l |F(hkl)|^2$ as the Fourier coefficients for the three sections respectively.

The three Harker Sections $P(uv\frac{1}{2})$, $P(u\frac{1}{2}w)$ and $P(\frac{1}{2}vw)$ are shown in figures III-5, III-6 and III-7 respectively. These could not be interpreted easily due to the occurrence of non Harker peaks i.e. incidental peaks corresponding to vectors between atoms not related by symmetry. However the molecule plotted with the final atomic parameters obtained by least squares method (chapter IV) is drawn on the same scale as in the Harker Section $P(uv\frac{1}{2})$ in figure III-5; the peaks could be explained from this molecule.

In addition to the peaks mentioned above the Patterson distribution $P(uvw)$ will have peaks at

$(\frac{1}{2}-2x, \frac{1}{2}, 0)$ due to the interaction between atoms at (x, y, z) and $(\frac{1}{2}-x, \frac{1}{2}+y, z)$ related by b glide. The appropriate Harker section is therefore the line $u, \frac{1}{2}, 0$ given by the expression

$$P(u\frac{1}{2}0) = \sum_h \left\{ \sum_l \sum_{k=-\infty}^{\infty} (-1)^k |F(hkl)|^2 \right\} \cos 2\pi hx$$

Similarly peaks are expected at $(0, \frac{1}{2}-2y, \frac{1}{2})$ in the line $P(0v\frac{1}{2})$ due to interaction between atoms related by c glide and at $(\frac{1}{2}, 0, \frac{1}{2}-2z)$ in the line $P(\frac{1}{2}ow)$ due to vector between atoms related by a glide. These two Harker lines are given by

$$P(0v\frac{1}{2}) = \sum_k \left\{ \sum_h \sum_l (-1)^l |F(hkl)|^2 \right\} \cos 2\pi ky$$

and

$$P(\frac{1}{2}ow) = \sum_l \left\{ \sum_k \sum_h (-1)^h |F(hkl)|^2 \right\} \cos 2\pi lx.$$

These Harker lines are present in the Harker sections discussed above. These Harker lines were computed with the hkl intensities giving half weight to hko, okl and hol intensities and quarter weight to those of hoo, oko and ool reflexions. For the line $P(u\frac{1}{2}0)$ the Fourier coefficients are $\sum_l \sum_k (-1)^k |F(hkl)|^2$. These were obtained by summing the weighted hkl intensities over all k's. These were then tabulated to sum over all l's.

Similarly the coefficients for the Harker lines

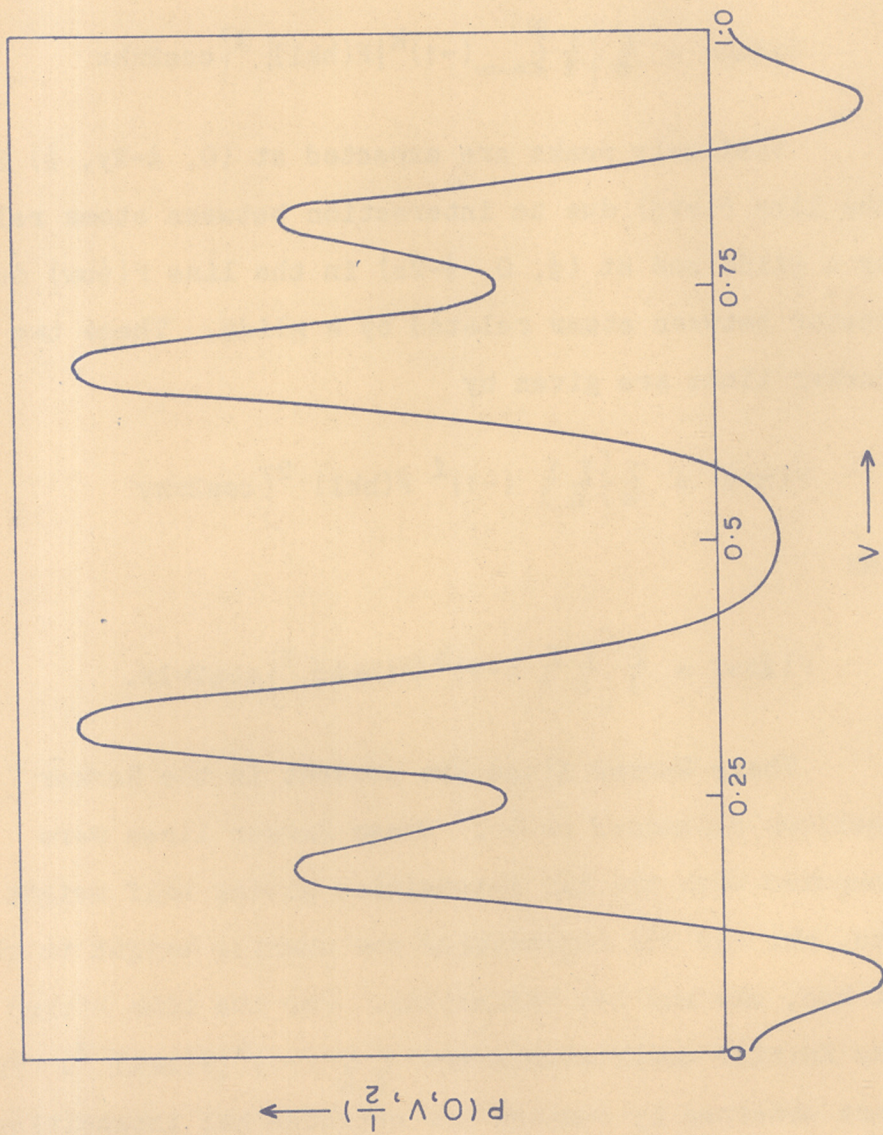


FIG. III · 8 $P(0, V, \frac{1}{2})$ HARKER LINE

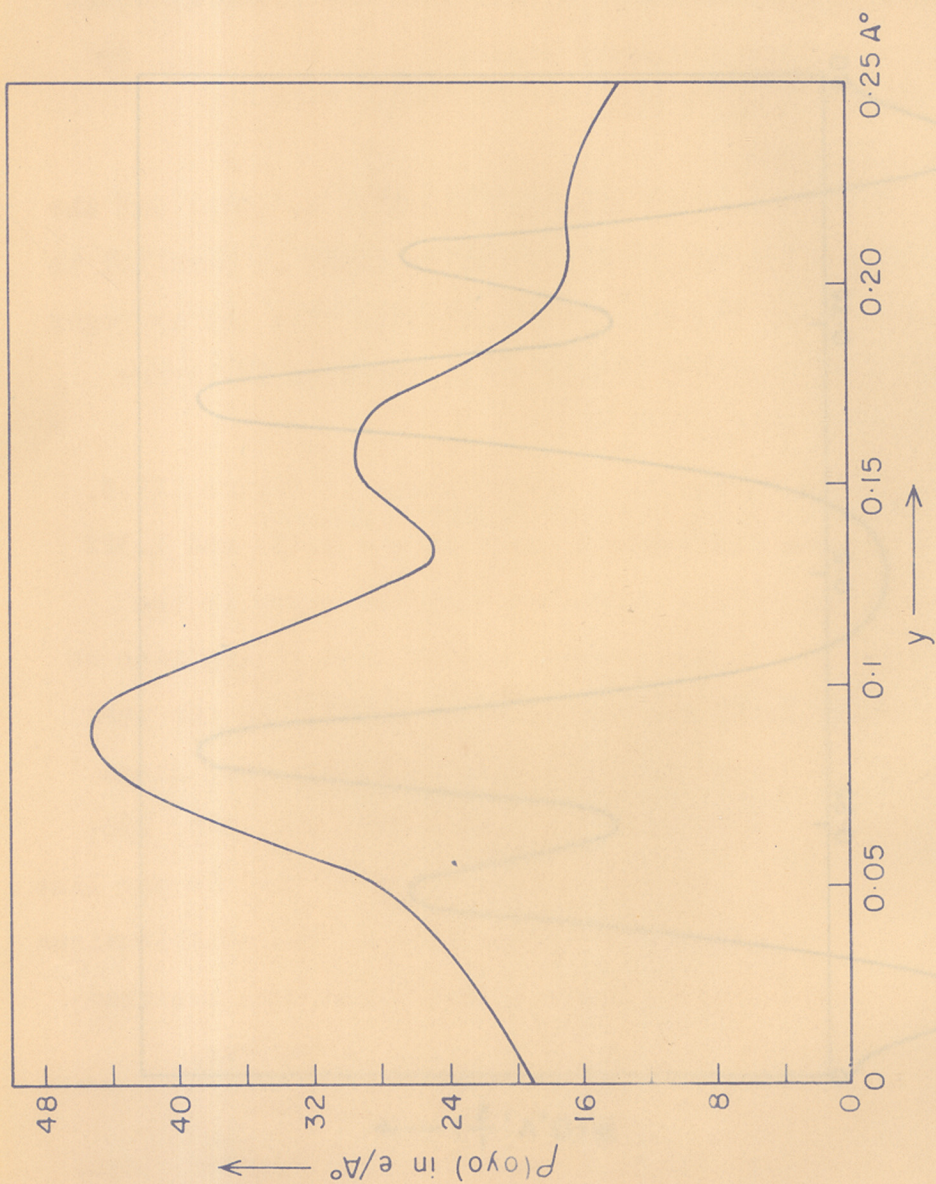


FIG. III-9 ρ (oyo) LINE SYNTHESIS

FIG. III-8 ρ (yo, y, $\frac{1}{2}$) HARKER LINE

$P(\text{ov}\frac{1}{2})$ and $P(\frac{1}{2}\text{ow})$ were obtained. The summation was done using Beevers and Lipson strips at intervals of 6° . The three Harker lines are shown in figures III.8, III.10 and III.12. Contours of $P(\text{u}\frac{1}{2}\text{o})$ etc. are drawn at equal intervals ^{on} of an arbitrary scale.

Trial structure:

The presence of cleavage parallel to (010) and the fact that α the smallest refractive index is parallel to b (McCrone and KRc Jr. 1950) indicated that the hydrogen bonded molecules are likely to be arranged in layers parallel to (010).

In the Harker line $P(\text{ov}\frac{1}{2})$ shown in figure III.8, there are two independent peaks at $v = 0.183$ and 0.322 respectively. This suggested that the atoms in the molecules lie in two groups, one of them giving rise to the peak at 0.183 and the other at 0.322 . As the peak at 0.322 is larger than the peak at 0.183 , more atoms were assumed at 0.322 . The planes 020 ; 040 ; 060 ; 080 ; $0,10,0$; $0,12,0$; and $0,16,0$ were drawn on this Harker line using a proper scale. By inspection of the contributions of different atoms to these planes signs were assigned to the structure factors as follows: $F(020)+ve$, $F(040)-ve$, $F(060)-ve$, $F(080)-ve$, $F(0,10,0)+ve$, $F(0,12,0)+ve$ and $F(0,16,0)-ve$. The line Fourier $\rho(\text{oyo})$ was plotted with these signs and observed values of $F(\text{oko})$. The summation was done using Beevers and Lipson strips. In the $\rho(\text{oyo})$ line (Figure III-9) there are two peaks

at $y = 0.089$ and 0.158 . From the areas under the peaks which were in the ratio ~~2:1~~ and the ratio of atomic numbers it was assumed that the larger peak corresponds to four atoms C_2 , C_3 , O_1 and O_2 (for numbering of atoms see figure III-11) and the smaller to Nitrogen and C_1 . This explained the two peaks at 0.183 and at 0.322 in the line $P(\text{ov}\frac{1}{2})$. The $F(\text{oko})$ were recalculated with the coordinates of C_2 , C_3 , O_1 and O_2 at 0.089 and N and C_1 at 0.158 . After two successive line $(F_o - F_c)$ syntheses N and C were separated to 0.153 and 0.162 respectively. As the four atoms at 0.089 were lying in deep negative region in the second $(F_o - F_c)$ line synthesis two atoms (one oxygen and one carbon) were shifted to 0.075 and the other two to 0.108 . With these coordinates $F(\text{oko})$ gave a reliability index R given by

$$\frac{\sum |F_o| - \sum |F_c|}{\sum |F_o|} \text{ of } 0.18.$$

The agreement for hko structure factors could not, however, be improved with these y coordinates. Hence the atoms were interchanged later to fit a proper molecular orientation. The complete structure analysis (chapter IV) shows that the weaker peak in $P(\text{ov}\frac{1}{2})$ corresponds to two methylene carbons and the stronger peak is due to carboxyl group and amino nitrogen.

From the expected bond lengths and bond angles and with the help of approximate y coordinates, a model of the molecule was made in (001) projection. The x coordinates for this orientation were those which explained the four peaks A , B , C and D in the $P(u, \frac{1}{2}, 0)$

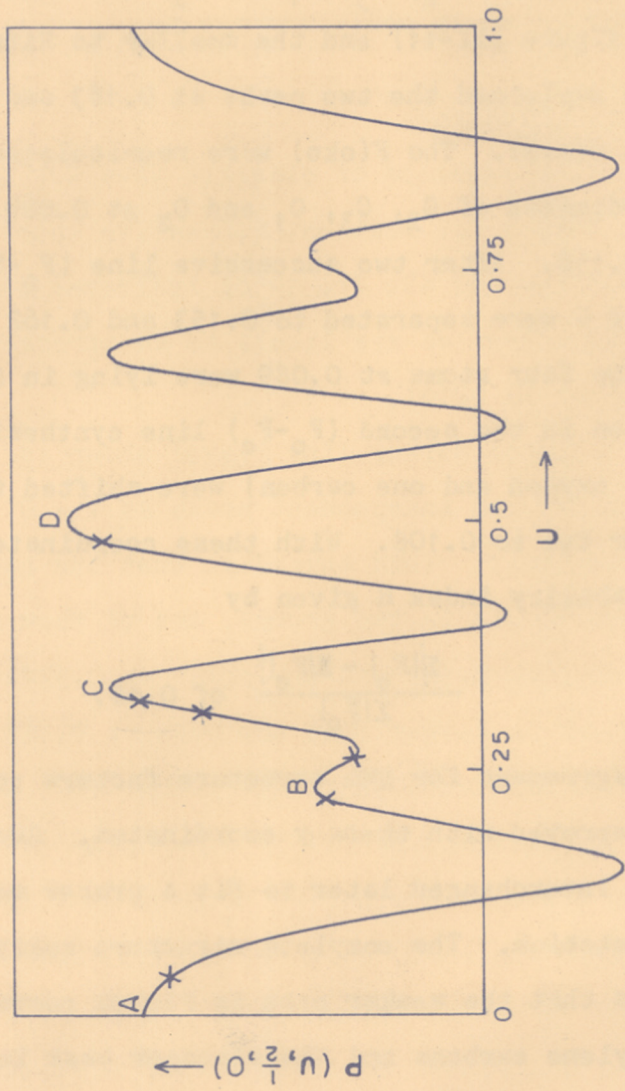


FIG. III-10. $P(u, \frac{1}{2}, 0)$ HARKER LINE

Harker line (Fig.III.10). The four peaks A, B, C and D are at $u = 0, 0.230, 0.332$ and 0.50 respectively. The x coordinates obtained from this Harker line were

Atom	x	$\frac{1}{2}-2x$
N	0.260	0.02
C ₁	0.142	0.216
C ₂	0.076	0.344
C ₃	0.085	0.33
O ₁	-0.01	0.48
O ₂	0.215	0.07

It is seen that atoms Nitrogen and O₂ fall at the origin peak, the peak B corresponds to C₁, C corresponds to carbons C₂ and C₃ and the peak D at 0.5 to O₁. Here again, with these x coordinates the agreement for hko structure factors could not be improved. After a few trials and with the help of a few $(F_o - F_c)$ line syntheses along x , the x coordinates of all atoms were changed to $N = .408$, $C_1 = 0.404$, $C_2 = 0.270$, $C_3 = 0.140$, $O_1 = 0.01$, $O_2 = 0.170$. The expected peaks in the Harker line with these coordinates are marked by crosses in the fig.III.10.

The hko structure factors were calculated with these values of x and y parameters and scattering factors corrected for $B = 3.4 \text{ \AA}^2$. The signs obtained from this calculation were used to take a Fourier map with the Eller photosommateur. The Fourier map showed that the molecular

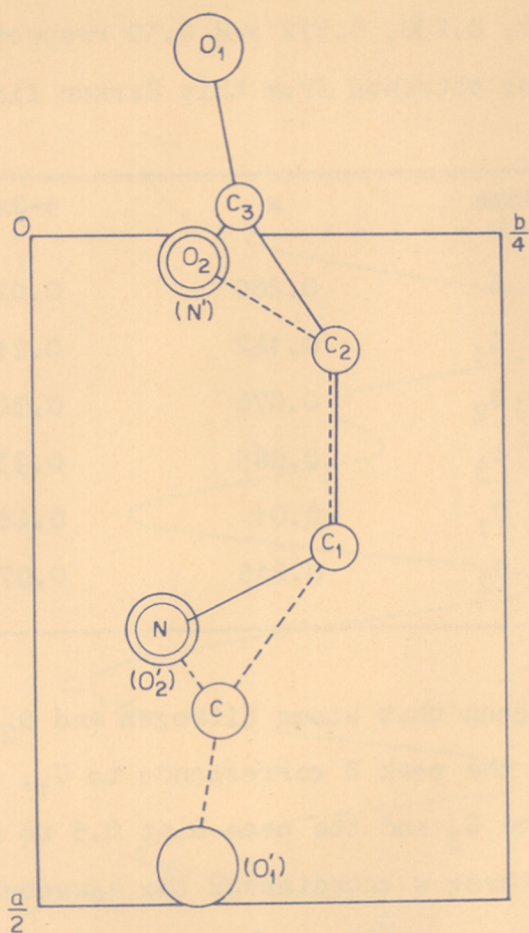


FIG. III -11 Two probable orientations of β -Alanine molecule

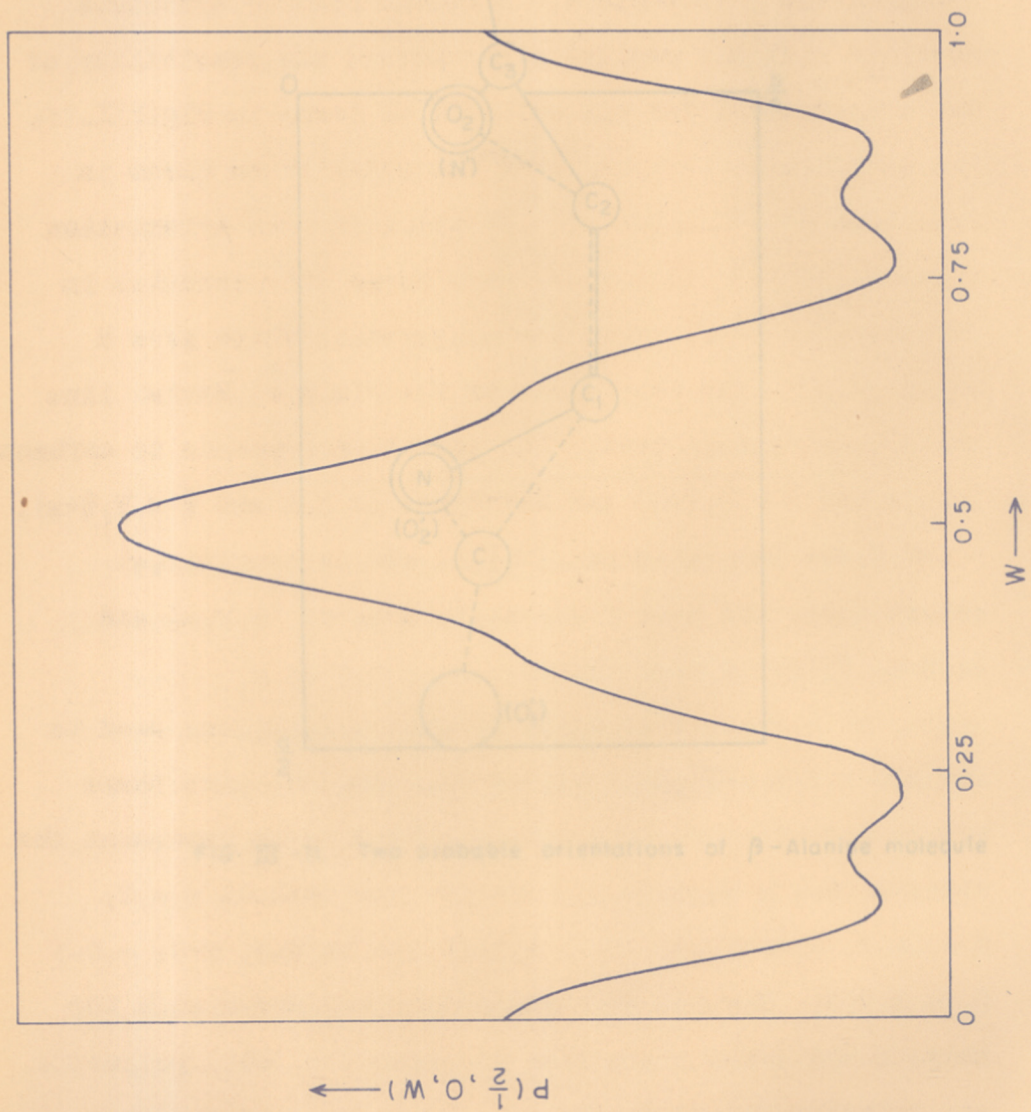


FIG. III-12 $P(\frac{1}{2}, 0, W)$ HARKER LINE

geometry was nearly correct but the whole molecule had to be shifted upwards along the x axis. The $F(hko)$ were recalculated with the new values of x-coordinates without changing the y parameters. A second Fourier synthesis obtained with the revised signs showed the possibility of two orientations for the molecule as drawn in Fig.III.11. The coordinates obtained from the orientation drawn in full line gave R value of 0.37 while for the orientation drawn in broken lines there were large discrepancies in structure factors. From the orientation which gave R value of 0.37 the four peaks in the $P(u, \frac{1}{2}, 0)$ Harker line could be explained thus: The peak A corresponds to carbons (x, y, z) and $(\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z)$ and Nitrogens (x, y, z) and $(\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z)$, B and C are due to oxygen $(\bar{x}, \bar{y}, \bar{z})$ and carbon (x, y, z) respectively and D corresponds to oxygens (x, y, z) and $(\bar{x}, \bar{y}, \bar{z})$ (Figure V-2).

The Harker line $P(\frac{1}{2}, w)$ (Figure III.12) was used to fix the trial in (100) projection. In this line there are two peaks at $w = 0$ and 0.5 . These peaks represent the coordinates $\frac{1}{2}, 0, \frac{1}{2}-2z$. Hence for the peak at $w = 0$, $\frac{1}{2}-2z = 0$ or $z = 0.25$ and for the peak at 0.5 , $\frac{1}{2}-2z = 0.5$ i.e. $z = 0$. A model of the molecule was drawn with the help of the known y-coordinates from the (001) projection and relative z-coordinates (taking z for nitrogen atom as zero) of atoms. The relative z-coordinates were obtained assuming expected bond lengths and bond angles in the molecule i.e. $C_1-N = 1.50\text{\AA}$, C_1-C_2 and $C_2-C_3 = 1.545\text{\AA}$, C_3-O and $C_3-C_2 = 1.25\text{\AA}$, the angles at C_3 120° ; and the

angles $N-C_1-C_2$ and $C_1-C_2-C_3$ 110° . The molecule was drawn on the same scale as $P(\frac{1}{2}vw)$ section and superposed on $P(\frac{1}{2}ow)$ line. The molecule was then shifted until z of O_2 was approximately 0.25 and z values of other atoms nearly zero. Thus the peak at $w = 0$ corresponds to oxygen O_2 at x, y, z and $\frac{1}{2}+x, y, \frac{1}{2}-z$ and that at 0.5 corresponds to the other five atoms at x, y, z and $\bar{x}, \bar{y}, \bar{z}$ (Figure V-3).

C H A P T E R - I V

Electron density projections and refinement of
β-Alanine structure.

The structure factor is given by the expression

$$F = \sum_{n=1}^N f_n \exp\{2\pi i(hx_n + ky_n + lz_n)\} \quad . \quad . \quad . \quad \text{IV.1}$$

where f_n is the scattering factor of the atom at x_n, y_n, z_n and the summation extends over all atoms of the unit cell. For purposes of calculation the structure factor is divided into real and imaginary parts, thus $F = A + iB$ where

$$A = \sum_{n=1}^N f_n \cos 2\pi(hx_n + ky_n + lz_n) \quad . \quad . \quad . \quad \text{IV.2}$$

and

$$B = \sum_{n=1}^N f_n \sin 2\pi(hx_n + ky_n + lz_n) \quad . \quad . \quad . \quad \text{IV.3}$$

For the space group Pbc₂a these expressions simplify to

$$A = 8f \cos 2\pi\left(hx - \frac{h-k}{4}\right) \cos 2\pi\left(ky - \frac{k-1}{4}\right) \cos 2\pi\left(lz - \frac{l-h}{4}\right)$$

$$B = 0$$

The structure factor formulae fall into four classes. They are

$$\Lambda = 8f \cos 2\pi hx \cos 2\pi ky \cos 2\pi lz \quad . \quad . \quad . \quad \text{IV.4}$$

for $h+k=2n, \quad k+l=2n$

$$\Lambda = -8f \cos 2\pi hx \sin 2\pi ky \sin 2\pi lz \quad . \quad . \quad . \quad \text{IV.5}$$

for $h+k=2n, \quad k+l=2n+1$

$$\Lambda = -8f \sin 2\pi hx \cos 2\pi ky \sin 2\pi lz \quad . \quad . \quad . \quad \text{IV.6}$$

for $h+k=2n+1, \quad k+l=2n$

$$\Lambda = -8f \sin 2\pi hx \sin 2\pi ky \cos 2\pi lz \quad . \quad . \quad . \quad \text{IV.7}$$

for $h+k=2n+1, \quad k+l=2n+1$

(001) Projection

The $F(hko)$'s were calculated according to the expressions

$$F(hko) = 8 \sum_{n=1}^{N/8} f_n \cos 2\pi hx \cos 2\pi ky$$

for reflexions $h+k = 2n$

and

$$= -8 \sum_{n=1}^{N/8} f_n \sin 2\pi hx \sin 2\pi ky$$

for reflexions $h+k = 2n+1$

with the atomic coordinates obtained from Harker lines
The summation is taken for all the atoms in the asymmetric unit.
 (Chapter III). In the calculation of structure factors
 McWeeny's (1951) values of the scattering factors for
 carbon, nitrogen and oxygen were used. ~~The scattering~~

factors for carbon, nitrogen and oxygen were used. The scattering factors were corrected for temperature factor according to the relation

$$f = f_0 \exp\left(-B \frac{\sin^2 \theta}{\lambda^2}\right)$$

where f is the scattering factor to be used in practice, f_0 , the scattering factor for the atom at rest and B is the temperature factor. The value of B obtained from Wilson's graph was 3.4 \AA^2 . The modified scattering factors were plotted against $\sin \theta$ for different types of atoms and the f values for all reflexions were read from the graph. The reliability index R given by

$$R = \frac{\sum |F_0| - \sum |F_c|}{\sum |F_0|}$$

where $|F_0|$ and $|F_c|$ are the moduli of the observed and calculated structure factors, was 0.37. With the revised signs a Fourier synthesis was carried out by Eller photosommateur.

(001) Electron density projection

The Fourier series in the (001) projection is given by the expression

$$\begin{aligned} \rho(x,y) &= \frac{1}{4} \left[F(000) + 2 \sum_0^{\infty} F(h00) \cos 2\pi hx + 2 \sum_0^{\infty} F(oko) \cos 2\pi ky \right. \\ &\quad \left. + 4 \sum_0^{\infty} \sum_0^{\infty} F(hko) \cos 2\pi hx \cos 2\pi ky - 4 \sum_0^{\infty} \sum_0^{\infty} F(hko) \sin 2\pi hx \sin 2\pi ky \right] \\ &= \frac{1}{4} \left[\frac{F(000)}{4} + \frac{1}{2} \sum F(h00) \cos 2\pi hx + \frac{1}{2} \sum F(oko) \cos 2\pi ky \right. \\ &\quad \left. + \sum_0^{\infty} \sum_0^{\infty} F(hko) \cos 2\pi ky \cos 2\pi hx - \sum_0^{\infty} \sum_0^{\infty} F(hko) \sin 2\pi hx \sin 2\pi ky \right] \dots \text{IV.8.} \end{aligned}$$

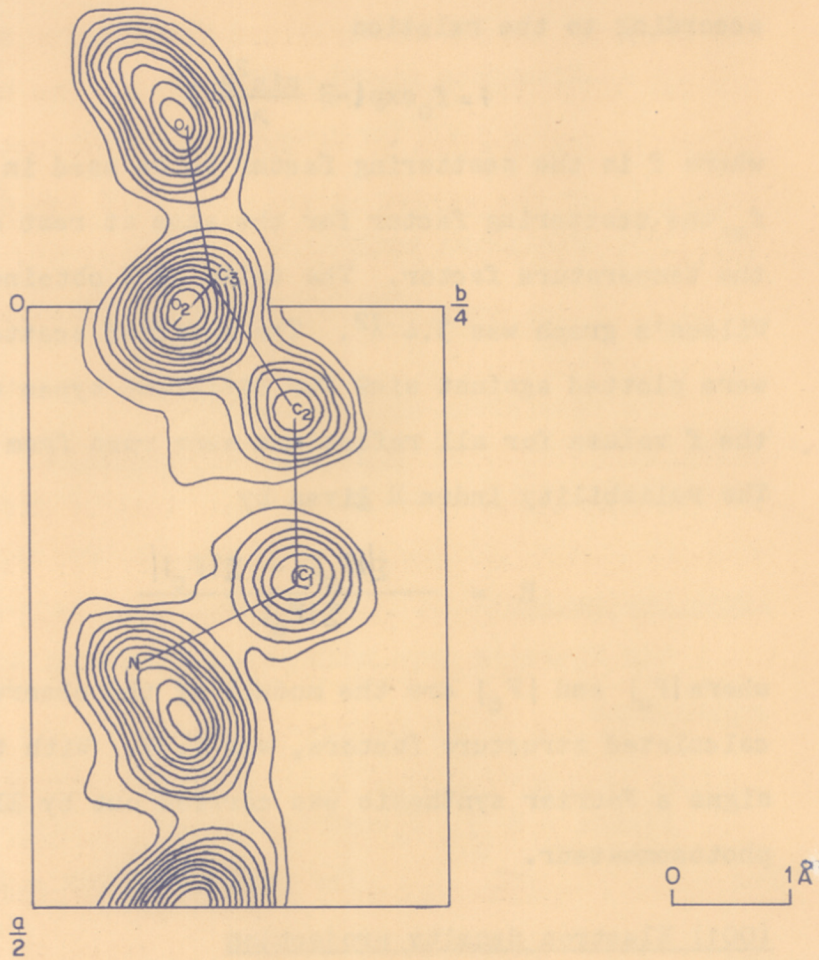


FIG. IV-1 (001) Electron density projection. Contours at intervals of $1e.\text{\AA}^{-2}$ starting from $2e./\text{\AA}^2$

The (001) electron density projection shown in figure IV-1 was computed using the final calculated signs and observed values of structure factors for all except 040 for which the final calculated value was used. Reflexion 040 appears to be subject to extinction. The summation of the series in equation IV.8 was done by using Beavers and Lipson strips at intervals of 6° . The contours (fig. IV.1) are drawn at intervals of 1 electron per \AA^2 starting from $2e/\text{\AA}^2$.

Difference syntheses by Eller photosommateur

First three refinements were done by difference Fourier syntheses (discussed in chapter VI) obtained with the help of von Eller photosommateur described in chapter III. $(F_o - F_c)$ values with the corresponding phases were written on the $a^* b^*$ reciprocal lattice. The ~~reciprocal~~ ^{exposures corresponding to} reciprocal lattice points were then exposed to the source of light with exposures proportional to $(F_o - F_c)$ values. Shifts in the atomic coordinates were approximate depending on the blackness or whiteness at the atomic position on the difference map. The shifts obtained from the first difference map gave an R value of 0.29 for 56 hko reflexions including unobserved ones at half the minimum observable value but excluding 040 as it appeared to suffer from extinction effect. After two further difference syntheses the R factor was 0.215. Further refinements were done by the least squares method.

(100) projection

The structure factor for (100) projection is given by the expression

$$F(okl) = 8 \sum_{n=1}^{N/8} f_n \cos 2\pi k y \cos 2\pi l z \quad \text{for } k+l=2n$$

and

$$F(okl) = -8 \sum_{n=1}^N (f_n \sin 2\pi k y \sin 2\pi l z \quad \text{for } k+l=2n+1$$

where N is the number of atoms in a molecule

The final y -coordinates from the (001) projection and the z -coordinates obtained from the Harker line $P(\frac{1}{2}ow)$ were used to calculate $F(okl)$. The z coordinates are listed below

<u>Atom</u>	<u>z/c</u>
N	-0.045
C ₁	0.0
C ₂	-0.108
C ₃	0.057
O ₁	-0.05
O ₂	0.232

A temperature factor of 0.9\AA^2 , obtained from Wilson's graph, was used throughout the course of refinement. The agreement index R for 42 reflexions including unobserved ones at half the minimum observable value was 0.30.

Reflexions 002 and 040 were left out of all calculations

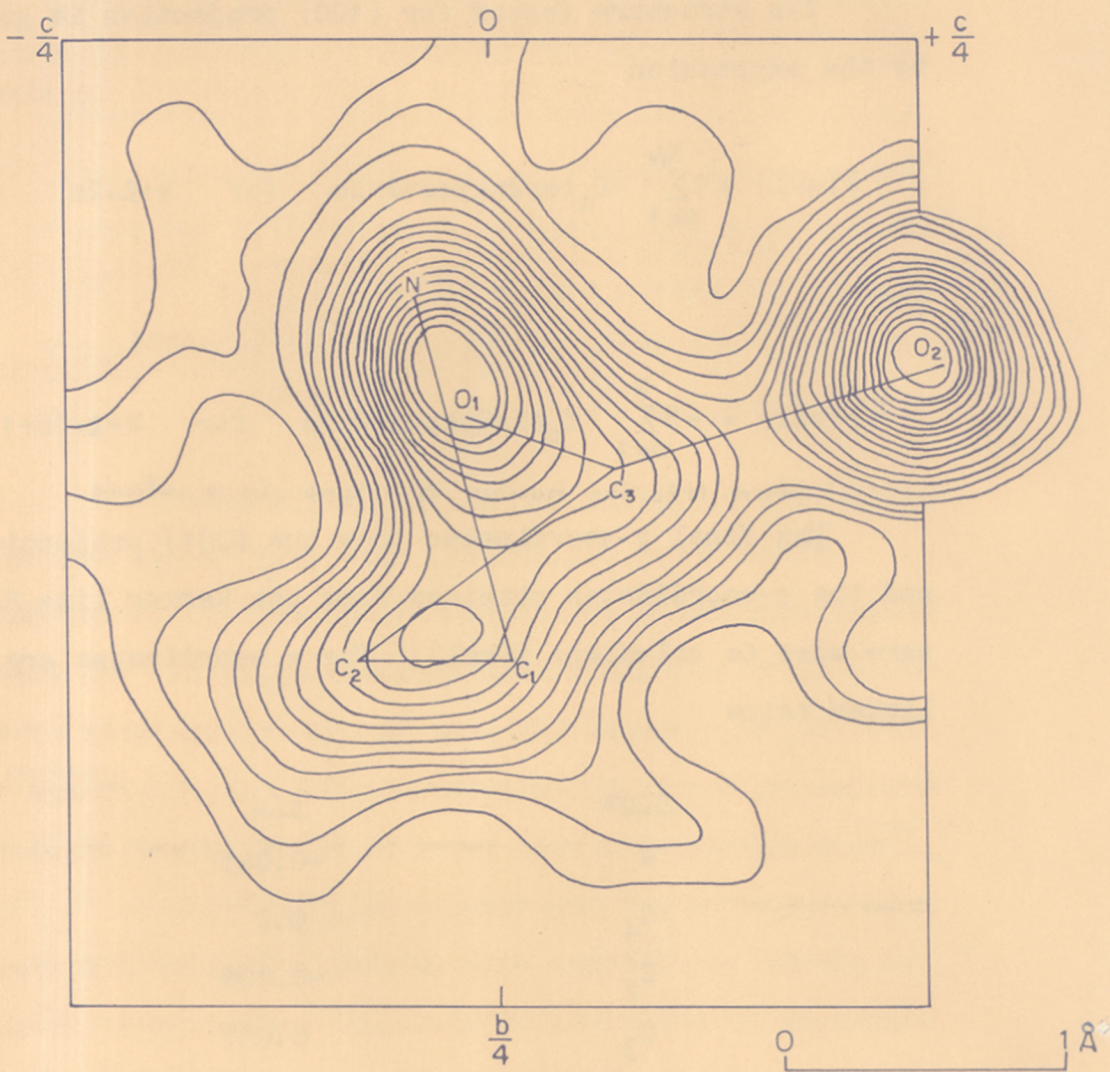


FIG. IV-2. (100) ELECTRON DENSITY PROJECTION
 CONTOURS AT INTERVALS OF $1 e \cdot \text{\AA}^{-2}$ STARTING FROM $.2 e \cdot \text{\AA}^{-2}$

as they suffer from extinction effect.

(100) electron density projection

The electron density in (100) projection is given by the expression

$$\rho(oyz) = \frac{4}{\Lambda} \left[\frac{F(000)}{4} + \frac{1}{2} \sum_0^{\infty} F(oko) \cos 2\pi ky + \frac{1}{2} \sum_0^{\infty} F(o0l) \cos 2\pi lz \right. \\ \left. + \sum_0^{\infty} \sum_0^{\infty} \frac{k+l=2n}{F(okl) \cos 2\pi ky \cos 2\pi lz} - \sum_0^{\infty} \sum_0^{\infty} \frac{k+l=2n+1}{F(okl) \sin 2\pi ky \sin 2\pi lz} \right]$$

The (100) electron density projection shown in figure IV-2 was computed using final calculated signs and observed values of structure factors for all except 002 and 040 for which the final calculated values were used. The summation was done using Beevers-Lipson strips at intervals of 6°. The intervals of division are 60 parts along b/2 and 15 parts along c/4. The contours in fig.IV.2 are drawn at intervals of $1e.\text{Å}^2$ starting from $2e.\text{Å}^{-2}$.

A few cycles of refinement were done by difference syntheses with the help of optical synthesiser. At the end of refinements by difference syntheses the R factor was 0.184. A further refinement was done by the method of least squares discussed in the next section.

Refinement of atomic coordinates by the least square method

In the earlier stages of structure determination by Fourier Syntheses small adjustments of the parameters are chosen in such a way as to improve as many of the outstanding discrepancies in structure factors as possible.

and F's are recalculated. The process is repeated until the best possible agreement between the observed and calculated structure factors is thought to have been obtained. However, to make all possible combinations of small displacements in a multiparameter structure and show that the agreement is best for the parameters proposed would be an impossible task. Under such circumstances the method of least squares is made use of. (Hughes 1941).

If the errors \bar{r}_x in the measured F_o 's follow the Gaussian Law, then the best atomic parameters are those which result in a minimisation of the quantity.

$$R = \sum_q \left[w(hkl) \left[|F_o(hkl)| - |F_c(hkl)| \right] \right]^2 \quad \dots \text{IV.10}$$

where $w(hkl)$ is a weighting factor and the sum is taken over all terms which lie within the limiting sphere.

Atomic parameters on which R depends include not only atomic coordinates but all quantities which influence the value of F_c 's such as temperature factor. Presently only the changes in atomic coordinates are considered. When the value of R is close to its minimum, systematic minimisation can be brought about.

A small change Δx_n in the x-coordinate of the n^{th} atom of a structure changes F_c by an amount $\frac{\partial F_c}{\partial x_n} \Delta x_n$.

Changes to all coordinates simultaneously result in a change in F_c of the amount

$$\Delta F_c = \sum_{n=1}^N \left[\frac{\partial F_c}{\partial x_n} \Delta x_n + \frac{\partial F_c}{\partial y_n} \Delta y_n + \frac{\partial F_c}{\partial z_n} \Delta z_n \right] \quad \dots \text{IV.11}$$

The correct values of x_n etc. are those which most nearly equate ΔF_c to $F_o - F_c$ for all the equations of this type that can be set up corresponding to all the measured values of F_o 's.

Multiplying both sides of the equation

$$\Delta F_c = F_o - F_c \quad \text{by} \quad w \frac{\partial F_c}{\partial x_n}$$

and adding all the equations, we have

$$\begin{aligned} \sum_m w \left\{ \frac{\partial F_c}{\partial x_n} \Delta x_n + \frac{\partial F_c}{\partial x_n} \frac{\partial F_c}{\partial y_n} \Delta y_n + \frac{\partial F_c}{\partial x_n} \frac{\partial F_c}{\partial z_n} \Delta z_n + \sum_m \frac{\partial F_c}{\partial x_n} \left(\frac{\partial F_c}{\partial x_m} \Delta x_m \right. \right. \\ \left. \left. + \frac{\partial F_c}{\partial y_m} \Delta y_m + \frac{\partial F_c}{\partial z_m} \Delta z_m \right) \right\} = \sum_q w (F_o - F_c) \frac{\partial F_c}{\partial x_n} \quad . . \quad \text{IV.12} \end{aligned}$$

where \sum_m denotes the sum over all other atoms except the n^{th} .

If the atoms are well resolved from one another the quantities such as $\sum_q w \frac{\partial F_c}{\partial x_n} \frac{\partial F_c}{\partial x_m}$ are very small compared to $\sum_q w \frac{\partial F_c}{\partial x_n}^2$ and hence can be neglected. If the axes are orthogonal or nearly so, $\sum_q w \frac{\partial F_c}{\partial x_n} \frac{\partial F_c}{\partial y_n}$ etc. can also be neglected so that the expression (IV.12) reduces to

$$\Delta x_n \sum_q w \left(\frac{\partial F_c}{\partial x_n} \right)^2 = \sum_q w (F_o - F_c) \frac{\partial F_c}{\partial x_n} \quad . . \quad \text{IV.13}$$

Expression IV.13 was used to calculate the shifts in atomic coordinates of β -Alanine.

(001) Projection

The structure factor $F(hko)$ is given by

$$F(hko) = \sum 8f \cos 2\pi h x \cos 2\pi k y \quad \text{for } h+k \text{ even and}$$

$$F(hko) = - \sum 8f \sin 2\pi h x \sin 2\pi k y \quad \text{for } h+k = 2n+1.$$

Differentiating with respect to x_n

$$\frac{\partial F}{\partial x_n} = - 8f \cos 2\pi k y_n \sin 2\pi h x_n \cdot 2\pi h \quad \text{for } h+k = 2n$$

and

$$\frac{\partial F}{\partial x_n} = - 8f \cos 2\pi h x_n \sin 2\pi k y_n \cdot 2\pi h. \quad \text{for } h+k = 2n+1.$$

Substituting these values of $\frac{\partial F}{\partial x_n}$ in the relation
IV.13

$$\Delta x_n = -\frac{1}{2\pi} \frac{\sum_{k=2n} (F_o - F_c) 8f \cdot h \cdot \sin 2\pi h x_n \cos 2\pi k y_n + \sum_{k=2n+1} (F_o - F_c) 8f \cdot h \cdot \cos 2\pi h x_n \sin 2\pi k y_n}{\sum_{k=2n} (8f \cdot h \cdot \sin 2\pi h x_n \cos 2\pi k y_n)^2 + \sum_{k=2n+1} (8f \cdot h \cdot \cos 2\pi h x_n \sin 2\pi k y_n)^2} \quad \text{IV.14}$$

Δx_n for the atoms N , C_1 , C_2 and O_1 were found out by means of the equation IV.14. Similarly an expression was derived for Δy_n

$$\Delta y_n = -\frac{1}{2\pi} \frac{\sum_{k=2n} (F_o - F_c) 8f \cdot h \cdot \cos 2\pi h x_n \sin 2\pi k y_n + \sum_{k=2n+1} (F_o - F_c) 8f \cdot h \cdot \sin 2\pi h x_n \cos 2\pi k y_n}{\sum_{k=2n} (8f \cdot h \cdot \cos 2\pi h x_n \sin 2\pi k y_n)^2 + \sum_{k=2n+1} (8f \cdot h \cdot \sin 2\pi h x_n \cos 2\pi k y_n)^2}$$

For the atoms C₃ and O₂ for which the quantity

$$\frac{\partial F_c}{\partial x_{c_3}} \quad \frac{\partial F_c}{\partial x_{o_2}} \quad \text{could not be neglected when compared with}$$

$$\sum \left(\frac{\partial F_c}{\partial x_{c_3}} \right)^2 \quad \text{or} \quad \sum \left(\frac{\partial F_c}{\partial x_{o_2}} \right)^2 \quad \text{the simultaneous equations}$$

$$\Delta x_{c_3} \sum \left(\frac{\partial F_c}{\partial x_{c_3}} \right)^2 + \Delta x_{o_2} \sum \frac{\partial F_c}{\partial x_{o_2}} \frac{\partial F_c}{\partial x_{c_3}} = \sum (F_o - F_c) \frac{\partial F_c}{\partial x_{c_3}}$$

and

$$\Delta x_{c_3} \sum \frac{\partial F_c}{\partial x_{c_3}} \frac{\partial F_c}{\partial x_{o_2}} + \Delta x_{o_2} \sum \left(\frac{\partial F_c}{\partial x_{o_2}} \right)^2 = \sum (F_o - F_c) \frac{F_c}{x_{o_2}}$$

were used to obtain Δx_{c_3} and Δx_{o_2} and similarly for Δy_{c_3} and Δy_{o_2} .

The shifts in atomic coordinates from the first least squares refinement gave a value for R of 0.204. At this stage the temperature factor was revised using observed and calculated structure factors by Wilson's method (Chapter II). The revised B value obtained from the graph of $\log_e \frac{\sum |F_o|}{\sum |F_c|}$ $\frac{\sin^2 \theta}{\lambda^2}$ was 2.4 Å². The F_c's were recalculated with the revised B value and gave an R value of 0.188. Two further cycles of least squares refinement were carried out at the end of which R was 0.169. The x and y parameters at the various stages of refinement are listed in Table IV.1.

T A B L E - IV.1

Changes in atomic parameters x/a and y/b

Atom	From (F-F _c) syntheses		After 1st least square refinement		After 2nd least square refinement		After 3rd least square refinement	
	x/a	y/b	x/a	y/b	x/a	y/b	x/a	y/b
N	0.293	0.072	0.2948	0.0689	0.2962	0.0670	0.2981	0.0638
C ₁	0.228	0.158	0.2241	0.1623	0.2281	0.1658	0.2289	0.1572
C ₂	0.085	0.160	0.0901	0.1594	0.0864	0.1575	0.0878	0.1589
C ₃	- 0.019	0.107	- 0.0222	0.1096	- 0.0172	0.1076	- 0.0212	0.1093
O ₁	- 0.140	0.100	- 0.1362	0.0972	- 0.1405	0.0964	- 0.1417	0.0970
O ₂	0.020	0.087	0.0186	0.0865	0.0214	0.0902	0.0175	0.0844
		R = 0.215		R = 0.204		R = 0.175		R = 0.169

(100) projection

y-coordinate was not refined from this projection. One least squares refinement was carried out for the z coordinate. The corrections Δz were obtained by the expression

$$\Delta z = \frac{\sum (F_o - F_c) \frac{\partial F_c}{\partial z}}{\sum \left(\frac{\partial F_c}{\partial z}\right)^2} \quad \text{IV.15}$$

$$F_c = \sum_{n=1}^{N/2} 8f \cos 2\pi ky \cos 2\pi lz \quad \text{for } k+l=2n, \quad \text{and}$$

$$= -\sum_{n=1}^{N/2} 8f \sin 2\pi ky \sin 2\pi lz \quad \text{for } k+l=2n+1$$

Hence

$$\frac{\partial F_c}{\partial z} = -8f \cos 2\pi ky \sin 2\pi lz \cdot 2\pi l \quad \text{for } k+l=2n \quad \text{and}$$

$$\frac{\partial F_c}{\partial z} = -8f \sin 2\pi ky \cos 2\pi lz \cdot 2\pi l \quad \text{for } k+l=2n+1.$$

Substituting for $\frac{\partial F_c}{\partial z}$ in the expression IV.15

$$\Delta z = -\frac{1}{2\pi} \frac{\sum_{l=2n} (F_o - F_c) 8f \cdot l \cdot \cos 2\pi ky \sin 2\pi lz + \sum_{l=2n+1} (F_o - F_c) 8f \cdot l \cdot \sin 2\pi ky \cos 2\pi lz}{\sum_{l=2n} (8f \cdot l \cdot \cos 2\pi ky \sin 2\pi lz)^2 + \sum_{l=2n+1} (8f \cdot l \cdot \sin 2\pi ky \cos 2\pi lz)^2}$$

The shifts in z from this refinement did not show any further improvement in the R factor. However these z coordinates were used for the final refinement using the general reflexions. The z -coordinates are

<u>Atom</u>	<u>z/c</u>
N	- 0.0446
C ₁	0.0114
C ₂	- 0.0827
C ₃	0.0766
O ₁	- 0.0184
O ₂	0.2285

As the atom O₂ ($z=0.2285$) lies close to the a -glide plane it was not possible to distinguish with certainty between O₂(xyz) and O₂($\frac{1}{2}+x, y, \frac{1}{2}-z$) from (100) projection from bond length considerations. This point was settled by the calculation of a few general structure factors. The z parameter of O₂ was taken as 0.2715 for further calculations.

Least squares refinement using the general reflexions

The atomic coordinates obtained from (001) and (100) projections were used to calculate $F(hkl)$. The formulae used for structure factor calculation are those given by the expressions IV.4, IV.5, IV.6 and IV.7. The observed structure factors for the data along the two axes were scaled separately with the F_c . For okl reflexions which

are common with the reflexions of the type hko, hk1, hk2 etc. (e.g. oko, ok1, ok2) a B value of 0.9\AA^2 was used. The two series of F_{ob} values were tabulated along with F_c . For 148 common reflexions the average of the two F_{ob} was taken to find the R factor. The R factor for 302 structure factors including unobserved ones at half the minimum observable value was 0.177. The agreement index ($\Sigma\Delta F/\Sigma F_o$) between 148 common F_{ob} was 0.166.

A least squares refinement was carried out with the general reflexions after giving half weight to all ($F_o - F_c$) values above 8 of which ^{there} were thirteen.

The corrections to the atomic coordinates were obtained using the equation (IV.13) for Δx and similar ones for Δy and Δz .

$\frac{\partial F_c}{\partial x}$ for the general reflexions fall into four classes which are derived by partial differentiation of the equations IV.4, IV.5, IV.6 and IV.7.

The four classes are

1. $\frac{\partial F_c}{\partial x} = - 8f \sin 2\pi hx \cos 2\pi ky \cos 2\pi lz \cdot 2\pi h. (A)$
for $h+k=2n, k+l=2n$
2. $\frac{\partial F_c}{\partial x} = 8f \sin 2\pi hx \sin 2\pi ky \sin 2\pi lz \cdot 2\pi h (B)$
for $h+k=2n, k+l=2n+1.$
3. $\frac{\partial F_c}{\partial x} = - 8f \cos 2\pi hx \cos 2\pi ky \sin 2\pi lz \cdot 2\pi h. (C)$
for $h+k=2n+1, k+l=2n;$
4. $\frac{\partial F_c}{\partial x} = - 8f \cos 2\pi hx \sin 2\pi ky \cos 2\pi lz \cdot 2\pi h. (D)$
for $h+k=2n+1, k+l=2n+1.$

Substituting for $\frac{\partial F}{\partial x}$ in the expression IV.13

$$\Delta x = -\frac{1}{2\pi} \frac{\sum_{\substack{h+k=2n \\ h+k=2n}} (F_o - F_c)A - \sum_{\substack{h+k=2n \\ k+l=2n+1}} (F_o - F_c)B + \sum_{\substack{h+k=2n+1 \\ k+l=2n}} (F_o - F_c)C + \sum_{\substack{h+k=2n+1 \\ k+l=2n+1}} (F_o - F_c)D}{\sum_{\substack{h+k=2n \\ k+l=2n}} (A)^2 + \sum_{\substack{h+k=2n \\ k+l=2n+1}} (B)^2 + \sum_{\substack{h+k=2n+1 \\ k+l=2n}} (C)^2 + \sum_{\substack{h+k=2n+1 \\ k+l=2n+1}} (D)^2}$$

where A, B, C and D represent the four classes of $\frac{\partial F_c}{\partial x}$ derived above.

Similar expressions were derived for Δy and Δz . All the calculations were done using a desk calculating machine. The maximum shift in atomic coordinates was about 0.03\AA . The reliability index after the refinement was 0.156 for 302 reflexions. The final atomic parameters are listed in Table IV.3 with their estimated standard deviations.

TABLE IV.3

Final atomic parameters and their estimated standard deviations.

	x/a	y/b	z/c
N	0.2955±0.0006	0.0663±0.0004	- 0.0450±0.0010
C ₁	0.2318±0.0007	0.1599±0.0005	0.0120±0.0012
C ₂	0.0850±0.0007	0.1601±0.0005	- 0.0796±0.0012
C ₃	-0.0214±0.0007	0.1107±0.0005	0.0717±0.0012
O ₁	-0.1393±0.0005	0.0960±0.0004	- 0.0156±0.0009
O ₂	0.0174±0.0005	0.0851±0.0004	0.2655±0.0009

Estimation of standard deviations

The agreement between the calculated and observed structure factors, so far taken as the reliability index, is to some extent a measure of the accuracy of the final results. Proper assessment of the accuracy of a structure determination, however, is the evaluation of the standard deviations of atomic coordinates, bond lengths and bond angles.

For a centro-symmetrical three dimensional synthesis the standard deviation $\sigma(x_n)$, of an atomic coordinate x_n is given by (Lipson and Cochran, 1953)

$$\sigma(x_n) = \frac{K}{\sqrt{2} Z_n} \left(\frac{\pi}{2p}\right)^{\frac{5}{4}} \left(\frac{1}{V} \sum_{n=1}^N Z_n^2\right)^{\frac{1}{2}}$$

where $K = \frac{\sigma(F_o)}{|F_o|}$ is taken equal to the final value of R. p is a constant which is given by Costain's (1941) formula

$$p = Z \left(\frac{p}{\pi}\right)^{\frac{3}{2}} \exp[-pr^2]$$

The value of this in practice is about 5.0\AA^2 . Z = atomic number of the atom concerned and V is volume of the unit cell.

The root mean square of $\sigma(x)$, $\sigma(y)$ and $\sigma(z)$ was taken as the standard deviation of the atomic position. The standard deviations are listed with the atomic parameters in table IV.3.

The standard deviation of the length of a bond between two atoms is given by

$$\sigma^2(d_{12}) = \sigma^2(x_1) + \sigma^2(x_2)$$

or $\sigma(d_{12}) = \sqrt{2} \sigma(x_1)$ when the atoms are the same. If the atoms are related by a mirror plane or a centre of symmetry then

$$\sigma(d_{12}) = 2\sigma(x_1).$$

The standard deviations in bond angles were estimated by the method of Darlow (1960). With isotropic standard deviations for each atom, the standard deviation of a bond angle θ subtended at atom 2 by bonds from atoms 1 and 3 is given by

$$\sigma^2(\theta) = \frac{\sigma^2(1)}{l_1^2} + \frac{l_{13}^2 \sigma^2(2)}{l_1^2 l_3^2} + \frac{\sigma^2(3)}{3}$$

where $\sigma(1)$, $\sigma(2)$ and $\sigma(3)$ are the standard deviations of any coordinate for atoms (1), (2) and (3) referred to orthogonal axes, l_1 is the length of bond between atoms, 1 and 2, l_3 and l_{13} are the bond lengths between atoms 2 and 3 and 1 and 3 respectively.

The standard deviations of the bond lengths and bond angles are given in chapter V.

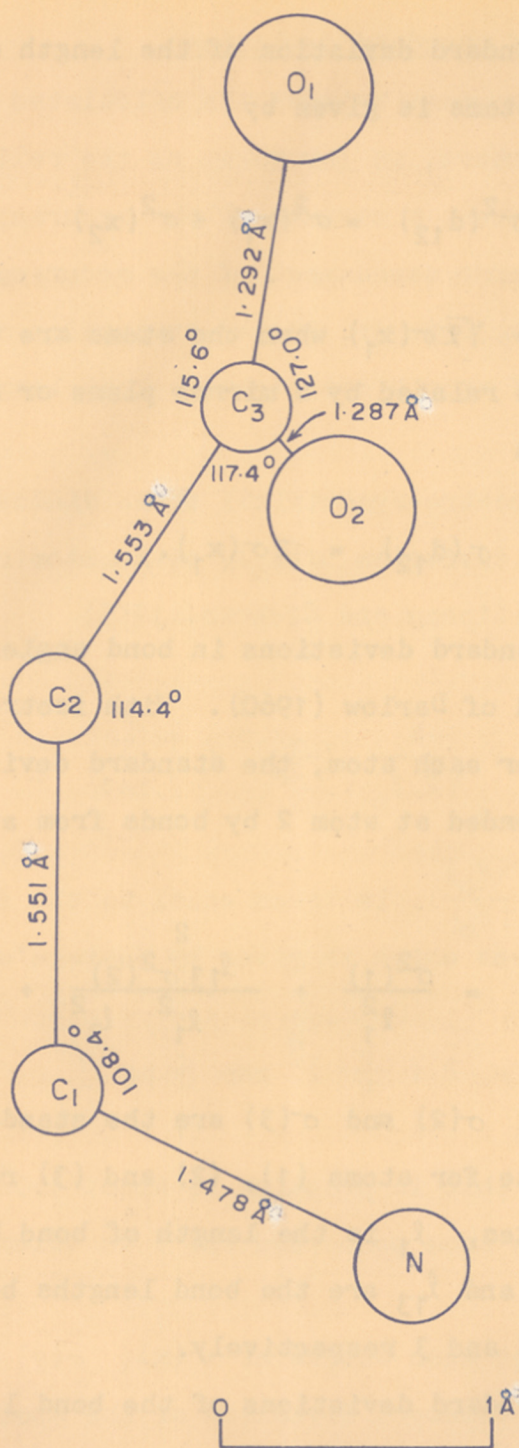


FIG. V-1. Bond lengths and bond angles in β -Alanine

C H A P T E R - V.

RESULTS AND DISCUSSION.

The final atomic coordinates in Angstrom units are listed in Table V.1

T A B L E - V.1

Atom	x in Å	y in Å	z in Å
N	2.9151	0.9156	- 0.2732
C ₁	2.2867	2.2082	0.0728
C ₂	0.8385	2.2110	- 0.4832
C ₃	- 0.2111	1.5288	0.4352
O ₁	- 1.3742	1.3382	- 0.0947
O ₂	0.1717	1.1752	1.6116

All interatomic distances were calculated from these. The intramolecular bond lengths and bond angles are indicated in Fig.V-1 and listed in Table V.2

T A B L E - V.2

Bond	Length	Bond angles
N - C ₁	1.478±0.010Å	N - C ₁ - C ₂ 108.4±0.6°
C ₁ - C ₂	1.551±0.010	C ₁ - C ₂ - C ₃ 114.4±0.6
C ₂ - C ₃	1.553±0.010	C ₂ - C ₃ - O ₁ 115.6±0.6
C ₃ - O ₁	1.292±0.009	C ₂ - C ₃ - O ₂ 117.4±0.6
C ₃ - O ₂	1.287±0.009	O ₁ - C ₃ - O ₂ 127.0±0.7

Molecular Structure

The bond lengths and angles are in general close to the expected values. The two C-O bonds of the carboxyl group are compared with those of Copper Nickel and Cobalt complexes in Table V.3

T A B L E-V.3

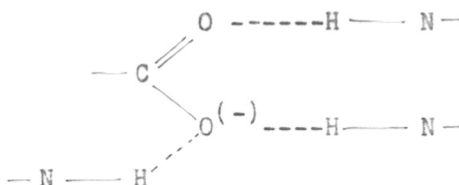
	C-O	C-O	Reference
Cu β -Alanine. 6H ₂ O	1.23Å	1.26Å	Tomita 1961
Ni β -Alanine. 2H ₂ O	1.215±0.038	1.279±0.038	Present work
Co β -Alanine. 2H ₂ O	1.277±	1.249±	"
β -Alanine	1.292±0.009	1.287±0.009	"

The two C-O bond lengths in β -Alanine are more nearly equal than in the complexes. The two bonds are compared with those in some other amino acids in Table V.4

T A B L E-V.4

Compound	C-O	C-O	Reference
α -Glycine	1.261	1.265	Marsh (1958).
Dl α -Alanine	1.26	1.23	Donohue J (1950).
Dl - Serine	1.268	1.261	Shoemaker et. al. (1953).
Threonine	1.25	1.24	Shoemaker et. al. (1950).
Hydroxy-L-Proline	1.27	1.25	Donohue and ^{Trueblood.} True blood (1952)
β -glycyl glycine	1.27	1.21	Hughes and Moore (1949).
N-acetyl glycine	1.31	1.19	Carpenter and Donohue (1950); Donohue and Marsh.(1962).
β -Alanine	1.292	1.287	Present work.

In the amino acids listed ^{in table V.4} above the two C-O bond lengths are more nearly equal in those structures which exist in the 'zwitterion' form (discussed under crystal structure) than in N-acetyl glycine which does not have the zwitterion structure. Part of the variation between the two C-O bond lengths in the others have been attributed to the particular intermolecular attractions. The inequality in DL-alanine, for example, has been attributed by Donohue (1950) to the lack of complete resonance arising from the fact that one of the oxygen atoms takes part in two hydrogen bonds while the second oxygen atom takes part in only one. The result is that the form



is favoured.

Equations of planes

The normal forms of equations of the various planes are given below:

1. The plane containing the atoms N, C₁ and C₂ can be represented by the equation

$$-0.332x - 0.352y + 0.870z + 1.563 = 0 \quad \text{and}$$

2. The plane passing through the atoms C₁, C₂ and C₃ has the equation

$$-0.172x + 0.874y + 0.453z - 1.570 = 0$$

where x, y and z represent the axes of the unit cell.

The angle between these two planes was found to be 83.8°. This is slightly larger than the corresponding angles in Copper β-Alanine. 6H₂O (70°, Tomita, 1961) Nickel β-Alanine.^{2H₂O} (73.7° present work) and Cobalt β-Alanine.^{2H₂O} (78°, present work).

3. The atoms C₃, C₂, O₁ and O₂ (figure V-1) are almost coplanar, the sum of the three angles around C₃ being 360.0°. This situation holds for many of the amino acids some of which are listed in Table V.5.

T A B L E - V.5

Angle	Hydroxy L-proline	L- Threonine	Dl- Alanine	Dl- Serine	β-Alanine
O ₁ -C ₃ -O ₂	126.1°	126.9°	125.4°	125.3°	127.0°
O ₁ -C ₃ -C ₂	118.5°	117.0	121.3	117.4	115.6
O ₂ -C ₃ -C ₂	115.4°	116.1	113.2	117.2	117.4

The mean plane through the atoms C₂, C₃, O₁ and O₂ is represented by

$$-0.290x + 0.891y + 0.348z - 1.563 = 0$$

The normal distances of the individual atoms from the mean plane are 0.013 Å for C₃ and -0.004 Å for C₂, O₁ and O₂. This plane makes an angle of 9.3° with the plane containing the atoms C₁, C₂ and C₃. This angle is much smaller than the corresponding angles in nickel and cobalt β-Alanine dihydrates (30.1° and 32.8°). The differences

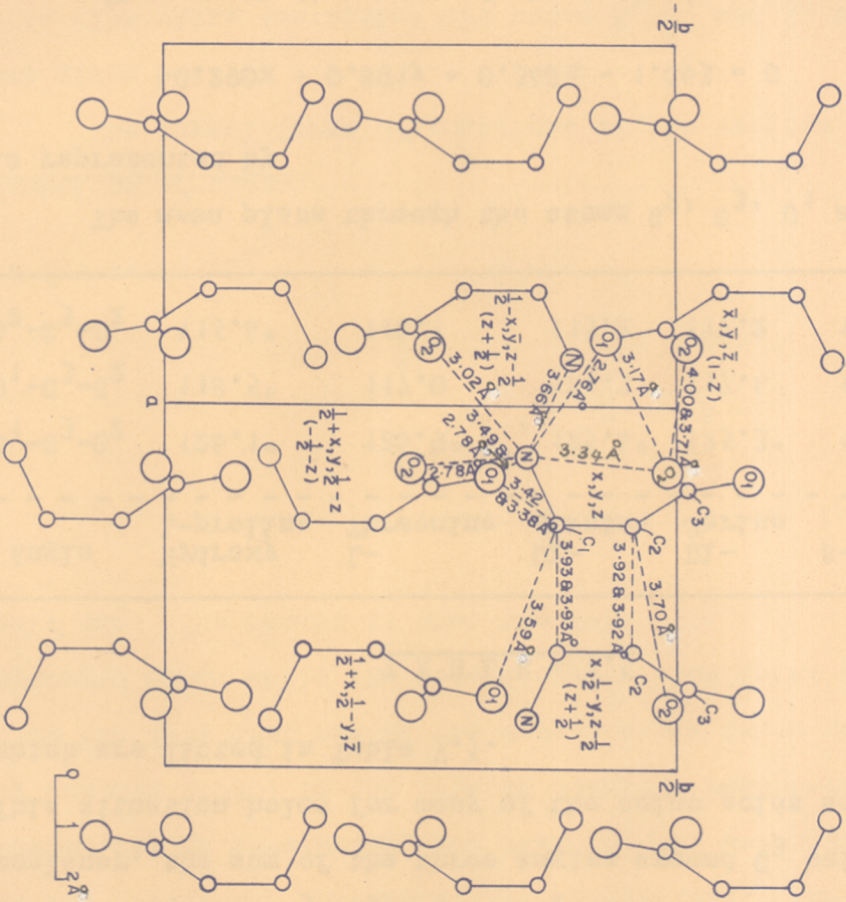


FIG. V-2. Structure projected on (001)

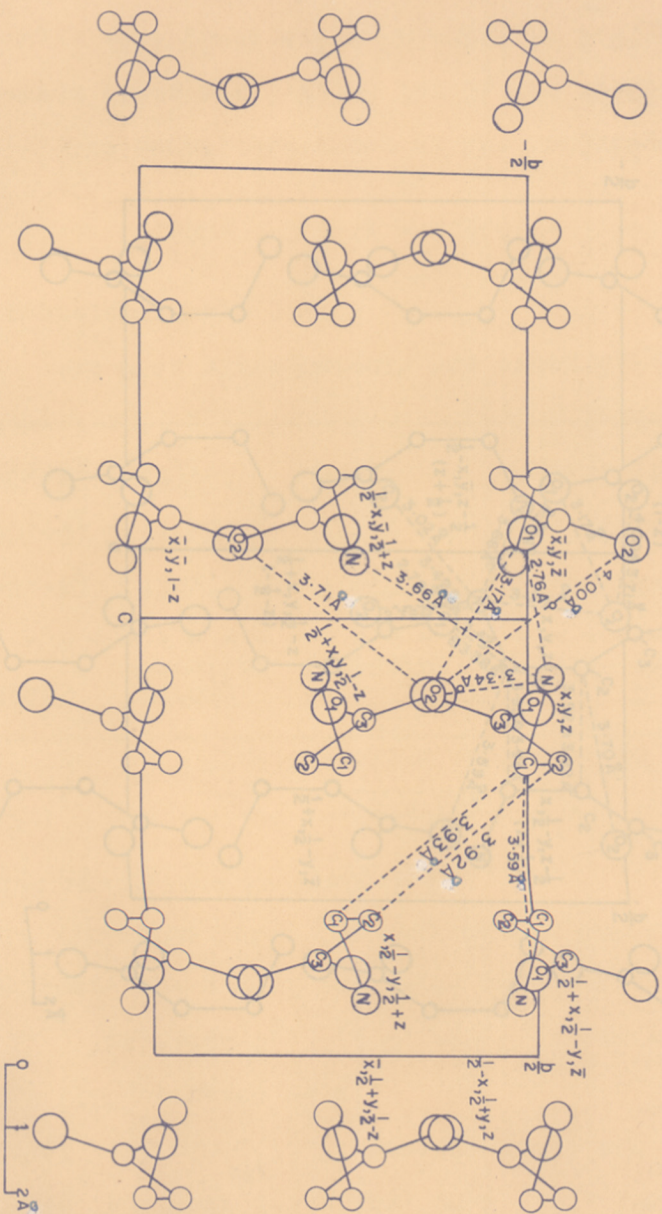


FIG. 3. Structure projected on (100)

FIG. 2. Structure projected on (001)

in the angles may be due to the coordination of nitrogen atom and oxygen atom (O_1) to the metal in the complex.

Crystal Structure

The projections of the structure along the c and a axes are shown in figures V.2 and V.3. All the symmetry related molecules in a unit cell and a few from neighbouring cells are also shown. Intermolecular distances are drawn by broken lines in these figures and listed in Table V.6.

T A B L E - V.6

Intermolecular distances

Contact	Bond length in Å
$N(x, y, z) - O_1(\frac{1}{2}+x, y, -\frac{1}{2}-z)$	$2.78 \pm 0.01 \text{Å}$
$N(x, y, z) - O_2(\frac{1}{2}+x, y, \frac{1}{2}-z)$	2.78 ± 0.01
$N(x, y, z) - O_1(\bar{x}, \bar{y}, \bar{z})$	2.76 ± 0.01
$N(x, y, z) - O_2(\frac{1}{2}-x, \bar{y}, z-\frac{1}{2})$	3.02 ± 0.01
$C_1(x, y, z) - O_1(\frac{1}{2}+x, y, -\frac{1}{2}-z)$	3.38 ± 0.01
$C_1(x, y, z) - O_1(\frac{1}{2}+x, y, \frac{1}{2}-z)$	3.42 ± 0.01
$C_2(x, y, z) - O_2(x, \frac{1}{2}-y, z-\frac{1}{2})$	3.70 ± 0.01
$O_2(x, y, z) - O_1(\bar{x}, \bar{y}, \bar{z})$	3.17 ± 0.01
$N(x, y, z) - N(\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z)$	3.66 ± 0.01
$C_1(x, y, z) - O_1(\frac{1}{2}+x, \frac{1}{2}-y, \bar{z})$	3.59 ± 0.01
$C_1(x, y, z) - C_1(x, \frac{1}{2}-y, \frac{1}{2}+z)$	3.93 ± 0.01
$C_2(x, y, z) - C_2(x, \frac{1}{2}-y, \frac{1}{2}+z)$	3.92 ± 0.01

Hydrogen bonds

The nitrogen atom (x,y,z) is immediately surrounded by four oxygens $O_1(\frac{1}{2}+x, y, -\frac{1}{2}-z)$, $O_2(\frac{1}{2}+x, y, \frac{1}{2}-z)$, $O_1(\bar{x}, \bar{y}, \bar{z})$ and $O_2(\frac{1}{2}-z, \bar{y}, z-\frac{1}{2})$ at distances 2.78Å, 2.78Å, 2.76Å and 3.02Å respectively (Figure V-2). In the absence of the knowledge about hydrogen positions the probable hydrogen bonds could be decided by the evaluation of angles which these bonds make with the C_1-N bond and with each other. The angles were found to be

Contacts	Angle
$C_1-N-O_1(\bar{x}, \bar{y}, \bar{z})$	$116.4 \pm 0.4^\circ$
$C_1-N-O_2(\frac{1}{2}+x, y, \frac{1}{2}-z)$	$96.4 \pm 0.4^\circ$
$C_1-N-O_1(\frac{1}{2}+x, y, -\frac{1}{2}-z)$	$101.0 \pm 0.4^\circ$
$O_1(\frac{1}{2}+x, y, -\frac{1}{2}-z)-N-O_2(\frac{1}{2}+x, y, \frac{1}{2}-z)$	$112.9 \pm 0.3^\circ$
$O_1(\bar{x}, \bar{y}, \bar{z})-N-O_2(\frac{1}{2}+x, y, \frac{1}{2}-z)$	$115.6 \pm 0.3^\circ$
$O_1(\bar{x}, \bar{y}, \bar{z})-N-O_1(\frac{1}{2}+x, y, -\frac{1}{2}-z)$	$112.4 \pm 0.3^\circ$
$O_2(\frac{1}{2}-x, \bar{y}, z-\frac{1}{2}) - N - C_1$	$162.3 \pm 0.5^\circ$
$O_2(\frac{1}{2}-x, \bar{y}, z-\frac{1}{2}) - N - O_1(\bar{x}, \bar{y}, \bar{z})$	$80.0 \pm 0.2^\circ$
$O_2(\frac{1}{2}-x, \bar{y}, z-\frac{1}{2}) - N - O_2(\frac{1}{2}+x, y, \frac{1}{2}-z)$	$79.4 \pm 0.2^\circ$
$O_2(\frac{1}{2}-x, \bar{y}, z-\frac{1}{2}) - N - O_1(\frac{1}{2}+x, y, -\frac{1}{2}-z)$	$66.3 \pm 0.2^\circ$

The angles which $N-O_2(\frac{1}{2}-x, \bar{y}, z-\frac{1}{2})$ (3.02Å) makes with the other possible hydrogen bonds and with C_1-N bond differ widely from the tetrahedral angle of 109.5° while the other three bonds make angles which are all close to it. This indicates that nitrogen takes part in the

formation of three strong hydrogen bonds. The nearly tetrahedral disposition of these hydrogen bonds establishes the fact that β -Alanine like most of the amino acids exists in the crystal in the zwitterion form $^+\text{NH}_3\text{CH}_2\text{CH}_2\text{COO}^-$.

The formation of hydrogen bonds in β -Alanine is different from that found in α , β and γ glycines, the three polymorphic forms of glycine which also have the zwitterion structure. In α and β glycines (Albrecht and Corey 1939; Marsh 1958, Iitaka 1960) strong hydrogen bonds (lengths 2.768 Å, 2.850 Å in α -glycine and 2.758 Å, 2.833 Å in β -glycine) involving two hydrogens of the NH_3 group are arranged nearly in tetrahedral directions with respect to C-N bond and hold the molecules together in a layer. The third hydrogen is situated between two neighbouring oxygens of adjacent layer forming a weak 'bifurcated' bond (which accounts for the formation of double layers). In γ glycine (Iitaka 1961) Nitrogen is surrounded by five oxygen atoms at short distances. Three of these take part in hydrogen bond formation and the other two are possibly linked by electrostatic attraction to the NH_3^+ group. The hydrogen bonds link the molecules into helical chains.

Packing of molecules

The β -Alanine molecules are held together in a layer parallel to (010) by the hydrogen bonds $\text{N-H}\dots\text{O}_1(\frac{1}{2}+x, y, \frac{1}{2}-z)$ and $\text{N-H}\dots\text{O}_2(\frac{1}{2}+x, y, \frac{1}{2}-z)$ (figure V.2). Each such layer is linked to the adjacent layer by the third hydrogen bond $\text{N-H}\dots\text{O}_3(\bar{x}, \bar{y}, \bar{z})$. The β -Alanine crystal is thus made up

of double layers of molecules firmly held by hydrogen bonds between nitrogen and oxygen atoms and also by electrostatic attraction between these same atoms. The double layers are connected to the neighbouring double layers by normal Van der Waal's distances (Table V.6). This description explains the observation of cleavage on (010) face. In DL-Serine (α -amino β -hydroxy propionic acid) (Shoemaker et al. 1953) which also has a layer structure, cleavage takes place across a hydrogen bond between amino nitrogen of one molecule and the hydroxyl oxygen of another molecule from the adjacent layer. This bond is explained to be weaker than the other hydrogen bonds (notwithstanding the apparently shorter distance) because the hydroxyl oxygen atom has no formal charge on it.

The double layer structure in β -Alanine is similar to that found in α and β glycines, norleucine (Mathieson, 1953) and α and β forms of methionine (Mathieson 1952).

C H A P T E R - VI.

The structures of Nickel and Cobalt complexes of
 β -Alanine

A. EXPERIMENTAL

Nickel β -Alanine complex

Nickel β -Alanine dihydrate was prepared by heating an aqueous solution of β -Alanine with freshly precipitated Nickel hydroxide in the stoichiometric ratio 2:1. The solution was filtered and concentrated. On slow evaporation, greenish blue needles which were analysed for carbon, hydrogen, nitrogen and oxygen giving the molecular formula $\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{COO})_2 \cdot 2\text{H}_2\text{O}$ were obtained.

The crystals belong to the triclinic system. For the collection of data along the needle axis a crystal having cross section of 0.1 mm x 0.18 mm and 1 mm in length was used. The data along the other two axes were obtained with crystals of dimensions between 0.1 mm and 0.25 mm along the different directions normal to the oscillation axes. Accurate setting of the crystal was done by the method of double oscillation (Davies, 1950). Preliminary values of axial lengths were obtained from rotation photographs taken around all the three axes with CuK_α radiation. Accurate values of the unit cell dimensions were determined from high angle spots in zero layer Weissenberg photographs. The angles α , β and γ were

calculated from the measured α^* , β^* and γ^* on the same photographs.

The expressions used for calculating the angles α , β and γ in a triclinic system are

$$\cos\alpha = \frac{\cos\beta^* \cos\gamma^* - \cos\alpha^*}{\sin\beta^* \sin\gamma^*}$$

$$\cos\beta = \frac{\cos\alpha^* \cos\gamma^* - \cos\beta^*}{\sin\alpha^* \sin\gamma^*}$$

$$\cos\gamma = \frac{\cos\alpha^* \cos\beta^* - \cos\alpha^*}{\sin\alpha^* \sin\beta^*}$$

and the relations used for axial lengths are

$$a = \frac{1}{\alpha^* \sin\beta^* \sin\gamma^*}$$

$$b = \frac{1}{\beta^* \sin\alpha^* \sin\gamma^*}$$

$$\text{and } c = \frac{1}{c^* \sin\alpha^* \sin\beta^*}$$

Volume of the unit cell, $V = abc \sin\alpha \sin\beta \sin\gamma$.

a^* was determined from the reflexions 900 and 800, b^* from 070 and 050 and c^* from 005 and 004, using the expressions

$$a^* = \frac{\lambda}{d_{100}}, \quad b^* = \frac{\lambda}{d_{010}} \quad \text{and} \quad c^* = \frac{\lambda}{d_{001}}$$

where λ is the wavelength of X-rays used.

The unit cell dimensions ^{and inter axial angles} are

$$a = 8.48, \quad b = 6.77, \quad c = 4.93 \text{ \AA}$$

$$\alpha = 103.0^\circ, \quad \beta = 95.2^\circ, \quad \gamma = 102.3^\circ$$

The density measured by flotation in a mixture of Ethylene dichloride and Ethylene dibromide was found to be 1.720 gm.cm^{-3} while that calculated for one unit of $\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{COO})_2 \cdot 2\text{H}_2\text{O}$ per cell is 1.689 gm.cm^{-3} .

The linear absorption coefficient μ of $\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{COO})_2 \cdot 2\text{H}_2\text{O}$ for CuK_α radiation is 30.1 cm^{-1} . Intensity data were collected from equatorial Weissenberg photographs taken around all the three axes with CuK_α radiation and using the multiple film technique. Weissenberg photographs of short exposures (2-3 hrs) were taken to estimate the intensities of strong reflexions. Intensity scales were prepared with the same crystals used for intensity data collection, in every case using a pack of 3 films. Of the 144 possible reflexions in the hko zone, 107 were observed and in the hol and okl zones 73 and 68 reflexions were observed respectively out of possible 100 and 87 reflexions.

Intensities were estimated visually with the help of scales obtained with the same crystals. The ratio of the intensities of the strongest to the weakest reflexion was 720:1. The observed intensities were corrected for Lorentz-polarization factor described in chapter II. No absorption correction was applied.

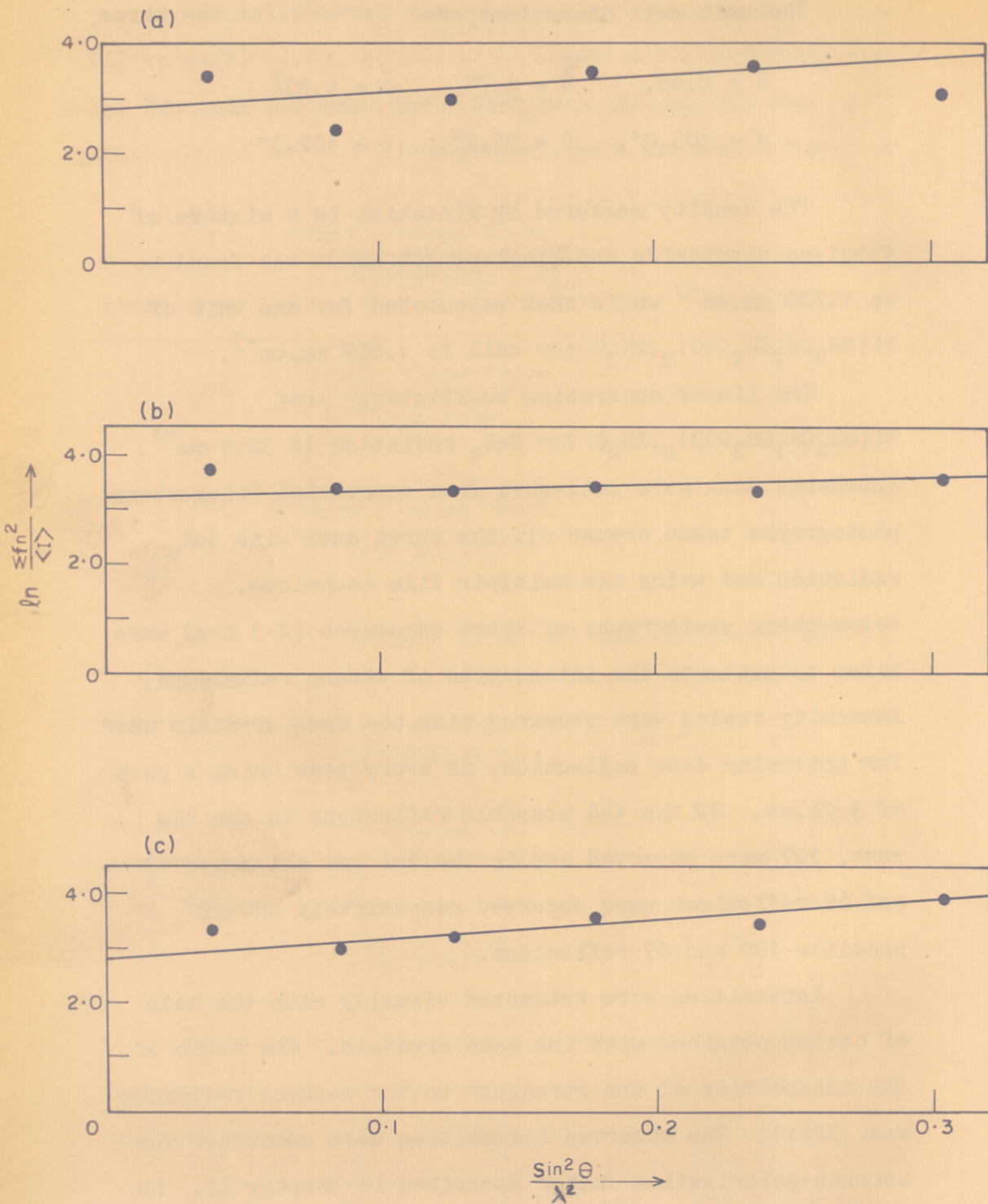


FIG. VII-1 Wilson's graphs for scale factors and temp.-factors for Ni- β -Alanine.
 (a) (001) projection; (b) (100) projection; (c) (010) projection

Temperature factors and scale factors for the three zones were obtained by Wilson's method (1942) (Chapter II). The plots of the $\log_e C$ against $\frac{\sin^2 \theta}{\lambda^2}$ for the hko, okl and hol reflexions are shown in figure VI-1. The corresponding data are given in Table VI-1.

T A B L E VI-1

Scale factor and temperature factor for hol reflexions

$\sin \theta$	$\frac{\sin^2 \theta}{\lambda^2}$	$\sum f_n^2$	$\langle I \rangle$	$C = \frac{\sum f_n^2}{\langle I \rangle}$	$\log_e C$
0.2-0.4	0.038	810	29.77	27.2	3.303
0.4-0.5	0.085	505	25.9	19.51	2.971
0.5-0.6	0.127	381	15.8	24.11	3.183
0.6-0.7	0.178	292	8.0	35.25	3.563
0.7-0.8	0.237	234	7.31	32.0	3.466
0.8-0.9	0.304	198	4.0	49.5	3.902

From the graph $B = 1.8 \text{ \AA}^2$; Scale factor = 4.2

Scale factor and temperature factor for okl reflexions

$\sin \theta$	$\frac{\sin^2 \theta}{\lambda^2}$	$\sum f_n^2$	$\langle I \rangle$	$C = \frac{\sum f_n^2}{\langle I \rangle}$	$\log_e C$
0.2-0.4	0.038	810	19.6	41.33	3.722
0.4-0.5	0.085	505	16.33	31.00	3.434
0.5-0.6	0.127	381	13.55	28.12	3.337
0.6-0.7	0.178	292	9.83	29.70	3.391
0.7-0.8	0.237	234	8.07	29.02	3.368
0.8-0.9	0.304	198	5.61	35.29	3.563

From the graph $2B = 1.1 \text{ \AA}^2$; Scale factor = 4.95

Scale factor and temperature factor for hko reflexions

$\sin\theta$	$\frac{\sin^2\theta}{\lambda^2}$	$\sum f_n^2$	$\langle I \rangle$	$C = \frac{\sum f_n^2}{\langle I \rangle}$	$\log_e C$
0.2-0.4	0.038	810	22.21	36.47	3.597
0.4-0.5	0.085	505	33.3	15.17	2.719
0.5-0.6	0.127	381	14.2	27.2	3.303
0.6-0.7	0.178	292	6.0	48.6	3.884
0.7-0.8	0.237	234	4.5	39.33	3.672
0.8-0.9	0.304	198	5.68	34.56	3.551

From the graph $B = 1.8\text{\AA}^2$; Scale factor = 4.3

Individual isotropic temperature factors for all atoms were obtained during the later stages of refinement.

The structure factors were calculated using McWeeny's values (1951) of scattering factors for Carbon, Nitrogen and Oxygen and Thomas and Umeda's (1957) values for Ni^{2+} . The atomic scattering factors of Nickel were corrected for dispersion by K electrons.

Dispersion Correction

If any atom in a crystal has an absorption edge which lies very close to the incident radiation but is shorter than the latter, the wave scattered by that atom has a phase shift of half a wave length. On the other hand when the wave length of X-rays is shorter than the absorption edge of any atom, there is a change of phase of

less than half a wavelength between the incident wave and the scattered wave. The resultant wave can be expressed in terms of normal wave f_0 with the aid of a real and imaginary correction $\Delta f'$ and $i\Delta f''$

$$f = f_0 + \Delta f' + i\Delta f''$$

f_0 is a function of $\sin\theta$. The corrections $\Delta f'$ and $i\Delta f''$ are nearly independent of θ because the tightly bound electrons responsible for these effects are concentrated in a small volume near the atomic nucleus; they are functions of λ . For $\frac{\lambda}{\lambda_k} > 1$, λ being the wave length of X-rays used and λ_k is ^{Ni}_k absorption edge $\Delta f'' = 0$. Hence in the case nickel ($\frac{\lambda}{\lambda_k} = 1.037$)

$$f = f_0 + \Delta f'$$

The value of $\Delta f'$ was obtained from tables given by James (1950) so that $f = f_0 - 3.5$.

Cobalt β -Alanine complex

Cobalt β -Alanine dihydrate was prepared by a method similar to that used for the Nickel complex using freshly precipitated cobalt hydroxide. On slow evaporation pink needles were obtained. Preliminary rotation photographs and equatorial Weissenberg photograph taken along the needle axis showed that Cobalt β -Alanine, molecular formula $\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{COO})_2 \cdot 2\text{H}_2\text{O}$, was isomorphous with Nickel β -Alanine dihydrate.

The unit cell dimensions and inter axial angles α , β and γ were determined from zero layer Weissenberg photographs using the same equations as those given for Nickel β -Alanine.

The reflexions used to obtain a^* , b^* and c^* are

900, 800 and 500 for a^*

080 and 070 for b^* and 006 for c^*

The values of unit cell dimensions and interaxial angles are

$$\begin{array}{lll} a = 8.54\text{\AA}, & b = 6.79\text{\AA}, & c = 4.96\text{\AA} \\ \alpha = 103.3^\circ & \beta = 95.8^\circ & \gamma = 101.3^\circ \end{array}$$

The density was measured by flotation method using a mixture of Ethylene dichloride and Ethylene dibromide at 24°C . The observed value is 1.69 gm/c.c. and that calculated for one molecule of $\text{Co}(\text{NH}_2\text{CH}_2\overset{\text{CH}_2}{\text{C}}\text{OO})_2 \cdot 2\text{H}_2\text{O}$, per unit cell is 1.66 gm.cm^{-3}

The linear absorption coefficient μ of $\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{COO})_2 \cdot 2\text{H}_2\text{O}$ for MoK_α radiation was found to be 16.7 cm^{-1} and optimum thickness $t = 0.12 \text{ cm.}$ and that for CuK_α radiation was calculated to be 142.1 cm^{-1} and $t = 0.14 \text{ mm.}$ Intensity data along the needle axis were obtained with both CuK_α and MoK_α radiations with needles having cross sectional area of 0.1 mm by 0.15 mm (for CuK_α radiation) and 0.2 mm x 0.3 mm (for MoK_α radiation). For the other two axes the specimens used were between 0.3 mm and 0.5 mm along the different directions normal to the oscillation axes. Intensity data along a and b axes were

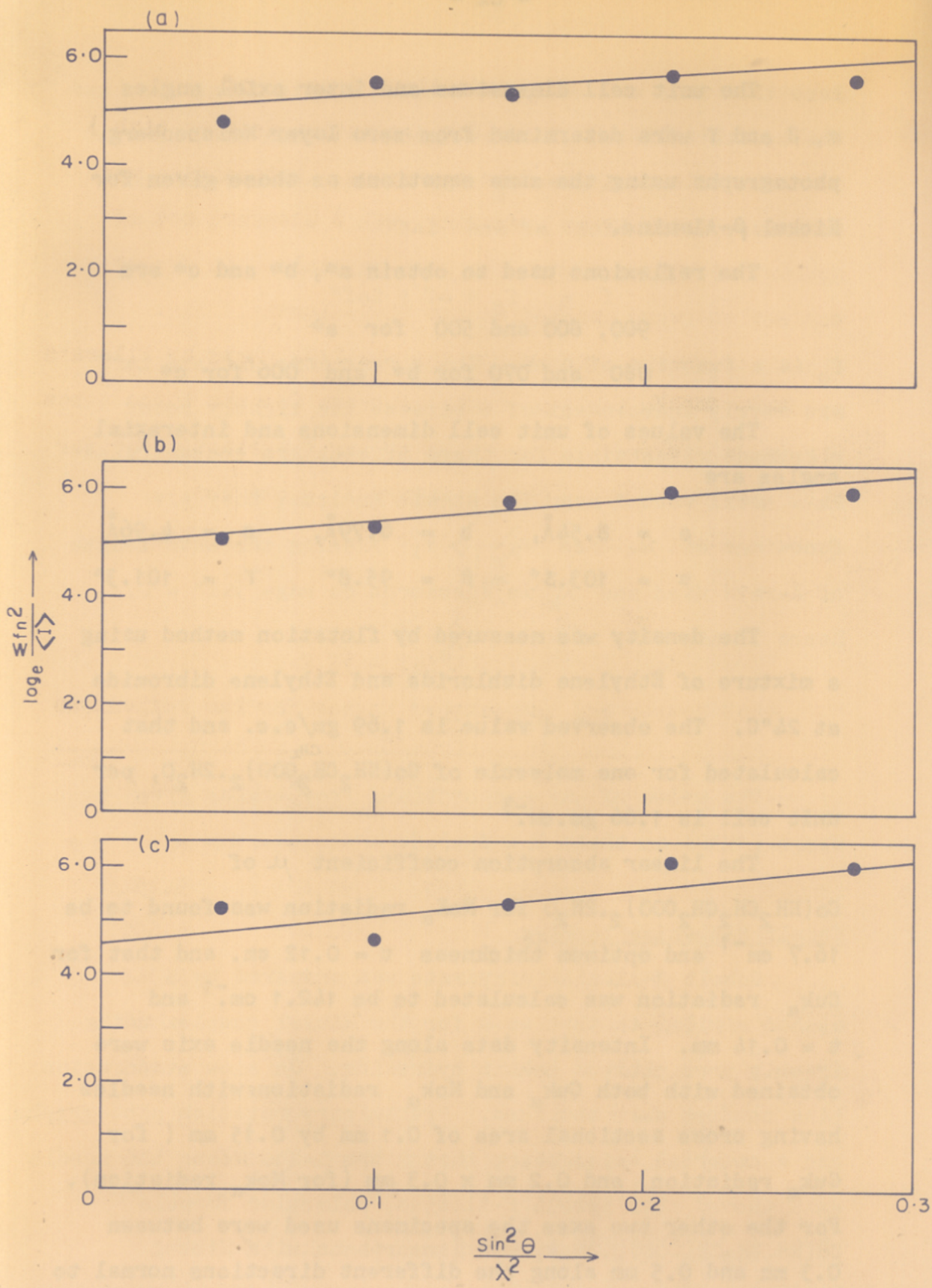


FIG. VI -2. (a) okl reflexions (b) hol reflexions (c) hko reflexions. (Co-β-Alanine)

collected only with Mok_{α} radiation (as μ of $Co(NH_2CH_2CH_2COO)_2 \cdot 2H_2O$ for CuK_{α} radiation is very high) and using the multiple film technique. Intensities were estimated visually by comparing with a standard set of reflexions obtained with the same crystals. Lp factor corrections were applied as for Ni- β -Alanine. The intensities were then put on the absolute scale by Wilson's method by which the temperature factors for the three zones were also obtained. The graphs of $\log_e C$ against $\frac{\sin^2 \theta}{\lambda^2}$ for the three zones are shown in figure VI.2 and the corresponding data given in Table VI.2. λ for Mok_{α} radiation was taken as 0.711 \AA .

T A B L E - VI.2

Scale factor and temperature factor for hko reflexions
(Mok_{α} radiation)

$\sin \theta$	$\frac{\sin^2 \theta}{\lambda^2}$	$\sum f_n^2$	$\langle I \rangle$	$C = \frac{\sum f_n^2}{\langle I \rangle}$	$\log_e C$
0.1-0.2	0.044	1144	5.977	191.4	5.254
0.2-0.25	0.100	960	9.181	104.6	4.650
0.25-0.3	0.1496	826	3.90	210.2	5.348
0.3-0.35	0.2089	710	1.52	467.1	6.147
0.35-0.4	0.278	605	1.412	428.5	6.060

From the graph $B = 2.7 \text{ \AA}^2$; Scale factor = 9.73

Scale factor and temperature factor for okl reflexions

Sin θ	$\frac{\text{Sin}^2\theta}{\lambda^2}$	$\sum f_n^2$	$\langle I \rangle$	$C = \frac{\sum f_n^2}{\langle I \rangle}$	$\log_e C$
0.1-0.2	0.044	1144	9.355	122.2	4.806
0.2-0.25	0.100	960	3.50	274.3	5.614
0.25-0.3	0.1496	826	3.81	216.8	5.379
0.3-0.35	0.2089	710	2.25	315.6	5.754
0.35-0.4	0.278	605	2.10	288.1	5.668

From the graph $B = 1.8\text{\AA}^2$, Scale factor = 12.2

Scale factor and temperature factor for hol reflexions

Sin θ	$\frac{\text{Sin}^2\theta}{\lambda^2}$	$\sum f_n^2$	$\langle I \rangle$	$C = \frac{\sum f_n^2}{\langle I \rangle}$	$\log_e C$
0.1-0.2	0.044	1144	7.185	159.2	5.070
0.2-0.25	0.100	960	4.573	209.9	5.347
0.25-0.3	0.1496	826	2.415	342.0	5.835
0.3-0.35	0.2089	710	1.661	402.7	5.998
0.35-0.4	0.298	605	1.482	408.2	6.012

From the graph $B = 2.4\text{\AA}^2$, Scale factor = 11.9

Space group

The space group was assumed to be $P\bar{1}$. As there is only one molecule per unit cell Nickel must be at the centre of symmetry. This was later confirmed from the Patterson and electron density projections.

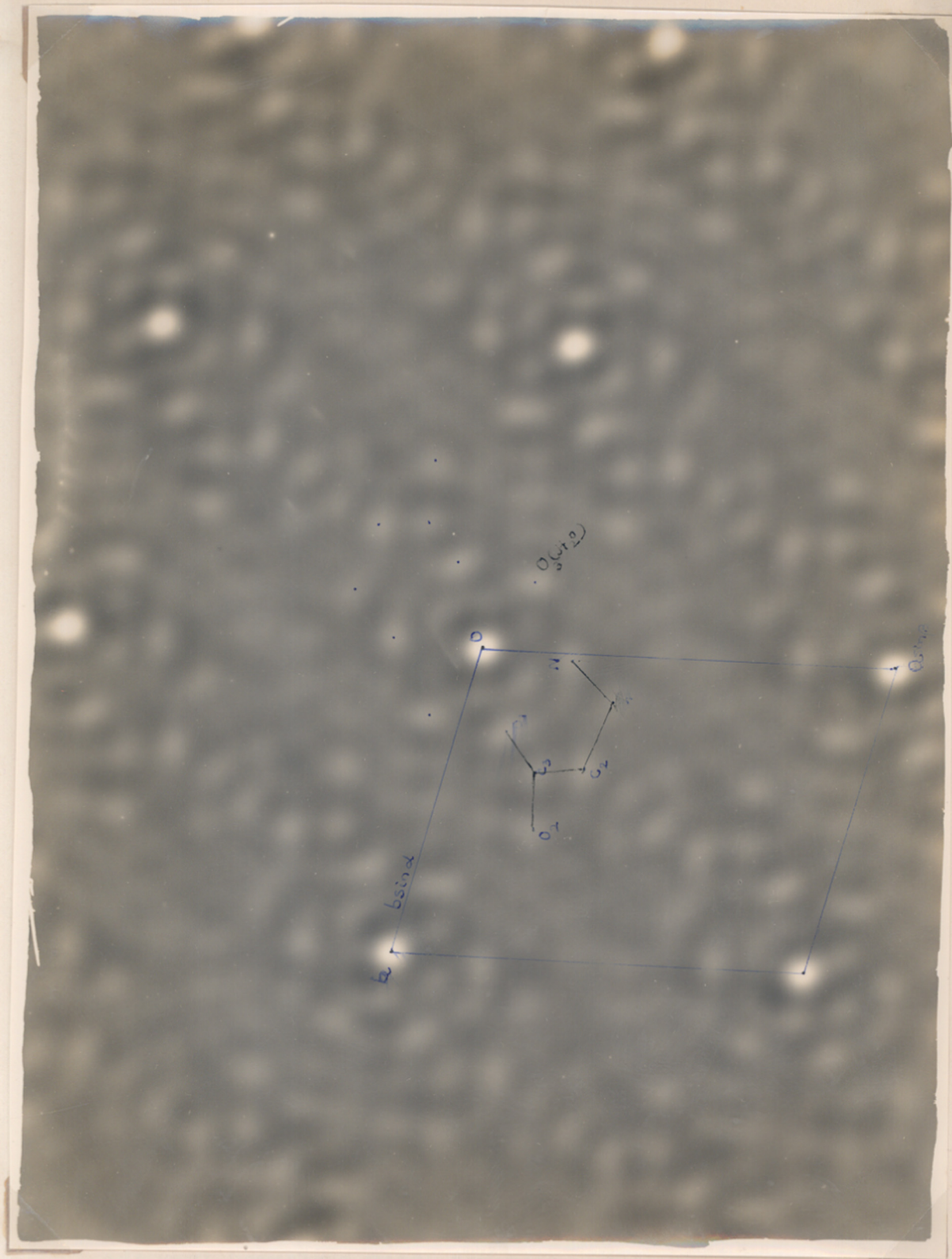


Fig. VI-3 Sharpened (001) Patterson projection

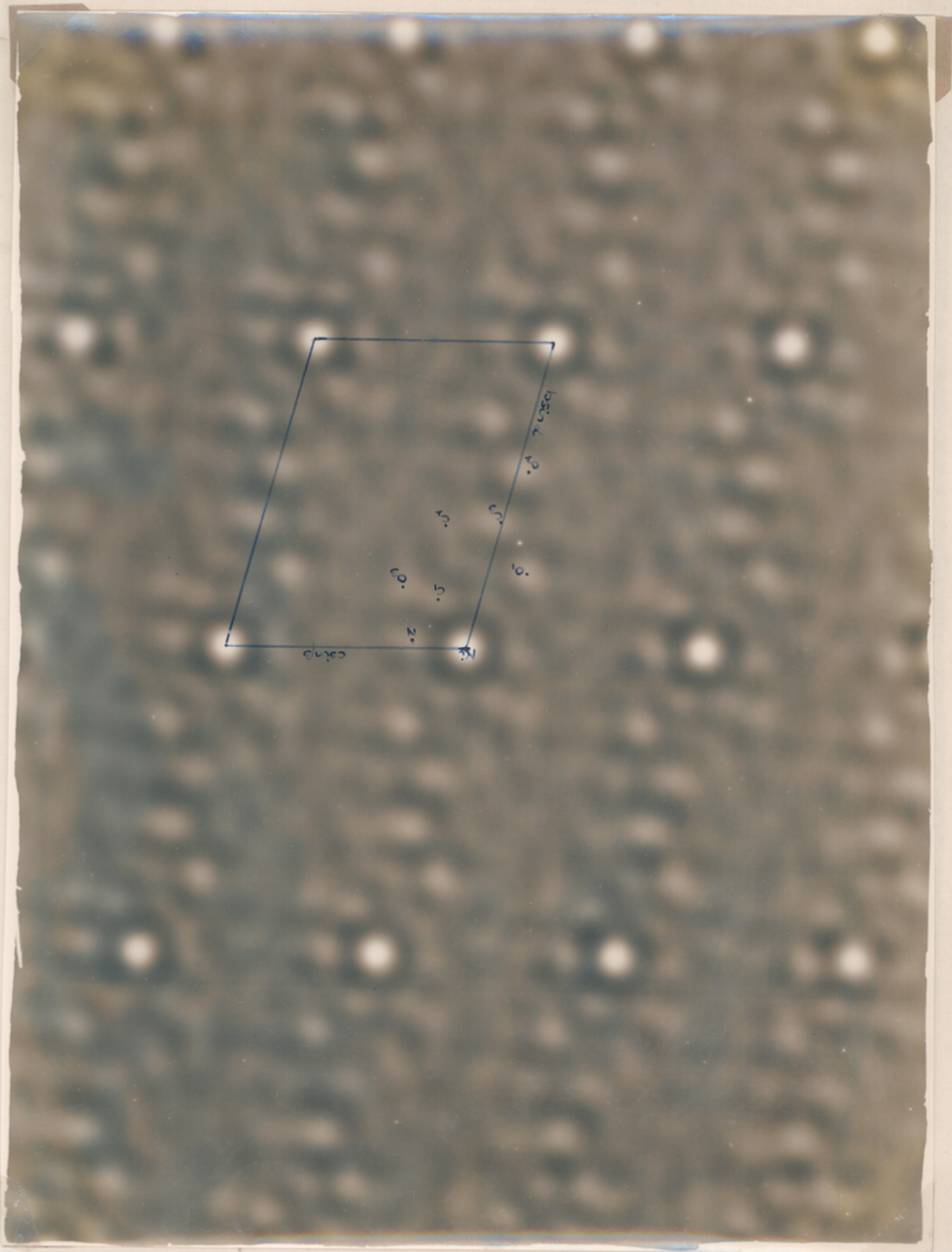


Fig. VI-4 Sharpened (100) Patterson projection

B. Determination of the structure of Nickel β -Alanine dihydrate and its refinement.

Patterson Projections

For the space group $P\bar{1}$, there are two equivalent positions. As there is only one molecule per unit cell Nickel must occupy the special position 0,0,0. The peaks in the two dimensional Patterson distribution due to the interaction between Nickel atom and the other atoms stand out against the background of weaker peaks due to the interaction between the lighter atoms. The approximate coordinates of all atoms could, therefore, be obtained directly from the three Patterson projections $P(uvo)$, $P(uow)$ and $P(ovw)$. These Patterson projections were obtained with the help of von Eller photosommateur. The Patterson maps were sharpened by using $S^2|F|^2$ where $S = 2 \sin\theta$ as Fourier coefficients instead of taking $|F|^2$. The Patterson maps for (001) and (100) projections are shown in figures VI-3 and VI-4 respectively.

Refinement of the structure

(001) Projection : For the space group $P\bar{1}$ the expression for the structure factor is

$$F(hkl) = 2 \sum_{n=1}^{N/2} f_n \cos 2\pi(hx_n + ky_n + lz_n) \quad \dots \quad \text{VI.1}$$

where N is the number of atoms in a molecule.

This expression in (001) projection simplifies to

$$F(hko) = 2 \sum_{n=1}^{N/2} f_n \cos 2\pi(hx_n + ky_n) \quad \dots \quad \text{VI.2}$$

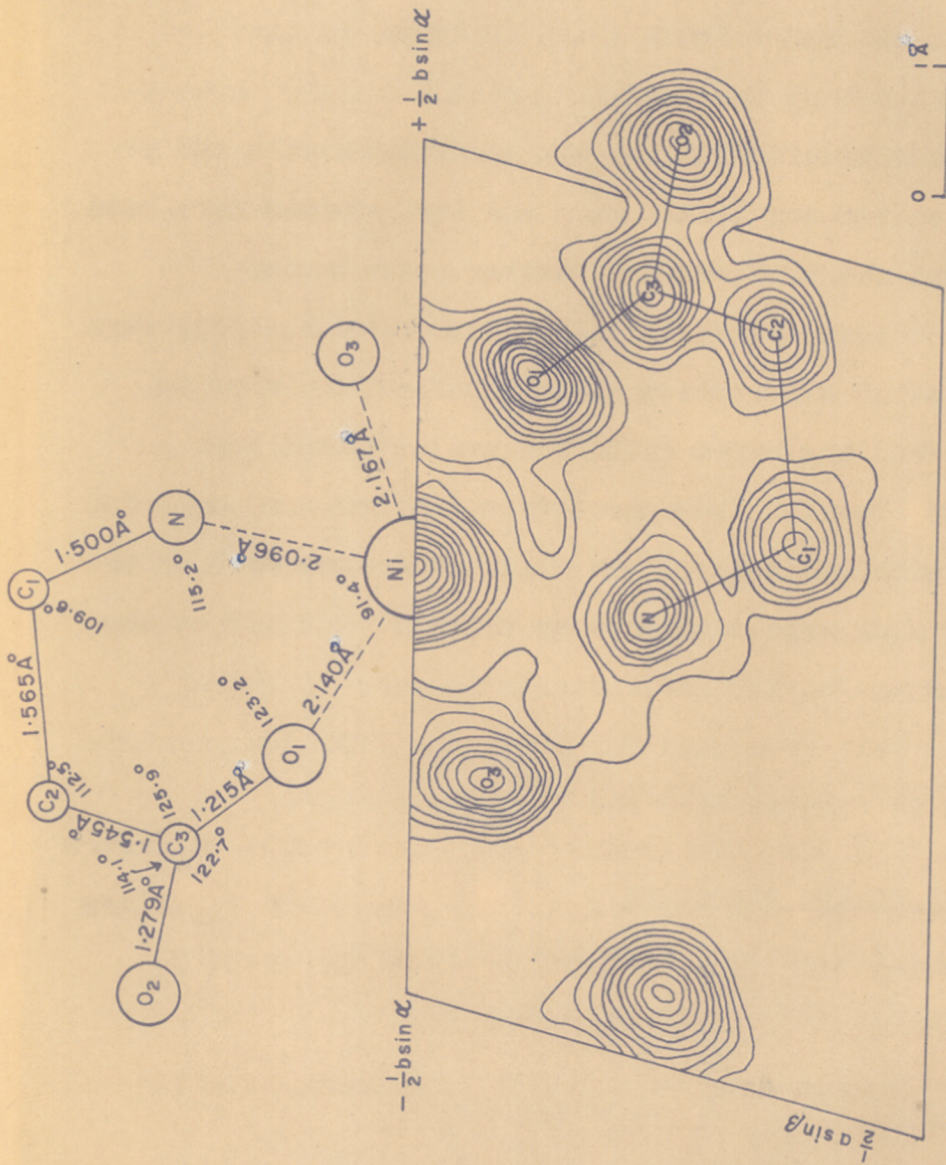


FIG. VI-5.(001) Electron density projection; contours drawn at intervals of $4 e \text{ \AA}^2$ for Ni and $1 e \text{ \AA}^2$ for the other atoms starting from $2 e \text{ \AA}^{-2}$

For Nickel β -Alanine^{dihydrate} the formula VI.2 can be written in the form

$$F(hko) = f_{Ni} + 2 \sum f_n \cos 2\pi(hx_n + ky_n)$$

where the summation extends over all atoms ^{except Nickel.} in one asymmetric unit.

To calculate $F(hko)$ the average values of x and y coordinates from the three Patterson projections were used. Scattering factors of Carbon, Nitrogen and Oxygen (McWeeny, 1951) and Nickel²⁺ (Thomas and Umeda, 1957) were corrected for a temperature factor of 1.8\AA^2 . Prior to this, scattering factors of Ni²⁺ were corrected for dispersion. The 100, 010 and $\bar{1}10$ reflexions were excluded from all calculations as they could not be recorded on the Weissenberg photograph on account of being cut off by the beam catcher.

(001) electron density projection

The (001) electron density projection shown in figure VI.5 was computed with the calculated phases and F_o values for all except 100, 010 and $\bar{1}10$ for which the final F_c values were used.

The electron density in (001) projection is given by

$$\rho(xyo) = \frac{2}{\lambda} \sum_{-\infty}^{\infty} F(hko) [\cos 2\pi hx \cos 2\pi ky - \sin 2\pi hx \sin 2\pi ky] \dots \text{VI.3}$$

For a centrosymmetrical structure F_c is given by

$$F_c = 2 \sum_{n=1}^{N/2} f_n \cos 2\pi \left(\frac{hx_n}{a} + \frac{ky_n}{b} + \frac{lz_n}{c} \right)$$

$$\frac{\partial F_c}{\partial x_n} = -\frac{4\pi}{a} f_n \cdot h \sin 2\pi \left(\frac{hx_n}{a} + \frac{ky_n}{b} + \frac{lz_n}{c} \right)$$

Substituting for $\frac{\partial F_c}{\partial x_n}$ in the equation VI.5

$$-\frac{4\pi}{a} \sum \frac{h}{f_n} (F_o - F_c) \sin 2\pi \left(\frac{hx_n}{a} + \frac{ky_n}{b} + \frac{lz_n}{c} \right) = 0$$

However the function $D = f_o - f_c = \frac{1}{V} \sum (F_o - F_c) \cos 2\pi (hx_n + ky_n + lz_n)$ has a slope in the x direction at the point (x_n, y_n, z_n) which is expressed by the relation

$$\left(\frac{\partial D}{\partial x} \right)_n = -\frac{2\pi}{V} \sum h (F_o - F_c) \sin 2\pi (hx_n + ky_n + lz_n) \dots \text{VI.6}$$

The condition for ϕ_n to be minimum with respect to the coordinates of the n^{th} atom is that $\frac{\partial D}{\partial x_n}, \frac{\partial D}{\partial y_n}, \frac{\partial D}{\partial z_n}$ should all be zero at (x_n, y_n, z_n) . However, when the slope of D is not zero at the atomic co-ordinates then the correction to the atomic co-ordinate Δx_n is given by

$$\Delta x_n = -\left(\frac{\partial D}{\partial x} \right)_n \bigg/ \left(\frac{\partial^2 \rho_c}{\partial x^2} \right)_n \dots \text{VI.7}$$

If ρ_c and ρ_o are assumed to be of the same shape

near an atomic centre, $\frac{\partial^2 \rho_c}{\partial x^2}$ in the expression IV.7 can be replaced by $\left(\frac{\partial^2 \rho_o}{\partial x^2}\right)_n$.

The electron density near the centre of an atom is approximated by the relation (Costain 1941, Booth 1946)

$$\rho = Z \left(\frac{p}{\pi}\right)^{3/2} \exp(-pr^2) \dots \dots \dots \text{VI.8}$$

where ρ is the density at a distance r from the centre of the atom, Z is the atomic number and p is a constant, its value in practice being about 5.0 \AA^{-2}

Hence

$$\left(\frac{\partial^2 \rho_o}{\partial x^2}\right)_n = -2p\rho_o(x_n \ y_n \ z_n)$$

The centre of an atom should therefore be moved by a distance

$$\Delta r_n = \frac{\left(\frac{\partial D}{\partial r}\right)_n}{2p(\rho_o)_n} \dots \dots \dots \text{VI.9}$$

where r denotes a distance measured in the direction in which D increases most rapidly.

When one or more successive corrections have reduced the values of $\left(\frac{\partial D}{\partial x}\right)_n$ etc. to zero at each atomic centre, the coordinates are free from series termination errors^r provided the values assumed for f_n 's are correct. The $(F_o - F_c)$ synthesis shows to a considerable extent when incorrect values of f_n are used. If the temperature factor B of an atom defined by $f_n = f_{o_n} \exp\left(-\frac{B \sin^2 \theta}{\lambda^2}\right)$ has been

over estimated in magnitude then $D = (\rho_o - \rho_c)$ near the atomic centre will be positive. If the thermal vibration of an atom is anisotropic but an isotropic temperature factor has been assumed for this atom contours of constant positive and negative D are seen around the atomic centre in mutually perpendicular directions.

Refinement of x and y parameters

The $(F_o - F_c)$ syntheses were summed by using Beevers and Lipson strips at intervals of 6° . On the difference map contours of constant $D (\rho_o - \rho_c)$ were drawn. The direction in which the n^{th} atom is to be moved is perpendicular to the contour passing through the atomic centre and in the direction of increasing D . The magnitude of correction was obtained from the expression

$$\Delta r_n = \frac{\left(\frac{\partial D}{\partial r}\right)_n}{2p(\rho_o)_n}$$

The values of ρ_o for carbon, nitrogen and oxygen were taken to be 8e. per \AA^2 , 9e. per \AA^2 , and 11e. per \AA^2 respectively. The corrections Δx_n and Δy_n for the x and y parameters were obtained from Δr_n on the difference Fourier map in the directions parallel to a and b axes. After five successive cycles of difference Fourier syntheses the R factor was 0.169. The x and y coordinates after each stage of refinement are listed in Table VI.3.

T A B L E VI.3(a)

Changes in the atomic co-ordinate x/a

Atom	From Patter- son maps	After I Differ- ence	After II differ- ence	After III differ- ence	After IV differ- ence	After V differ- ence
N1	0.0	0.0	0.0	0.0	0.0	0.0
N	0.2248	0.2201	0.2201	0.2237	0.2257	0.2257
C ₁	0.390	0.3677	0.3601	0.3698	0.3656	0.3656
C ₂	0.3695	0.3361	0.3572	0.3391	0.3301	0.3359
C ₃	0.2270	0.2121	0.2056	0.220	0.2146	0.2179
O ₁	0.1195	0.1116	0.1173	0.1140	0.1095	0.1095
O ₂	0.250	0.2386	0.2161	0.2456	0.2456	0.2456
O ₃ (H ₂ O)	-0.0575	-0.0696	-0.0645	-0.0714	-0.0714	-0.0690

T A B L E VI.3(b)

Changes in atomic co-ordinate y/b

Atom	From Patter- son maps	After I differ- ence	After II differ- ence	After III differ- ence	After IV differ- ence	After V differ- ence
N1	0.0	0.0	0.0	0.0	0.0	0.0
N	0.038	0.0267	0.0324	0.0236	0.0217	0.0217
C ₁	0.190	0.1601	0.1619	0.1643	0.1639	0.1639
C ₂	0.3860	0.3755	0.3849	0.3868	0.3856	0.3875
C ₃	0.416	0.3937	0.3772	0.3987	0.4098	0.4098
O ₁	0.259	0.2622	0.2637	0.2629	0.2575	0.2575
O ₂	0.582	0.5762	0.5762	0.5835	0.5804	0.5804
O ₃ (H ₂ O)	0.203	0.2191	0.2249	0.2134	0.2134	0.2163

The fifth difference map showed that the overall temperature factor of 1.8\AA^2 for all the atoms was incorrect. Individual isotropic temperature factors for the other atoms and anisotropic temperature factor for Nickel were obtained by the least squares method.

Refinement of thermal parameters by least square method

The value of R, the minimum function mentioned in the discussion on the least squares method (Chapter IV) depends not only on the atomic co-ordinates but other quantities which influence the value of F_c , for instance the temperature factor.

The value of B which make the function $\sum(F_o - F_c)^2$ minimum can be derived as follows:

$$\sum(F_o - F_c) = \sum\left(\frac{\partial F_c}{\partial B_1}\right)\Delta B_1 + \left(\frac{\partial F_c}{\partial B_2}\right)\Delta B_2 + \dots \quad \text{VI.10}$$

where B_1, B_2 etc. are the individual temperature factors of the different atoms.

Multiplying both sides of ^{Equation} VI.10 by $\left(\frac{\partial F_c}{\partial B_1}\right)$ we have

$$\sum(F_o - F_c)\left(\frac{\partial F_c}{\partial B_1}\right) = \sum\left(\frac{\partial F_c}{\partial B_1}\right)^2\Delta B_1 + \sum\left(\frac{\partial F_c}{\partial B_1}\right)\left(\frac{\partial F_c}{\partial B_2}\right)\Delta B_2 + \dots \quad \text{VI.11}$$

If the atoms are well resolved, terms like $\left(\frac{\partial F_c}{\partial B_1}\right)\left(\frac{\partial F_c}{\partial B_2}\right)\Delta B_2$ can be neglected. Hence VI.11 reduces to

$$\Delta B_n = \frac{\sum\left(\frac{\partial F_c}{\partial B_n}\right)(F_o - F_c)}{\sum\left(\frac{\partial F_c}{\partial B_n}\right)^2} \dots \dots \dots \text{VI.12}$$

In the case of Nickel β -Alanine, for (001) projection

$$F = f_{oNi} \exp\left(-\frac{B \sin^2 \theta}{\lambda^2}\right) + 2 \sum f_n (\cos 2\pi h x \cos 2\pi k y - \sin 2\pi h x \sin 2\pi k y)$$

$\frac{\partial F}{\partial B_n}$ for Nickel is given by

$$\frac{\partial F}{\partial B_{Ni}} = f_o \exp\left(-\frac{B \sin^2 \theta}{\lambda^2}\right) \left(-\frac{\sin^2 \theta}{\lambda^2}\right) \text{ so that}$$

$$\Delta B_{Ni} = \frac{\sum (F_o - F_c) f_o \exp\left(-\frac{B \sin^2 \theta}{\lambda^2}\right) \cdot \frac{\sin^2 \theta}{\lambda^2}}{\sum \left[f_o \exp\left(-\frac{B \sin^2 \theta}{\lambda^2}\right) \cdot \left(\frac{\sin^2 \theta}{\lambda^2}\right) \right]^2} \dots \text{VI.13}$$

The expression VI.13 was written in the form

$$\Delta B_{Ni} = -4\lambda^2 \frac{\sum (F_o - F_c) f(2\sin\theta)^2}{\sum [f(2\sin\theta)^2]^2}$$

for the purposes of calculation, where $f = f_o \exp\left(-\frac{B \sin^2 \theta}{\lambda^2}\right)$ the value of B being the average value of 1.8 \AA^2 . $2\sin\theta$ is directly measured on the $a^* b^*$ reciprocal lattice for different reflexions.

For other atoms

$$\frac{\partial F}{\partial B_n} = f_o \exp\left(-\frac{B \sin^2 \theta}{\lambda^2}\right) \left(-\frac{\sin^2 \theta}{\lambda^2}\right) (\cos 2\pi h x \cos 2\pi k y - \sin 2\pi h x \sin 2\pi k y)$$

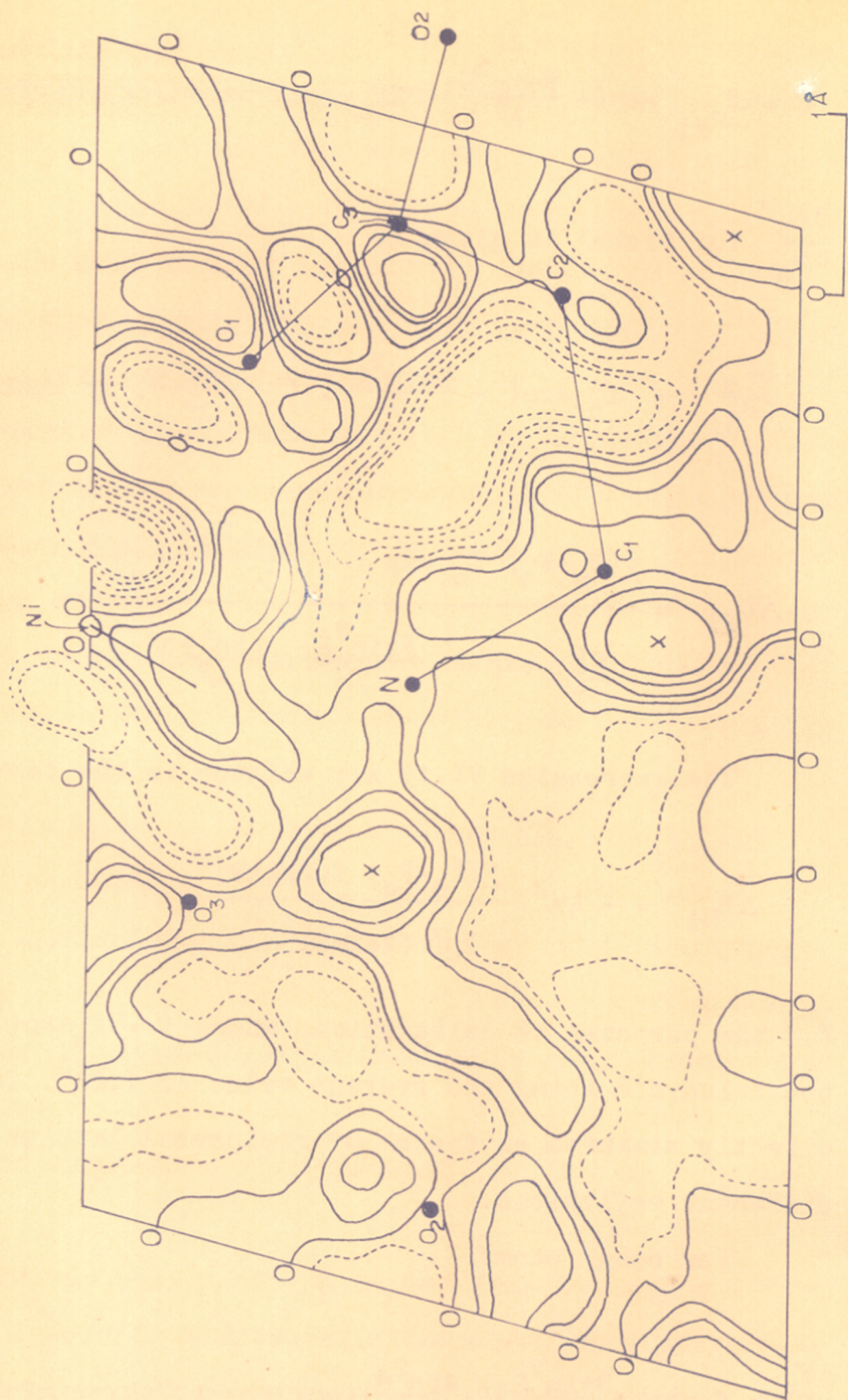


FIG. VI - 6 Final $(F_0 - F_c)$ synthesis of (001) projection. Contours at intervals of $0.25e/\text{Å}^2$, the zero contour is indicated by 0 and negative contours are dotted. Atomic centres are indicated by dots.

and

$$\Delta B_n = - \frac{2\lambda^2 \sum (F_o - F_c) f(2\sin\theta)^2 (\cos 2\pi hx \cos 2\pi ky - \sin 2\pi hx \sin 2\pi ky)}{\sum [f(2\sin\theta)^2 (\cos 2\pi hx \cos 2\pi ky - \sin 2\pi hx \sin 2\pi ky)]^2} \dots \dots \dots \text{VI.14}$$

The individual temperature factors thus obtained are listed in table VI.4. The structure factors based on the new f values for each atom were recalculated. A further refinement was done by difference Fourier synthesis. The R factor after this refinement was 0.152. The final difference map is shown in figure VI.6. The contours are drawn at intervals of 0.25e.Å⁻². The negative contours are dotted and the zero contour is indicated by o. This map shows that the slope of D near the atomic centres is small.

The contours around Nickel, O₁ and O₂ indicate that the thermal vibration of these atoms are anisotropic, the directions of maximum vibrations being parallel. This indicates the possibility of the whole molecule vibrating in this direction. This point is discussed in chapter VII. The contours marked by crosses indicate the possible positions of the hydrogen atoms but these were not included in the calculation.

As the contribution of Nickel to the structure factor is large the scattering factors of Nickel were corrected for anisotropic temperature factors by means of the expression

$$f = f_o \exp \left[-(A \cos^2 \phi + B \sin^2 \phi) \frac{\sin^2 \theta}{\lambda^2} \right]$$

where f_o is the scattering factor of the stationary atom, A and B are constants. ϕ is the angle between the direction of maximum vibration and the normal to the reflecting plane. Similar expressions were used by Hughes (1941) and by Cochran (1951a) in the structures of melamine and adenine hydrochloride to account for thermal anisotropy. A and B were chosen as 1.8\AA^2 to start with. The corrections ΔA and ΔB were obtained from the expressions

$$\Delta A = \frac{\sum (F_o - F_c) \left(\frac{\partial F_c}{\partial A} \right)}{\sum \left(\frac{\partial F_c}{\partial A} \right)^2} \quad \text{VI.15}$$

and

$$\Delta B = \frac{\sum (F_o - F_c) \left(\frac{\partial F_c}{\partial B} \right)}{\sum \left(\frac{\partial F_c}{\partial B} \right)^2} \quad \text{VI.16}$$

The structure factor formula can be written in the form

$$F_c = f_{Ni} \exp \left[- (A \cos^2 \phi + B \sin^2 \phi) \frac{\sin^2 \theta}{\lambda^2} \right] + 2 \sum f_n (\cos 2\pi h x \cos 2\pi k y - \sin 2\pi h x \sin 2\pi k y)$$

For the nickel atom

$$\frac{\partial F_c}{\partial A} = f_{oNi} \exp \left[- (A \cos^2 \phi + B \sin^2 \phi) \frac{\sin^2 \theta}{\lambda^2} \right] \left(-\cos^2 \phi \frac{\sin^2 \theta}{\lambda^2} \right)$$

Similarly

$$\frac{\partial F_c}{\partial B} = f_{oNi} \exp \left[- (A \cos^2 \phi + B \sin^2 \phi) \frac{\sin^2 \theta}{\lambda^2} \right] \left(-\sin^2 \phi \frac{\sin^2 \theta}{\lambda^2} \right)$$

Substituting for $\frac{\partial F_c}{\partial A}$, $\frac{\partial F_c}{\partial B}$ in the equations VI.15 and VI.16 we get the following relations for ΔA , and ΔB

$$\Delta A = - \frac{4\lambda^2 \sum (F_c - F_c) f_{Ni} e^{-(A \cos^2 \phi + B \sin^2 \phi) \frac{\sin^2 \theta}{\lambda^2}} \cos^2 \phi \cdot (2 \sin \theta)^2}{\sum \left[f_{Ni} e^{-(A \cos^2 \phi + B \sin^2 \phi) \frac{\sin^2 \theta}{\lambda^2}} \cos^2 \phi (2 \sin \theta)^2 \right]^2}$$

This on simplification becomes

$$\Delta A = \frac{-4\lambda^2 \sum (F_o - F_c) f_{Ni} \cos^2 \phi \cdot (2 \sin \theta)^2}{\sum \left[f_{Ni} \cos^2 \phi (2 \sin \theta)^2 \right]^2} \quad \text{VI.17}$$

where f_{Ni} is the scattering factor of Ni corrected for $B = 1.8 \text{ \AA}^2$.

Similarly

$$\Delta B = \frac{-4\lambda^2 \sum (F_o - F_c) f_{Ni} \sin^2 \phi (2 \sin \theta)^2}{\sum \left[f_{Ni} \sin^2 \phi (2 \sin \theta)^2 \right]^2} \quad \text{VI.18}$$

The $a^* b^*$ reciprocal lattice was plotted superposed on the final difference map. The direction of maximum vibration was marked on the difference map and the angle which ^{the line joining the origin to} each reflexion makes with the direction of maximum vibration was measured. The values of ΔA and ΔB were found to be 0.5 and -0.4 \AA^2 so that the temperature factor changed from $1.8 \cos^2 \phi + 1.8 \sin^2 \phi$ to $2.3 \cos^2 \phi + 1.4 \sin^2 \phi$. The structure factors were recalculated with the changed thermal parameters for Nickel. The R factor dropped from 0.152 to 0.138. The final x and y parameters along with

thermal parameters are listed in table VI.4

TABLE - VI.4

Atomic and thermal parameters for (001) projection

Atom	x/a	y/b	B in \AA^2
Ni	0.0	0.0	1.8
N	0.2257	0.0217	1.7
C ₁	0.3656	0.1639	2.2
C ₂	0.3359	0.3875	2.9
C ₃	0.2179	0.4036	0.9
O ₁	0.1095	0.2575	2.1
O ₂	0.2456	0.5804	2.3
O ₃ (H ₂ O)	- 0.0690	0.2163	2.7

(100) projection

The structure factor formula for the okl reflexions is

$$F(0kl) = f_{Ni} + 2 \sum_n (\cos 2\pi ky \cos 2\pi lz - \sin 2\pi ky \sin 2\pi lz)$$

The final y parameters from the (001) projection given in table VI.4 were used to calculate okl structure factors. The z parameters were obtained from the Patterson projections P(ovw) and P(uow). The averages of the z values obtained from the Patterson projections were used to calculate F(okl). The scattering factors were

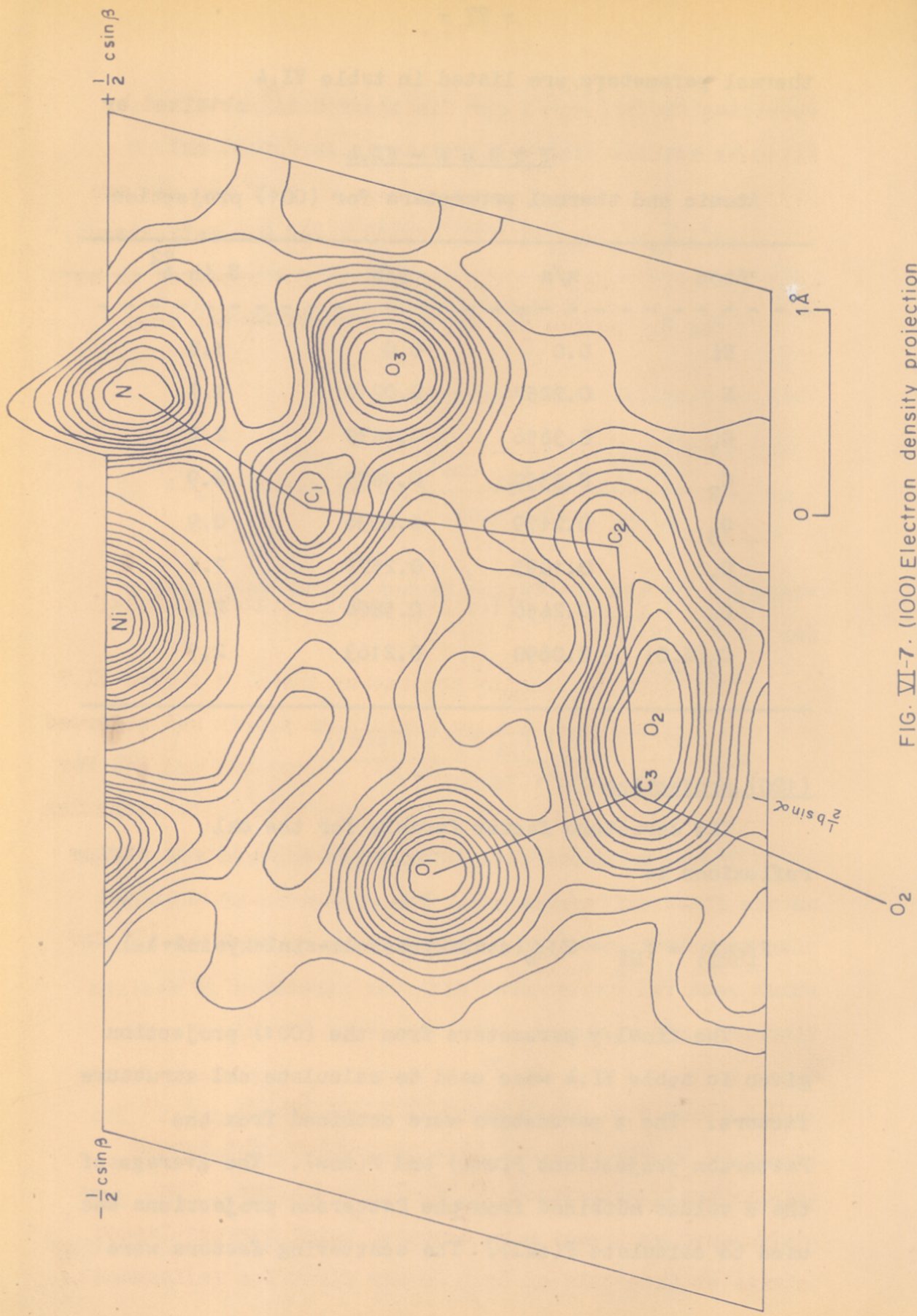


FIG. VI-7. (100) Electron density projection

corrected for a temperature factor of 0.6\AA^2 obtained by Wilson's method. The reliability index for 80 okl reflexions including unobserved ones at half the minimum observable value was 18.2 %. The 001 and 010 reflexions were excluded from all calculations as 001 appeared to be subject to extinction and 010 was cut off by the beam catcher and hence could not be recorded.

(100) electron density projection

The electron density $\rho(\text{oyz})$ is given by the expression

$$\rho(\text{oyz}) = \frac{2}{\text{\AA}} \sum_{-\infty}^{\infty} F(\text{okl}) (\cos 2\pi ky \cos 2\pi lz - \sin 2\pi ky \sin 2\pi lz)$$

The electron density projection shown in figure VI.7 was computed using the final calculated phases and observed values of structure factors for all except 001 and 010 for which the final calculated values were used. The summation of Fourier Series was done by using Beevers-Lipson strips at intervals of $\frac{1}{60}$ of cell edge. The contours in the electron density map are drawn at intervals of $4e.\text{\AA}^{-2}$ for Nickel and $1e/\text{\AA}^2$ for the other atoms starting from 2 electron / \AA^2 .

(100) difference electron density projection

As in the case of (001) projection, the atomic parameters were refined by $(F_o - F_c)$ syntheses. The difference syntheses were computed using Beevers-Lipson strips at intervals of 6° . In the first few refinements

y-coordinate was not refined from this projection. But as there were shifts in the y coordinates after the third difference synthesis y-coordinate was also refined during the later refinements. At the end of four cycles of refinement the R factor was 0.15. At this stage the individual isotropic temperature factors were obtained by the least squares method.

Refinement of thermal parameters for (100) projection

The structure factor $F(okl)$ can be written as

$$F(okl) = f_{O_{Ni}} \exp\left(-\frac{B \sin^2 \theta}{\lambda^2}\right) + 2 \sum f_o \exp\left(-\frac{B \sin^2 \theta}{\lambda^2}\right) (\cos 2\pi k y \cos 2\pi l z - \sin 2\pi k y \sin 2\pi l z)$$

From this expression we get $\frac{\partial F_c}{\partial B}$ for Nickel as

$$\frac{\partial F_c}{\partial B} = f_{O_{Ni}} \exp\left[-\frac{B \sin^2 \theta}{\lambda^2}\right] \left(-\frac{\sin^2 \theta}{\lambda^2}\right)$$

so that

$$\Delta B_{Ni} = \frac{\sum (F_o - F_c) f_{O_{Ni}} \exp\left[-\frac{B \sin^2 \theta}{\lambda^2}\right] \left(-\frac{\sin^2 \theta}{\lambda^2}\right)}{\sum \left[f_{O_{Ni}} \exp\left(-\frac{B \sin^2 \theta}{\lambda^2}\right) \frac{\sin^2 \theta}{\lambda^2} \right]^2} \quad \dots \text{VI.19}$$

This can be simplified in the form

$$\Delta B_{Ni} = \frac{4\lambda^2 \sum (F_o - F_c) f_{Ni} (2\sin\theta)^2}{\sum [f_{Ni} (2\sin\theta)^2]^2} \quad \dots \text{VI.20}$$

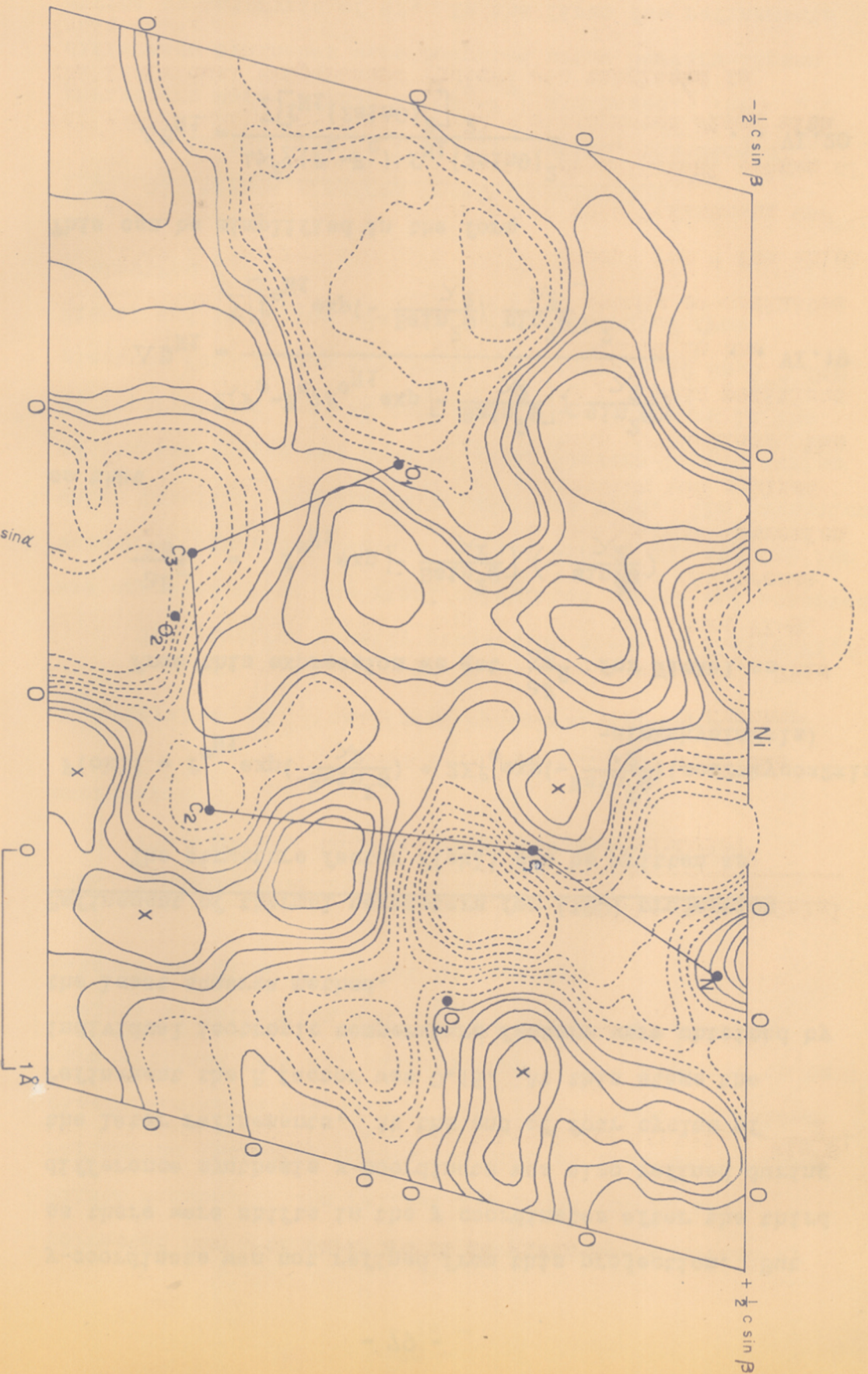


FIG. VI-8 ($F_o - F_c$) synthesis of (100) projection. Contours at intervals of $0.25/\text{\AA}^2$, zero contours are indicated by O and negative contours are dotted.

TABLE VI.5

Changes in the atomic parameter z/c

Atom	From Patter- son maps	After I differ- ence	After II differ- ence	After III differ- ence	After IV differ- ence
Ni	0.0	0.0	0.0	0.0	0.0
N	0.2545	0.2551	0.2424	0.2424	0.2517
C ₁	0.2242	0.1911	0.1911	0.1911	0.1909
C ₂	0.1724	0.1877	0.1989	0.2133	0.2133
C ₃	-0.0296	-0.0388	-0.0388	-0.0322	-0.0322
O ₁	-0.1454	-0.1653	-0.1653	-0.1653	-0.1740
O ₂	-0.0616	-0.0616	-0.0692	-0.0692	-0.0786
O ₃ (H ₂ O)	0.3393	0.3490	0.3210	0.3283	0.3283

TABLE VI.6.

Final values of y/b and z/c from (100) projection and individual B values.

Atom	y/b	z/c	B(okl)
Ni	0.0	0.0	0.5Å ²
N	0.0194	0.2468	1.4
C ₁	0.1636	0.1766	1.2
C ₂	0.3880	0.2152	0.8
C ₃	0.4039	-0.0284	0.8
O ₁	0.2535	-0.1680	1.2
O ₂	0.5817	-0.0847	1.3
O ₃ (H ₂ O)	0.2189	0.3306	1.0

Refinement of (010) projection

The structure factor for hol reflexions is given by

$$F(\text{hol}) = f_{\text{Ni}} + 2\sum f_n (\cos 2\pi hx \cos 2\pi lz - \sin 2\pi hx \sin 2\pi lz)$$

To calculate the hol structure factors the final values of x and z coordinates from the preceding projections were used. The scattering factors were modified using a temperature factor of 1.8\AA^2 . The R value for 85 hol reflexions including unobserved ones was 0.194. (001) and (100) were excluded from the calculations as (001) appears to suffer from extinction and 100 was not recorded on the Weissenberg photographs. One cycle of refinement by difference synthesis was carried out after which R was 0.176. Individual isotropic temperature factors were obtained by the least squares method.

ΔB for Nickel is given by

$$\Delta B_{\text{Ni}} = \frac{-4\lambda^2 \sum (F_o - F_c) f_{\text{Ni}} (2\sin\theta)^2}{\sum [f_{\text{Ni}} (2\sin\theta)^2]^2}$$

and for the other atoms

$$\Delta B = \frac{-2\pi^2 \sum (F_o - F_c) f_n (2\sin\theta)^2 (\cos 2\pi hx \cos 2\pi lz - \sin 2\pi hx \sin 2\pi lz)}{\sum [f_n (2\sin\theta)^2 (\cos 2\pi hx \cos 2\pi lz - \sin 2\pi hx \sin 2\pi lz)]^2}$$

After the refinement of temperature factors a further ~~stage~~ of refinement was carried out for x and z coordinates. The final R factor was 0.153. The x and z coordinates and the B values for (010) projection are tabulated in Table VI.7.

TABLE - VI.7

Final x and z parameters from (010) projection and B values.

Atom	x/a	z/c	B in Å ²
Ni	0	0	1.5
N	0.2180	0.2388	0.9
C ₁	0.3695	0.1859	2.7
C ₂	0.3387	0.2194	2.6
C ₃	0.2131	- 0.0210	1.0
O ₁	0.1095	- 0.0582	2.1
O ₂	0.2456	- 0.0847	3.2
O ₃ (H ₂ O)	- 0.0690	0.3403	3.3

The final atomic co-ordinates used in the calculation of interatomic distances were the mean values from the three projections. The average atomic co-ordinates are listed in table VI.8 with their estimated standard deviations. The thermal parameters for the three zones are also listed in this table.

TABLE - VI.8(a)

Final atomic parameters with their estimated standard deviations

Atom	x/a	y/b	z/c
Ni	0	0	0
N	0.2219±0.0031	0.0260±0.0039	0.2428±0.0053
C ₁	0.3675±0.0036	0.1638±0.0045	0.1813±0.0062
C ₂	0.3373±0.0036	0.3878±0.0045	0.2173±0.0062
C ₃	0.2155±0.0036	0.4038±0.0045	-0.0247±0.0062
O ₁	0.1095±0.0027	0.2555±0.0034	-0.1631±0.0047
O ₂	0.2456±0.0027	0.5811±0.0034	-0.0847±0.0047
O ₃ (H ₂ O)	-0.0690±0.0027	0.2165±0.0034	0.3355±0.0047

TABLE - VI.8(b)

Thermal parameters

Atom	B(hko)	B(okl)	B(hol)
Ni	1.8 Å ²	0.5 Å ²	1.5 Å ²
N	1.7	1.4	0.9
C ₁	2.2	1.2	2.7
C ₂	2.9	0.8	2.6
C ₃	0.9	0.8	1.0
O ₁	2.1	1.2	2.1
O ₂	2.3	1.3	3.2
O ₃ (H ₂ O)	2.7	1.0	3.3

C. Refinement of Cobalt β -Alanine structure

As Cobalt β -Alanine $2H_2O$ was found to be isomorphous with Nickel β -Alanine $2H_2O$, refinement of its structure was started from the final atomic parameters obtained for Nickel β -Alanine.

(001) projection

The hko structure factors were calculated with the final average x and y coordinates given in table VI.8. The structure factor formulae are similar to those used in ^{the case} Nickel β -Alanine. A temperature factor of 2.0\AA^2 obtained by Wilson's method was used ~~for~~ to correct the scattering factor for the first three refinements which were done with the intensity data collected with CuK_{α} radiation. At the end of these refinements by difference syntheses the R factor was 0.15. Further refinements were done with the intensity data obtained with MoK_{α} radiation.

The scale and temperature factors were obtained by Wilson's graph (figure VI.2) for the observed intensities obtained with MoK_{α} radiation. Using the x and y coordinates from the third difference synthesis and revised scattering factors the F_c 's ^{were} ~~was~~ recalculated. The R factor for 94 reflexions including unobserved ones at half the minimum observable value was 0.15. Twelve low angle reflexions 100, 200, 110, 210, 220, 120, 010, 020, $\bar{1}10$, $\bar{1}20$, $\bar{2}10$, and $\bar{2}20$ could not be recorded in the Weissenberg photograph with MoK_{α} radiation as they were cut off by the beam catcher. These were, therefore,

excluded from further refinements. A further cycle of refinement was carried out by difference synthesis after which the R factor was 0.137. Isotropic temperature factors for all atoms were derived by the least squares method. The expressions for ΔB of Cobalt and other atoms are similar to those used in the corresponding cases in Nickel β -Alanine. The structure factors recalculated with the revised thermal parameters gave R factor of 0.121. The final x and y parameters along with the temperature factors for this projection are listed in table VI.9.

T A B L E - VI.9

Atomic parameters x/a and y/b and temperature factors

Atom	x/a	y/b	B(hko)
Co	0	0	2.6 \AA^2
N	0.2273	0.0147	1.8
C ₁	0.3698	0.1611	1.8
C ₂	0.3392	0.3854	3.6
C ₃	0.2247	0.4062	1.0
O ₁	0.1108	0.2470	3.4
O ₂	0.2484	0.5824	3.1
O ₃ (H ₂ O)	- 0.0558	0.2158	4.5

(100) and (010) projections

(100) projection : The y-coordinates from (001) projection (table VI.9) and final average z-coordinates

obtained for Nickel β -Alanine were used to calculate $F(0kl)$. A temperature factor of 1.8\AA^2 obtained from Wilson's graph was used. A refinement of y and z parameters was done by difference synthesis. Isotropic temperature factors were obtained by the method of least squares and a further refinement of atomic parameters was carried out by (100) difference electron density projection. The final R factor was 0.125.

(010) projection: The $h0l$ structure factors were calculated with the x and z coordinates obtained from the preceding projections. A B-factor of 2.4\AA^2 obtained from Wilson's graph was used. The R factor for 75 reflexions including unobserved ones was 0.20. Individual temperature factors were obtained, as in the preceding projections, by the least squares method. One refinement by the difference synthesis of the x and z parameters brought the R factor to 0.16.

The final average atomic co-ordinates with their estimated standard deviations are listed in Table VI.10. The individual B values are also given in this table.

T A B L E - VI.10(a)

Atomic parameters with their estimated standard deviations

Atom	x/a	y/b	z/c
Co	0	0	0
N	0.2285±0.0029	0.0147±0.0036	0.2362±0.0049
C ₁	0.3698±0.0033	0.1588±0.0042	0.1774±0.0057
C ₂	0.3392±0.0033	0.3848±0.0042	0.2212±0.0057
C ₃	0.2241±0.0033	0.4047±0.0042	-0.0326±0.0057
O ₁	0.1098±0.0028	0.2493±0.0035	-0.1618±0.0048
O ₂	0.2469±0.0028	0.5802±0.0035	-0.0799±0.0048
O ₃ (H ₂ O)	-0.0581±0.0028	0.2163±0.0035	0.3267±0.0048

T A B L E - VI.10(b)

Thermal parameters

Atom	B(hko)	B(okl)	B(hol)
Co	2.6Å ²	1.8Å ²	2.3Å ²
N	1.8	2.1	3.7
C ₁	1.8	2.2	2.5
C ₂	3.6	2.1	2.2
C ₃	1.0	1.8	1.5
O ₁	3.4	2.2	0.8
O ₂	3.1	3.6	4.5
O ₃ (H ₂ O)	4.5	2.7	3.1

Estimation of standard deviations

For a centrosymmetrical two dimensional synthesis the standard deviation $\sigma(x_n)$ of an atomic co-ordinates x_n is given by (Lipson and Cochran, 1953).

$$\sigma(x_n) = \frac{K}{\sqrt{2} Z_n} \frac{\pi}{2p} \left[\frac{1}{A} \sum_{n=1}^N Z_n^2 \right]^{\frac{1}{2}}$$

where A is the area of the projection, Z_n the atomic number of the n^{th} atom and K is taken equal to the final R factor for the particular projection. p is a constant the value of which was taken as 5.0\AA^2 . The standard deviations were estimated from all the three projections. A root mean square of $\sigma(x)$, $\sigma(y)$ and $\sigma(z)$ was taken as the standard deviation of the atomic position. The standard deviations of bond lengths and bond angles were estimated by means of the same expressions as those used in the case of β -Alanine, described in chapter IV.

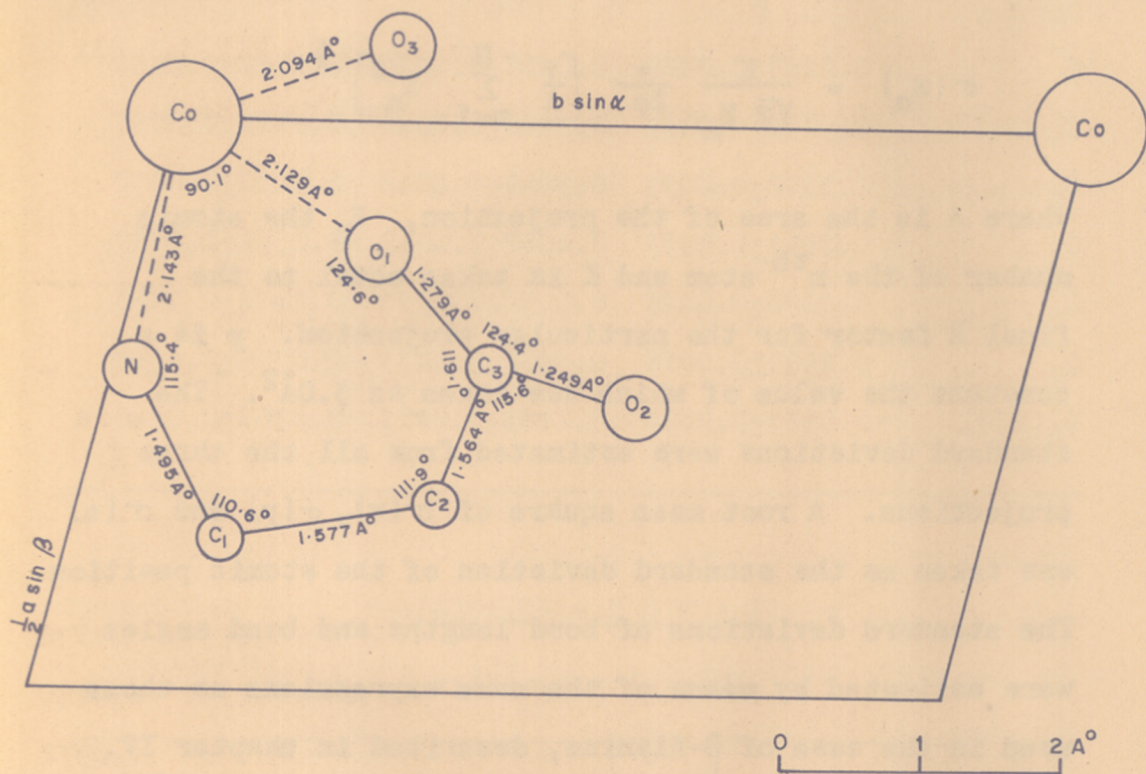


FIG. VII-1 Bond lengths and bond angles in Cobalt β -Alanine dihydrate.

C H A P T E R - V I I

Results and discussion of Nickel and Cobalt β -Alanine complexes

The atomic co-ordinates in Angstrom units referred to the axes of unit cell are listed in Table VII.1. All the interatomic distances were calculated from these.

T A B L E - V I I . 1

Ni β -Alanine, 2H ₂ O				Co β -Alanine, 2H ₂ O			
Atom	x in \AA	y in \AA	z in \AA	Atom	x in \AA	y in \AA	z in \AA
Ni	0	0	0	Ni	0	0	0
N	1.881	0.1395	1.197	N	1.9514	1.0998	1.1716
C ₁	3.117	1.109	0.8937	C ₁	3.1581	1.0783	0.8799
C ₂	2.861	2.625	1.071	C ₂	2.8968	2.6128	1.0972
C ₃	1.827	2.734	-0.1217	C ₃	1.9138	2.7479	-0.1617
O ₁	0.9287	1.730	-0.8041	O ₁	0.9377	1.6927	-0.8025
O ₂	2.083	3.934	-0.4176	O ₂	2.1085	3.9395	-0.3963
O ₃	-0.5851	1.473	1.654	O ₃	-0.4963	1.4687	1.6204
(H ₂ O)				(H ₂ O)			

The intramolecular bond lengths and bond angles in Ni β -Alanine^{dihydrate} are shown in figures VI-5 (Chapter VI) and those of Co β -Alanine^{dihydrate} in figure VII.1 and listed in table VII.2 with their estimated standard deviations.

T A B L E - VII.2

Ni β -Alanine $2H_2O$		Co β -Alanine $2H_2O$	
Bond	Length in \AA	Bond	Length in \AA
N-C ₁	1.500 \pm 0.040 \AA	N-C ₁	1.495 \pm 0.037 \AA
C ₁ -C ₂	1.565 \pm 0.043	C ₁ -C ₂	1.577 \pm 0.040
C ₂ -C ₃	1.545 \pm 0.043	C ₂ -C ₃	1.564 \pm 0.036
C ₃ -O ₁	1.215 \pm 0.038	C ₃ -O ₁	1.279 \pm 0.036
C ₃ -O ₂	1.279 \pm 0.038	C ₃ -O ₂	1.249 \pm 0.036
Ni-O ₁	2.140 \pm 0.023	Co-O ₁	2.129 \pm 0.021
Ni-N	2.096 \pm 0.026	Co-N	2.143 \pm 0.024
Ni-O ₃	2.167 \pm 0.023	Co-O ₃	2.094 \pm 0.021

Bond angles

Ni β -Alanine, $2H_2O$	
Contact	angle
N-C ₁ -C ₂	109.6 \pm 2.4°
C ₁ -C ₂ -C ₃	112.5 \pm 2.5
C ₂ -C ₃ -O ₁	125.9 \pm 2.8
C ₂ -C ₃ -O ₂	114.1 \pm 2.5
O ₁ -C ₃ -O ₂	122.7 \pm 2.9
O ₁ -Ni-N	91.4 \pm 1.0
Ni-N-C ₁	115.2 \pm 1.9
Ni-O ₁ -C ₃	123.2 \pm 2.1

Bond angles

Co β -Alanine, $2H_2O$	
Contact	angle
N-C ₁ -C ₂	110.6 \pm 2.3°
C ₁ -C ₂ -C ₃	111.9 \pm 2.3
C ₂ -C ₃ -O ₁	119.1 \pm 2.4
C ₂ -C ₃ -O ₂	115.6 \pm 2.4
O ₁ -C ₃ -O ₂	124.4 \pm 2.6
O ₁ -Co-N	90.1 \pm 0.9
Co-N-C ₁	115.4 \pm 1.8
Co-O ₁ -C ₃	124.6 \pm 2.1

The sides of the octahedron around the metal are

	Ni β -Alanine, 2H ₂ O	Co β -Alanine 2H ₂ O
O ₃ -N	2.96 \pm 0.04 and 3.07 \pm 0.04 \AA	2.94 \pm 0.04 and 3.01 \pm 0.04 \AA
O ₃ -O ₁	3.03 \pm 0.03 and 3.06 \pm 0.03 \AA	3.01 \pm 0.03 and 2.86 \pm 0.03 \AA
O ₁ -N	3.03 \pm 0.04 and 2.96 \pm 0.04 \AA	2.996 \pm 0.04 and 3.02 \pm 0.04 \AA

Equations of planes

The various planes in the two complexes are represented by the following equations:

Ni- β -Alanine

1. $0.594x' - 0.006y' + 2.129z' = 3.492$ passing through N₁, C₁ and C₂,

2. $-1.719x' - 0.847y' + 1.125z' = -4.572$ passing through C₁, C₂ and C₃,

3. $3.564x' - 0.588y' - 2.969z' = 3.341$ is the equation of the the mean plane through the atoms C₂, C₃, O₁ and O₂. In all these equations x', y' and z' are atomic co-ordinates in \AA with reference to the orthogonal axes a, b' and c' such that ab plane and ab' plane are the same. The normal distances of O₁, O₂ and C₂ are 0.022 \AA and of C₃ -0.023 \AA from the mean plane.

Co β -Alanine

1. $0.623x' - 0.054y' + 2.119z' = 3.528$ passing through N, C₁ and C₂,

2. $-1.846x' - 0.889y' + 1.015z' = -5.158$ passing through C_1, C_2 and C_3 and

3. $3.670x' - 0.640y' - 3.042z' = 3.748$ is the equation of the mean plane passing through the atoms C_2, C_3, O_1 and O_2 where x', y' and z' have the same significance as in Nickel β -Alanine. The normal distances of C_2, O_1 and O_2 are -0.016\AA from the mean plane and of C_3 $+0.015\text{\AA}$.

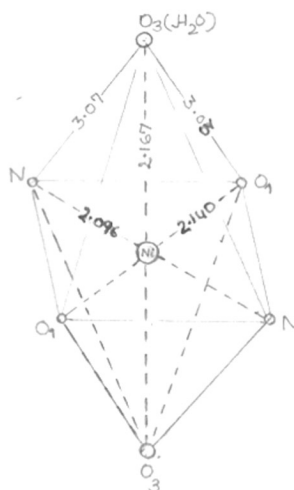
The angles between the planes represented by equations 1 and 2 is 73.7° in Ni β -Alanine and 78° in Co β -Alanine (70° in Copper β -Alanine, $6H_2O$; Tomita, 1961). The angle between the planes given by 2 and 3 is 30.3° and 32.8° respectively in Nickel and Cobalt complexes. These indicate that β -Alanine molecule has the gauche configuration in the complexes ^{as well in state} and as free acid (~~33.8° and 30.3°~~).

DISCUSSION

Molecular structure:

The intramolecular bond lengths and bond angles are normal within experimental error. Two nitrogen atoms and two carboxylic oxygens (one from each β -Alanine molecule) form a square planer trans-configuration around the metal. Similar trans-configurations are formed in the complexes Copper β -Alanine hexahydrate (Tomita 1961) bis(β -Aminobutyrate) Copper II dihydrate, Copper-Proline dihydrate. But in the structures of Copper glycine monohydrate (Tomita and Nitta 1961) and Nickel di α -amino isobutyrate tetrahydrate (Noguchi, 1961) the chelation of the amino acids is of the cis form.

Together with the two water molecular oxygens the nitrogens and carboxylic oxygens form an octahedron around the metal as indicated in the figure below. This is similar to the structures of Nickel glycine dihydrate (Stosick 1945) Nickel di α -aminoisotybutyrate tetrahydrate (Noguchi 1962)



In these complexes the distortion from octahedral symmetry is very slight as can be seen from the distances given below:

	Me-N	Me-O	Me-O(H ₂ O)	Reference
Nickel-glycine. 2H ₂ O	2.09Å	2.08Å	2.12Å	Stosick (1945)
Nickel di- α -amino iso-butyrate, 4H ₂ O	2.10	2.01	2.14	Noguchi (1962)
Ni- β -Alanine. 2H ₂ O	2.096	2.140	2.167	Present work
Co- β -Alanine. 2H ₂ O	2.143	2.129	2.094	Present work

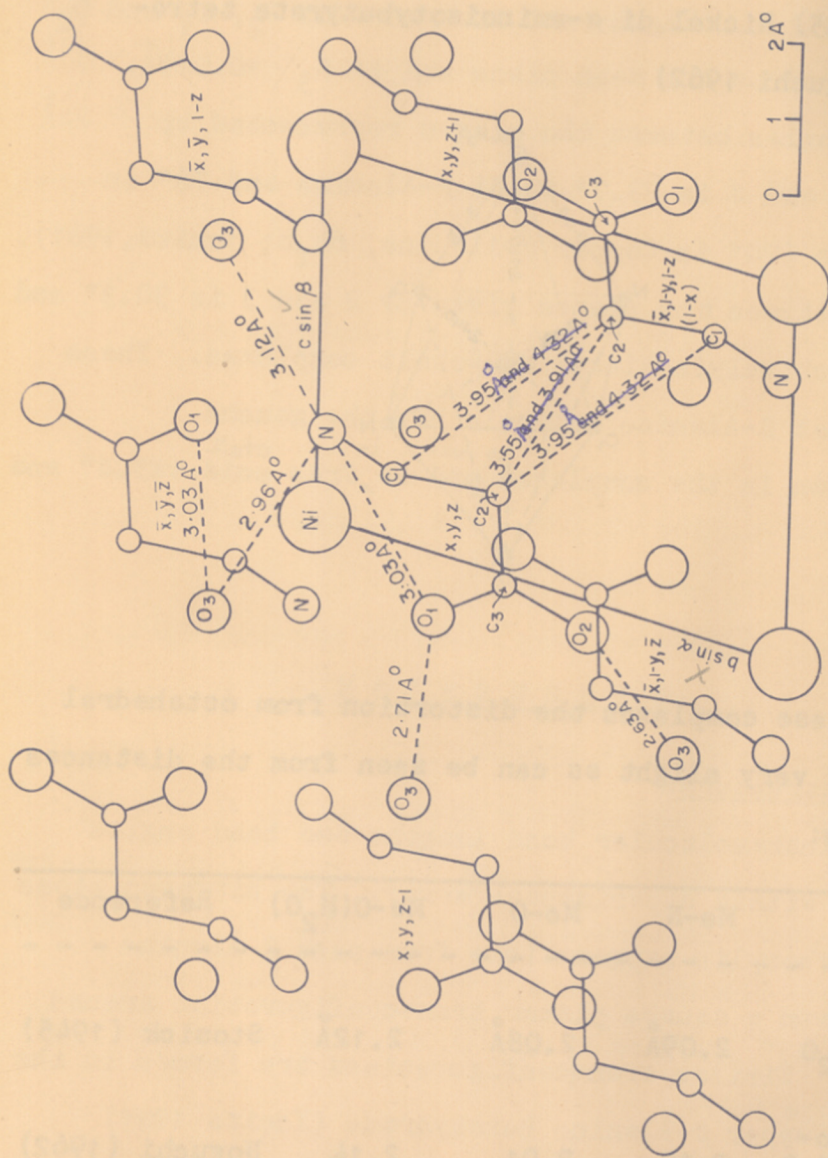


FIG. VII-3. STRUCTURE PROJECTED ON (100) SHOWING INTERMOLECULAR INTERATOMIC DISTANCES FOR Ni β -ALANINE DIHYDRATE.

In the copper complexes of amino acids, however, the octahedra are very much distorted with the water oxygen atoms at about 2.5Å, nitrogen and Carboxylic oxygens at about 2.0Å from the metal ion. These distances for some copper complexes are listed below:

	Me-N	Me-O	Me-O(H ₂ O)	Reference
Copper β-Alanine. 6H ₂ O	2.04Å	2.01Å	2.53Å	Tomita (1961)
Copper Proline. 2H ₂ O	1.99	2.03	2.52	Mathieson and Welsh (1952)
bis-(β-amino-butyrates) Copper II. 2H ₂ O	1.99	2.00	2.45	Bryan, Poljak and Tomita (1961)

The almost regular octahedral arrangement of ligands in the nickel and cobalt complexes and the distorted octahedral arrangement is the case of copper complexes are in accord with the theoretical considerations put forward by Orgel (1952) based on the crystal field theory and Jahn-Teller effect (Orgel and Dunitz 1957).

Crystal structure:

The projections of the structure, viewed along c axis and along a axis are shown in figures VII-2 and VII-3 respectively. The intermolecular distances for Nickel β-Alanine dihydrate are indicated in these figures, and are, for both the compounds, listed in table VII.3.

T A B L E - VII.3

Contact	Ni β -Alanine	Co β -Alanine
$O_1(x, y, z) - O_3(\bar{x}, \bar{y}, z-1)$	$2.71 \pm 0.03 \text{ \AA}$	$2.72 \pm 0.03 \text{ \AA}$
$N(x, y, z) - O_3(\bar{x}, \bar{y}, 1-z)$	3.12 ± 0.04	3.25 ± 0.04
$O_2(x, y, z) - O_3(\bar{x}, 1-y, \bar{z})$	2.63 ± 0.03	2.69 ± 0.03
$N(x, y, z) - O_2(x, y-1, z)$	3.11 ± 0.04	3.05 ± 0.04
$C_1(x, y, z) - O_2(1-x, 1-y, \bar{z})$	3.47 ± 0.04	3.54 ± 0.04
$C_2(x, y, z) - O_2(1-x, 1-y, \bar{z})$	3.62 ± 0.04	3.65 ± 0.04
$C_2(x, y, z) - C_2(1-x, 1-y, \bar{z})$	3.99 ± 0.06	3.99 ± 0.06
$C_2(x, y, z) - C_2(1-x, 1-y, 1-z)$	3.55 ± 0.06	3.52 ± 0.06
$C_2(x, y, z) - C_1(1-x, 1-y, \bar{z})$	4.32 ± 0.06	4.59 ± 0.06
$C_1(x, y, z) - C_1(1-x, \bar{y}, \bar{z})$	3.77 ± 0.06	3.69 ± 0.06
$C_1(x, y, z) - C_2(1-x, 1-y, 1-z)$	3.95 ± 0.06	3.99 ± 0.06

Nitrogen atom of one molecule makes three short contacts with oxygen atoms in the neighbouring molecules $N-O_3(\bar{x}, \bar{y}, \bar{z})$ (side of the octahedron around the metal atom), $N-O_3(\bar{x}, \bar{y}, 1-z)$ and $N-O_2(x, y-1, z)$. The angles which these bonds make with the C_1-N bond and Ni-N bond are listed in Table VII-4.

T A B L E - VII.4

Contact	Angle
Ni-N-C ₁	115.2 ± 1.9°
Ni-N-O ₂ (x, y-1, z)	82.9 ± 1.0°
Ni-N-O ₃ (\bar{x} , \bar{y} , 1-z)	96.0 ± 1.1°
Ni-N-O ₃ (\bar{x} , \bar{y} , \bar{z})	46.0 ± 0.6°
C ₁ -N-O ₂ (x, y-1, z)	103.3 ± 1.7°
C ₁ -N-O ₃ (\bar{x} , \bar{y} , 1-z)	147.6 ± 1.9°
C ₁ -N-O ₃ (\bar{x} , \bar{y} , \bar{z})	100.6 ± 1.7°
O ₂ (x, y-1, z)-N-O ₃ (\bar{x} , \bar{y} , \bar{z})	51.3 ± 0.6°
O ₂ (x, y-1, z)-N-O ₃ (\bar{x} , \bar{y} , 1-z)	86.4 ± 1.0°

If the arrangement of the bonds around Nitrogen is assumed to be tetrahedral then the angles which N-O₃(\bar{x} , \bar{y} , \bar{z}) makes with the other bonds show wide variations from the tetrahedral value, except C₁-N-O₃(\bar{x} , \bar{y} , \bar{z}) (100.6°). This may be due to the fact that N-O₃(\bar{x} , \bar{y} , \bar{z}) is a side of the octahedron around the metal. The contacts N-O₂(x, y-1, z) and N-O₃(\bar{x} , \bar{y} , 1-z) make angles which are reasonably close to the tetrahedral angle. It would therefore, appear likely that N-O₂(x, y-1, z) and N-O₃(\bar{x} , \bar{y} , 1-z) are the possible hydrogen bonds.

The configuration of the bonds around the water molecular oxygen is shown in figure VII.4 and the various angles are listed in table VII.5.

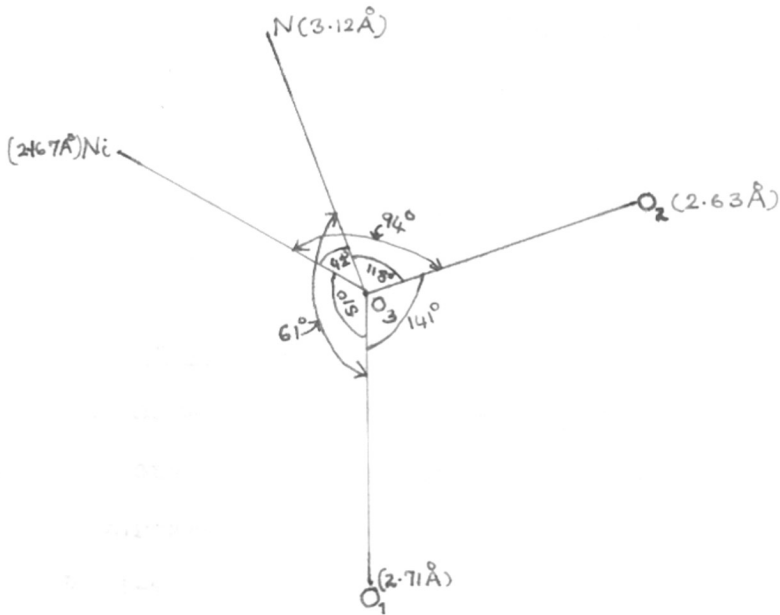


Fig. VII-4

T A B L E - VII.5

Contact	Angle
Ni-O ₃ (2.167 Å) and O ₃ -N (3.12 Å)	42.0 ± 0.5°
Ni-O ₃ (2.167 Å) and O ₃ -O ₂ (2.63 Å)	94.0 ± 1.1°
Ni-O ₃ (2.167 Å) and O ₃ -O ₁ (2.71 Å)	50.5 ± 0.6°
O ₂ -O ₃ (2.63 Å) and O ₃ -O ₁ (2.71 Å)	140.7 ± 1.2°
O ₁ -O ₃ (2.71 Å) and O ₃ -N (3.12 Å)	60.7 ± 0.8°
O ₂ -O ₃ (2.63 Å) and O ₃ -N (3.12 Å)	118.5 ± 1.1°
O ₂ -O ₃ (2.63 Å) and O ₃ -O ₁ (3.03 Å) (side of the octahedron)	79.6 ± 1.0°
Ni-O ₃ (2.16 Å) and O ₃ -O ₁ (3.03 Å)	44.9 ± 0.6°

In view of the large deviations of the angles from the tetrahedral value it is rather difficult to decide as to which of these contacts are the hydrogen bonds though the interatomic distances O_3-O_1 (2.71Å and 2.72Å) and O_3-O_2 (2.63Å in Ni β -Alanine and 2.69Å in Co β -Alanine) suggest that these are the hydrogen bonds.

Packing of molecules

The nickel and cobalt β -Alanine dihydrate units are held in a stable layer structure parallel to (100) plane by the hydrogen bonds $N-O_2(x,y-1,z)$, $O_1-O_3(x,y,z-1)$ and $O_2-O_3(\bar{x}, 1-y, \bar{z})$. The stacking of the layers normal to (100) plane is governed by Van der Waal's bonds of the type CH_2-CH_2 and CH_2-O . The layer structure is similar to those found in Nickel glycine dihydrate (Storick 1945), Copper Proline dihydrate (Mathieson and Welsh, 1952), and bis(β -amino butyrate) Copper II dihydrate (Bryan, Poljak and Tomita 1961).

Thermal vibration of the molecules

On comparison of the B values for the three projections (Table VI, Chapter VI) it is seen that the B values for okl reflexions are in general smaller than those for the hko and hol reflexions. This indicates that the amplitude of thermal vibration is larger in a direction normal to the layers of molecules i.e. roughly along the a axis (figure VII-2). This direction coincides with the direction of maximum vibration of nickel and oxygen atoms O_1 and O_2 (figure VI-6) in the difference map

of (001) projection. From the structure projected on (001) (figure VII.2) the absence of any bonds in this direction can be seen. This accounts for the larger thermal vibration of the molecules in this direction.

A P P E N D I X

The observed and calculated structure factors are given for the structures of β -Alanine, Nickel β -Alanine dihydrate and Cobalt β -Alanine dihydrate. For the unobserved reflexions the estimated minimum observable values have been given.

Table of Observed and Calculated Structure Factors
for β -Alanine

h	k	l	$ F_o $	F_c	h	k	l	F_o	F_c
2	0	0	17	24	2	4	0	31	-33
4	0	0	41	43	4	4	0	12	-15
6	0	0	18	20	6	4	0	17	-13
8	0	0	18	18	8	4	0	12	-18
10	0	0	13	-8	2	5	0	47	41
2	1	0	<8	6	4	5	0	24	-23
4	1	0	36	-30	6	5	0	15	11
6	1	0	17	-14	8	5	0	31	-29
8	1	0	18	17	0	6	0	60	-64
0	2	0	62	56	2	6	0	34	-31
2	2	0	10	11	4	6	0	10	-11
4	2	0	9	12	6	6	0	54	-51
6	2	0	31	31	8	6	0	12	-11
8	2	0	<12	4	2	7	0	42	-40
2	3	0	59	63	4	7	0	<10	2
4	3	0	37	-46	6	7	0	<13	10
6	3	0	9	-10	0	8	0	23	-23
8	3	0	<12	-1	2	8	0	22	18
0	4	0	94	-154*	4	8	0	<12	-10

Reflexions marked (*) appear to suffer from extinction.

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
6	8	0	<12	3	8	1	1	<22	-6
8	8	0	<6	6	0	2	1	31	-38
10	8	0	10	-8	1	2	1	36	-37
2	9	0	27	-22	2	2	1	47	-57
4	9	0	18	17	3	2	1	56	52
6	9	0	<12	8	4	2	1	54	-48
0	10	0	16	13	5	2	1	36	-41
2	10	0	24	27	6	2	1	30	-28
4	10	0	<12	-5	7	2	1	21	16
6	10	0	28	26	8	2	1	<23	-14
8	10	0	16	12	9	2	1	41	30
2	11	0	14	15	1	3	1	48	-58
4	11	0	19	18	2	3	1	17	-15
0	12	0	35	36	3	3	1	19	16
6	13	0	12	-14	4	3	1	16	-10
8	13	0	12	11	5	3	1	10	-7
0	14	0	<17	-1	0	4	1	38	-42
0	16	0	21	-25	1	4	1	25	24
1	1	1	<43	59	2	4	1	56	-56
2	1	1	<10	-9	3	4	1	34	35
3	1	1	<14	4	4	4	1	22	-21
5	1	1	24	-25	6	4	1	13	-9
6	1	1	15	-15	1	5	1	29	-36
7	1	1	29	25	2	5	1	15	15

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
5	5	1	11	-9	1	15	1	21	-16
7	5	1	37	31	0	0	2	64	108*
0	6	1	13	12	1	0	2	31	39
1	6	1	26	-25	2	0	2	66	-80
2	6	1	<12	-2	3	0	2	22	18
4	6	1	15	11	4	0	2	32	-32
1	7	1	17	-15	5	0	2	21	22
2	7	1	18	16	6	0	2	20	-18
5	7	1	24	18	7	0	2	14	-6
7	7	1	33	-23	8	0	2	<13	2
0	8	1	30	36	1	1	2	12	9
1	8	1	35	-42	2	1	2	27	22
2	8	1	35	-33	3	1	2	<9	-6
3	8	1	<20	-18	4	1	2	<9	-4
4	8	1	19	18	5	1	2	27	-22
1	9	1	19	-16	6	1	2	<10	-1
5	9	1	13	15	7	1	2	<13	-4
0	10	1	<16	-8	8	1	2	22	-23
1	10	1	<23	20	0	2	2	<8	-1
0	12	1	<17	-11	1	2	2	12	8
1	12	1	25	27	2	2	2	29	-24
0	14	1	<17	-7	3	2	2	21	-16
3	5	2	16	15	4	1	3	39	40

Reflexions marked (*) appear to suffer from extinction.

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
4	2	2	24	-23	6	5	2	21	20
5	2	2	< 9	4	7	5	2	14	14
6	2	2	< 10	6	8	5	2	17	-14
7	2	2	< 13	7	0	6	2	< 12	9
1	3	2	16	- 8	2	6	2	25	32
2	3	2	53	62	3	6	2	20	19
4	3	2	< 10	-10	4	6	2	36	41
5	3	2	22	-18	6	6	2	13	-12
6	3	2	13	14	7	6	2	14	-13
7	3	2	< 13	7	1	7	2	16	14
8	3	2	17	20	2	7	2	33	36
10	3	2	20	21	3	7	2	14	14
0	4	2	43	-53	0	8	2	< 15	3
1	4	2	< 9	- 4	2	8	2	26	30
2	4	2	23	24	6	8	2	12	10
3	4	2	17	-15	2	9	2	24	-26
4	4	2	20	21	0	10	2	< 16	- 9
5	4	2	12	-14	4	10	2	21	-25
6	4	2	< 10	6	2	11	2	< 14	8
7	4	2	< 13	- 6	0	12	2	< 17	7
1	5	2	16	19	0	14	2	< 16	- 8
2	5	2	29	29	1	1	3	25	28
3	5	2	14	15	4	1	3	39	40
4	5	2	16	-10	5	1	3	11	- 7

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
7	1	3	19	20	6	5	3	15	16
8	1	3	19	16	7	5	3	23	-24
0	2	3	<45	52	0	6	3	20	16
1	2	3	<11	-7	1	6	3	14	-13
2	2	3	8	-8	4	6	3	16	16
3	2	3	31	-34	2	7	3	15	15
4	2	3	<11	-6	5	7	3	<18	11
5	2	3	27	-33	0	8	3	<15	-10
9	2	3	12	11	1	8	3	21	-26
1	3	3	<17	-13	6	8	3	<14	-15
2	3	3	17	-19	6	9	3	15	18
3	3	3	12	-14	0	10	3	42	-36
4	3	3	16	-14	0	12	3	21	-17
5	3	3	<14	-9	1	12	3	19	19
0	4	3	29	-35	0	14	3	22	18
1	4	3	13	-14	0	0	4	61	66
2	4	3	19	-8	1	0	4	<20	13
3	4	3	11	-5	2	0	4	<9	-9
4	4	3	<22	23	3	0	4	<10	5
6	4	3	<21	-18	4	0	4	14	14
8	4	3	<16	5	5	0	4	18	14
1	5	3	21	-25	6	0	4	17	15
4	5	3	16	-19	7	0	4	<12	-9
5	5	3	10	-7	8	0	4	15	20

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
9	0	4	<13	-16	3	6	4	19	23
2	1	4	13	13	6	6	4	16	-18
3	1	4	<10	-11	1	7	4	21	16
4	1	4	<12	-4	2	7	4	11	-10
5	1	4	24	-24	3	7	4	17	20
6	1	4	18	-16	4	7	4	18	14
0	2	4	25	23	0	8	4	<17	-14
2	2	4	11	11	4	8	4	12	-12
3	2	4	15	-16	4	9	4	14	13
5	2	4	<11	-2	0	10	4	<17	11
6	2	4	12	-10	4	10	4	14	-14
1	3	4	19	-19	0	12	4	25	23
2	3	4	21	19	3	1	5	19	-21
3	3	4	<12	-13	4	1	5	18	15
4	3	4	20	-19	5	1	5	<9	-7
5	3	4	23	-28	6	1	5	13	-9
6	3	4	19	-16	0	2	5	<16	-2
0	4	4	38	-34	2	2	5	24	-24
2	4	4	<12	5	3	2	5	22	23
4	4	4	<12	-3	4	2	5	24	-26
3	5	4	12	9	5	2	5	15	-15
4	5	4	15	-16	6	2	5	15	-11
0	6	4	34	-35	3	3	5	14	10
2	6	4	19	-21	5	3	5	9	-8

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
0	4	5	<16	2	6	1	6	9	-10
2	4	5	30	-31	0	2	6	<17	-4
3	5	5	22	20	2	2	6	<8	-1
5	5	5	17	16	4	2	6	15	-15
4	6	5	12	13	2	3	6	12	10
2	7	5	9	14	5	3	6	10	-8
5	7	5	11	13	6	3	6	9	-8
2	8	5	21	22	0	4	6	<17	7
5	9	5	11	-14	2	4	6	19	22
0	0	6	<17	-12	4	4	6	13	10
2	0	6	35	-33	4	6	6	23	28
4	0	6	19	-14	4	7	6	12	11
5	0	6	9	10	0	2	7	21	16
2	1	6	14	11	0	4	7	24	28
1	1	0	25	25	7	2	0	10	11
0	1	0	10	11	8	2	0	<4	11
7	1	0	8	9	7	2	0	9	11
8	1	0	10	10	7	2	0	18	-11
9	1	0	<4	1	3	2	0	6	11
2	1	1	24	25	4	2	0	31	33
3	1	1	25	20	5	2	0	25	20
4	1	0	6	5	3	2	0	9	11

II. Table of Observed and Calculated Structure Factors for Nickel β -Alanine. $2H_2O$

h	k	l	F_o	F_c	h	k	l	F_c	F_c
2	0	0	6	-10	$\bar{5}$	1	0	< 3	0
3	0	0	18	19	$\bar{6}$	1	0	8	9
4	0	0	17	16	$\bar{7}$	1	0	4	5
5	0	0	12	11	$\bar{8}$	1	0	< 4	2
6	0	0	< 4	- 1	$\bar{9}$	1	0	5	5
7	0	0	5	- 4	$\bar{10}$	1	0	8	9
8	0	0	10	10	0	2	0	15	13
9	0	0	13	11	1	2	0	< 2	2
10	0	0	5	2	2	2	0	5	- 2
1	1	0	9	7	3	2	0	14	17
2	1	0	33	35	4	2	0	28	32
3	1	0	8	12	5	2	0	19	18
4	1	0	10	12	6	2	0	8	9
5	1	0	25	25	7	2	0	10	10
6	1	0	10	11	8	2	0	< 4	4
7	1	0	8	9	$\bar{1}$	2	0	5	5
8	1	0	10	10	$\bar{2}$	2	0	18	-15
9	1	0	< 4	1	$\bar{3}$	2	0	6	4
$\bar{2}$	1	0	24	25	$\bar{4}$	2	0	31	32
$\bar{3}$	1	0	25	20	$\bar{5}$	2	0	25	29
$\bar{4}$	1	0	6	5	$\bar{6}$	2	0	9	11

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
$\bar{7}$	2	0	< 4	3	1	4	0	18	18
$\bar{8}$	2	0	10	10	2	4	0	< 10	10
$\bar{9}$	2	0	12	13	3	4	0	< 6	7
0	3	0	15	17	4	4	0	5	5
1	3	0	15	14	5	4	0	5	- 3
2	3	0	9	9	6	4	0	3	4
3	3	0	9	7	7	4	0	8	8
4	3	0	15	15	$\bar{1}$	4	0	29	31
5	3	0	< 8	9	$\bar{2}$	4	0	31	30
6	3	0	< 4	- 1	$\bar{3}$	4	0	3	3
7	3	0	< 4	2	$\bar{4}$	4	0	10	10
8	3	0	6	7	$\bar{5}$	4	0	12	13
$\bar{1}$	3	0	20	18	$\bar{6}$	4	0	3	2
$\bar{2}$	3	0	3	- 1	$\bar{7}$	4	0	5	5
$\bar{3}$	3	0	8	9	$\bar{8}$	4	0	5	6
$\bar{4}$	3	0	24	22	$\bar{10}$	4	0	16	6
$\bar{5}$	3	0	15	14	0	5	0	25	24
$\bar{6}$	3	0	< 17	18	1	5	0	10	11
$\bar{7}$	3	0	10	15	2	5	0	5	- 5
$\bar{8}$	3	0	< 4	3	3	5	0	6	8
$\bar{9}$	3	0	8	7	4	5	0	15	12
10	3	0	6	6	5	5	0	8	8
0	4	0	18	17	6	5	0	16	15

Values marked (*) probably suitable for extraction

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
1	5	0	10	11	3	7	0	6	5
2	5	0	9	9	1	7	0	< 4	5
3	5	0	10	12	2	7	0	< 4	- 2
4	5	0	10	11	3	7	0	< 4	2
5	5	0	10	11	4	7	0	8	7
6	5	0	3	- 1	5	7	0	11	10
7	5	0	< 4	- 4	6	7	0	6	5
8	5	0	5	5	0	8	0	8	5
0	6	0	< 4	2	2	8	0	< 2	4
1	6	0	< 4	- 1	1	8	0	< 9	12
2	6	0	15	11	2	8	0	< 6	6
3	6	0	15	13	3	8	0	6	5
4	6	0	6	6	4	8	0	5	4
5	6	0	9	8	5	8	0	4	2
1	6	0	6	7	0	0	1	27	50*
2	6	0	< 8	8	1	0	1	10	13
3	6	0	3	4	2	0	1	24	25
4	6	0	< 4	2	3	0	1	25	23
5	6	0	6	9	4	0	1	23	24
6	6	0	10	11	5	0	1	21	23
7	6	0	5	6	6	0	1	< 3	- 1
0	7	0	10	10	7	0	1	< 3	2
1	7	0	6	6	8	0	1	12	13
2	7	0	3	2	9	0	1	6	8

Reflexion marked (*) probably suffers from extinction.

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
$\bar{1}$	0	1	16	25	$\bar{7}$	0	2	15	17
$\bar{2}$	0	1	31	-34	$\bar{8}$	0	2	6	8
$\bar{3}$	0	1	3	-4	0	0	3	11	8
$\bar{4}$	0	1	11	8	1	0	3	27	32
$\bar{5}$	0	1	10	7	2	0	3	15	12
$\bar{6}$	0	1	14	16	3	0	3	< 3	2
$\bar{7}$	0	1	10	10	4	0	3	16	15
$\bar{8}$	0	1	9	9	5	0	3	14	13
$\bar{9}$	0	1	10	12	6	0	3	8	10
0	0	2	< 2	1	7	0	3	< 2	3
1	0	2	18	20	$\bar{1}$	0	3	< 2	- 2
2	0	2	18	20	$\bar{2}$	0	3	13	13
3	0	2	< 3	- 1	$\bar{3}$	0	3	18	17
4	0	2	15	14	$\bar{4}$	0	3	22	22
5	0	2	17	14	$\bar{5}$	0	3	10	9
6	0	2	< 3	2	$\bar{6}$	0	3	< 3	0
7	0	2	6	6	$\bar{7}$	0	3	7	8
8	0	2	4	5	$\bar{8}$	0	3	5	7
$\bar{1}$	0	2	9	9	0	0	4	14	10
$\bar{2}$	0	2	4	5	1	0	4	14	12
$\bar{3}$	0	2	18	18	2	0	4	< 3	- 1
$\bar{4}$	0	2	26	28	3	0	4	6	3
$\bar{5}$	0	2	12	13	4	0	4	13	10
$\bar{6}$	0	2	12	15	5	0	4	14	13

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
6	0	4	<14	12	0	3	1	<9	8
$\bar{1}$	0	4	<3	-2	0	$\bar{4}$	1	14	14
$\bar{2}$	0	4	7	6	0	5	1	17	17
$\bar{3}$	0	4	13	11	0	6	1	<4	-3
$\bar{4}$	0	4	11	11	0	7	1	7	9
$\bar{5}$	0	4	15	12	0	$\bar{1}$	1	19	22
$\bar{6}$	0	4	<3	13	0	$\bar{2}$	1	22	27
$\bar{8}$	0	4	16	16	0	$\bar{3}$	1	29	32
0	0	5	13	10	0	$\bar{4}$	1	<4	-4
1	0	5	6	2	0	$\bar{5}$	1	14	15
2	0	5	<3	0	0	$\bar{6}$	1	10	10
$\bar{1}$	0	5	9	8	0	$\bar{7}$	1	17	16
$\bar{2}$	0	5	10	19	0	$\bar{8}$	1	10	10
$\bar{3}$	0	5	14	9	0	1	2	15	19
$\bar{4}$	0	5	19	16	0	2	2	26	25
$\bar{5}$	0	5	<7	8	0	3	2	<14	-4
$\bar{6}$	0	5	<7	6	0	4	2	6	6
0	0	6	9	9	0	5	2	10	11
$\bar{1}$	0	6	8	8	0	6	2	6	5
$\bar{2}$	0	6	9	6	0	7	2	6	5
$\bar{3}$	0	6	6	6	0	$\bar{1}$	2	10	-8
$\bar{4}$	0	6	6	2	0	$\bar{2}$	2	15	18
0	1	1	13	-11	0	$\bar{3}$	2	29	33
0	2	1	21	22	0	$\bar{4}$	2	<4	-1

Table of observed and calculated structure factors for K_2AlF_6 - AlF_6^{3-}

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
0	$\bar{5}$	2	< 4	0	0	5	4	< 2	2
0	$\bar{6}$	2	< 4	2	0	$\bar{1}$	4	17	17
0	$\bar{7}$	2	11	12	0	$\bar{2}$	4	17	19
0	$\bar{8}$	2	6	7	0	$\bar{3}$	4	10	9
0	1	3	14	12	0	$\bar{4}$	4	7	6
0	2	3	14	15	0	$\bar{5}$	4	19	20
0	3	3	10	10	0	$\bar{6}$	4	10	9
0	4	3	10	10	0	$\bar{7}$	4	6	6
0	5	3	10	8	0	1	5	9	8
0	6	3	6	8	0	2	5	10	8
0	$\bar{1}$	3	10	9	0	3	5	7	7
0	$\bar{2}$	3	14	13	0	$\bar{1}$	5	8	8
0	$\bar{3}$	3	12	11	0	$\bar{2}$	5	6	5
0	$\bar{4}$	3	6	8	0	$\bar{3}$	5	10	10
0	$\bar{5}$	3	14	15	0	$\bar{4}$	5	10	9
0	$\bar{6}$	3	< 4	2	0	$\bar{5}$	5	12	12
0	$\bar{7}$	3	< 4	4	0	$\bar{6}$	5	7	7
0	1	4	7	7	0	$\bar{1}$	6	6	8
0	2	4	13	15	0	$\bar{2}$	6	< 3	1
0	3	4	17	18	0	$\bar{3}$	6	< 3	2
0	4	4	< 5	4	0	$\bar{4}$	6	10	9

III. Table of Observed and calculated Structure Factors for Cobalt β -Alanine, $2H_2O$

h	k	l	$ F_o $	F_c	h	k	l	F_o	F_c
2	0	0*	6	-7	$\bar{4}$	1	0	8	8
3	0	0	16	23	$\bar{5}$	1	0	< 3	1
4	0	0	19	20	$\bar{6}$	1	0	10	10
5	0	0	15	15	$\bar{7}$	1	0	< 5	4
6	0	0	< 5	1	$\bar{8}$	1	0	< 5	2
7	0	0	< 5	-2	$\bar{10}$	1	0	6	7
8	0	0	12	13	0	2	0*	14	12
9	0	0	12	11	1	2	0	3	1
10	0	0	< 6	2	2	2	0	6	-4
0	1	0*	15	13	3	2	0	13	14
1	1	0*	9	7	4	2	0	30	30
2	1	0*	28	36	5	2	0	18	18
3	1	0	9	12	6	2	0	9	8
4	1	0	13	13	7	2	0	10	9
5	1	0	25	25	8	2	0	10	11
6	1	0	12	13	$\bar{4}$	2	0	4	4
7	1	0	10	11	$\bar{2}$	2	0	12	-13
8	1	0	11	9	$\bar{3}$	2	0	9	9
9	1	0	< 6	2	$\bar{4}$	2	0	29	32
$\bar{3}$	1	0	22	24	$\bar{5}$	2	0	24	25

For the reflexions marked (*) the $|F_o|$ and F_c values for CuK_α radiation are given.

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
$\bar{6}$	2	0	11	9	1	4	0	18	20
$\bar{7}$	2	0	4	2	2	4	0	9	11
$\bar{9}$	2	0	12	12	3	4	0	7	7
0	3	0	15	17	4	4	0	7	6
1	3	0	15	14	5	4	0	5	0
2	3	0	10	9	6	4	0	7	5
3	3	0	9	8	$\bar{1}$	4	0	25	27
4	3	0	13	15	$\bar{2}$	4	0	23	25
5	3	0	9	9	$\bar{3}$	4	0	<4	4
6	3	0	<5	0	$\bar{4}$	4	0	12	12
7	3	0	<5	2	$\bar{5}$	4	0	14	14
$\bar{1}$	3	0	15	16	$\bar{6}$	4	0	26	24
$\bar{2}$	3	0	<4	-2	$\bar{7}$	4	0	27	28
$\bar{3}$	3	0	10	9	0	5	0	21	25
$\bar{4}$	3	0	23	23	1	5	0	12	12
$\bar{5}$	3	0	<15	15	2	5	0	<5	-4
$\bar{6}$	3	0	<20	17	3	5	0	<9	7
$\bar{7}$	3	0	15	14	4	5	0	13	11
$\bar{8}$	3	0	<5	4	5	5	0	<6	7
$\bar{9}$	3	0	10	9	$\bar{1}$	5	0	12	11
0	4	0	16	15	$\bar{2}$	5	0	29	29
3	0	1	25	26	$\bar{3}$	0	1	21	21

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
3	5	0	10	11	5	0	1	18	20
4	5	0	12	12	6	0	1	< 4	2
5	5	0	11	12	7	0	1	< 5	3
0	6	0	< 5	3	8	0	1	14	10
1	6	0	< 5	11	9	0	1	5	6
2	6	0	11	9	10	0	1	10	11
3	6	0	9	10	11	0	1	7	6
4	6	0	< 6	4	12	0	1	11	12
1	6	0	7	7	13	0	1	9	9
2	6	0	8	9	14	0	1	< 8	10
3	6	0	< 5	6	15	0	1	9	11
4	6	0	< 5	3	16	0	2	21	22
5	6	0	19	29	17	0	2	20	20
6	6	0	10	18	18	0	2	< 3	1
0	7	0	< 12	9	19	0	2	17	16
1	7	0	< 5	2	20	0	2	18	14
2	7	0	< 5	- 2	21	0	2	< 5	1
4	7	0	10	7	22	0	2	5	4
5	7	0	12	9	23	0	2	3	3
0	8	0	< 7	6	24	0	2	16	17
2	0	1	25	27	25	0	2	21	27
3	0	1	25	26	26	0	2	11	14
4	0	1	19	23	27	0	2	12	16

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
$\bar{7}$	0	2	14	16	6	0	4	12	10
$\bar{8}$	0	2	8	8	$\bar{7}$	0	4	<5	-1
0	0	3	11	10	$\bar{2}$	0	4	8	7
1	0	3	25	29	$\bar{3}$	0	4	10	12
2	0	3	12	10	$\bar{4}$	0	4	9	11
3	0	3	<4	3	$\bar{5}$	0	4	8	9
4	0	3	17	17	$\bar{6}$	0	4	<5	2
5	0	3	14	13	0	0	5	12	10
6	0	3	10	7	1	0	5	<5	3
7	0	3	<5	2	2	0	5	<5	0
$\bar{2}$	0	3	14	14	$\bar{7}$	0	5	8	7
$\bar{3}$	0	3	16	19	$\bar{2}$	0	5	10	9
$\bar{4}$	0	3	18	22	$\bar{3}$	0	5	11	10
$\bar{5}$	0	3	10	12	$\bar{4}$	0	5	7	7
$\bar{6}$	0	3	<5	4	0	0	6	10	7
$\bar{7}$	0	3	6	8	1	0	6	8	5
$\bar{8}$	0	3	<7	5	2	0	6	10	6
0	0	4	11	9	$\bar{7}$	0	6	8	7
1	0	4	14	11	$\bar{2}$	0	6	6	5
2	0	4	<5	-1	$\bar{3}$	0	6	6	6
3	0	4	8	5	0	2	1	22	23
4	0	4	14	10	0	3	1	7	8
5	0	4	14	10	0	4	1	15	16

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
0	5	1	16	17	0	6	2	< 6	3
0	6	1	< 6	1	0	7	2	12	12
0	7	1	6	8	0	1	3	15	14
0	8	1	< 7	5	0	2	3	14	15
0	3	1	29	32	0	3	5	9	10
0	4	1	< 4	1	0	4	3	10	10
0	5	1	15	14	0	5	3	8	10
0	6	1	10	10	0	7	3	11	8
0	7	1	15	14	0	2	3	17	16
0	8	1	9	9	0	3	3	15	12
0	1	2	14	11	0	4	3	8	8
0	2	2	24	25	0	5	3	15	14
0	3	2	< 5	- 2	0	6	3	6	3
0	4	2	8	6	0	1	4	9	8
0	5	2	11	11	0	2	4	11	14
0	6	2	6	6	0	3	4	18	17
0	7	2	< 7	4	0	4	4	6	6
0	1	2	7	- 8	0	7	4	17	17
0	2	2	18	22	0	2	4	18	18
0	3	2	30	34	0	3	4	9	9
0	4	2	< 5	4	0	4	4	7	6
0	5	2	< 5	1	0	5	4	17	18

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
0	$\bar{6}$	4	12	10	0	$\bar{4}$	5	8	9
0	1	5	8	9	0	$\bar{5}$	5	14	10
0	2	5	9	9	0	1	6	<7	6
0	3	5	6	8	0	$\bar{1}$	6	6	8
0	$\bar{1}$	5	11	10	0	$\bar{2}$	6	<6	1
0	$\bar{2}$	5	8	6	0	$\bar{3}$	6	<6	3
0	$\bar{3}$	5	11	9	0	$\bar{4}$	6	10	8

REFERENCES

- Albrecht, G and Corey, R.B. (1939). J. Am. Chem. Soc. 61, 1087
- Bernal, J.D. (1927). Proc. Roy. Soc. A. 113, 117
- Booth, A.D. (1946). Proc. Roy. Soc. A. 188, 77
- Bragg, W.H. (1915). Phil. Trans. Roy. Soc. A. 215, 253
- Bragg, W.H. (1921). Proc. Phys. Soc. (Lond.). 34, 33.
- Bragg, W.H. (1922). Proc. Phys. Soc. (Lond.). 35, 167.
- Bragg, W. L. (1929a). Z. Krist. 70, 483.
- Bragg, W. L. (1929b). Proc. Roy. Soc. A 123, 537
- Bryan, R.F., Poljak, R.J. and Tomita, K. (1961). Acta Cryst. 14, 1125
- Carpenter, G.B. and Donohue, J. (1950). J. Am. Chem. Soc. 72, 2315.
- Cochran, W. (1948). J. Sc. Instr. 25, 253.
- Cochran, W. (1951a). Acta. Cryst. 4, 81.
- Cochran, W. (1951b). Acta Cryst. 4, 408.
- Costain, W. (1941). Ph.D. Thesis, University of Birmingham.
- Crowfoot, D., Bunn, C.W., Rogers-Low, B.W. and Turner Jones A. (1949). The Chemistry of Penicillin, Princeton University Press, p.310; Pitt, G.J. (1952). Acta. Cryst. 5, 770.
- Cruickshank, D.W.J. (1956). Acta. Cryst. 9, 915.
- Cruickshank, D.W.J. (1957). Acta. Cryst. 10, 504.
- Darlow, S.F. (1960). Acta. Cryst. 13, 683.
- Davies, P.T. (1960). J.Sc.Instru. 27, 338.
- Donohue, J. (1950). J. Am. Chem. Soc. 72, 949.
- Donohue, J. and Trueblood, K.N. (1952). Acta Cryst. 5, 414
- Donohue, J. and Marsh, R.E. (1962) Acta. Cryst. 15, 941.
- Harker, D. (1936). J. Chem. Phys. 4, 381.

- Hodgkin, D.C., Kamper, J., Lindsey, J., Mackay, M.,
Pickworth, J., Robertson, J.H., Shoemaker, C.B.,
White, J.G., Prosen, R.J. and Trueblood, K.N.
(1957) Proc. Roy. Soc. A 242, 228
- Huggins, M.L. (1944). J. Chem. Phys. 12, 520.
- Hughes, E.W. (1941). J. Am. Chem. Soc. 63, 1737
- Hughes, E.W. and Moore, W.J. (1949). J. Am. Chem. Soc.
71, 2618.
- James, R.W. (1950). The Optical principles of the
diffraction of X-rays, p. 608. London: Bell.
- Lipson, H. and Cochran, W. (1953). The Determination of
the Crystal Structures, pp.288, 309. London: Bell.
- Lonsdale, K. (1928). Nature, 122, 810.
- Lonsdale, K. (1929). Proc. Roy. Soc. A. 123, 494.
- Marsh, R.E. (1958). Acta. Cryst. 11, 654.
- Mathieson, A.M. (1952). Acta. Cryst. 5, 382.
- Mathieson, A.M. (1953). Acta. Cryst. 6, 399.
- Mathieson, A.M. and Welsh, H.K. (1952). Acta. Cryst.
5, 599.
- McCrone, W.C. and KRe. J. Jr. (1950). Anal. Chem.
22, 730.
- McWeeny, R. (1951). Acta. Cryst. 4, 513.
- Noguchi, T. (1962). Bull. Chem. Soc. Japan. 35, 99.
- Orgel, L.E. (1952). J. Chem. Soc. p. 4756.
- Orgel, L.E. and Dunitz, J. D. (1957). J. Chem. Phys.
26, 293.
- Patterson, A.L. (1934). Phys. Rev. 46, 372.
- Pauling, L. and Corey, R.B. (1951). Proc. Nat. Acad.
Sci. U.S. 37, 235, 241, 251, 256, 261, 272,
282, 729.
- Phillips, D.C. (1954). Acta. Cryst. 7, 746.
- Phillips, D.C. (1956). Acta. Cryst. 9, 819.
- Robertson, J.M. (1933). Proc. Roy. Soc. A. 140, 179.
A. 141, 594.

- Robertson, J.M. and Woodward, I. (1937). J. Chem. Soc. p. 219.
- Shoemaker, D.P., Donohue, J., Schomaker, V. and Corey, R.B. (1950). J. Am. Chem. Soc. 72, 2328.
- Shoemaker, D.P., Barieau, R.E., Donohue, J. and Lu, C.S. (1953). Acta. Cryst. 6, 241.
- Stosick, A.J. (1945). J. Am. Chem. Soc. 67, 365.
- Thomas, L.H. and Umeda, K. (1957). J. Chem. Phys. 26, 293.
- Tomita, K. (1961). Bull. Chem. Soc. Japan, 34, 297.
- Tomita, K. and Nitta, I. (1961). Bull. Chem. Soc. Japan, 34, 286.
- von Eller, G. (1955). Bull. Soc. Franc. Mineral. Crist. 128, 157.
- Weissenberg, K. (1924). Z. Physik. 23, 229.
- Wilson, A.J.C. (1942). Nature, Lond. 150. 152.