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AN INVESTIGATION OF THE CRYSTAL STRUCTURE
OF SODIUM HYPONITRITE

by

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A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

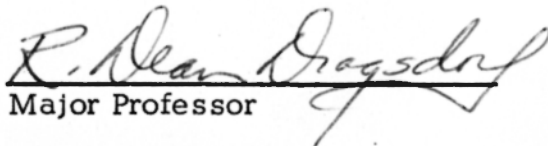
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INTRODUCTION

X-ray Diffraction from Single Crystals

The Fourier transform and the reciprocal lattice. Whenever radiation falls upon matter it is scattered. Conversely, whenever we see radiation being scattered, we infer the existence of matter. By analyzing the pattern of scattered waves it may be possible to find out some things about the matter that is scattering the radiation.

In crystal structure analysis, a beam of radiation is allowed to fall on a small (usually less than 1 mm^3) single crystal. The crystal scatters the radiation in many directions and this so-called "diffraction pattern" is recorded. In order to obtain a meaningful diffraction pattern the wavelength of the radiation used must be of the same magnitude as the scattering objects (atoms in the crystal). X-rays fulfill this requirement and are the most common type of radiation employed, although electrons and thermal neutrons are sometimes used. Figure 1 schematically illustrates the diffraction process.

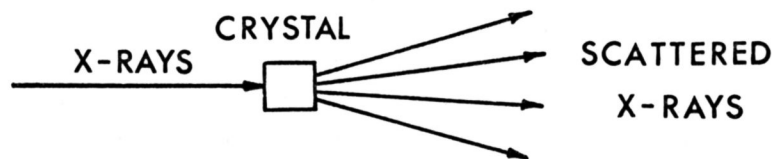


Fig. 1

The aim of crystal structure analysis is to find the arrangement of atoms in the crystal that produced the diffraction pattern. The scattering experiment produces a diffraction pattern, and the task is to synthesize an image of the

crystal given the diffraction pattern. Figure 2 illustrates the reciprocal nature of these two operations.

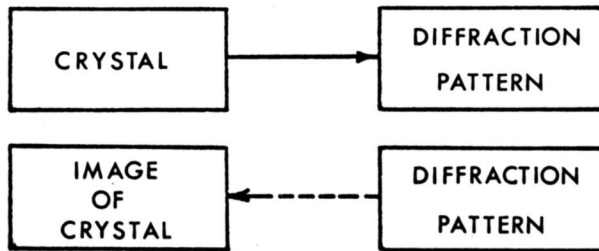


Fig. 2

In the case of optics, scattered light emanating from an object can be focussed by means of a lens to produce an image of the object. For X-rays there exists no such "lens". The lens must be replaced by a mathematical transformation. Before discussing the exact nature of this transformation, it is well to examine how X-rays are scattered. The full mathematical treatment of X-ray scattering is covered thoroughly in such books as Compton and Allison (1935), Buerger (1960) and McLachlan (1960). Because the material is voluminous, only an outline of the theory is presented in what follows.

Consider a plane wave \vec{s}_0 incident upon a particle at the origin of coordinates, and another particle at some general position A. (See Fig. 3). If \vec{r} is a vector between 0 and A, the path difference between the rays striking 0 and A will be $|\vec{r}|\cos\psi - |\vec{r}|\cos\phi$ as shown. The phase difference will be $2\pi/\lambda$ times the path difference. In other words a path difference of one wave length corresponds to a phase difference of 2π . If we replace the point scatterer at A with an electron distribution $\rho(\vec{r})dV$ and integrate, we arrive at the

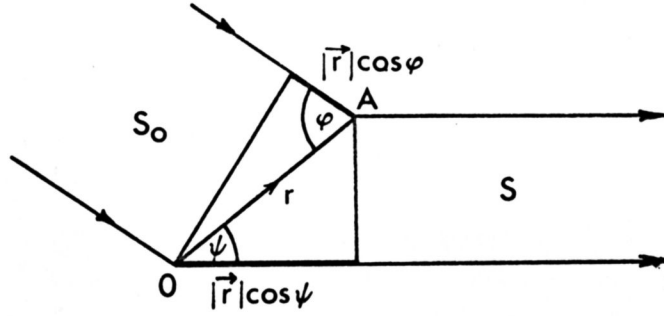


Fig. 3

expression for the total scattered wave:

$$\begin{aligned} G &= \int \rho(\vec{r}) \exp \frac{2\pi i |\vec{r}|}{\lambda} (\cos \psi - \cos \phi) dV \\ &= \int \rho(\vec{r}) \exp 2\pi i \vec{r} \cdot \left(\frac{\vec{s}}{\lambda} - \frac{\vec{s}_0}{\lambda} \right) dV . \end{aligned}$$

Replacing $\vec{s}/\lambda - \vec{s}_0/\lambda$ by \vec{H} we obtain

$$G(\vec{H}) = \int \rho(\vec{r}) \exp 2\pi i \vec{r} \cdot \vec{H} dV . \quad (1)$$

For the wave scattered from the n^{th} atom relative to the origin, we have

$$\begin{aligned} G(\vec{H}) &= \int \rho(\vec{r}) \exp 2\pi i (\vec{r} + \vec{r}_n) \cdot \vec{H} dV \\ &= \left\{ \int \rho(\vec{r}) \exp 2\pi i \vec{r} \cdot \vec{H} dV \right\} \exp 2\pi i \vec{r}_n \cdot \vec{H} \\ &= f_n(\vec{H}) \exp 2\pi i \vec{r}_n \cdot \vec{H} . \end{aligned} \quad (2)$$

The factor $f_n(\vec{H}) = \int \rho(\vec{r}) \exp (2\pi i \vec{r} \cdot \vec{H}) dV$ is the atomic scattering factor for the n^{th} atom type. Values of $f_n(\vec{H})$ have been calculated for all the elements by Hartree-Fock self-consistent field theory and other methods (Henry and Lonsdale, International Tables for X-ray Crystallography). Summing over the N atoms in the unit cell, we obtain

$$G(\vec{H}) = \sum_{n=1}^N f_n(H) \exp 2\pi i \vec{r}_n \cdot \vec{H} \quad (3)$$

for the scattering from the entire unit cell. Note that the vector \vec{r}_n ranges over the space of the crystal (real space) while the vector \vec{H} is defined in the space of the Fourier transform of $\rho(\vec{r})$. This space is commonly called "reciprocal space". The intensity of the scattered radiation is the product of the transform and its complex conjugate:

$$I = G(\vec{H}) \cdot G^*(\vec{H}) . \quad (4)$$

Because the crystal is made up of many unit cell building blocks, the observed transform is not that of a single unit cell, but that of the entire crystal. It can be shown [see Lipson and Taylor, (1958)], for example, that the observed diffraction pattern is a sampling of the modulus of the transform of a single unit cell by a three-dimensional periodic delta function. That is, one can observe the modulus of the transform only at discrete points and nowhere between these points. The points themselves are referred to as "reciprocal lattice points". Because the diffraction pattern is defined at these points only, the reciprocal lattice vector \vec{H} can assume only certain values:

$$\vec{H} = a^* h + b^* k + c^* l \quad (5)$$

where $a^* = 1/a$, $b^* = 1/b$, $c^* = 1/c$, ($a, b,$ and c are the lengths of the edges of the unit cell) and $h, k,$ and l are integers. If

$$\vec{r}_n = a x_n + b y_n + c z_n \quad (6)$$

is a vector from the origin of the unit cell to the n^{th} atom in the cell, the transform becomes

$$G(\mathbf{H}) \rightarrow F_{hkl} = \sum_{n=1}^N f_n(hkl) \exp 2\pi i (hx_n + ky_n + lz_n) . \quad (7)$$

The magnitude of each sampling point of the transform is called a "structure factor" and is indexed by h , k , and l . The intensity of each discrete beam of radiation is given by

$$I_{hkl} \propto F_{hkl} F_{hkl}^* . \quad (8)$$

It is clear that the concept of the Fourier transform is intimately connected with the diffraction process. The experimenter measures the intensities of the discrete beams of radiation coming from the crystal, and converts them to F_{hkl} values. (A number of factors including polarization and the geometry of the X-ray recording device must be considered here). He must then use an inverse Fourier transformation from reciprocal space to real space to obtain $\rho(\vec{r}) = \rho(x, y, z)$, the electron density.

The electron density function provides the crystal "image" that is sought. The great obstacle to the routine application of the inverse transformation is discussed next.

The phase problem. In general, the structure factors F_{hkl} are complex quantities. When the intensity

$$I_{hkl} \propto F_{hkl} F_{hkl}^*$$

is measured, all phase dependency is lost. That is,

$$I_{hkl} \propto |F_{hkl}|^2.$$

This phase dependency must be recovered in order to make the correct inverse transformation. Herein lies what is known as "the phase problem of X-ray crystal structure analysis".

The actual form of the inverse transformation is that of a Fourier series since the F_{hkl} are discrete:

$$\begin{aligned} \rho(xyz) &= \sum_h \sum_k \sum_l F_{hkl} \exp(-2\pi i(hx + ky + lz)) \\ &= \sum_h \sum_k \sum_l |F_{hkl}| \cos[2\pi(hx + ky + lz) - \alpha_{hkl}], \end{aligned} \quad (9)$$

where

$$\alpha_{hkl} = \text{Tan}^{-1} \left[\frac{\sum_n f_n \sin 2\pi(hx_n + ky_n + lz_n)}{\sum_n f_n \cos 2\pi(hx_n + ky_n + lz_n)} \right] = ? \quad (10)$$

The phase angles α_{hkl} are seen to be a function of the $3N$ atom coordinates which are, of course, unknown. The calculation of $\rho(xyz)$ cannot be carried out here because these α_{hkl} cannot be measured experimentally.

Many crystals are centrosymmetric. That is,

$$\rho(x, y, z) = \rho(\bar{x}, \bar{y}, \bar{z}). \quad (11)$$

This implies that

$$F_{hkl} = \pm |F_{hkl}| \quad (12)$$

is a real quantity. Thus in a centrosymmetric crystal, the phase problem reduces to a problem of giving either a + or a - sign to each of the measured

$|F_{hkl}|$. The problem appears, offhand, to be indeterminate by reason of the missing phases. W. L. Bragg, in his presidential address before the section on Physics and Mathematics of the British Association for the Advancement of Science, said in 1948:

The inherent difficulty of such work consists in its being very rarely possible to deduce the structure directly from the observations. On a strictly analytical basis, the observed diffractions might be caused by an infinity of structures since the relative phases of the periodicities do not effect the strengths of the diffracted beams, and the solution only becomes unique when we impose certain conditions, in general that the pattern-unit consists of a discrete number of atoms of known form. No way has as yet been found of arriving directly at a solution consistent with these conditions, by a mathematical treatment, though attempts to do so have been made, and crystallographers have to fall back on a process of trial and error. In effect, one has to guess a likely structure, calculate how it would diffract, and compare with observation. If there is no correspondence, a fresh guess has to be made. So in solving a crystal with one-hundred parameters, one is trying to guess successfully all their values simultaneously. [From Buerger (1959), page 2].

The possibility of trying out all possible sign combinations until the "correct" combination is found is futile. For a centrosymmetric crystal with 100 F_{hkl} , there are 2^{100} sign combinations. If each combination could be checked within 1 microsecond, it would require 10^{18} years to exhaust all combinations.

Fortunately, although the phase problem has not yet been solved, A. L. Patterson and others have discovered that certain clues pertaining to the missing phases were contained in the intensity data. Some of these clues can be uncovered by several ingenious approaches developed by many workers in the field. Primary to all of these approaches was the discovery by Patterson of a

functional relationship between the observed data and the electron density. [See Buerger (1960)]. If F_{hkl} is replaced by $F_{hkl}F_{hkl}^*$ in the electron density function, a phaseless Fourier series (Patterson function) results which is equal to the auto-convolution of the electron density function.

$$\begin{aligned}
 P(xyz) &= \sum_h \sum_k \sum_l F_{hkl} F_{hkl}^* \exp -2\pi i(hx + ky + lz) \\
 &= \rho \star \rho' = \iiint \rho(uvw) \rho(u+x, v+y, w+z) dudvdw .
 \end{aligned}
 \tag{13}$$

Let us assume that the electron density function consists of 5 discrete peaks outlining the molecule as in Fig. 4a.

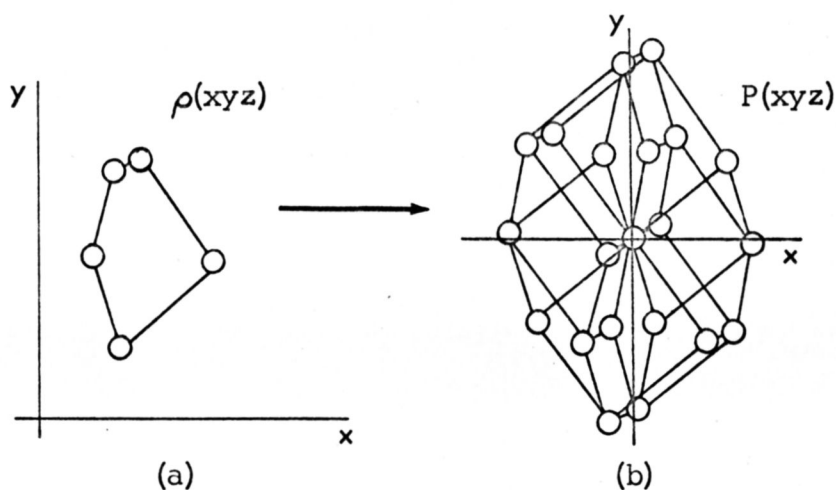


Fig. 4

Then the Patterson function will contain 20 peaks besides the peak at the origin (Fig. 4b). Further, it will contain 5 interwoven images of the electron density function, plus 5 centrosymmetrical equivalent images. In general, if the electron density function contains N discrete peaks denoting atom locations, the Patterson function will contain $N \cdot (N-1)$ non-origin peaks. The Patterson function contains a characteristic origin peak which is higher than

any of the other peaks of the function. This is caused by atoms folding with themselves. Another property of the Patterson function is that it is always centrosymmetric regardless of whether the crystal itself is centrosymmetric.

The calculation of the Patterson function is straightforward, though tedious and time consuming. This calculation is described in Appendix I.

With the Patterson function calculated, it is then a matter of de-convoluting or "unfolding" the function to obtain the electron density function. This process amounts to finding one of the images of the electron density function within the Patterson function. If the atoms were point scatterers, this task could be carried out without too much difficulty. In actuality, the electron density distribution of each atom is more or less Gaussian shaped, so the volume of a Patterson peak due to the folding of two atoms with each other is roughly eight times the volume of an electron density peak. Thus, a great amount of overlapping occurs for crystals with more than just a few atoms per unit cell. Except for simple cases, this overlapping tends to obliterate all images of the electron density function. Buerger (1959) has developed "image-seeking functions" which "seek out an image" of the crystal despite overlapping. This has resulted in only limited success. Harker and Kasper (1947) have developed certain methods based on the recognition that the F_{hkl} are related to each other by the Fourier transform of the unit cell. Several other procedures have been developed, but it is beyond the scope of this thesis to discuss these methods in detail. Only the procedures used in the study of sodium hyponitrite will be discussed.

Sodium Hyponitrite

Infrared Studies. Several plausible structures for the $\text{N}_2\text{O}_2^{--}$ ion have been postulated by workers using infrared and Raman spectra studies. Figure 5 shows (a) trans-structure, (b) cis-structure, and (c) isoelectronic structure.

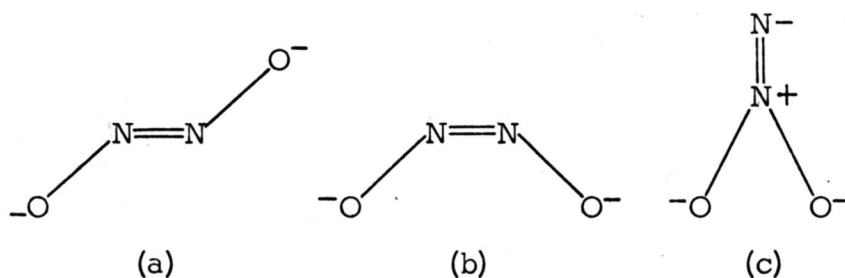


Fig. 5

Hunter and Partington (1933) concluded from chemical evidences that the trans-structure (Fig. 5a) is present in the hyponitrous acid. Also indicated was the possibility of free rotation around the oxygen bonds.

Kuhn and Lippincott (1956) worked with sodium, silver, and mercury hyponitrites in addition to an aqueous solution of $\text{Na}_2\text{N}_2\text{O}_2$. Here again, the trans-structure was indicated.

Goubeau and Laitenberger (1963) measured the infrared spectrum of sodium nitrosyl prepared by a reaction of NO with Na in liquid ammonia. The existence of the dimeric ion $\text{N}_2\text{O}_2^{--2}$ is derived as not being identical with the hyponitrite ion, but the cis form is the preferred structure. The resonance structure proposed is shown in Fig. 6.

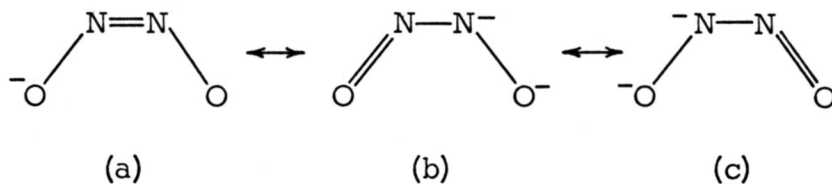


Fig. 6

From these evidences, it seemed that either the trans- or the cis-structures were possible for the hyponitrite ion. Further investigation utilizing X-ray diffraction is necessary to determine the correct structure.

X-ray Studies. Unit cell and reciprocal lattice. Cox, Jeffrey and Stadler (1949) performed an X-ray study of crystalline potassium dinitrosulphite, $K_2SO_3N_2O_2$. Their work indicated that the N_2O_2 group was planar and was of the cis form. The valence diagram for the molecule can be represented as a hybrid of the following three molecular structures shown in Fig. 7. Figure 7a was thought to be the most likely.

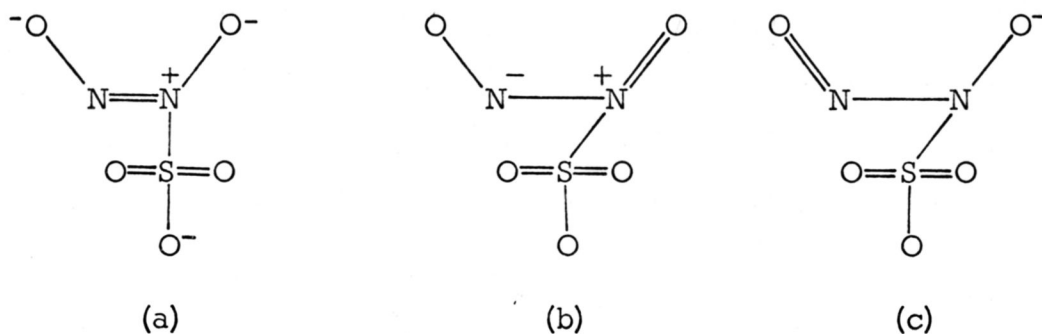


Fig. 7

The bond lengths of N=N and N-O were found to be 1.33 Å and 1.28 Å, respectively.

Lee (1958) attempted to solve the crystal structure of ammonium hydrogen hyponitrite, but no definite result followed.

Chang (1963) conducted an extensive X-ray diffraction study of sodium hyponitrite. Powder patterns were taken of anhydrous $\text{Na}_2\text{N}_2\text{O}_2$ with $\text{CuK}\alpha$ radiation and diffraction patterns were taken using single crystals prepared by evaporating an aqueous solution in a desiccator over sulfuric acid. Rotation, Weissenberg and precession photographs were obtained. The intensities of the diffraction spots were measured both visually by comparison with a calibrated film strip and by using an optical densitometer. Crystalline structure factors $|F|$ were calculated from the measured intensities using the relation

$$I = Lpc^2|F|^2\exp\left[-2B\frac{\sin^2\theta}{\lambda^2}\right], \quad (14)$$

where I is the intensity read from the recording photographic film, c^2 is an absolute scale factor obtained from a Wilson plot [see for example, Buerger (1960)], B is the temperature factor obtained from the Wilson plot, L is the Lorentz factor which depends upon the geometry of the recording device, and p is the polarization factor obtained from Thomson scattering theory.

In addition, the unit cell parameters were calculated from the reciprocal lattice spacings. The results are shown as follows:

$$a = 7.22 \pm 0.03 \text{ \AA}$$

$$b = 17.10 \pm 0.07 \text{ \AA}$$

$$c = 6.01 \pm 0.02 \text{ \AA}$$

$$\alpha = 90^\circ$$

$$\beta = 90^\circ$$

$$\gamma = 107.5 \pm 0.40^\circ$$

$$v = 706 \pm 10 \text{ \AA}^3$$

It was found that there were systematic extinctions on the recording film due to the presence of symmetry elements in the crystal. The conditions restricting possible reflections are as follows:

h k l, no conditions

h k 0, k = 2n

0 0 l, l = 2n

The last of the above conditions was found from a precession photograph. these conditions indicated that the space group of the crystal was $P2_1/b$, no. 14 in the International Tables for X-Ray Crystallography. The symmetry elements of $P2_1/b$ are shown in plate I, along with the symmetry equivalent molecular positions. For this space group, there are 4 molecules per unit cell.

Possible bond lengths and waters of hydration. Bond lengths for N-N, N-O, and Na-O have been obtained from X-ray, infrared and chemical studies of several compounds. These are reported in the International Tables for X-Ray Crystallography, Vol. III and are reproduced here in Table I. From these values it was concluded that the N-N separation for $\text{Na}_2\text{N}_2\text{O}_2$ should be $1.23 \sim 1.40 \text{ \AA}$, the N-O separation should be $1.22 \sim 1.45 \text{ \AA}$, and the Na-O separation should be $2.3 \sim 2.4 \text{ \AA}$.

EXPLANATION OF PLATE I

- Fig. 1. This figure shows the symmetry elements of space group $P2_1/b$. Circles denote inversion centers, while the symbols (\S) denote 2-fold screw axes.
- Fig. 2. This figure shows the equivalent positions of space group $P2_1/b$. Numbers denote the z -coordinates of the molecules with respect to the base plane. The symbols (\ominus) denote left-handed molecules.

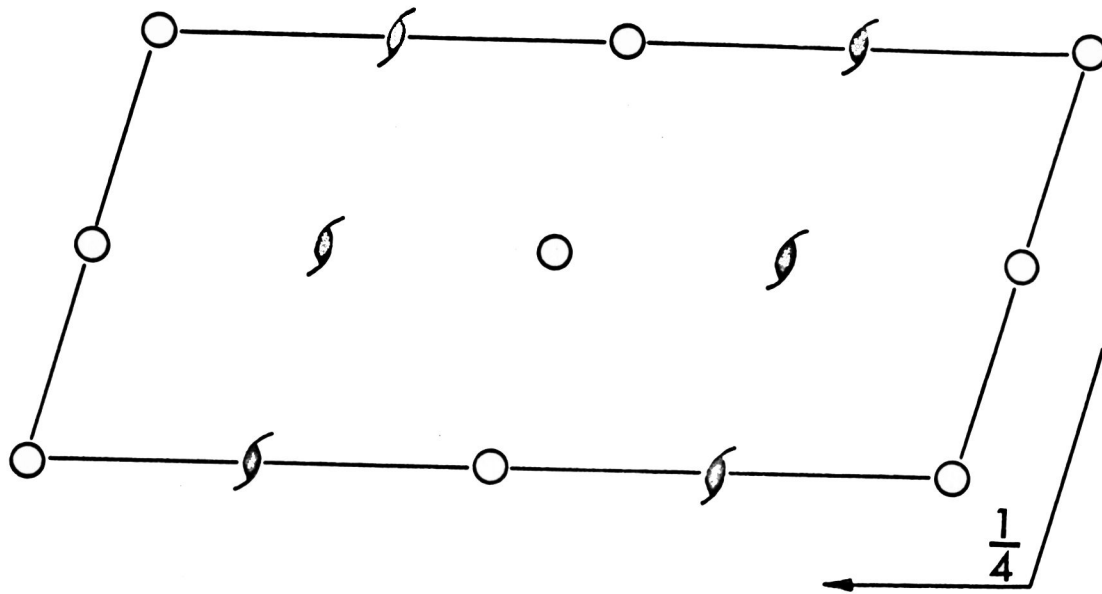


Fig. 1

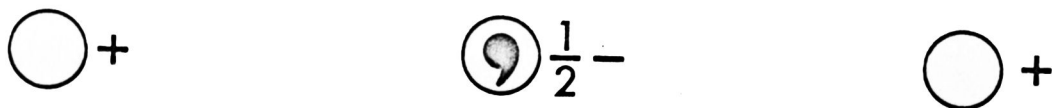
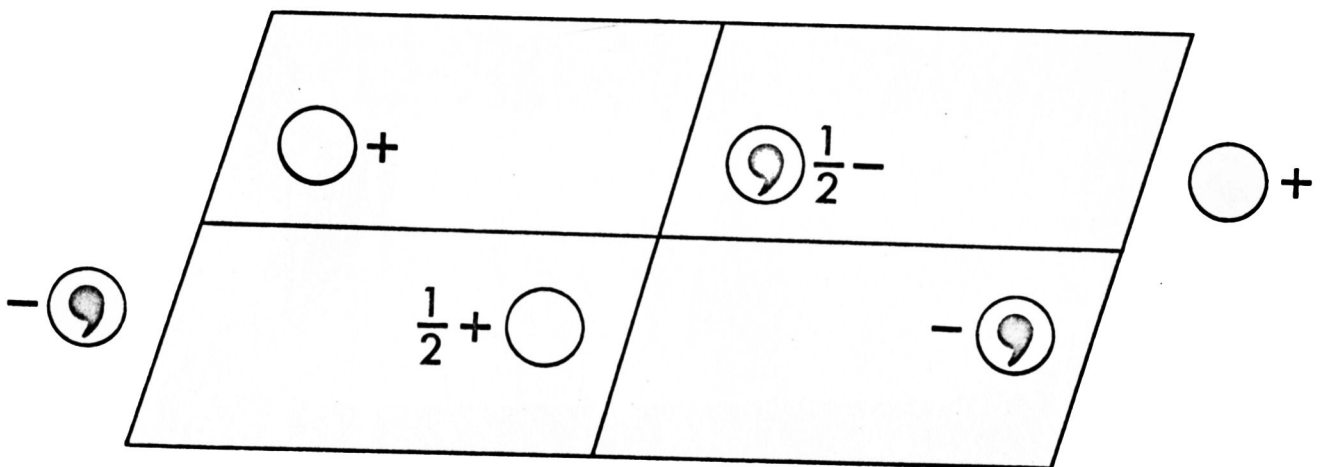
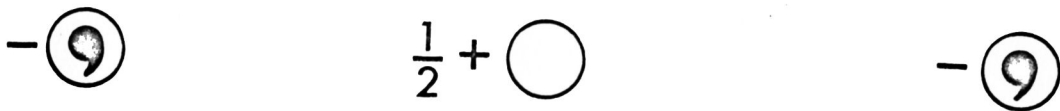


Fig. 2

TABLE I. Bond lengths for N-N, N-O, and Na-O.

	Bond Type	Avg. Distance	No. of Deter.
N-N	triple	1.0976	1
	partial triple	1.131	10
	double	1.24	1
	single	1.44	4
	extended single in:		
	N_2O_4 (g)	1.64	3
N_2O_4 (s)	1.75	1	
N-O	in NO (g)	1.1507	4
	in NO_2 (g) & nitrosyl compounds	1.18	8
	in NO_2 and NO_3^-	1.24	7
	N-O in HNO_3 (s)	1.29	6
	N-O in nitryls & HNO_3	1.22	20
	N-OH in HNO_3 (g)	1.41	2
	in NH_2OH	1.47	3
	in NH_3OCl	1.45	4
	in KSO_3NHOH	1.51	4
Na-O	4-fold coordination	2.38	2
	5-fold "	2.37	2
	6-fold "	2.44	16
	7-fold "	2.53	1

The density of sodium hyponitrite was found by Chang to be $\rho = 1.85 \pm 0.03 \text{ gm/cm}^3$ based on 4 molecules per unit cell. This value favors the presence of a pentahydrate state. Data obtained by Shah (1946) and others indicated the possibility of a trihydrate state. Because of its great affinity for water and carbon dioxide present in the air, exact density measurements of $\text{Na}_2\text{N}_2\text{O}_2 \cdot n\text{H}_2\text{O}$ and determination of the number of waters of hydration n could not be carried out. Further work of both experimental and theoretical nature was carried out by G. Stucky, G. P. Reese and the present author to determine the number of waters of hydration and is presented in the following pages.

Purpose of the Thesis

With the unit cell parameters, space group and probable bond lengths determined, the theory and technique of X-ray methods can be used to determine the electron density function and the atom locations referred to the unit cell axes. This eventual elucidation of the exact structure of the crystal is contingent, of course, on the solution of the phase problem. The purpose of this thesis is to explain various phase-determining techniques that were applied during the work and what their effect was on the problem, to present results obtained to date, and to point out areas where future work can be conducted.

EXPERIMENTAL & CALCULATIONS

Data

The table of structure factors prepared by S. C. Chang were used. They were found from the relation [see Eq. (14)]

$$|F|^2 = \frac{I}{Lpc^2} \exp\left[+2B \frac{\sin^2\theta}{\lambda^2}\right]. \quad (15)$$

The Lorentz factor for the Weissenberg recording method is given in general by

$$\frac{1}{L} = \frac{\xi}{2} \sqrt{4\cos^2\nu - \xi^2}, \quad (16)$$

where ν is the angle of inclination from the zero-level line in reciprocal space, and ξ is the distance between the tips of the unit vectors \vec{s} and \vec{s}_0 (see Fig. 3) projected to the plane perpendicular to the rotation axis.

The polarization factor is

$$p = (1 + \cos^2 2\theta)/2. \quad (17)$$

Scale and temperature factors were determined from the Wilson plot and solving the relations

$$\left. \begin{aligned} c^2 \langle I_0 \rangle &= \sum_{i=1}^N f_i^2 \exp\left[-2B \frac{\sin^2\theta}{\lambda^2}\right] \\ \frac{2B \sin^2\theta}{\lambda^2} &= \ln \left[\frac{\sum f_i^2}{\langle I_0 \rangle} \right] - \ln c^2, \end{aligned} \right\} (18)$$

where θ is a zone of reciprocal space about a given diffraction point, $\langle I_o \rangle$ is the average observed intensities in this zone modified by the L_p factor, and f_i is the atomic scattering factor for the i^{th} atom. For the 468 observed reflections it was found

$$B = 1.95 \text{ \AA}^2 \qquad c = 6.6$$

After substituting these values into Equ. (15), a table of corrected intensities was obtained (see Table II). Table II thus provided the basic starting point for all the calculations to follow.

Patterson Functions

The patterson function of the crystal was calculated by squaring each $|F|$ and substituting into Eq. (13). While this seems on the outset to be a simple task, in actuality great care must be taken in order to perform the calculation in a reasonably short time. Appendix I is a detailed description of this calculation.

If only the $hk0$ class of reflections are used, Eq. (13) reduces to

$$P(x,y) = \sum_h \sum_k F_{hk} F_{hk}^* \exp -2\pi i(hx + ky) \quad . \quad (19)$$

When this is done, a projection of the function in the direction of the z -axis is obtained. For sodium hyponitrite this is a most useful projection since it lies in the direction of the symmetry elements (see Plate I).

Table II. The observed structure factors of $\text{Na}_2\text{N}_2\text{O}_2$ as rendered to absolute scale and corrected for thermal vibration.

h	k	l	F	:	h	k	l	F	:	h	k	l	F
0	2	0	5.94		6	0	0	0		$\bar{5}$	6	0	8.15
0	4	0	18.92		6	2	0	14.92		$\bar{5}$	8	0	8.50
0	6	0	63.53		6	4	0	28.92		$\bar{5}$	10	0	0
0	8	0	5.61							$\bar{5}$	12	0	0
0	10	0	0		7	0	0	24.42		$\bar{5}$	14	0	23.28
0	12	0	89.68		7	2	0	18.26					
0	14	0	18.40							$\bar{6}$	2	0	0
0	16	0	40.59		$\bar{1}$	4	0	47.32		$\bar{6}$	4	0	9.09
					$\bar{1}$	6	0	59.09		$\bar{6}$	6	0	0
1	0	0	19.34		$\bar{1}$	8	0	17.44		$\bar{6}$	8	0	122.66
1	2	0	15.75		$\bar{1}$	10	0	16.36		$\bar{6}$	10	0	16.76
1	4	0	8.93		$\bar{1}$	12	0	14.12					
1	6	0	14.41		$\bar{1}$	14	0	41.26		$\bar{7}$	2	0	18.97
1	8	0	56.46		$\bar{1}$	16	0	43.81		$\bar{7}$	4	0	26.83
1	10	0	30.70							$\bar{7}$	6	0	0
1	12	0	25.95		$\bar{2}$	2	0	9.49		$\bar{7}$	8	0	15.47
1	14	0	0		$\bar{2}$	4	0	109.51					
1	16	0	24.48		$\bar{2}$	6	0	129.86		0	2	1	18.35
					$\bar{2}$	8	0	23.74		0	3	1	51.39
2	0	0	76.85		$\bar{2}$	10	0	0		0	4	1	22.05
2	2	0	19.70		$\bar{2}$	12	0	0		0	5	1	8.81
2	4	0	20.77		$\bar{2}$	14	0	25.68		0	6	1	23.12
2	6	0	0		$\bar{2}$	16	0	73.83		0	7	1	25.86
2	8	0	51.74		$\bar{2}$	18	0	42.81		0	8	1	45.04
2	10	0	8.63							0	9	1	56.72
2	12	0	21.53		$\bar{3}$	2	0	31.62		0	10	1	19.17
2	14	0	54.33		$\bar{3}$	4	0	4.97		0	11	1	33.86
					$\bar{3}$	6	0	74.64		0	12	1	19.37
3	0	0	29.07		$\bar{3}$	8	0	64.38		0	13	1	33.69
3	2	0	23.60		$\bar{3}$	10	0	0		0	14	1	8.92
3	4	0	20.98		$\bar{3}$	12	0	0		0	15	1	15.14
3	6	0	15.65		$\bar{3}$	14	0	0		0	16	1	8.09
					$\bar{3}$	16	0	8.50					
4	0	0	0							1	0	1	4.72
4	2	0	7.22		$\bar{4}$	2	0	80.31		1	1	1	50.75
4	4	0	35.24		$\bar{4}$	4	0	96.55		1	2	1	12.91
4	6	0	0		$\bar{4}$	6	0	19.92		1	3	1	21.63
4	8	0	81.45		$\bar{4}$	8	0	20.36		1	4	1	52.88
4	10	0	29.28		$\bar{4}$	10	0	0		1	5	1	4.58
					$\bar{4}$	12	0	0		1	6	1	10.25
5	0	0	9.88		$\bar{4}$	14	0	0		1	7	1	24.94
5	2	0	0		$\bar{4}$	16	0	35.27		1	8	1	22.25
5	4	0	0							1	9	1	0
5	6	0	26.24		$\bar{5}$	2	0	38.18		1	10	1	23.72
5	8	0	38.83		$\bar{5}$	4	0	23.12		1	11	1	17.17

Table II (Cont.)

h	k	l	F	:	h	k	l	F	:	h	k	l	F
1	12	1	15.59		4	9	1	12.65		$\frac{2}{2}$	1	1	72.43
1	13	1	23.93		4	10	1	12.09		$\frac{2}{2}$	2	1	9.01
1	14	1	0		4	11	1	20.57		$\frac{2}{2}$	3	1	30.27
1	15	1	0		4	12	1	9.08		$\frac{2}{2}$	4	1	28.26
1	16	1	19.54							$\frac{2}{2}$	5	1	4.33
					5	0	1	29.32		$\frac{2}{2}$	6	1	48.52
2	0	1	22.31		5	1	1	0		$\frac{2}{2}$	7	1	54.33
2	1	1	36.33		5	2	1	0		$\frac{2}{2}$	8	1	8.02
2	2	1	98.71		5	3	1	12.80		$\frac{2}{2}$	9	1	50.00
2	3	1	60.63		5	4	1	0		$\frac{2}{2}$	10	1	43.57
2	4	1	20.34		5	5	1	0		$\frac{2}{2}$	11	1	23.10
2	5	1	109.54		5	6	1	21.96		$\frac{2}{2}$	12	1	0
2	6	1	42.22		5	7	1	0		$\frac{2}{2}$	13	1	21.70
2	7	1	0		5	8	1	0		$\frac{2}{2}$	14	1	8.98
2	8	1	22.69		5	9	1	18.98		$\frac{2}{2}$	15	1	0
2	9	1	11.60		5	10	1	8.43		$\frac{2}{2}$	16	1	0
2	10	1	0							$\frac{2}{2}$	17	1	0
2	11	1	0		6	0	1	18.26		$\frac{2}{2}$	18	1	14.24
2	12	1	9.07		6	1	1	24.25					
2	13	1	12.28		6	2	1	11.05		$\frac{3}{3}$	1	1	21.77
2	14	1	27.61		6	3	1	22.53		$\frac{3}{3}$	2	1	32.67
					6	4	1	0		$\frac{3}{3}$	3	1	0
3	0	1	7.21		6	5	1	14.16		$\frac{3}{3}$	4	1	27.24
3	1	1	56.90		6	6	1	13.08		$\frac{3}{3}$	5	1	0
3	2	1	20.38							$\frac{3}{3}$	6	1	13.65
3	3	1	42.77		7	0	1	15.57		$\frac{3}{3}$	7	1	29.11
3	4	1	18.43		7	1	1	0		$\frac{3}{3}$	8	1	24.81
3	5	1	14.91		7	2	1	6.59		$\frac{3}{3}$	9	1	44.83
3	6	1	18.72							$\frac{3}{3}$	10	1	7.53
3	7	1	44.03		$\frac{1}{1}$	1	1	13.06		$\frac{3}{3}$	11	1	33.21
3	8	1	8.78		$\frac{1}{1}$	2	1	9.49		$\frac{3}{3}$	12	1	8.58
3	9	1	12.76		$\frac{1}{1}$	3	1	12.24		$\frac{3}{3}$	13	1	9.02
3	10	1	20.49		$\frac{1}{1}$	4	1	0		$\frac{3}{3}$	14	1	18.23
3	11	1	0		$\frac{1}{1}$	5	1	0		$\frac{3}{3}$	15	1	27.99
3	12	1	0		$\frac{1}{1}$	6	1	15.59		$\frac{3}{3}$	16	1	8.37
3	13	1	7.84		$\frac{1}{1}$	7	1	10.86		$\frac{3}{3}$	17	1	10.57
3	14	1	13.87		$\frac{1}{1}$	8	1	46.48					
					$\frac{1}{1}$	9	1	0		$\frac{4}{4}$	1	1	41.68
4	0	1	13.61		$\frac{1}{1}$	10	1	12.08		$\frac{4}{4}$	2	1	34.35
4	1	1	34.73		$\frac{1}{1}$	11	1	0		$\frac{4}{4}$	3	1	24.09
4	2	1	12.88		$\frac{1}{1}$	12	1	0		$\frac{4}{4}$	4	1	14.03
4	3	1	7.79		$\frac{1}{1}$	13	1	17.79		$\frac{4}{4}$	5	1	18.82
4	4	1	27.04		$\frac{1}{1}$	14	1	17.96		$\frac{4}{4}$	6	1	0
4	5	1	44.62		$\frac{1}{1}$	15	1	8.92		$\frac{4}{4}$	7	1	17.48
4	6	1	15.48		$\frac{1}{1}$	16	1	0		$\frac{4}{4}$	8	1	0
4	7	1	0		$\frac{1}{1}$	17	1	18.14		$\frac{4}{4}$	9	1	5.56
4	8	1	0		$\frac{1}{1}$	18	1	14.65		$\frac{4}{4}$	10	1	37.87

Table II (Cont.)

h	k	l	F	:	h	k	l	F	:	h	k	l	F
$\bar{4}$	11	1	30.21		0	6	2	20.11		3	5	2	0
$\bar{4}$	12	1	27.02		0	7	2	4.23		3	6	2	44.93
$\bar{4}$	13	1	59.88		0	8	2	73.23		3	7	2	0
$\bar{4}$	14	1	20.61		0	9	2	60.51		3	8	2	0
$\bar{4}$	15	1	19.31		0	10	2	16.87		3	9	2	9.98
$\bar{4}$	16	1	20.86		0	11	2	37.36		3	10	2	26.04
					0	12	2	9.79		3	11	2	0
$\bar{5}$	1	1	24.92		0	13	2	0		3	12	2	0
$\bar{5}$	2	1	0		0	14	2	0		3	13	2	29.00
$\bar{5}$	3	1	9.95		0	15	2	16.63					
$\bar{5}$	4	1	19.04		0	16	2	40.69		4	0	2	32.13
$\bar{5}$	5	1	0							4	1	2	32.13
$\bar{5}$	6	1	17.54		1	0	2	19.03		4	2	2	0
$\bar{5}$	7	1	28.05		1	1	2	51.50		4	3	2	0
$\bar{5}$	8	1	0		1	2	2	65.99		4	4	2	22.72
$\bar{5}$	9	1	34.50		1	3	2	5.33		4	5	2	19.12
$\bar{5}$	10	1	0		1	4	2	5.01		4	6	2	33.80
$\bar{5}$	11	1	19.16		1	5	2	37.91		4	7	2	69.84
$\bar{5}$	12	1	23.89		1	6	2	0		4	8	2	20.48
$\bar{5}$	13	1	10.80		1	7	2	34.60		4	9	2	17.12
$\bar{5}$	14	1	0		1	8	2	0		4	10	2	0
$\bar{5}$	15	1	15.87		1	9	2	0		4	11	2	7.46
					1	10	2	0					
$\bar{6}$	1	1	31.94		1	11	2	0		5	0	2	9.71
$\bar{6}$	2	1	30.32		1	12	2	21.88		5	1	2	0
$\bar{6}$	3	1	0		1	13	2	34.90		5	2	2	11.98
$\bar{6}$	4	1	0							5	3	2	34.12
$\bar{6}$	5	1	25.83		2	0	2	54.51		5	4	2	27.86
										5	5	2	0
$\bar{6}$	6	1	0		2	1	2	12.76		5	6	2	32.66
$\bar{6}$	7	1	0		2	2	2	14.66		5	7	2	11.06
$\bar{6}$	8	1	0		2	3	2	8.00		5	8	2	0
$\bar{6}$	9	1	0		2	4	2	64.76		5	9	2	6.43
$\bar{6}$	10	1	28.23		2	5	2	0					
$\bar{6}$	11	1	24.51		2	6	2	0		6	0	2	43.11
$\bar{6}$	12	1	0		2	7	2	8.22		6	1	2	19.08
$\bar{6}$	13	1	18.37		2	8	2	39.91		6	2	2	9.43
					2	9	2	16.25		6	3	2	0
$\bar{7}$	1	1	12.71		2	10	2	39.84		6	4	2	0
$\bar{7}$	2	1	13.11		2	11	2	37.04		6	5	2	0
$\bar{7}$	3	1	0		2	12	2	0		6	6	2	17.16
$\bar{7}$	4	1	13.42		2	13	2	9.16					
										7	1	2	15.16
0	1	2	31.31		3	0	2	10.89					
0	2	2	14.14		3	1	2	53.98		$\bar{1}$	1	2	12.27
0	3	2	70.55		3	2	2	18.23		$\bar{1}$	2	2	36.33
0	4	2	56.15		3	3	2	14.60		$\bar{1}$	3	2	28.09
0	5	2	4.82		3	4	2	15.57		$\bar{1}$	4	2	5.06

This calculation was carried out using the computer program described in Appendix I. Plate II shows the results, in terms of a contour map. Peaks in this map represent foldings between the electron density distributions of all the atoms in the unit cell. Because of the great number of foldings, there is much overlapping and superposition of Patterson densities. While the actual unit cell axes are inclined at an angle of $107.5 \pm 0.40^\circ$ it was found convenient to make a transformation from the actual space of the crystal to a rectilinear space with orthogonal axes. In this way it was possible to print maps on the output device of the computer which were then contoured directly. The small numerals and letters visible in Plate II are the actual computer print-outs. (See Appendix I).

Because of the great amount of overlapping present in the Patterson projection, any interpretation was difficult. It was decided to compute the entire three-dimensional Patterson function in order to eliminate overlapping. Using the computer program described in Appendix I, 149,810 values of the function were computed in less than seven hours. Forty sections were taken through the unit cell perpendicular to the z-axis. Each section was plotted by the computer and contoured directly onto a 24" x 30" glass sheet. These 40 sheets, when stacked together in the proper order, comprised a "picture" of the function. Three dimensions of space were present, and the functional values were represented by the contour levels creating a "fourth dimension". Plate III shows the completed array of glass sheets.

EXPLANATION OF PLATE II

This plate shows the projection of the Patterson function of sodium hyponitrite on the x-y plane. Contour intervals are arbitrary but equal. Symbols (\odot) denote screw axes; (\circ) denote inversion centers.

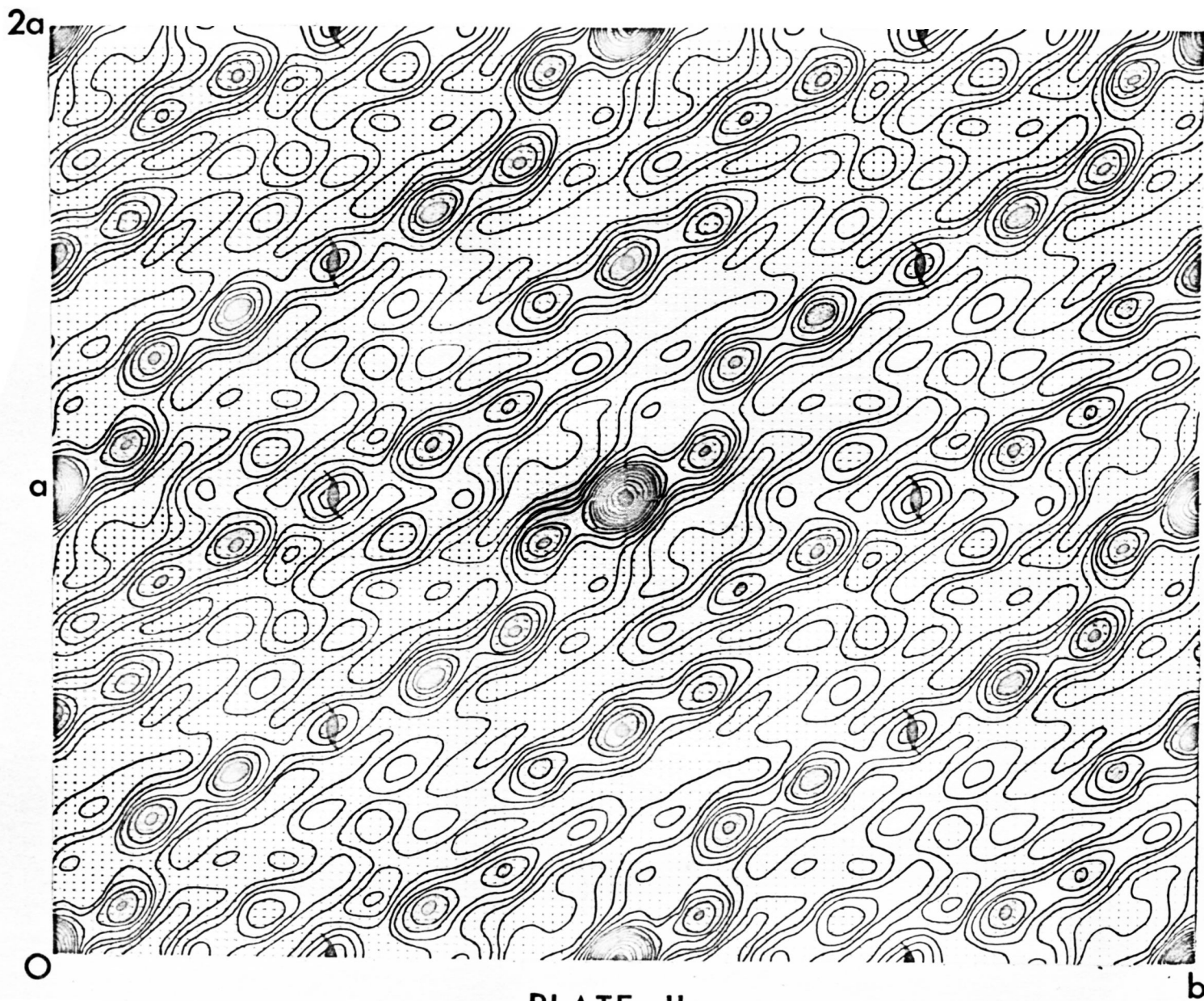


PLATE II

EXPLANATION OF PLATE III

This plate shows the 4-dimensional graph of the 3-dimensional Patterson function of sodium hyponitrite. Forty glass sheets were used to create 40 contoured sections through the function. Individual slabs through the function were illuminated by an edge-lighting technique.

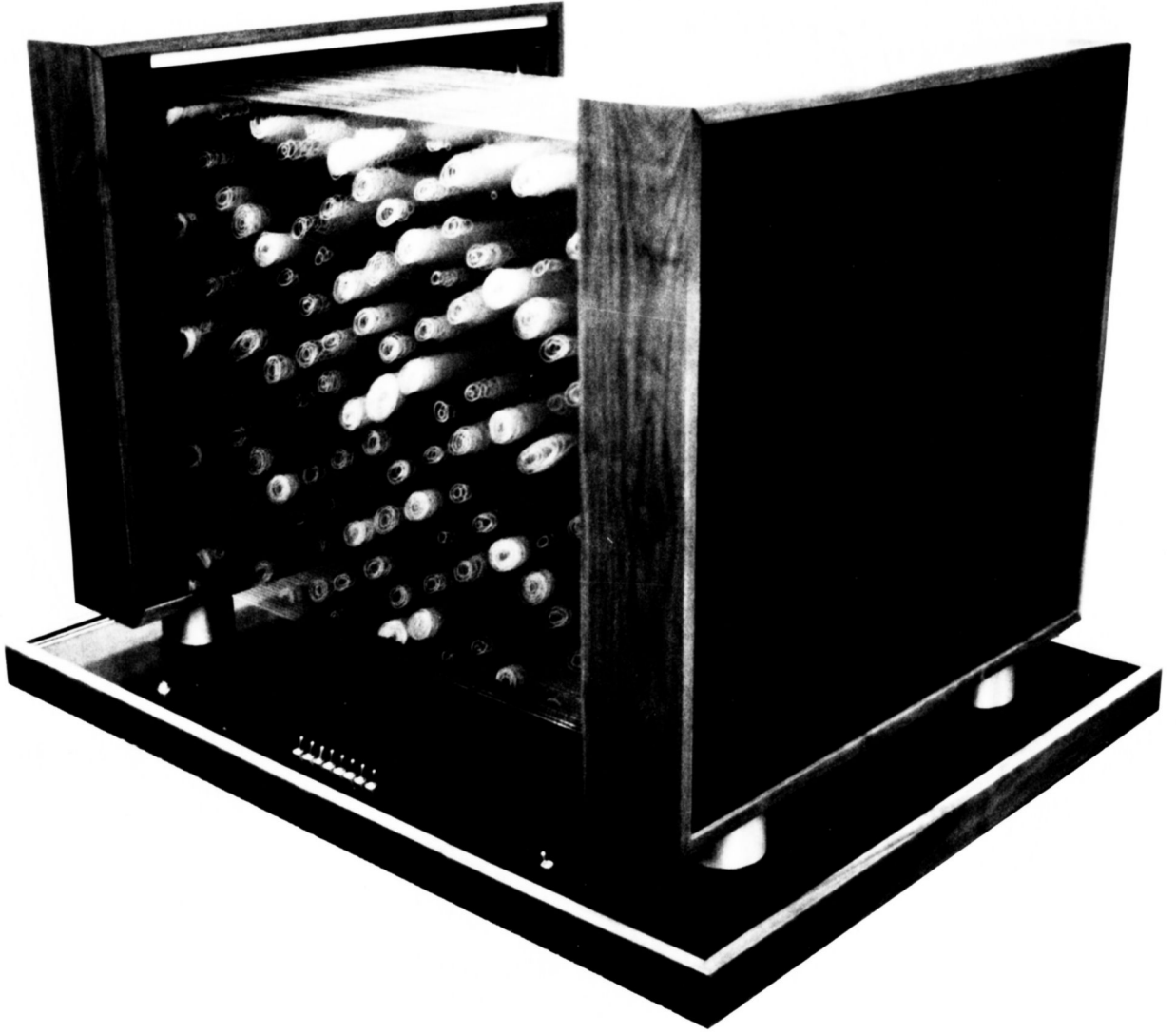


PLATE III

The three-dimensional function provided an exact knowledge of the distribution, sizes, and shapes of the Patterson peaks with much greater resolution than that provided by the projection alone.

Methods of Solution

Interpretation of Peak Heights. An attempt was made to calibrate the heights of the various peaks present in the three-dimensional Patterson function. The height of a Patterson peak is roughly proportional to the product of the number of electrons in each of the two atoms folding together to make up the Patterson peak. The height of the origin peak in a Patterson map is proportional to the sum of the squares of the electron counts of each atom in the unit cell. Thus it is possible to predict the heights of peaks appearing in the Patterson maps by knowing what types of atoms are present in the crystal. The relation governing peak heights is

$$H_{ij} = \frac{H_0}{\sum Z_k^2} Z_i Z_j \quad (20)$$

where H_{ij} is the height of the Patterson peak resulting from the folding of the i^{th} atom with the j^{th} atom, H_0 is the height of the origin peak in the Patterson map, $\sum Z_k^2$ is the sum of the squares of the number of electrons in each atom. Z_i and Z_j are the electron counts of the i^{th} and j^{th} atoms, respectively.

For sodium hyponitrite, assuming 3 waters of hydration per molecule,

$$\sum Z_k^2 = 2040$$

$$\begin{aligned}
 Z_{\text{Na}} Z_{\text{Na}} &= 100 \\
 Z_{\text{Na}} Z_{\text{O}} &= 90 \\
 Z_{\text{Na}} Z_{\text{N}} &= 70 \\
 Z_{\text{O}} Z_{\text{O}} &= 81 \\
 Z_{\text{O}} Z_{\text{N}} &= 63 \\
 Z_{\text{N}} Z_{\text{N}} &= 49 .
 \end{aligned}$$

Using the height of the Patterson origin, H_{ij} were calculated for all possible combinations of atom types and were compared with the actual observed peak heights in the three-dimensional Patterson map. In nearly all cases the peaks on the map were higher than the predicted peaks. This was thought to be due to the large symmetry present which permitted overlapping to occur even in the three-dimensional function. Further analysis of the various peaks in the Patterson function revealed clues for possible atom foldings which were later used to help determine trial structures.

Application of Harker-Kasper Inequalities. Harker and Kasper (1947, 1948) showed that there exist relations between the structure factors for centrosymmetrical crystals. They began by making use of the well known Schwarz inequality

$$\left| \int fg \, d\tau \right|^2 \leq \left(\int |f|^2 \, d\tau \right) \left(\int |g|^2 \, d\tau \right). \quad (21)$$

The fundamental scattering from the crystal can be written

$$F_{hkl} = \int_0^1 \int_0^1 \int_0^1 \rho(xyz) \exp 2\pi i (hx + ky + lz) \, dx dy dz. \quad (22)$$

For Schwarz's inequality, let

$$\left. \begin{aligned} f &= \rho(xyz)^{\frac{1}{2}}, \\ g &= \rho(xyz)^{\frac{1}{2}} \exp 2\pi i(hx + ky + lz), \\ d\tau &= dx dy dz. \end{aligned} \right\} (23)$$

Substitution in Eq. (21) gives

$$\begin{aligned} |F_{hkl}|^2 &\leq \left[\iiint_{\circ}^1 \rho(xyz) dx dy dz \right] \\ &\times \left[\iiint_{\circ}^1 \rho(xyz) |\exp 2\pi i(hx + ky + lz)|^2 dx dy dz \right], \\ \text{or} \quad |F_{hkl}|^2 &\leq \left[\iiint_{\circ}^1 \rho(xyz) dx dy dz \right]^2. \end{aligned} \quad (24)$$

Letting

$$Z = \iiint_{\circ}^1 \rho(xyz) dx dy dz \quad (25)$$

be the electron content of the unit cell, we obtain

$$|F_{hkl}|^2 \leq Z^2. \quad (26)$$

Introducing the unitary structure factor

$$U_{hkl} = \frac{F_{hkl}}{Z} \quad (27)$$

we obtain

$$U_{hkl} = \frac{1}{Z} \iiint_{\circ}^1 \rho(xyz) \exp 2\pi i(hx + ky + lz) dx dy dz. \quad (28)$$

Sodium hyponitrite has 2-fold screw axes parallel to c . Thus we may write

$$\rho(x, y, z) = \rho(x, y, z + \frac{1}{2}). \quad (29)$$

The unitary structure factor then reduces to

$$U_{hkl} = \frac{1}{Z} \int_0^1 \int_0^1 \int_0^1 \rho(xyz) \exp 2\pi i l (z + \frac{1}{2}) \cos 2\pi (hx + ky) dx dy dz.$$

For substitution into Schwarz's inequality, let

$$\left. \begin{aligned} f &= \frac{1}{Z} \rho(xyz)^{\frac{1}{2}}, \\ g &= \frac{1}{Z} \rho(xyz)^{\frac{1}{2}} \exp 2\pi i l (z + \frac{1}{2}) \cos 2\pi (hx + ky), \\ dr &= dx dy dz. \end{aligned} \right\} (30)$$

Substituting in Eq. (21), we obtain

$$\begin{aligned} |U_{hkl}|^2 &\leq \left[\frac{1}{Z} \int_0^1 \int_0^1 \int_0^1 \rho(xyz) dx dy dz \right] \\ &\times \left[\frac{1}{Z} \int_0^1 \int_0^1 \int_0^1 \rho(xyz) \left| \exp 2\pi i l (z + \frac{1}{2}) \right| \cos^2 2\pi (hx + ky) dx dy dz \right]. \end{aligned} \quad (31)$$

Using the identity

$$\cos^2 \xi = (1 + \cos 2\xi)/2 \quad (32)$$

we have

$$\begin{aligned} |U_{hkl}|^2 &\leq \left[\frac{1}{Z} \int_0^1 \int_0^1 \int_0^1 \rho(xyz) dx dy dz \right] \left[\frac{1}{2Z} \int_0^1 \int_0^1 \int_0^1 \rho(xyz) dx dy dz \right. \\ &\quad \left. + \frac{1}{2Z} (-1)^l \int_0^1 \int_0^1 \int_0^1 \rho(xyz) \cos 2\pi (2hx + 2ky) dx dy dz \right]. \end{aligned} \quad (33)$$

From Eqs. (25) and (28), this becomes

$$|U_{hkl}|^2 \leq [1] \left[\frac{1}{2} + \frac{1}{2}(-1)^k U_{2h \ 2k \ 0} \right]. \quad (34)$$

Equation (34) is the desired inequality and can be used to determine phases. For example, suppose that $|U_{hkl}|^2$ is known for a particular reflection. If l is even and $|U_{hkl}|^2 > \frac{1}{2}$, then $U_{2h \ 2k \ 0}$ is positive. If $|U_{hkl}|^2 \leq \frac{1}{2}$, then $U_{2h \ 2k \ 0}$ may be either positive or negative and no information is obtained.

For sodium hyponitrite, a table of unitary structure factors $|U_{hkl}|$ were calculated, but unfortunately, so few were large enough to satisfy Eq. (34) that the method had to be abandoned.

Application of the Karle-Hauptman symbolic addition procedure. The application of this procedure to the solution of the phase problem has been described by Karle, Britts, and Brenner (1964) and by Sax, Beurskens, and Chu (1964) in the solutions of the crystal structures of 1-cyclohexenyl-1-cyclobutenedione and ortho-nitroperoxybenzoic acid, respectively. The theoretical derivation of the method is beyond the scope of this thesis but the application of the method is straightforward.

First, a complete set of normalized structure factors E_{hkl}^2 were obtained from the relation given by Karle,

$$E_{hkl}^2 = \frac{F_{hkl}^2}{\epsilon \sum_{j=1}^N f_{hkl}^{(j)2}} \quad (35)$$

where F_{hkl} are the structure factor magnitudes previously obtained, $f_{hkl}^{(j)}$ is the atomic scattering factor for the j^{th} atom evaluated at the scattering angle determined by h, k, l ; N is the number of atoms in the unit cell, and ϵ is a constant which depends on the symmetry of the crystal. For $P2_1/b$, $\epsilon = 1$ except for the $hk0$ and $00l$ reflections where $\epsilon = 2$.

The distribution of the normalized structure factor magnitudes was as follows:

	<u>Experimental</u>	<u>Theoretical</u>
$ E > 3$.87%	.3%
$ E > 2$	3.3	5.0
$ E > 1$	31.1	32.0

The theoretical values are those for a centrosymmetric crystal with atoms located randomly. Statistical averages for the normalized structure factors are as follows:

	<u>Experimental</u>	<u>Centrosymmetric</u>	<u>Noncentrosymmetric</u>
$\langle E \rangle$	0.748	0.798	0.886
$\langle E^2 - 1 \rangle$	1.039	0.968	0.736
$\langle E^2 \rangle$	1.012	1.000	1.000

The experimental values were in close agreement with the theoretical values indicating that the Wilson plot was probably correct.

To initiate the phase-determining procedure, three linearly independent $|E_{hkl}|$ were chosen to specify the origin of coordinates. Plus (+) signs were given arbitrarily to these three reflections. Since the probability of a correct sign depends on the magnitude of E_{hkl} , the three initial $|E_{hkl}|$ were chosen to be large. From these initial signs, other signs were generated for

the large $|E_{hkl}|$'s from the relation [Karle & Karle (1963)]:

$$sE(h+h', k+k', l+l') \sim sE(h, k, l) \cdot sE(h', k', l')$$

where s = "sign of" and \sim = "is given by". The greater the number of interactions with Eq. (36), the greater is the probability that a phase is correctly determined. The probability that a phase determined by Eq. (36) is positive is given by [Woolfson (1961)]:

$$P_+[E(h, k, l)] = \frac{1}{2} + \frac{1}{2} \tanh \frac{E(h, k, l) \sum_{h'k'l'} E(h', k', l') E(h-h', k-k', l-l')}{\sqrt{N}} \quad (37)$$

where N is the number of interactions.

Once a starting set of signs was established, these were used in Eq. (36) to generate even more phases until all possible interactions were exhausted. Because of the scarcity of data for the ℓ Miller index (see Table II) in sodium hyponitrite, not enough interactions were established with high enough probabilities to be successful in solving the structure. Accordingly, this approach was eventually discontinued.

While the more direct methods of Harker and Kasper or Karle and Hauptman offer many advantages, they could not be applied to the available sodium hyponitrite data with success. Particularly, the Harker-Kasper inequalities depended upon large unitary structure factors, and these in turn depended upon the presence of heavy atoms or planar groups in the crystal. Overlying the difficulty in interpreting the Patterson function directly was the uncertainty in the number of waters of hydration present. Because of these considerations,

it was decided to study in detail the Harker section of the Patterson function, and to relate it to the Patterson projection.

Harker Section. [See Buerger (1959)]. Certain special sections through the three-dimensional Patterson function do not suffer from overlap of peaks as do projections. To explain the nature of a Harker section consider two equivalent sets of atoms, A and B, related to each other by a two-fold rotation axis parallel to c . The coordinates of the atoms in the equivalent sets are:

$$\begin{array}{ll} \text{Set A:} & x_a y_a z_a \quad \bar{x}_a \bar{y}_a z_a \\ \text{Set B:} & x_b y_b z_b \quad \bar{x}_b \bar{y}_b z_b. \end{array}$$

It will be recalled that the Patterson function can be considered to be an auto-convolution of the electron density function. That is, the Patterson function contains peaks located at the ends of all the interatomic vectors in the unit cell, where each vector has its tail located at the Patterson origin. The coordinates of the interatomic vectors are:

Symmetrical Vectors:

$$\begin{array}{ll} 2x_a, 2y_a, 0 & 2x_a, 2y_a, 0 \\ 2x_b, 2y_b, 0 & 2x_b, 2y_b, 0 \end{array}$$

Unsymmetrical Vectors:

$$\begin{array}{lll} x_b - x_a & y_b - y_a & z_b - z_a \\ x_a - x_b & y_a - y_b & z_a - z_b \\ x_b + x_a & y_b + y_a & z_b - z_a \\ -x_a - x_b & -y_a - y_b & z_a - z_b \\ -x_b + x_a & -y_b + y_a & z_b - z_a \end{array}$$

$$\begin{array}{lll}
 -x_a+x_b & -y_a+y_b & z_a-z_b \\
 -x_b-x_a & -y_b-y_a & z_b-z_a \\
 x_a+x_b & y_a+y_b & z_a-z_b.
 \end{array}$$

All the unsymmetrical vectors have a very general form, whereas the symmetrical vectors all contain a z-coordinate of zero. If a section of $P(xyz)$ were computed at the section $z=0$, it would contain peaks due to the symmetrical vectors, but in general would not contain peaks of the more general unsymmetrical vectors. This Harker section $P(xyp)$ at $p=0$ is a great simplification of the Patterson function which materially aids in its interpretation.

The general form of the full three-dimensional Patterson synthesis is

$$P(xyz) = \sum_h \sum_k \sum_l |F_{hkl}|^2 \cos 2\pi(hx + ky + lz). \quad (38)$$

Expanding by means of the identity

$$\cos(\alpha + \beta) = \cos\alpha \cos\beta - \sin\alpha \sin\beta \quad (39)$$

with $\alpha = 2\pi(hx + ky)$ and $\beta = 2\pi lz = 2\pi lp$ where p is constant, we obtain

$$\begin{aligned}
 P(xyp) = \sum_h \sum_k \sum_l |F_{hkl}|^2 \{ & \cos 2\pi(hx + ky) \cos 2\pi lp \\
 & - \sin 2\pi(hx + ky) \sin 2\pi lp \}, \quad (40)
 \end{aligned}$$

or

$$\begin{aligned}
 P(xyp) = \sum_h \sum_k \{ & \left[\sum_l |F_{hkl}|^2 \cos 2\pi lp \right] \cos 2\pi(hx + ky) \\
 & - \left[\sum_l |F_{hkl}|^2 \sin 2\pi lp \right] \sin 2\pi(hx + ky) \}. \quad (41)
 \end{aligned}$$

The terms in brackets are simple numerical summations and can be

represented by coefficients C_{hk} and C'_{hk} :

$$C_{hk} = \sum_l |F_{hkl}|^2 \cos 2\pi lp, \quad (42)$$

$$C'_{hk} = \sum_l |F_{hkl}|^2 \sin 2\pi lp. \quad (43)$$

With this simplification we have

$$P(xyp) = \sum_h \sum_k \left\{ C_{hk} \cos 2\pi(hx + ky) - C'_{hk} \sin 2\pi(hx + ky) \right\}. \quad (44)$$

For sodium hyponitrite, p equals $1/2$ due to the two-fold screw axes. In this case,

$$C = \sum_{l=2N} |F_{hkl}|^2 - \sum_{l=2N+1} |F_{hkl}|^2,$$

$$C' = 0.$$

The $P(xy\frac{1}{2})$ section was computed by means of the program described in Appendix I, and is shown in Plate IV.

It is likely that much non-Harker background was present in the Harker section due to chance foldings between non-symmetry related atoms that differed by $1/2$ in their z -coordinates. In spite of this possibility the Harker section should have contained an image of the electron density function.

A comparison was made between the Patterson projection (Plate II) and the Harker section (Plate IV). Many similarities between the two functions exist and certain distributions of peaks suggest foldings by chemically reasonable atom groupings. At this stage in the work, many trial structures were inferred from peaks in the Harker section. A calculation was made for each trial structure to see how it would scatter X-rays. The calculated

EXPLANATION OF PLATE IV

This plate shows the $(x, y, 1/2)$ Harker section of sodium hyponitrite. Contour intervals are arbitrary but equal. Lowest contour levels have been omitted for clarity.

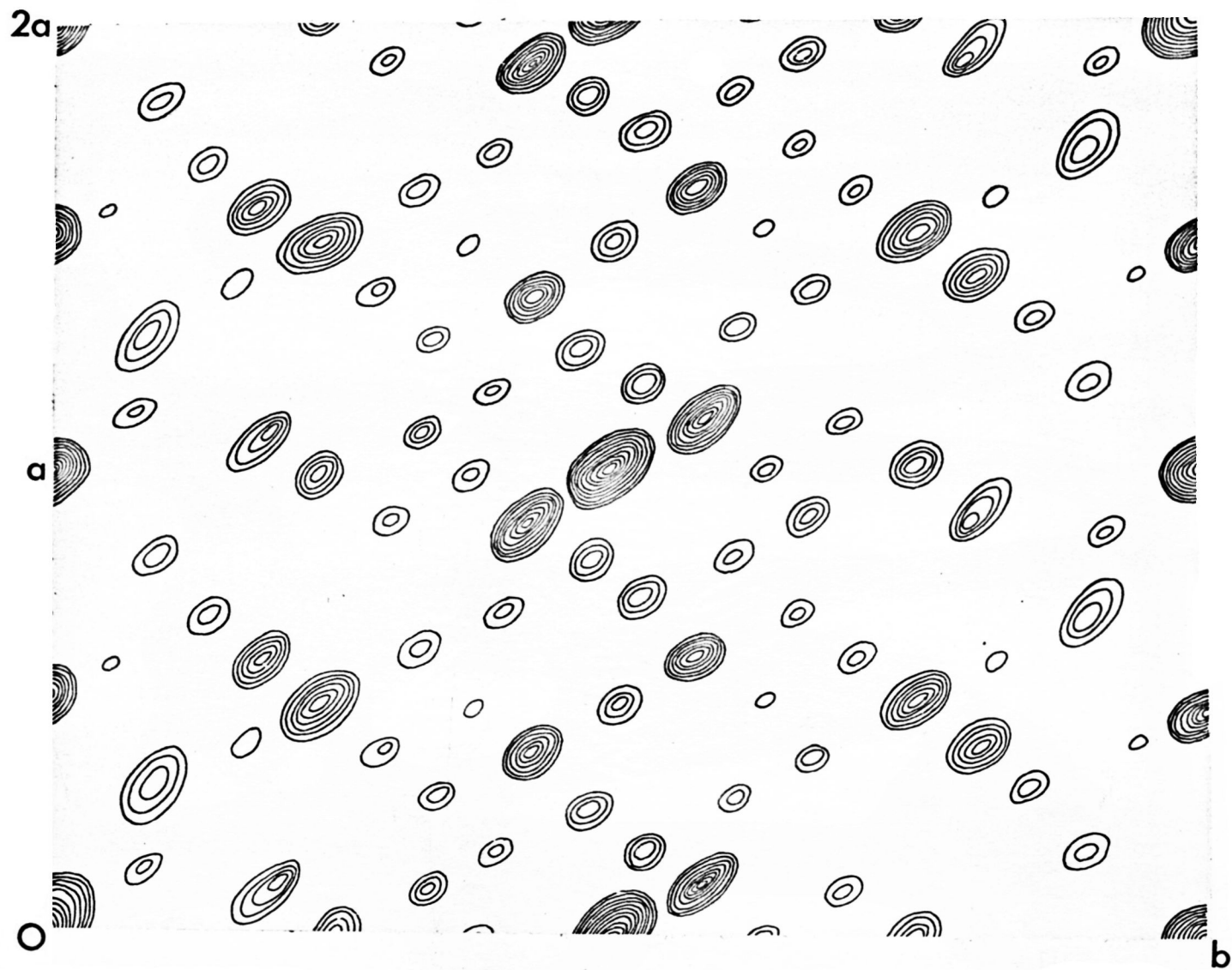


PLATE IV

scattering was compared with the observed scattering from the crystal. In this way a measure of fit was obtained. Reasonably good agreements were obtained for several trial structures and the most promising was singled out for further investigation.

Trial Structure and Refinement Processes. The chosen (2-dimensional) trial structure scattered X-rays in good agreement with the observed scattering and at the same time agreed closely with the postulated bond distances for sodium hyponitrite given in Table I. The $hk0$ structure factors for the proposed structure were calculated using the computer program described in Appendix II. The expression for the structure factor is that given by Eq. (7):

$$F_{hkl} = \sum_{n=1}^N f_n(hkl) \exp 2\pi i (hx_n + ky_n + lz_n), \quad (46)$$

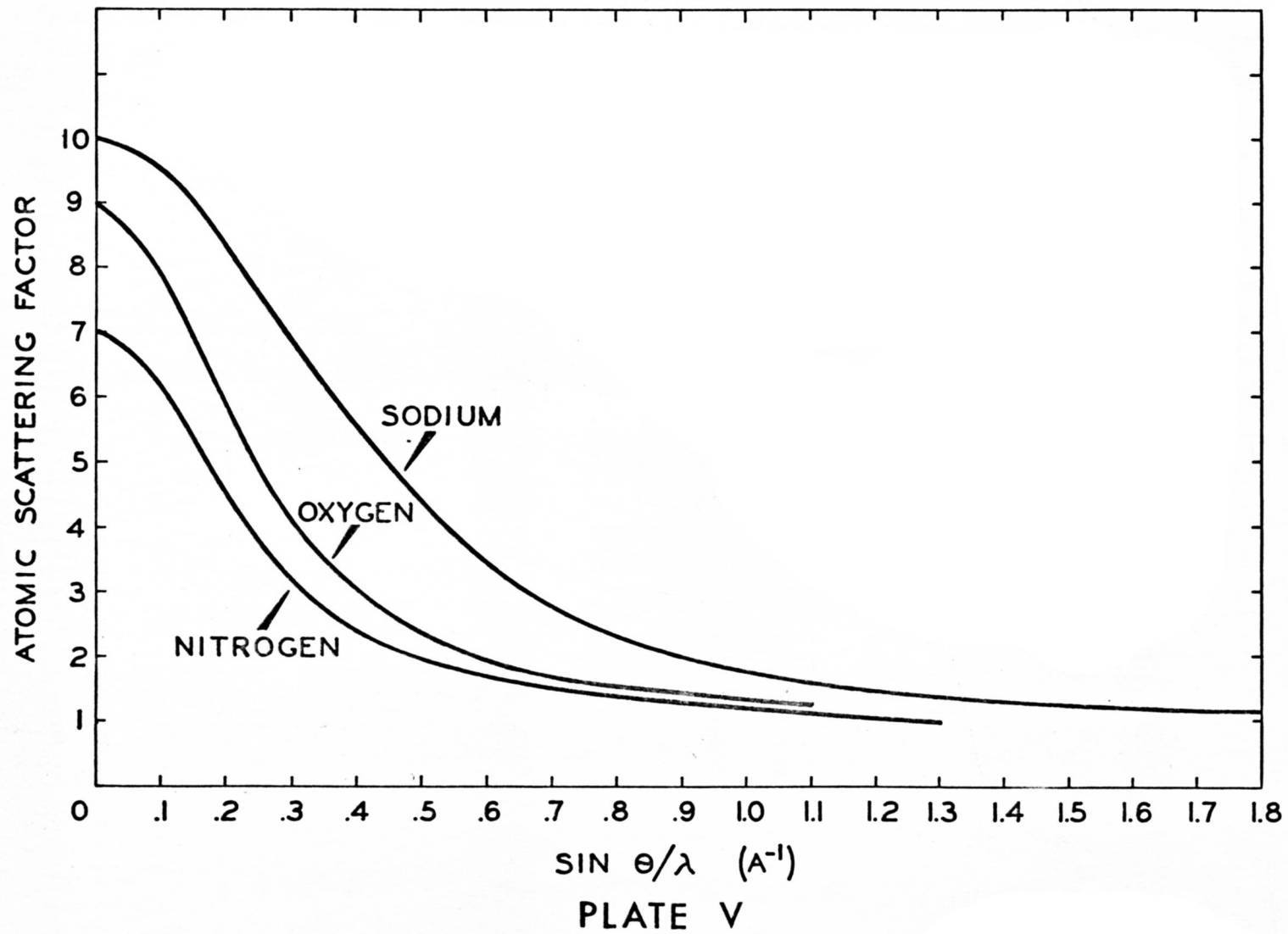
where $f_n(hkl)$ is the atomic scattering factor for the n^{th} atom; x_n, y_n, z_n , are the coordinates of the n^{th} atom, and N is the number of atoms in the unit cell. The atomic scattering factors are those based on Hartree-Fock self-consistent field calculations [see Norman and Lonsdale (1952)], and are shown as functions of $(\sin \theta)/\lambda$ in Plate V.

The criterion used to determine how closely a trial structure matched the observed scattering was based on the definition of a residual R given by

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad (47)$$

EXPLANATION OF PLATE V

This plate shows the atomic scattering factor curves for the elements sodium, oxygen and nitrogen as functions of $\sin \theta / \lambda$.



where the F_o are the observed structure factors, and the F_c are the calculated structure factors (see Appendix II). In general, the lower the value of R , the better was the trial solution. The R value calculated for the proposed solution was $R = .49$. Buerger (1960) states that centrosymmetric models with an R value less than 0.5 are worth attempting to refine.

Refinement for the trial structure was carried out in a number of ways. Computer programs were written by R. D. Dragsdorf and G.P. Reese of the Kansas State University Physics Department based on least-square methods, steepest descents, and differential synthesis. The mathematics of convergence of a crystal structure model is beyond the scope of this thesis. [See, for example, Buerger (1960)]. These programs greatly speeded up the many calculations necessary for the convergence process and made possible the ultimate refinement of the structure.

At many steps during the refinement, the validity of the structure was tested by the structure factor program (Appendix II). The output of this program consisted of a list of observed and calculated structure factors for $hk0$ reflections. (These are the reflections which define the x - y projection of the crystal). If for a particular $hk0$, $|F_c|$ agreed closely with $|F_o|$, the algebraic sign of F_c was transferred to $|F_o|$. In this way the observed structure factors supplied magnitudes, while the calculated structure factors furnished the missing algebraic signs. The validity of this process lies in the assumption that the trial structure is "close" to the actual structure. If this is the case, small changes in the atom locations of the trial structure

produce changes in the magnitudes of the F_c 's but unless the F_c 's are small, their signs will remain unaltered.

From Eq. (9), it is seen that the electron density function is expressible as a Fourier series. In order to synthesize an approximation to the actual electron density function, it is not necessary to include all of the Fourier coefficients F_{hkl} . Consequently, if one includes only those F_{hkl} for which F_o and F_c agree closely, and these happen to be among the larger F_o 's, a trial electron density map can be constructed which should yield an approximate "picture" of the molecule.

During the refinement process several trial electron density maps were calculated in this manner using the program described in Appendix I. As the value of R became lower, the outline of the sodium hyponitrite molecule became clearer. These trial maps are shown in Plate VI.

Karl-Fischer Titration Study. It became apparent during the refinement process that several of the higher peaks in the trial electron density maps could be attributed to the waters of hydration. It became necessary to know from a chemical viewpoint, just how many waters of hydration per molecule to expect in the crystal. Work of this nature was carried out by Stucky, Lambert, and Dragsdorf (1965) of Kansas State University Departments of Chemistry and Physics. This work was closely related to the X-ray investigation of the crystal and is presented here in summary form as it relates to the trial electron density maps.

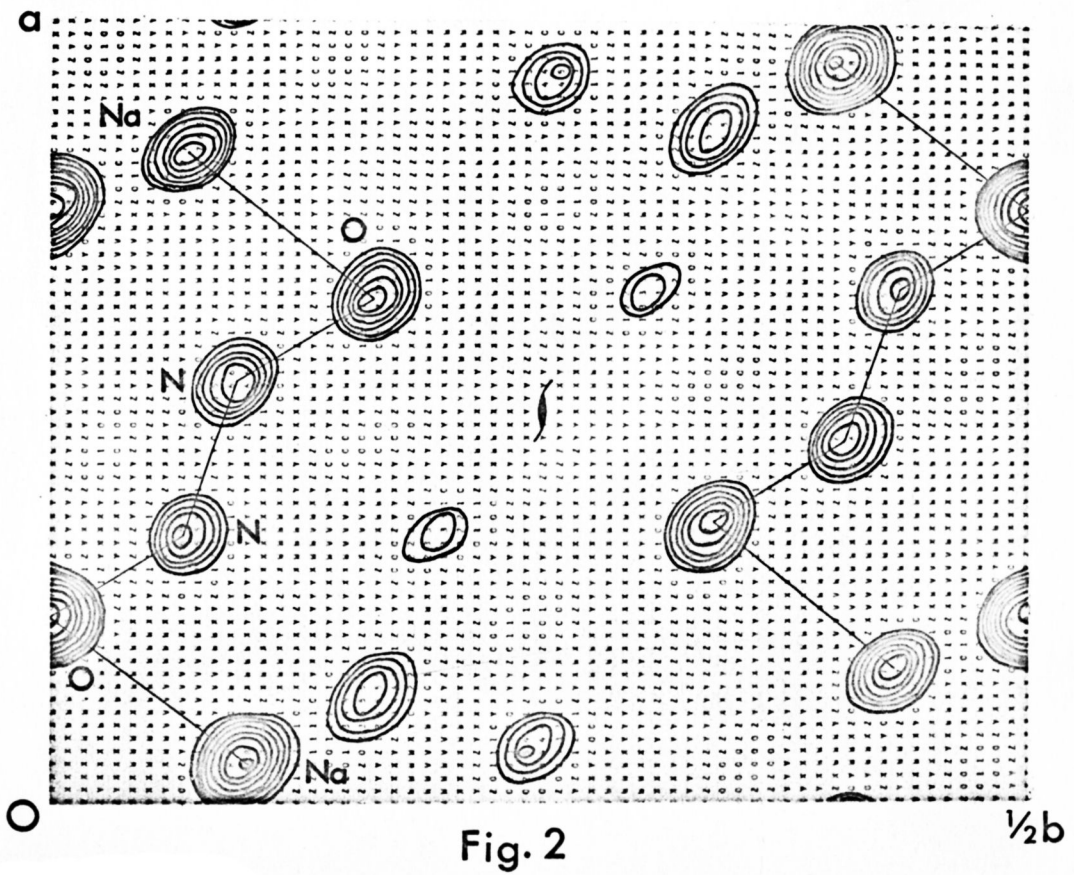
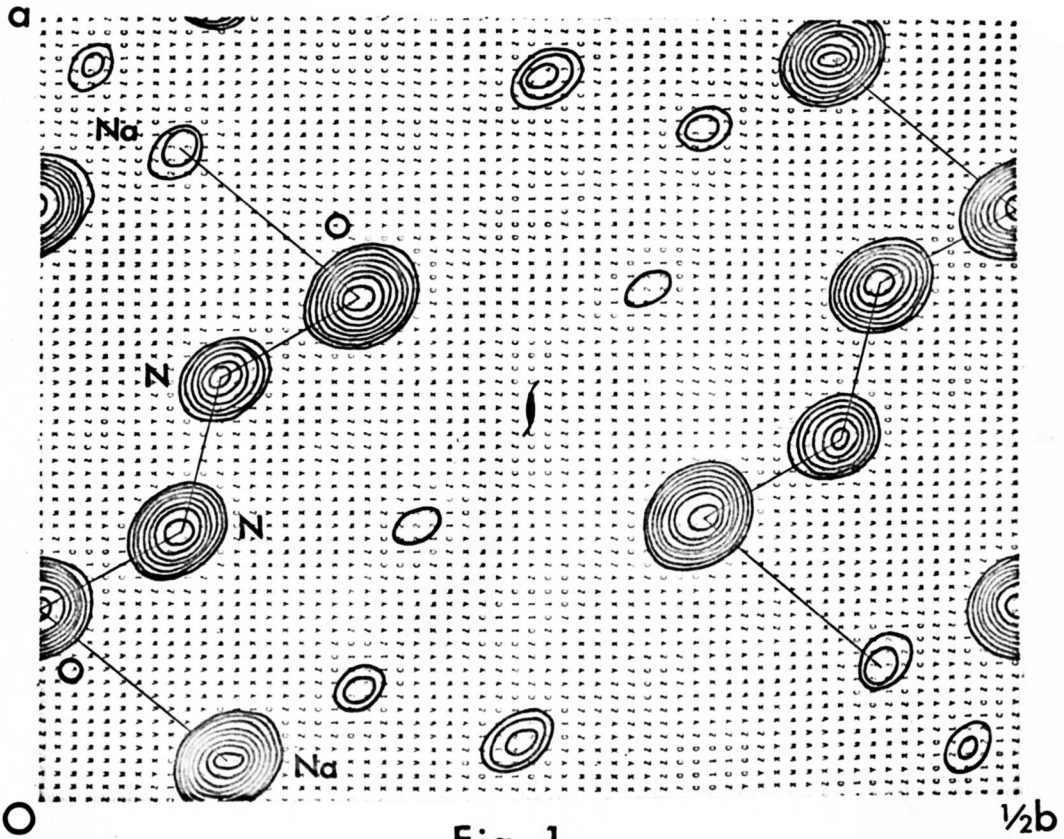
EXPLANATION OF PLATE VI

Trial electron density maps for sodium hyponitrite.

Fig. 1. $R = .49$

Fig. 2. $R = .42$

PLATE VI



Karl-Fischer titrations for water content were performed using Karl-Fischer reagent standardized against Fisher ACS reagent $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$. The titrations were performed on samples taken fresh from a constant humidity dessicator. The samples were stored in a nitrogen atmosphere to prevent contamination by CO_2 present in the atmosphere.

The results obtained indicated that no hydrates greater than the 5-hydrate exist in a well-defined form and that 3 or $3\frac{1}{2}$ waters of hydration per molecule was quite likely.

In accordance with these findings, three of the larger peaks in the trial electron density maps were assigned to waters of hydration. Upon including these coordinates in the structure factor calculations, a reduction of the value of R was apparent and a trial electron density map was made (Plate VII, Fig. 1). At this point an attempt was made to locate a water molecule on an inversion center of the crystal to be shared by two sodium hyponitrite molecules. This attempt was not successful. Plate VII, Fig. 2 shows the current map with $R = .3179$.

RESULTS AND CONCLUSION

Molecular Configuration and Atom Locations

Plates VI and VII indicated a highly symmetric trans-structure with three waters of hydration for the sodium hyponitrite molecule. The peak heights were acceptable although not quite the same for equivalent atom types.

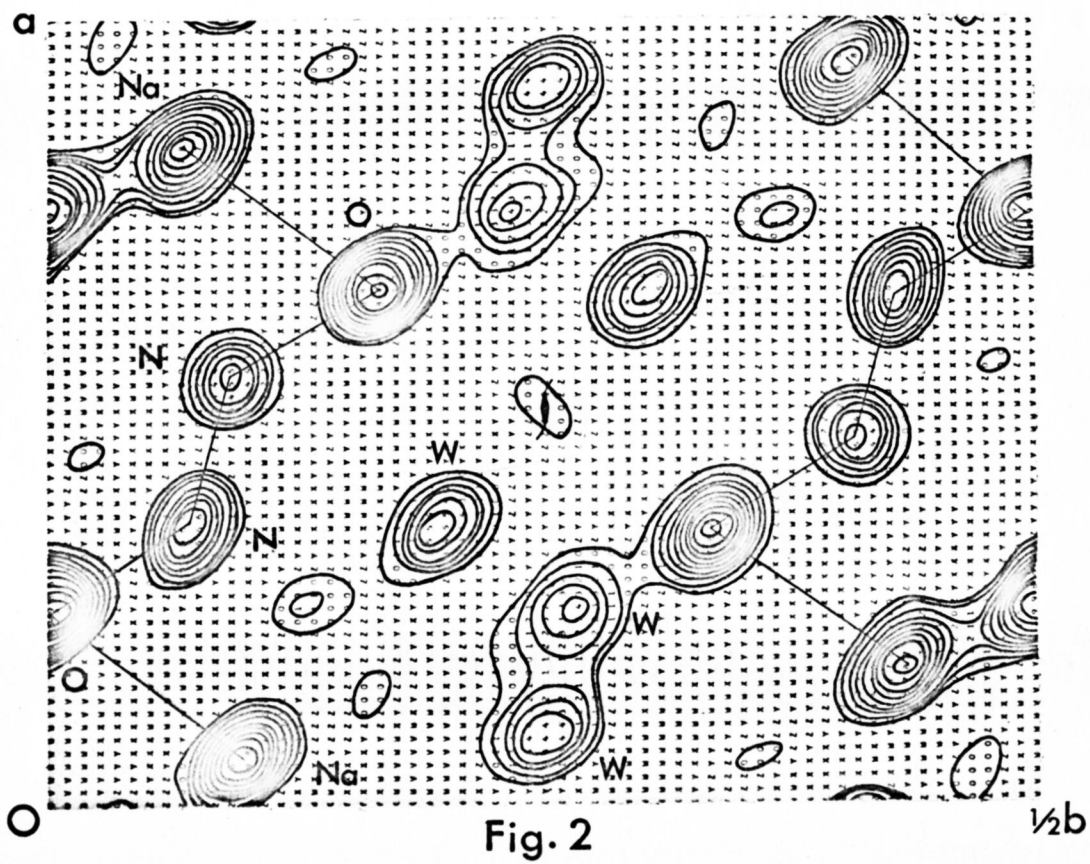
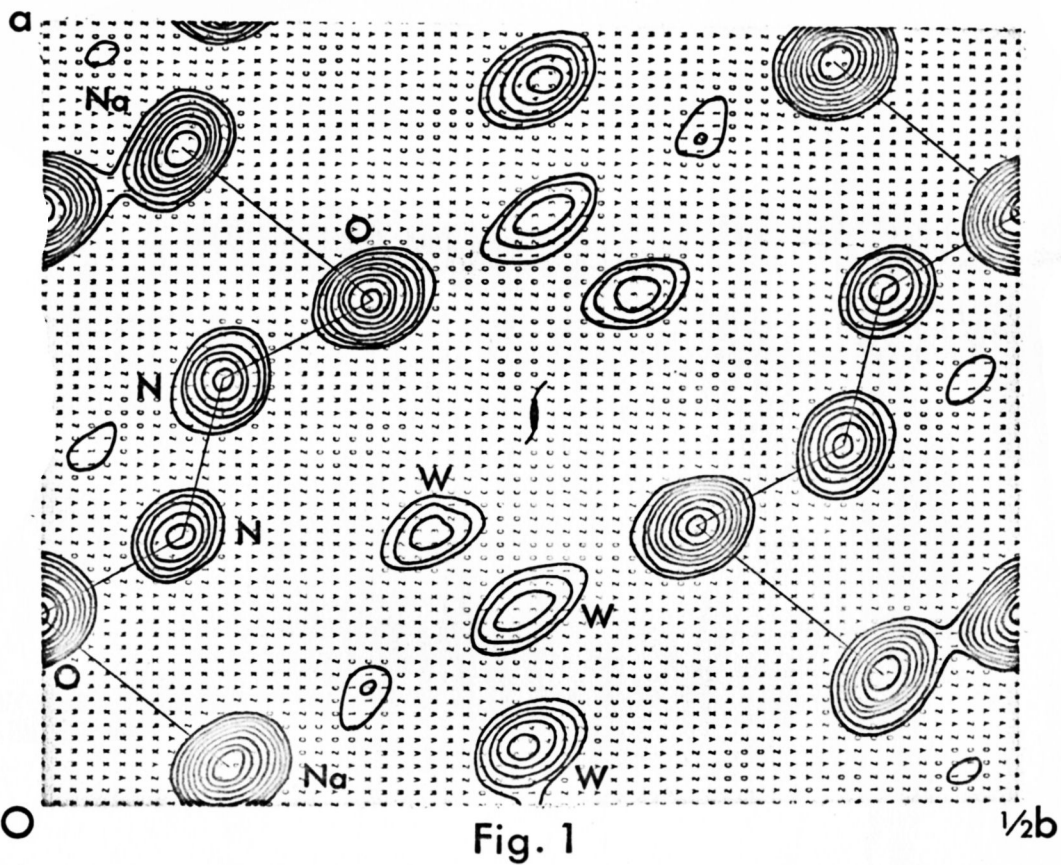
EXPLANATION OF PLATE VII

Trial electron density maps for sodium hyponitrite.

Fig. 1. $R = .34$

Fig. 2. $R = .3179$

PLATE VII



The bond distances from the trial electron density projection (Plate VII, Fig. 2) were as follows:

$$\text{N-N} = 1.32 \text{ \AA}$$

$$\text{N-O} = 1.44 \text{ \AA}$$

$$\text{Na-O} = 1.84 \text{ \AA}.$$

These values were compared with the postulated bond lengths in Table I. The N-N and N-O lengths were acceptable. The Na-O length was short and indicated that the Na atoms were in a different z-plane than the rest of the molecule. For a bond length of 2.3 \AA , the Na atoms would have to be 1.17 \AA above or below the oxygen atoms.

A careful inspection of the sequence of trial electron density maps starting with Plate VI, Fig. 1 and ending with Plate VII, Fig. 2 revealed that the symmetry of the molecule itself became slightly distorted as R went from $R = .49$ to $R = .3179$. While this asymmetry in no way violated the mathematical symmetry of the space group, it was unlikely that the molecule would actually suffer this distortion. Also, at this stage in the refinement process, small displacements of the atoms did not yield a significantly lower R value. These observations pointed out the likelihood that one or more water molecules were incorrectly located, or that perhaps a water molecule that should be present had been left out entirely. It was likely that during the convergence process, all of the atom locations were "strained" slightly out of their true positions in trying to compensate for a missing or incorrectly placed water molecule.

Attempts were made to find other locations for water molecules and both the Patterson projection and the Harker section were checked for inconsistencies.

Because the waters of hydration were extremely loosely bound in sodium hyponitrite, they were likely to have large thermal vibration parameters. This manifested itself by a broadening and lowering of the water molecule peaks. There was some conjecture that at least some of the water molecules were bound in the lattice in a random fashion, or free to move in the lattice. This would introduce a random component in the scattered X-rays which could only be interpreted in terms of statistical averages.

The final atom locations calculated from the work to date are as follows:

	x	y	z
Na ₁	.823	.068	---
Na ₂	.057	.098	---
O ₁	.651	.167	---
O ₂	.245	.000	---
N ₁	.542	.091	---
N ₂	.357	.071	---
W ₁	.350	.195	---
W ₂	.248	.263	---
W ₃	.090	.250	---

plus centrosymmetrical equivalent locations. Calculations for the z-coordinates have not been carried out at this time because it was thought best to resolve the water molecule difficulty before making the more elaborate three-dimensional calculations.

Three-Dimensional Representation

In order to visualize atom groupings and trial structures during the work, a universal crystal model was designed and constructed by G.P. Reese, M. F. Roth and the author. (See Plates VIII and IX). This model was unique and offered several advantages over other modelling schemes that have been suggested in the past. Atoms were represented by painting cork balls. These balls were mounted on vertical glass rods between horizontal sheets of plexi-glass. The rods were equipped with spring-loaded rubber feet so that the cork balls could be stationed anywhere within the volume defined by the model. Bonds between the "atoms" were provided by spring-loaded telescoping brass tubes. Plate VIII, Figs. 1 and 2 show the proposed crystal structure viewed from the 100 projection axis, and the 010 projection axis. Plate IX, Figs. 1 and 2 show the proposed crystal structure viewed from the 001 projection axis, and the 110 projection axis. Plate IX, Fig. 1 is to be compared with Plates VI and VII.

Observed and Calculated Scattering

A comparison between observed and calculated scattering (structure factors) as functions of $(\sin \theta)/\lambda$ is shown in Plate X. There was fairly good agreement, especially on the larger structure factors. Overall, there was a tendency for the observed scattering to be slightly higher than the calculated scattering. This could be due to a missing water molecule in the proposed structure.

EXPLANATION OF PLATE VIII

This plate shows the 3-dimensional tentative structure of sodium hyponitrite on the universal crystal model.

Fig. 1. 100 projection.

Fig. 2. 010 projection.

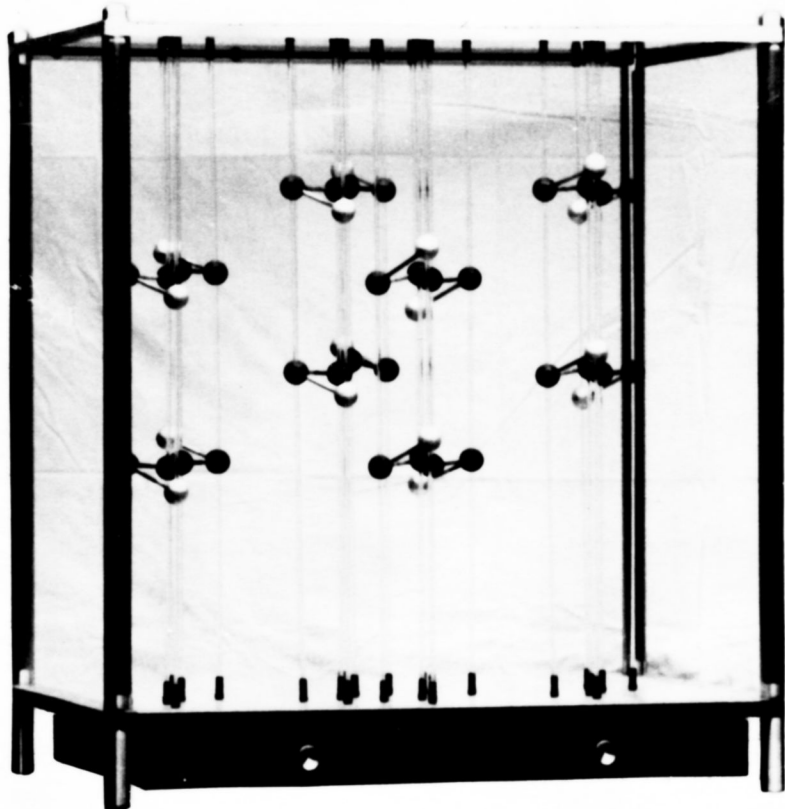


Fig. 1

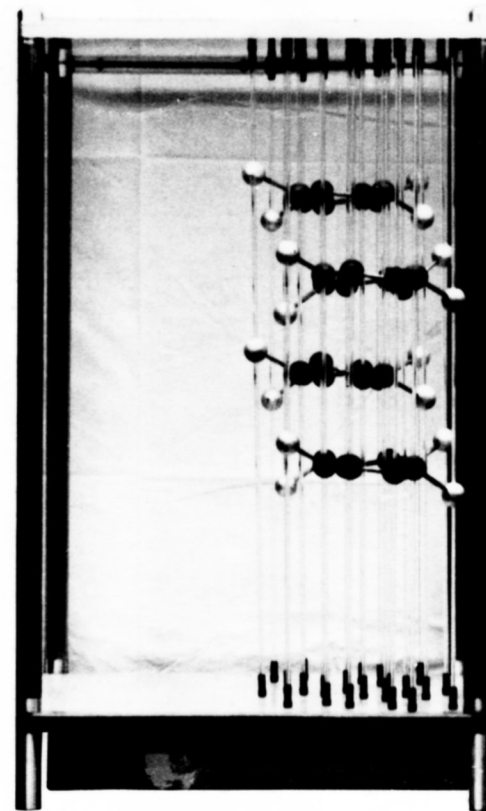


Fig. 2

PLATE VIII

EXPLANATION OF PLATE IX

This plate shows the 3-dimensional tentative structure of sodium hyponitrite on the universal crystal model.

Fig. 1. 001 projection.

Fig. 2. 110 projection.

PLATE IX

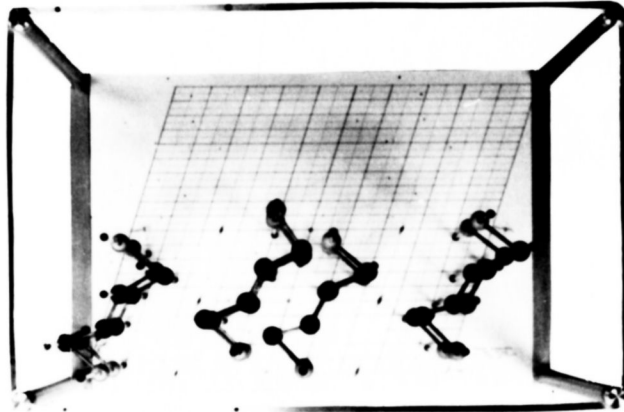


Fig. 1

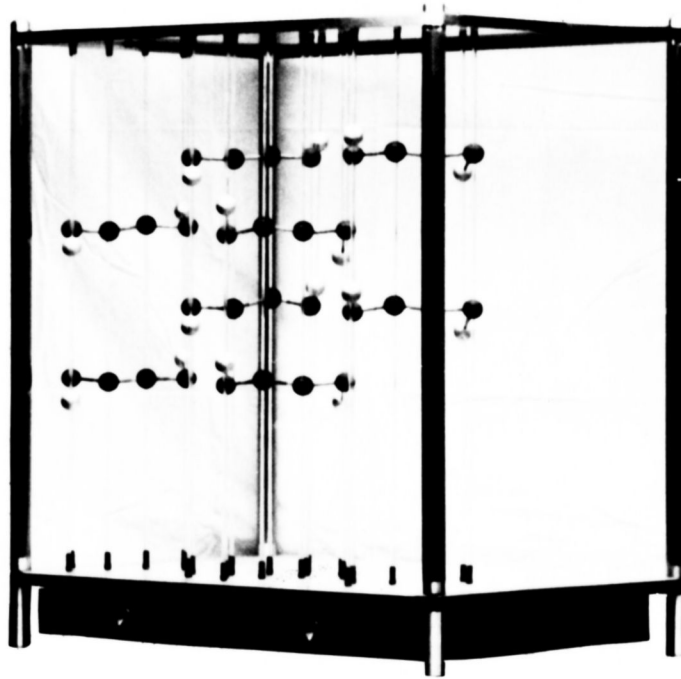
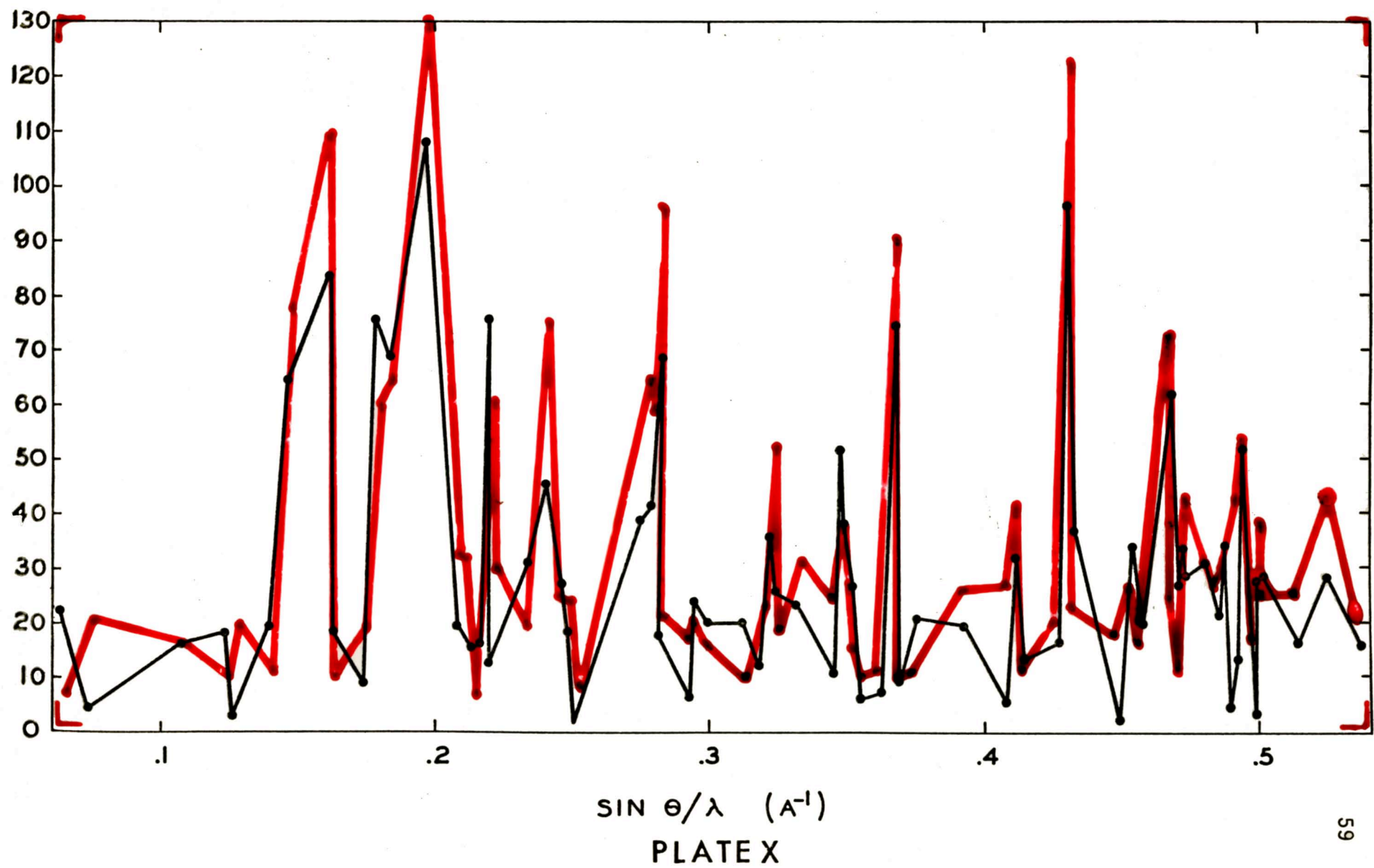


Fig. 2

EXPLANATION OF PLATE X

This plate is a comparison between the observed x-ray scattering and the calculated x-ray scattering from the proposed model, as functions of $\sin \theta / \lambda$. The magnitude of F_{hkl} is plotted for each reciprocal lattice point. Calculated values are shown in black, while the observed values are shown on the transparent overlay in red.



The residual factor R defined by Eq. (47) has been given additional meaning by Luzzati [See Buerger (1960), p. 586]. If

$$|\sigma_{hkl}| = (2\sin\theta/\lambda) \quad (48)$$

is the distance of a point hkl from the origin of reciprocal space, and if $|\overline{\Delta r}|$ is the mean of the absolute errors in atomic position, then the values of R are related to the values of $|\overline{\Delta r}| \cdot |\sigma_{hkl}|$ as shown in Table III. Thus a totally incorrect structure would have $R = .828$ for the centrosymmetrical case whereas R would have the value $R = 0.000$ for a completely correct structure. The best value for sodium hyponitrite obtained to date is $R = .3179$. Further conclusions about the structure cannot be made until the ultimate refinement in three dimensions is carried out.

EXTENSIONS

Primary to extending the work is the need of additional data for the Miller index. This can only be obtained by regrowing sodium hyponitrite crystals under the same carefully controlled conditions and taking X-ray data by means of Weissenberg or single crystal orienter methods.

The search for possible water locations should be continued and refinement in three dimensions by a general least squares approach should be undertaken.

Isotropic and anisotropic temperature factors for each atom should be taken into consideration and attention should be paid to the possibility of free water molecules in the lattice.

Table III. Relation of R to mean displacement $|\overline{\Delta r}|$, and to σ_{hkl} (from Luzzati, 1952). (See Buerger, 1960, p. 586).

R				$ \overline{\Delta r} \cdot \sigma_{hkl}$
Centric		Acentric		
2 dimen	3 dimen	2 dimen	3 dimen	
0.000	0.000	0.000	0.000	0.00
.050	.039	.031	.025	.01
.098	.078	.062	.050	.02
.145	.115	.093	.074	.03
.191	.152	.124	.098	.04
.234	.188	.155	.122	.05
.276	.223	.185	.145	.06
.317	.256	.214	.168	.07
.356	.288	.243	.191	.08
.394	.320	.270	.214	.09
.430	.350	.296	.237	.10
.494	.410	.342	.281	.12
.552	.462	.384	.319	.14
.603	.510	.420	.353	.16
.647	.554	.452	.385	.18
.686	.595	.480	.414	.20
.715	.631	.504	.440	.22
.742	.662	.524	.463	.24
.763	.689	.540	.483	.26
.781	.713	.552	.502	.28
.794	.735	.560	.518	.30
.816	.776	.574	.548	.35
.824	.802	.580	.564	.40
---	.817	---	.574	.45
---	.823	---	.580	.50
.828	.828	.586	.586	∞

APPENDIX I -- THE FOURIER-PATTERSON CALCULATION

Introduction

One of the most tedious and time-consuming jobs of the crystallographer is the Fourier calculation of Patterson- and electron-density functions. Until recent years, these calculations were limited to one and two dimensions, and the calculation of a function involving, say, 400 terms at a grid interval of $1/30$ of the unit cell required days of effort.

The advent of the high-speed computing machine has made possible the routine calculation of these functions in a matter of hours or minutes. Complex organic crystals with 50 or more atoms per asymmetric unit are now being solved with the aid of the computer.

Many programs have been written to carry out the Fourier-Patterson calculations. The following is a representative although incomplete listing of these programs:

Ahmed, F. R., (National Research Council, Ottawa, Canada.) Written for IBM 650.

S. Block and J. R. Holden, (U. S. Bureau of Standards and U. S. Naval Ordnance Laboratory), Written for IBM 704.

L. Born and E. Hellner, (Min. u. Petrogr. Inst., Kiel, Germany). Patterson functions, monoclinic or orthorhombic space groups. Written for IBM 704.

J. H. Bryden, (U. S. Naval Ordnance Testing Station, California). Written for IBM 704.

R. D. Dragsdorf and R. L. Hollis, here described.

R. E. Jones, R. P. Dodge, and D. H. Templeton, (Univ. of California). Written for IBM 701.

R. Shiono, D. H. Hall, and S. C. Chu, (University of Pittsburgh, Pittsburgh, Pa.). Written for IBM 1620.

W. G. Sly and D. P. Shoemaker, (M.I.T., Cambridge, Mass.). Written for IBM 704.

R. G. Treuting and S. C. Abrahams, (Brookhaven National Laboratories, Bell Telephone Laboratories). Calculates the electron density on any one general plane. Written for IBM 704.

D. Van Der Helm and A. L. Patterson, (Dept. of Chemistry, Univ. of Oklahoma, Norman, Okla.). Written for IBM 1620.

A. Zalkin, (Univ. of Calif. Radiation Lab., Livermore, Calif.). Written for IBM 704.

As can be inferred from this list, most of the programs have been written for either small computers (IBM 650, 1620) or very large computers (IBM 701, 704). Many of the programs written for the IBM 704 have been re-written for the IBM 709, 7090, and 7094. Recently, many medium-scale computers (such as IBM 1410) have become available for use. With respect to the IBM 1620 and IBM 7090, these computers are intermediate in speed and storage capacity. The present program arose out of the need for a Fourier-Patterson program suitable for the medium-scale computer.

FOURIER is a very flexible program written in FORTRAN II language, and is therefore readily adaptable to many machines. It may easily be upgraded to large-scale machines, where advantage may be taken of increased core storage and speed. The decision to write the program in FORTRAN II symbolic language was based upon two reasons. First, it was thought very desirable to have a program which could be run on a variety of machines with few or no modifications and second, the programming time and de-bugging time was

considerably shortened over what it would have been had the program been written in a more machine-oriented assembly language.

The requirement of speed has made essential the Beevers-Lipson (1934) transformation into triple-products of sines and cosines, and factorization into three one-dimensional summations. It has been estimated by D. Van Der Helm and A. L. Patterson that this results in twenty times fewer steps than without the transformation. Also, it was decided to use integer arithmetic throughout the program to eliminate time-consuming floating additions and multiplications. It was decided to use a fixed word length of 8 decimal digits, and to incorporate automatic scaling wherever necessary. It has been found that this results in a final accuracy of 3 or 4 significant figures, which is at least equal to the accuracy of the input data. In addition, a grid of 120 divisions in the x-, y-, and z-directions was accepted which restricted the required angles to a small number which could be stored in a table. Thus general sine-cosine subroutines could be replaced by a fast table look-up operation.

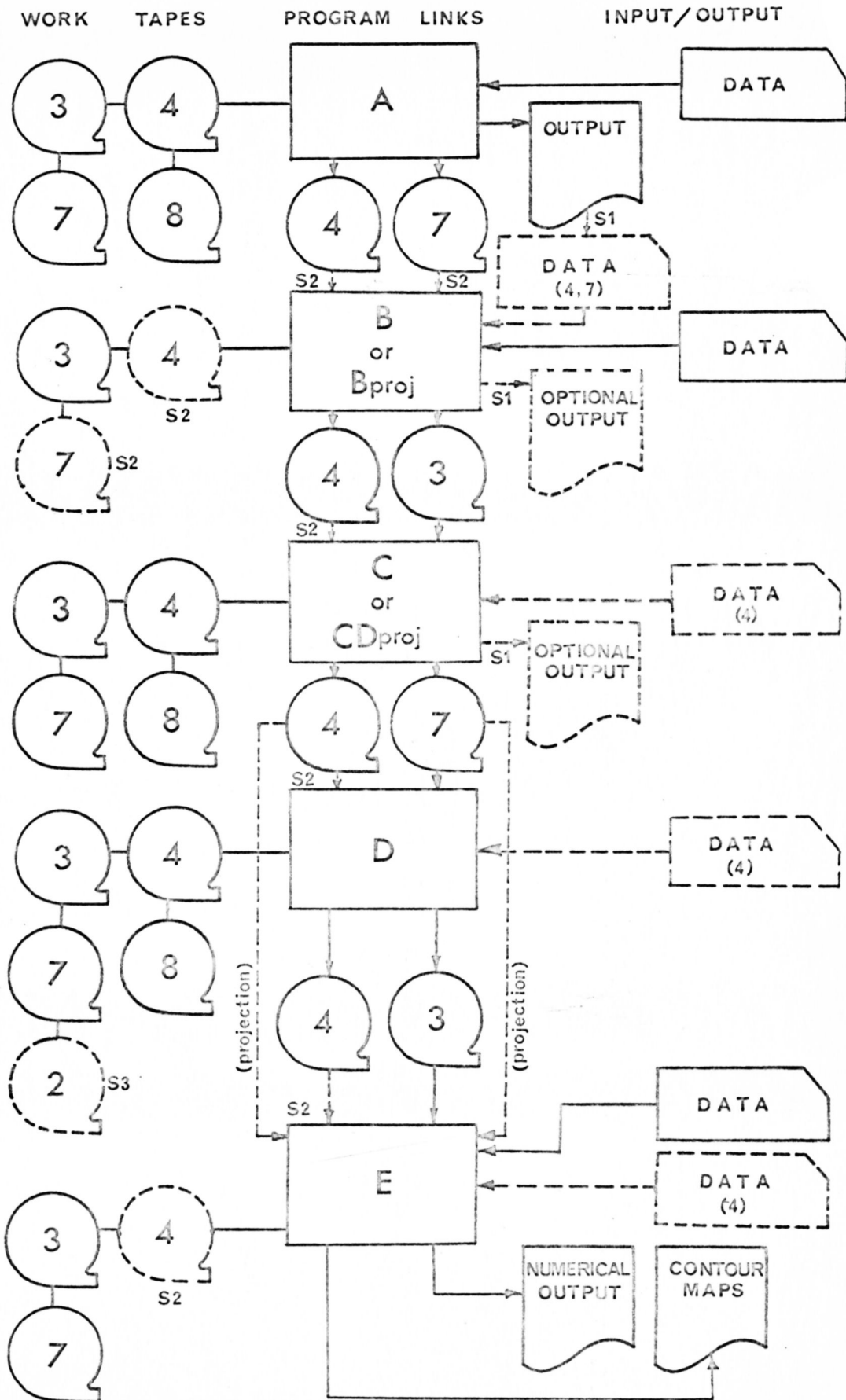
The program as it is presently written is now being run on an IBM 1410 data processing system with 40,000 decimal digits of core storage and seven magnetic tape units. Four units are used as working files, one unit for input, one unit for output, and one unit for the System Operating File. This should be considered the minimum machine configuration. Operated in this minimum configuration, the program will accept almost any size problem, limited only by the time involved in carrying out the calculation. Any number of X-ray reflections may be included, subject to the requirement that no Miller index exceeds 99. There are no restriction with regard to space groups.

Because of core-storage limitations, the program is segmented into five links which are chained together serially to perform the calculation. In this way, only one link resides in core at any time. Plate XI shows the linkage sequence of the program. Individual links are represented by rectangular boxes. For the calculation of a three-dimensional function or section links A, B, C, D, and E are required. These same five links may be used for calculating a projection, but with some loss in efficiency. For maximum efficiency in projection, link B is replaced by link B_{proj} , link C is replaced by link CD_{proj} , and link D is omitted. No other changes are necessary. Work tapes required by the respective links are shown at the left of each link. The input and output for each link is shown at the right. Machine-coded input tapes required for a given link are shown directly above that link. Thus program link D, for example, requires tape units 4 and 7 for operation. The files on units 4 and 7 are prepared by link C or link CD_{proj} . Anything that is illustrated with a dashed line is optional and is controlled by the setting of the sense switch indicated next to the dashed line. Thus if switch 1 is turned on in link A, punched output will be produced in addition to the printed output. If switch 1 is off, no punched output will result. In link B or B_{proj} , if sense switch 2 is turned on, the machine-coded tapes produced by link A will be read as input. If switch 2 is off, input will be from the cards punched by link A. These cards then take the place of tape units 4 and 7, and since no intermediate files are written on units 4 and 7 during the execution of link B or B_{proj} , these units are shown in dashed lines. As another example, if switch 2 is turned on in link D,

EXPLANATION OF PLATE XI

This plate shows the logical linkage and information flow of the program. Details are explained in the text.

PLATE XI



the machine-coded file on unit 4 will be read. If switch 2 is off, cards will take the place of the file on unit 4. The file on unit 7 is required by link D and cannot be replaced by card input. Program links B, B_{proj} , C, and C_{proj} have provision for intermediate output useful for observing the results of partial summation, and for diagnostic purposes. Because the program is divided into separate links, each link may be run independently. This is advantageous for a long calculation if a continuous time period is not available.

In addition, the ranges of calculation in the x-, y-, and z-directions are independently variable. Thus for a large problem portions of the unit cell may be calculated independently of other portions. Also, in this way, advantage may be taken of symmetry elements.

The increments in the x-, y-, and z-directions can be independently varied and are restricted to $1/120$, $1/60$, $1/40$, $1/30$, or $1/15$ of the unit cell edge.

It is difficult to estimate the actual running time of the program because of the large number of factors involved. As an example, the calculation of the three-dimensional Patterson function of sodium hyponitrite on the IBM 1410 computer involved 460 x-ray reflections and required 13.2 minutes per section with 3600 points in each section. A "brute-force" application of the un-factored Patterson equation using floating point arithmetic and power series sub-routines for sine and cosine would have taken over a year of continuous running time on the IBM 1410!

Mathematical Treatment

The electron density may be written

$$\rho(x, y, z) = K \sum_h \sum_k \sum_l F_{hkl} \exp -2\pi i(hx+ky+lz), \quad (49)$$

where K is a scale factor. The Patterson density may be obtained by substituting $F_{hkl} F_{hkl}^*$ for F_{hkl} in the electron density equation. Separating into real and imaginary parts,

$$\rho(x, y, z) = K \left[\sum_h \sum_k \sum_l A_{hkl} \cos 2\pi(hx+ky+lz) + \sum_h \sum_k \sum_l B_{hkl} \sin 2\pi(hx+ky+lz) \right], \quad (50)$$

where the imaginary unit i is included in B_{hkl} . Here the sums are taken over positive and zero values of all three Miller indices h , k , and l , and over negative values of at least two of them in the most general case (P1). The sine and cosine terms can then be expanded as triple products of sines and cosines.

When this is done, the summations can be factored so that the electron density may be written

$$\begin{aligned} \rho(x, y, z) = K \sum_l \left\{ \sum_k \left[\sum_h (m_{hkl} A_{hkl}^{(1)} \cos 2\pi hx + m_{hkl} B_{hkl}^{(2)} \sin 2\pi hx) \cos 2\pi ky \right. \right. \\ + \left. \sum_h (m_{hkl} A_{hkl}^{(4)} \sin 2\pi hx + m_{hkl} B_{hkl}^{(3)} \cos 2\pi hx) \sin 2\pi ky \right] \cos 2\pi lz \\ + \sum_k \left[\sum_h (m_{hkl} A_{hkl}^{(2)} \cos 2\pi hx + m_{hkl} B_{hkl}^{(1)} \sin 2\pi hx) \sin 2\pi ky \right. \\ + \left. \left. \sum_h (m_{hkl} A_{hkl}^{(3)} \sin 2\pi hx + m_{hkl} B_{hkl}^{(4)} \cos 2\pi hx) \cos 2\pi ky \right] \sin 2\pi lz \right\}, \quad (51) \end{aligned}$$

(Beevers and Lipson (1934)). Here the summations are taken only over zero and positive values of the Miller indices. The coefficients are given by

$$\begin{aligned}
A_{hkl}^{(1)} &= A(hkl) + A(\bar{h}kl) + A(h\bar{k}l) + A(hk\bar{l}) \\
A_{hkl}^{(2)} &= -A(hkl) - A(\bar{h}kl) + A(h\bar{k}l) + A(hk\bar{l}) \\
A_{hkl}^{(3)} &= -A(hkl) + A(\bar{h}kl) - A(h\bar{k}l) + A(hk\bar{l}) \\
A_{hkl}^{(4)} &= -A(hkl) + A(\bar{h}kl) + A(h\bar{k}l) - A(hk\bar{l})
\end{aligned}
\tag{52}$$

$$\begin{aligned}
B_{hkl}^{(1)} &= -B(hkl) + B(\bar{h}kl) + B(h\bar{k}l) + B(hk\bar{l}) \\
B_{hkl}^{(2)} &= B(hkl) - B(\bar{h}kl) + B(h\bar{k}l) + B(hk\bar{l}) \\
B_{hkl}^{(3)} &= B(hkl) + B(\bar{h}kl) - B(h\bar{k}l) + B(hk\bar{l}) \\
B_{hkl}^{(4)} &= B(hkl) + B(\bar{h}kl) + B(h\bar{k}l) - B(hk\bar{l})
\end{aligned}$$

In the factored equation, summations are performed over indices ranging from zero to the maximum values of h , k , and l , and no summations are taken over negative indices. For this reason, the $0kl$, $h0l$, $hk0$, $h00$, $0k0$, and $00l$ reflections must be given special consideration. Terms including these reflections are modified by the multiplier m_{hkl} and are treated as follows:

0kl Reflections:

$$\begin{aligned}
A_{hkl}^{(1)} &= A(0kl) + A(0k\bar{l}) + A(0\bar{k}l) + A(0k\bar{l}) \\
A_{hkl}^{(2)} &= -A(0kl) - A(0k\bar{l}) + A(0\bar{k}l) + A(0k\bar{l}) \\
A_{hkl}^{(3)} &= -A(0kl) + A(0k\bar{l}) - A(0\bar{k}l) + A(0k\bar{l}) \\
A_{hkl}^{(4)} &= -A(0kl) + A(0k\bar{l}) + A(0\bar{k}l) - A(0k\bar{l})
\end{aligned}
\tag{53}$$

$$\begin{aligned}
B_{hkl}^{(1)} &= -B(0kl) + B(0k\bar{l}) + B(0\bar{k}l) + B(0k\bar{l}) \\
B_{hkl}^{(2)} &= B(0kl) - B(0k\bar{l}) + B(0\bar{k}l) + B(0k\bar{l}) \\
B_{hkl}^{(3)} &= B(0kl) + B(0k\bar{l}) - B(0\bar{k}l) + B(0k\bar{l})
\end{aligned}$$

$$B_{hkl}^{(4)} = B(0kl) + B(0k\bar{l}) + B(0\bar{k}l) - B(0k\bar{l}) \quad (53 \text{ cont.})$$

Utilizing the relations

$$\begin{aligned} A(hkl) &= A(\bar{h}\bar{k}\bar{l}), \\ -B(hkl) &= B(\bar{h}\bar{k}\bar{l}), \end{aligned} \quad (54)$$

$$\begin{aligned} A_{hkl}^{(1)} &= 2A(0kl) + 2A(0\bar{k}l) & B_{hkl}^{(1)} &= 0 \\ A_{hkl}^{(2)} &= -2A(0kl) + 2A(0\bar{k}l) & B_{hkl}^{(2)} &= 0 \\ A_{hkl}^{(3)} &= 0 & B_{hkl}^{(3)} &= 2B(0kl) - 2B(0\bar{k}l) \\ A_{hkl}^{(4)} &= 0 & B_{hkl}^{(4)} &= 2B(0kl) + 2B(0\bar{k}l) \end{aligned} \quad (55)$$

h0l Reflections:

Similarly for h0l reflections, we have

$$\begin{aligned} A_{hkl}^{(1)} &= 2A(h0l) + 2A(\bar{h}0l) & B_{hkl}^{(1)} &= 0 \\ A_{hkl}^{(2)} &= 0 & B_{hkl}^{(2)} &= 2B(h0l) - 2B(\bar{h}0l) \\ A_{hkl}^{(3)} &= -2A(h0l) + 2A(\bar{h}0l) & B_{hkl}^{(3)} &= 0 \\ A_{hkl}^{(4)} &= 0 & B_{hkl}^{(4)} &= 2B(h0l) + 2B(\bar{h}0l) \end{aligned} \quad (56)$$

hk0 Reflections:

For hk0 reflections,

$$\begin{aligned} A_{hkl}^{(1)} &= 2A(hk0) + 2A(\bar{h}\bar{k}0) & B_{hkl}^{(1)} &= 0 \\ A_{hkl}^{(2)} &= 0 & B_{hkl}^{(2)} &= 2B(hk0) - 2B(\bar{h}\bar{k}0) \\ A_{hkl}^{(3)} &= 0 & B_{hkl}^{(3)} &= 2B(hk0) + 2B(\bar{h}\bar{k}0) \\ A_{hkl}^{(4)} &= -2A(hk0) + 2A(\bar{h}\bar{k}0) & B_{hkl}^{(4)} &= 0 \end{aligned} \quad (57)$$

If two indices are simultaneously zero, we have the following additional relationships:

h00 Reflections:

$$\begin{array}{ll}
 A_{hkl}^{(1)} = 4A(h00) & B_{hkl}^{(1)} = 0 \\
 A_{hkl}^{(2)} = 0 & B_{hkl}^{(2)} = 4B(h00) \\
 A_{hkl}^{(3)} = 0 & B_{hkl}^{(3)} = 0 \\
 A_{hkl}^{(4)} = 0 & B_{hkl}^{(4)} = 0
 \end{array} \tag{58}$$

0k0 Reflections:

$$\begin{array}{ll}
 A_{hkl}^{(1)} = 4A(0k0) & B_{hkl}^{(1)} = 0 \\
 A_{hkl}^{(2)} = 0 & B_{hkl}^{(2)} = 0 \\
 A_{hkl}^{(3)} = 0 & B_{hkl}^{(3)} = 4B(0k0) \\
 A_{hkl}^{(4)} = 0 & B_{hkl}^{(4)} = 0
 \end{array} \tag{59}$$

00l Reflections:

$$\begin{array}{ll}
 A_{hkl}^{(1)} = 4A(00l) & B_{hkl}^{(1)} = 0 \\
 A_{hkl}^{(2)} = 0 & B_{hkl}^{(2)} = 0 \\
 A_{hkl}^{(3)} = 0 & B_{hkl}^{(3)} = 0 \\
 A_{hkl}^{(4)} = 0 & B_{hkl}^{(4)} = 4B(00l)
 \end{array} \tag{60}$$

Terms of the form

$$A_{hkl}^{(n)} \begin{Bmatrix} \cos \\ \sin \end{Bmatrix} 2\pi \begin{Bmatrix} hx \\ ky \\ lz \end{Bmatrix} \tag{61}$$

must be summed over h, k , and l only once. If this is the case, we see from the above considerations that the multiplier m_{hkl} must be defined as follows:

$$\begin{aligned} m_{hkl} &= 1 \\ m_{0kl} &= m_{h0l} = m_{hk0} = 1/2 \\ m_{h00} &= m_{0k0} = m_{00l} = 1/4 \end{aligned} \tag{62}$$

In program link A, the input data is arranged in the following order on each 80-column card:

$$A(hkl), A(\bar{h}kl), A(h\bar{k}l), A(hk\bar{l}), B(hkl), B(\bar{h}kl), B(h\bar{k}l), B(hk\bar{l}).$$

As far as the input data are concerned, zero indices are to be treated as positive indices. Thus the real part of an $0kl$ reflection would be registered with $A(hkl)$ and no entry would be made for $A(\bar{h}kl)$. Similarly, the imaginary part of an $h0l$ reflection would be registered with $B(hkl)$ and no entry would be made for $B(h\bar{k}l)$. If this procedure is followed, the multiplication by m_{hkl} will be accomplished implicitly.

Operation of the Program

If a three-dimensional function or a section through a three-dimensional function is being computed, links A, B, C, D, and E are used. For a projection, greater efficiency will result by using links A , B_{proj} , CD_{proj} , and E as described in the introduction. The following are brief descriptions of the operation of each program link.

Link A. Input to link A consists of the Miller indices h , k , and l of the reflecting planes of the crystal, and the coefficients F_{hkl} or F_{hkl}^2 depending, respectively, on whether an electron density or Patterson function is desired. The order of these coefficients is irrelevant. A scaling factor variable from 0 to 1 may be included and will multiply all of the coefficients. Also, the direction of projection or sectioning and the "handedness" of the coordinate system is entered.

As described in the mathematical treatment, the input data is arranged on each 80-column card as follows:

$$A(hkl), A(\bar{h}kl), A(h\bar{k}l), A(hk\bar{l}), B(hkl), B(\bar{h}kl), B(h\bar{k}l), B(hk\bar{l}).$$

Thus for example, a $\bar{4}81$ reflection would appear on the same card as a 481 reflection. Since all of the terms necessary for the calculation of Eqs. (52) are together on each card, they are calculated immediately after each card is read. These calculated coefficients are then modified according to whether h , k , or l is zero, as discussed in the mathematical treatment.

Three tests of validity are then performed:

- (1) Check to see if any h , k , or l is negative. (Summations are performed over positive indices only).
- (2) Check to see if all h , k , and l are zero. (This is a safeguard against accidental inclusion of a blank card. F_{000} cannot be included).
- (3) Check to see if the coefficient just calculated is too large for the operation of link B. (All coefficients must have magnitudes less than 10^4 in order for the automatic scaling procedures in links B, C, and D to work properly. For

greatest numerical accuracy, the scaling factor should be adjusted so that the largest coefficient is equal to 9999).

The program terminates with an error message if any of these three checks are violated. After passing these checks, h , k , and l are permuted to agree with the selected direction of sectioning or projection, and then the permuted indices and the coefficients are written on a work tape. (See comment cards in program listing). This procedure continues until all of the data have been read.

The work file containing the permuted indices and coefficients is then rewound and a three-level sort is initiated using three additional tape units. This sorting procedure results in a file containing the indices and coefficients, ordered so that the **third** index varies least rapidly, the second index varies more rapidly, and **the** first index varies most rapidly. This **sort operation** is necessary for **calculations** using the factored Eq. (51) and is an integral part of the **entire program**. The terms "first index", "second index", and "third index" refer to the first, second, and third permuted indices. Thus if h, k, l , has been permuted to h, l, k ; h is the first index, l is the second index, and k is the third index. During the sort operation a 4th check is performed:

- (4) Check to see if any Miller indices are duplicate. (This guards against the accidental inclusion of a card with a mispunched structure factor but with correctly punched h, k, l ; along with a correctly punched card).

During and after the sort operation, tables are prepared containing all of the unique values of the Miller indices, and the number of unique values of each index. Along with the sorted coefficients, this information is transmitted to link B for further use.

Link B. To greatly simplify discussions of program links B, C, and D, it will be assumed that h, k, and l have been left unpermuted. That is, arrangement XYZ, ITEM = 1, has been selected (see link A listing) and that a continuous run through all five links is desired.

With the coefficients properly prepared by link A available on a work file, storage is cleared by the System Monitor and link B is placed in core.

Link B requires, in addition to the output of link A; the minimum and maximum values of x, y, and z (in $1/120^{\text{th}}$ s of the unit cell) and the increments to be taken in the x-, y-, and z-directions. Link B also requires a deck of 150 cosine values, starting from the cosine of 3 degrees and going 3 degree increments to 450 degrees. Each cosine value must be multiplied by 10^4 .

All of the coefficients associated with the first value of k and l are read and stored. Then input is suspended and summation is carried out over all values of h associated with the first value of k and l. When this summation is completed, input is resumed until all values of the coefficients associated with the second value of k and the first value of l are read and stored. Then another summation over h takes place, and so on. Thus by summing over the h index link B reduces the electron density function

[Eq. (51)] to the form

$$\rho(x, y, z) = K \sum_l \left\{ \sum_k \left[C_{kl}^{(1)} \cos 2\pi ky + C_{kl}^{(2)} \sin 2\pi ky \right] \cos 2\pi lz + \sum_k \left[C_{kl}^{(3)} \cos 2\pi ky + C_{kl}^{(4)} \sin 2\pi ky \right] \sin 2\pi lz \right\}. \quad (63)$$

These summations are carried out for all values of x , and the results of the summations are written on a work file. The sums for all values of x are stored in core until they are written out. Before the summation is performed for each value of x , a brief table of sines and cosines necessary for the summation is extracted from the main table of cosines. The program also keeps track of the largest summation occurring and transmits this information to link C for scaling purposes.

Link C. Link C begins by determining a scale factor based upon the magnitude of the largest sum computed in link B. This scale factor is used on all data to keep the results of link C less than or equal to 8 digits in length.

At this point, summation over h has been carried out for all values of x . The next task is to sum over k for all values of y . Because of the very large number of sums involved, it is no longer possible to store the sums for all values of y in core at the same time. Thus sums must be formed for all y associated with each value of x , and the results written on a work tape. However, in this case even the coefficients for each summation require more core storage than is available. If the program is restricted to calculating

single terms of the summation for each value of x and writing them on tape for all values of y , the time involved in reading and writing becomes a dominating factor which seriously interferes with the speed of the program. The most efficient utilization of core storage and magnetic tape dictates that a compromise be made between these several alternatives.

The procedure used in the program is to read in blocks of coefficients (1st dimension sums) and sum over blocks of k values within each range of constant l . The larger these blocks are, the less reading and writing on magnetic tape, and hence the faster the calculation. The size of the blocks is controlled by a parameter (MMM) within the program and is limited by the amount of core storage available. (See listing for links C and CD_{proj}). Since link C usually requires more running time than the other links, careful adjustment of this parameter to take advantage of the core storage available will result in a considerable saving of time.

In the operation of link C, a block of coefficients is read and partial sums are formed. These partial sums are written on a work file. When the sums for all values of x and y are written, this tape is rewound and the next block of coefficients (1st dimension sums) are read. These coefficients are then summed and combined with the partial sums from the work file. The new partial sums are written on a different work file. When the third block of coefficients is read, the identities of these two files are switched and the procedure continues. When the value of l is about to change (the last block for the current l value has been read) the program declares that

summation is completed and the sums are written on a file for use by link D. The process is then repeated for the new value of l and calculation continues until all of the input data to link C is exhausted.

By summing over the k index, link C reduces the electron density function [Eq. (63)] to the form

$$\rho(x, y, z, t) = K \sum_l (D_l^{(1)} \cos 2\pi lz + D_l^{(2)} \sin 2\pi lz). \quad (64)$$

The summations from link C form the coefficients for link D.

Link D. The plan of action for link D is different from that of link C and B. Instead of ranging over all values of z for each term of the summation over l is performed. In this way, sections through the three-dimensional function are calculated independently of each other.

Link D begins by determining the scale factor to be used. No scheme such as that used in link C can be used for working with blocks of coefficients, because of the huge quantity of numbers that are now available for coefficients. The output file from link C is read and terms of the form

$$D_l^{(1)} \cos 2\pi lz + D_l^{(2)} \sin 2\pi lz$$

are created and written on a work file. Then the tape is rewound, the value of l is changed, new terms are formed and added to the previous terms read from the work file and the results are written on a different work file. For the next value of l , the identities of the tape units are switched and the process is repeated. When the last l value is encountered, the final results

are written on a file to be read by link E. At this point, a section through the three-dimensional function has been calculated. If only a single section is desired, the program exits to link E. If more than one section is desired, the value of z is changed and the whole process is repeated. The maximum and minimum values of the entire function are now available and are transmitted to link E.

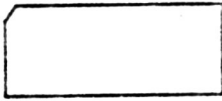
Link E. Link E converts the output from link D into a usable form. Two output tapes are provided. One output consists of a numerical listing of the functional values; the other output is in the form of contour maps. From the maximum and minimum values of the function, a scale factor is computed. This scale factor divides the function into 45 contouring intervals. An alphameric symbol is selected for each of the 45 levels and is printed out to form a continuous map that can be contoured directly. The available symbols are those which follow:

-. ,+*=)(\$ABCDEFGHIJKLMN0PQRSTUVWXYZ0123456789

No provision is made for skew axes or adjustment of the length of the unit cell edges.

Logical Diagrams and Fortran II Coding

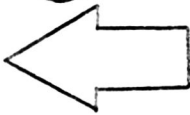
In this section, each link is outlined by block diagrams using more or less standard flow charting symbols. These symbols are defined as follows:



Card image on the input tape unit.



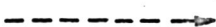
Print image on the output tape unit.



Entry point for each program link.



This symbol specifies the direction of normal program flow.



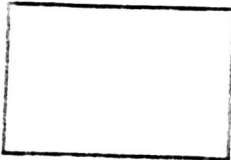
This symbol specifies the direction of optional program flow or conditional flow in program loops.



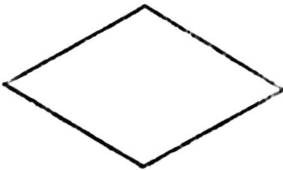
Major connector. The number within this symbol is an actual statement number of the program.



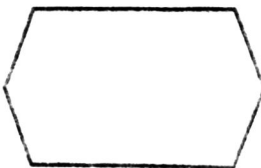
Off-page connector. This is not an actual connector point of the program.



Arithmetic calculation or defined procedure.



Logical decision point.



FORTRAN do loop statement. The range of the do loop is specified and terminates with a major connector. Return to the do loop statement is specified by a conditional flow symbol.



Tape unit operation. A W appearing within the symbol denotes a write operation on the unit specified. An R denotes a read operation.



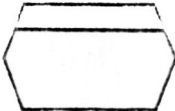

	Rewind specified tape unit.
	Backspace specified tape unit one logical record.
	Externally defined subroutine.
	Stop.

Plate XII shows the assembled program deck ready for operation. The form of the input cards for each link is specified in the FORTRAN listing by comment cards. It is intended that the actual coding be self-explanatory since comments are included liberally. Many of these comments can be keyed directly to the flow diagrams. For details of the FORTRAN coding see IBM manual J24-1468-1 IBM 1410/7010 Operating System (1410-PR-108) FORTRAN.

EXPLANATION OF PLATE XII

This plate shows the card deck sequence necessary for the operation of the program, using the IBM 1410-PR-108 monitor system. Card decks shown in parentheses are normally replaced by the corresponding tape file if a continuous run is desired.

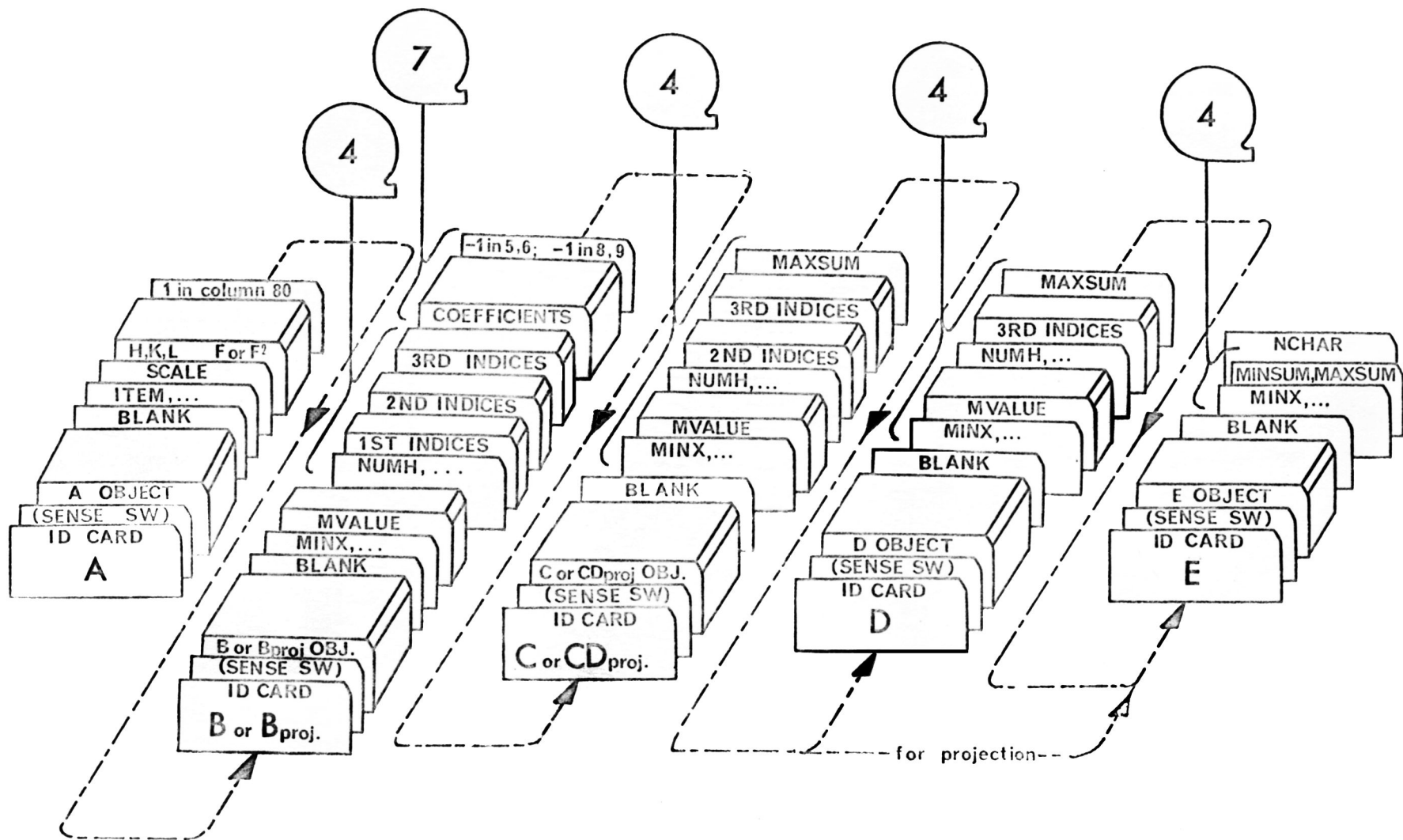
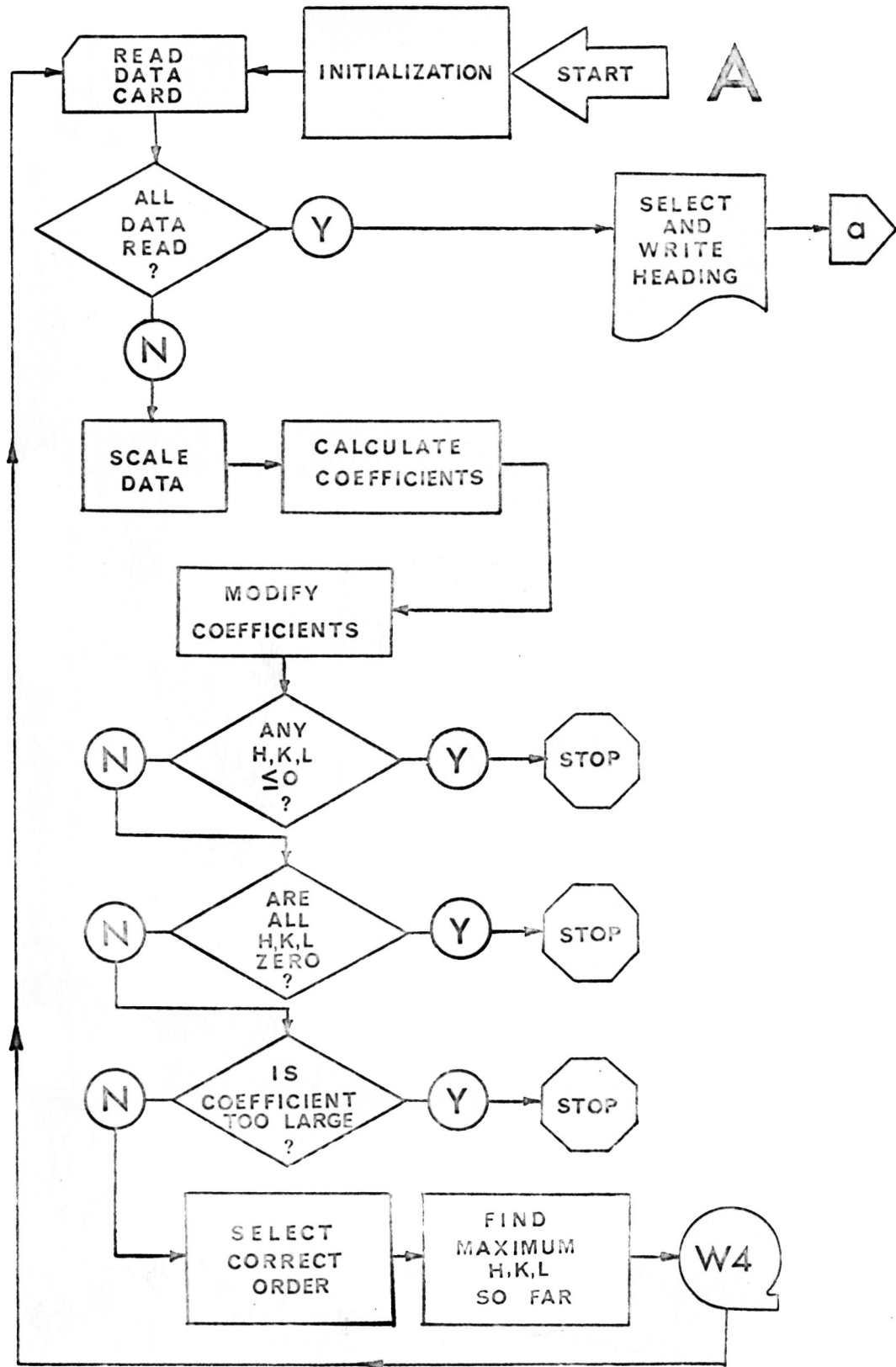


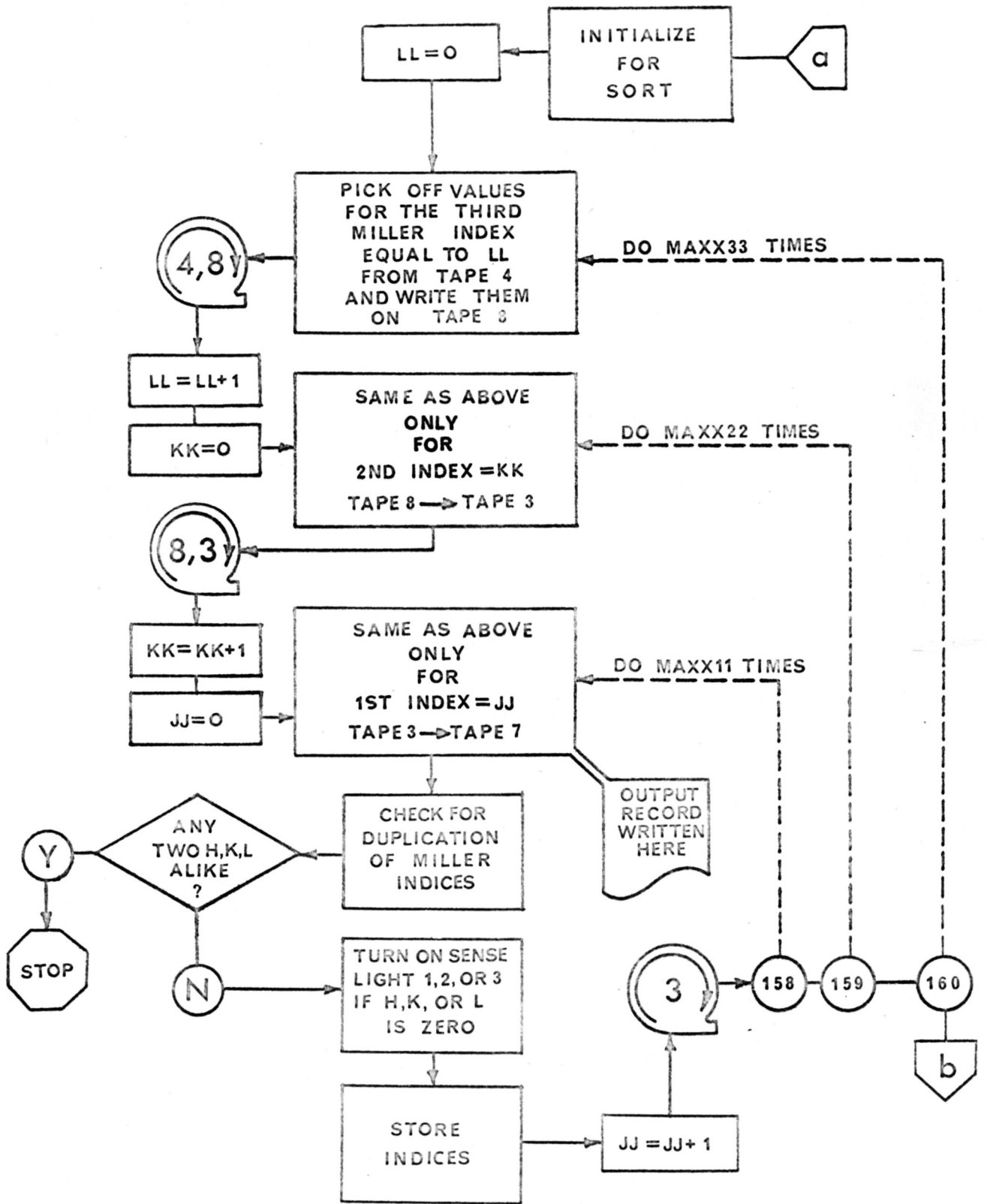
PLATE XII

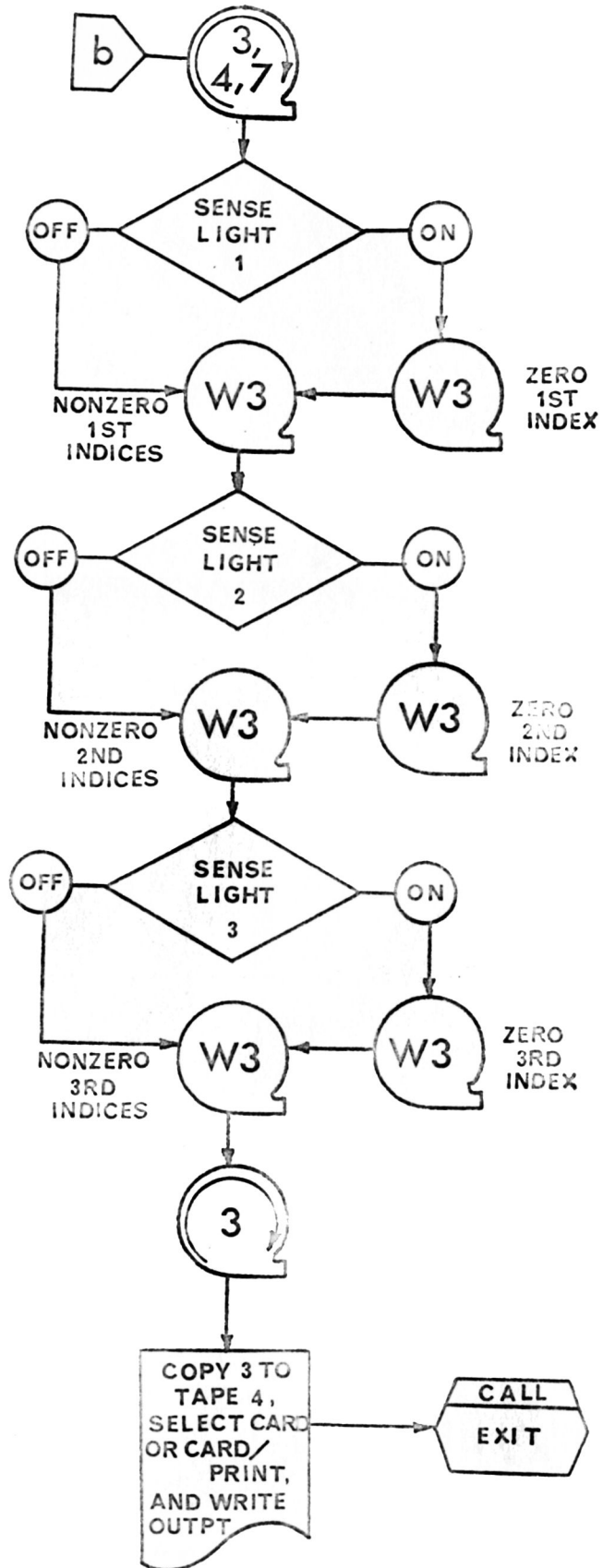
EXPLANATION OF PLATE XIII

This plate (next three pages) shows the logical steps and flow of information within program link A. The pentagonal boxes carry the program flow from page to page.

PLATE XIII







EXPLANATION OF PLATE XIV

This plate (next 9 pages) is the FORTRAN II symbolic coding for program link A.

BOP FOURIER A 08 08

C ***** FOURIER A *****
 C WRITTEN MARCH, 1964 RALPH L. HOLLIS
 C MODIFIED JULY 18, 1964
 C THIS PROGRAM ASSEMBLES THE STRUCTURE FACTORS INTO THE FOURIER
 C COEFFICIENTS FOR PROGRAM FOURIER B.
 C SENSE SWITCH 1 ON FOR BOTH CARD AND TAPE OUTPUT.
 C SENSE SWITCH 1 OFF FOR TAPE OUTPUT TO FOURIER B.
 C NH = ACTUAL H MILLER INDEX OF CRYSTAL.
 C NK = ACTUAL K MILLER INDEX OF CRYSTAL.
 C NL = ACTUAL L MILLER INDEX OF CRYSTAL.

C NA1ST = A(+H,+K,+L)
 C NA2ND = A(-H,+K,+L)
 C NA3RD = A(+H,-K,+L)
 C NA4TH = A(+H,+K,-L)
 C NB1ST = B(+H,+K,+L)
 C NB2ND = B(-H,+K,+L)
 C NB3RD = B(+H,-K,+L)
 C NB4TH = B(+H,+K,-L)

C-----PERMUTATION TABLE FOR XYZ...
 C LABEL2 IS MAPPED ACROSS THE PAGE, LABEL1 IS MAPPED DOWN THE
 C PAGE, AND PROJECTION OR SECTIONING IS DONE IN THE LABEL3
 C DIRECTION. THE COEFFICIENTS FOR FOURIER B ARE NUMBERED ONE
 C THRU EIGHT AND WILL MULTIPLY TRIPLE PRODUCTS OF SINES (S) AND
 C COSINES (C) AS SHOWN IN THE TABLE BELOW.

	LLL								
C	1 AAA	NA1	NA2	NA3	NA4	NB1	NB2	NB3	NB4
C	T BBB								
C	E EEE	1	2	3	4	5	6	7	8
C	M LLL								
C	123								
C	1 XYZ	CCC	CSS	SCS	SSC	SSS	SCC	CSC	CCS
C	2 YZX	CCC	SSC	CSS	SCS	SSS	CCS	SCC	CSC
C	3 ZXY	CCC	SCS	SSC	CSS	SSS	CSC	CCS	SCC
C	4 XZY	CCC	CSS	SSC	SCS	SSS	SCC	CCS	CSC
C	5 YXZ	CCC	SCS	CSS	SSC	SSS	CSC	SCC	CCS
C	6 ZYX	CCC	SSC	SCS	CSS	SSS	CCS	CSC	SCC

C-----THE ORDER OF THE CARDS AT OBJECT TIME IS AS FOLLOWS...
 C (1) ID CARD.
 C (2) SENSE SWITCH SETTINGS CARD (IF ONE).
 C (3) OBJECT DECK FOURIER A.
 C (4) A BLANK CARD.
 C (5) CARD CONTAINING ITEM, LABEL1, LABEL2, AND LABEL3,
 C PER FORMAT 52.
 C (6) CARD CONTAINING SCALING FACTOR TO BE USED ON DATA,
 C PER FORMAT 55.
 C (7) DATA DECK---NH, NK, NL, NA1ST..ETC., PER FORMAT 1.
 C COLUMN 80 MUST BE LEFT BLANK.
 C (8) A CARD WITH 1 PUNCHED IN COLUMN 80.

C AT THE COMPLETION OF THIS PROGRAM, TAPES 4 AND 7 WILL CONTAIN
C DATA FOR THE OPERATION OF FOURIER B.
C

```

DIMENSION NN1(100),NN2(100),NN3(100)
1 FORMAT(3I3,8(3X,I5),6X,I1)
2 FORMAT(1X,40HH, K, CR L NEGATIVE -- CORRECT AND RERUN)
6 FORMAT(1X,41HH, K, AND L ALL ZERO -- CORRECT AND RERUN)
8 FORMAT(1X,46HTWO CARDS HAVE SAME MILLER INDICES -- CORRECT ,
19HAND RERUN)
50 FORMAT(1X,43HOUTPUT TOO LARGE FOR OPERATION OF FOURIER B/
1 1X,47HCHOOSE A SMALLER SCALE FACTOR AND RERUN PROGRAM)
51 FORMAT(I1,3X,3A1)
52 FORMAT(1X,46HTHE OUTPUT IS BEING AUTOMATICALLY ORIENTED TO ,
1 13HCONFIGURATION,1X,3A1,1H./
21X,41HTHE OUTPUT OF FOURIER E WILL BE SUCH THAT,1X,A1,1X,
326HIS MAPPED ACROSS THE PAGE,,1X,A1,1X,
428HIS MAPPED DOWN THE PAGE, AND/
51X,A1,1X,31HIS MAPPED AS OVERLAPPING PAGES./
61X,53HIF A PROJECTION IS CALCULATED, PROJECTION WILL BE IN ,
73HTHE,1X,A1,11H-DIRECTION.)
53 FORMAT(2H $,3I3,8(3X,I5)3X,I4)
54 FORMAT(1H0,14HTOTAL COUNT = ,I4)
55 FORMAT(F6.3)
56 FORMAT(2H $,3I3,8(3X,I5),3X,I4)
57 FORMAT(2X,3I3,8(3X,I5),3X,I4)
61 FORMAT(1H0,3X,1HH,2X,1HK,2X,1HL,5X,3HNA1,5X,3HNA2,5X,3HNA3,
1 5X,3HNA4,5X,3HNB1,5X,3HNB2,5X,3HNB3,5X,3HNB4,2X,5HCOUNT)
62 FORMAT(1H0,3X,1HK,2X,1HL,2X,1HH,5X,3HNA1,5X,3HNA4,5X,3HNA2,
15X,3HNA3,5X,3HNB1,5X,3HNB4,5X,3HNB2,5X,3HNB3,2X,5HCOUNT)
63 FORMAT(1H0,3X,1HL,2X,1HH,2X,1HK,5X,3HNA1,5X,3HNA3,5X,3HNA4,
15X,3HNA2,5X,3HNB1,5X,3HNB3,5X,3HNB4,5X,3HNB2,2X,5HCOUNT)
64 FORMAT(1H0,3X,1HH,2X,1HL,2X,1HK,5X,3HNA1,5X,3HNA2,5X,3HNA4,
15X,3HNA3,5X,3HNB1,5X,3HNB2,5X,3HNB4,5X,3HNB3,2X,5HCOUNT)
65 FORMAT(1H0,3X,1HK,2X,1HH,2X,1HL,5X,3HNA1,5X,3HNA3,5X,3HNA2,
15X,3HNA4,5X,3HNB1,5X,3HNB3,5X,3HNB2,5X,3HNB4,2X,5HCOUNT)
66 FORMAT(1H0,3X,1HL,2X,1HK,2X,1HH,5X,3HNA1,5X,3HNA4,5X,3HNA3,
15X,3HNA2,5X,3HNB1,5X,3HNB4,5X,3HNB3,5X,3HNB2,2X,5HCOUNT)
67 FORMAT(2H $,I3)
68 FORMAT(1X,I3)
69 FORMAT(2H $,3I3)
70 FORMAT(1X,3I3)

```

C-----INITIALIZATION.

```

REWIND 4
REWIND 8
NCOUNT=0
READ INPUT TAPES,51,ITEM,LABEL1,LABEL2,LABEL3
WRITE OUTPUT TAPE6,52,LABEL1,LABEL2,LABEL3,LABEL2,LABEL1,
1 LABEL3,LABEL3
READ INPUT TAPE5,55,SCALE
MAX11=0
MAX22=0
MAX33=0

```

C-----INITIALIZATION COMPLETE.

```

40 READ INPUT TAPE5,1,NH,NK,NL,NA1ST,NA2ND,NA3RD,NA4TH,NB1ST,
1 NB2ND,NB3RD,NB4TH,M
C-----IF M IS NOT ZERO, WRITE HEADINGS AND START SORT OPERATION.
IF(M)5,7,5
7 NCOUNT=NCOUNT+1
C-----BEGIN SCALING OF DATA.
NA1ST=SCALE*FLOATF(NA1ST)
NA2ND=SCALE*FLOATF(NA2ND)
NA3RD=SCALE*FLOATF(NA3RD)
NA4TH=SCALE*FLOATF(NA4TH)
NB1ST=SCALE*FLOATF(NB1ST)
NB2ND=SCALE*FLOATF(NB2ND)
NB3RD=SCALE*FLOATF(NB3RD)
NB4TH=SCALE*FLOATF(NB4TH)
C-----SCALING COMPLETE.
C-----CALCULATE COEFFICIENTS FOR FOURIER B
NA1=+NA1ST+NA2ND+NA3RD+NA4TH
NA2=-NA1ST-NA2ND+NA3RD+NA4TH
NA3=-NA1ST+NA2ND-NA3RD+NA4TH
NA4=-NA1ST+NA2ND+NA3RD-NA4TH
NB1=-NB1ST+NB2ND+NB3RD+NB4TH
NB2=+NB1ST-NB2ND+NB3RD+NB4TH
NB3=+NB1ST+NB2ND-NB3RD+NB4TH
NB4=+NB1ST+NB2ND+NB3RD-NB4TH
C-----MODIFY FOURIER COEFFICIENTS ACCORDING TO WHETHER H, K, OR L
C ARE ZERO.
IF(NH)72,73,72
73 NA3=0
NA4=0
NB1=0
NB2=0
72 IF(NK)74,75,74
75 NA2=0
NA4=0
NB1=0
NB3=0
74 IF(NL)76,77,76
77 NA2=0
NA3=0
NB1=0
NB4=0
C-----COEFFICIENTS ARE NOW CALCULATED.
C-----CHECK TO SEE IF H, K, AND L ARE ALL ZERO.
76 IF(NH+NK+NL)12,4,12
4 TYPE 6
WRITE OUTPUT TAPE6,6
STOP 00001
C-----CHECK TO SEE IF ANY H, K, OR L IS NEGATIVE.
12 IF(NH)300,301,301
301 IF(NK)300,302,302
302 IF(NL)300,303,303
300 TYPE 2
WRITE OUTPUT TAPE6,2

```

```

                STOP 00002
C-----CHECK TO SEE IF ANY COEFFICIENT IS TOO LARGE FOR THE
C      OPERATION OF FOURIER B.
      303 IF(NA1-9999)14,14,13
          14 IF(NA2-9999)15,15,13
          15 IF(NA3-9999)16,16,13
          16 IF(NA4-9999)17,17,13
          17 IF(NB1-9999)18,18,13
          18 IF(NB2-9999)19,19,13
          19 IF(NB3-9999)20,20,13
          20 IF(NB4-9999)21,21,13
      13 TYPE 50
          WRITE OUTPUT TAPE6,50
          STOP 00003

C
C-----SELECT CORRECT ARRANGEMENT FOR COEFFICIENTS ACCORDING TO THE
C      VALUE OF ITEM, AND WRITE THEM ON A WORK TAPE.  ITEM CONTROLS
C      THE DIRECTION OF PROJECTION OR SECTIONING, AND THE
C      HANDEDNESS OF THE COORDINATE SYSTEM. (SEE PERMUTATION TABLE
C      FOR XYZ).  IN EACH CASE, THE MAXIMUM VALUE OF H, K, AND L
C      IS DETERMINED, AND CONTROL IS RETURNED TO STATEMENT 40.
C      A NON-ZERO M WILL SEND CONTROL TO STATEMENT 5.
C
      21 GO TO(101,102,103,104,105,106),ITEM
      101 WRITE TAPE 4,NH,NK,NL,NA1,NA2,NA3,NA4,NB1,NB2,NB3,NB4
          MAX11=XMAXOF(NH,MAX11)
          MAX22=XMAXOF(NK,MAX22)
          MAX33=XMAXOF(NL,MAX33)
          GO TO 40
      102 WRITE TAPE 4,NK,NL,NH,NA1,NA4,NA2,NA3,NB1,NB4,NB2,NB3
          MAX11=XMAXOF(NK,MAX11)
          MAX22=XMAXOF(NL,MAX22)
          MAX33=XMAXOF(NH,MAX33)
          GO TO 40
      103 WRITE TAPE 4,NL,NH,NK,NA1,NA3,NA4,NA2,NB1,NB3,NB4,NB2
          MAX11=XMAXOF(NL,MAX11)
          MAX22=XMAXOF(NH,MAX22)
          MAX33=XMAXOF(NK,MAX33)
          GO TO 40
      104 WRITE TAPE 4,NH,NL,NK,NA1,NA2,NA4,NA3,NB1,NB2,NB4,NB3
          MAX11=XMAXOF(NH,MAX11)
          MAX22=XMAXOF(NL,MAX22)
          MAX33=XMAXOF(NK,MAX33)
          GO TO 40
      105 WRITE TAPE 4,NK,NH,NL,NA1,NA3,NA2,NA4,NB1,NB3,NB2,NB4
          MAX11=XMAXOF(NK,MAX11)
          MAX22=XMAXOF(NH,MAX22)
          MAX33=XMAXOF(NL,MAX33)
          GO TO 40
      106 WRITE TAPE 4,NL,NK,NH,NA1,NA4,NA3,NA2,NB1,NB4,NB3,NB2
          MAX11=XMAXOF(NL,MAX11)
          MAX22=XMAXOF(NK,MAX22)
          MAX33=XMAXOF(NH,MAX33)

```



```

      GO TO 40
C
C-----SELECT A HEADING AND WRITE IT.
      5 WRITE OUTPUT TAPE6,54,NCOUNT
      GO TO(501,502,503,504,505,506),ITEM
      501 WRITE OUTPUT TAPE6,61
      GO TO 750
      502 WRITE OUTPUT TAPE6,62
      GO TO 750
      503 WRITE OUTPUT TAPE6,63
      GO TO 750
      504 WRITE OUTPUT TAPE6,64
      GO TO 750
      505 WRITE OUTPUT TAPE6,65
      GO TO 750
      506 WRITE OUTPUT TAPE6,66
      750 ICOUNT=0
C
C *****
C * START SORT OPERATION *
C *****
C
C-----THE MAXIMUM VALUES OF H, K, AND L FOR ALL THE DATA HAVE NOW
C BEEN DETERMINED. UNITY IS ADDED TO THESE VALUES.
      MAXX11=MAX11+1
      MAXX22=MAX22+1
      MAXX33=MAX33+1
C-----SET CERTAIN STORAGE LOCATIONS TO ZERO IN PREPARATION FOR
C SUMMING AND WORKING WITH PARTIALLY FILLED ARRAYS.
      IXX=0
      IYY=0
      IZZ=0
      ITWIN1=0
      ITWIN2=0
      ITWIN3=0
      DO 700 IX=1,MAXX11
700 NN1(IX)=0
      DO 701 IY=1,MAXX22
701 NN2(IY)=0
      DO 702 IZ=1,MAXX33
702 NN3(IZ)=0
C-----GET THREE WORK TAPES READY AND REWIND TAPE 4 WHICH CONTAINS
C THE COEFFICIENTS FOR FOURIER B.
      REWIND 8
      REWIND 7
      REWIND 3
      REWIND 4
C
      LL=0
      DO 160 NNN=1,MAXX33
      MCOUNT=0
C-----PICK OFF VALUES OF THE THIRD MILLER INDEX THAT ARE EQUAL TO
C LL AND WRITE THEM ON WORK TAPE 8. MCOUNT WILL BE THE NUMBER

```

```

C      OF WRITE-OUTS.
200 DO 151 N=1,NCOUNT
    READ TAPE 4, N1,N2,N3,M1,M2,M3,M4,M5,M6,M7,M8
    IF(N3-LL)151,150,151
150 WRITE TAPE 8, N1,N2,N3,M1,M2,M3,M4,M5,M6,M7,M8
    MCOUNT=MCOUNT+1
151 CONTINUE
C-----PICK OFF COMPLETED FOR A PARTICULAR VALUE OF LL.
    REWIND 4
    REWIND 8
C-----INCREMENT LL IN PREPARATION FOR NEXT GO-AROUND.
    LL=LL+1
C-----IF ANY VALUES WERE PICKED OFF, START WORKING WITH 2ND MILLER
C      INDEX. OTHERWISE, GO TO 160 AND START ON NEXT VALUE OF THE
C      THIRD INDEX.
    IF(MCOUNT)250,160,250
C-----STATEMENTS 250 TO 251 ARE ANALOGOUS TO STATEMENTS ABOVE
C      STARTING WITH LL=0 TO 250.
250 KK=0
    DO 159 MMM=1,MAXX22
    JCOUNT=0
201 DO 152 M=1,MCOUNT
    READ TAPE 8, N1,N2,N3,M1,M2,M3,M4,M5,M6,M7,M8
    IF(N2-KK)152,154,152
154 WRITE TAPE 3, N1,N2,N3,M1,M2,M3,M4,M5,M6,M7,M8
    JCOUNT=JCOUNT+1
152 CONTINUE
    REWIND 3
    REWIND 8
    KK=KK+1
    IF(JCOUNT)251,159,251
C-----STATEMENT 251 THRU WRITE TAPE 7 ARE ANALOGOUS TO SOME OF THE
C      STATEMENTS ABOVE.
251 JJ=0
    DO 158 JJJ=1,MAXX11
    DO 155 J=1,JCOUNT
    READ TAPE3,N1,N2,N3,M1,M2,M3,M4,M5,M6,M7,M8
    IF(N1-JJ)610,157,610
157 ICOUNT=ICOUNT+1
    WRITE TAPE 7,N1,N2,N3,M1,M2,M3,M4,M5,M6,M7,M8,ICOUNT
C-----AT THIS TIME ANY ACCIDENTAL DUPLICATION OF MILLER INDICES IN
C      THE INPUT DATA WILL HAVE BEEN SORTED SO AS TO BE SIDE BY
C      SIDE ON TAPE 7. WE NOW CHECK FOR THIS POSSIBLE OCCURANCE.
    IF(N1-ITWIN1)980,981,980
981 IF(N2-ITWIN2)980,982,980
982 IF(N3-ITWIN3)980,983,980
983 TYPE 8
    WRITE OUTPUT TAPE6,8
    STOP 00004
980 ITWIN1=N1
    ITWIN2=N2
    ITWIN3=N3
C-----END OF CHECK ROUTINE.

```

```

C-----IF CARD OUTPUT IS DESIRED, GO TO 400.
      IF(SENSE SWITCH 1)400,401
      400 WRITE OUTPUT TAPE6,56,N1,N2,N3,M1,M2,M3,M4,M5,M6,M7,M8,ICOUNT
          GO TO 156
      401 WRITE OUTPUT TAPE6,57,N1,N2,N3,M1,M2,M3,M4,M5,M6,M7,M8,ICOUNT
C-----CHECK TO SEE IF ANY MILLER INDEX IS ZERO.
C      IF SQ, TURN ON SENSE LIGHT.
      156 IF(N1)800,801,800
          801 SENSE LIGHT 1
          800 IF(N2)802,803,802
          803 SENSE LIGHT 2
          802 IF(N3)804,805,804
          805 SENSE LIGHT 3
C-----CHECKING COMPLETED.
C-----STORE MILLER INDICES IN LOCATIONS ONE HIGHER THAN THE VALUE
C      OF THE INDICES THEMSELVES.
      804 NN1(N1+1)=N1
          NN2(N2+1)=N2
          NN3(N3+1)=N3
      610 CONTINUE
      155 CONTINUE
          JJ=JJ+1
      158 REWIND 3
      159 CONTINUE
      160 CONTINUE
C-----END OF NESTED DO-LOOPS.
      REWIND 3
      REWIND 4
      NSTPCD=-1
      NDUMMY=0
C-----WRITE A DUMMY RECORD ON TAPE 7. THIS RECORD IS THE LAST
C      RECORD ON TAPE 7 AND IS USED BY FOURIER B TO SENSE THE END
C      OF THE FILE.
      WRITE TAPE7,NDUMMY,NSTPCD,NSTPCD,NDUMMY,NDUMMY,NDUMMY,
          INDUMMY,NDUMMY,NDUMMY,NDUMMY,NDUMMY,NDUMMY
      REWIND 7
C-----TAPE 7 IS NOW READY FOR FOURIER B.
C-----IF THERE WAS A FIRST MILLER INDEX EQUAL TO ZERO (SENSE LIGHT
C      1 TURNED ON) WRITE IT ON TAPE 3.
      IF(SENSE LIGHT 1)851,852
      851 WRITE TAPE 3,NN1(1)
          IXX=1
C-----WRITE ALL REMAINING NON-ZERO FIRST INDICES ON TAPE 3.
      852 DO 850 IX=2,MAXX11
          IF(NN1(IX))856,850,856
      856 WRITE TAPE 3,NN1(IX)
          IXX=IXX+1
      850 CONTINUE
C-----IXX IS NOW THE TOTAL NUMBER OF DIFFERENT VALUES OF THE FIRST
C      MILLER INDEX.
C-----STATEMENTS THRU 860 ARE ANALOGOUS TO THE STATEMENTS FROM
C      IF(SENSE LIGHT 1)851,852 TO STATEMENT 850.
          IF(SENSE LIGHT 2)861,862

```

```

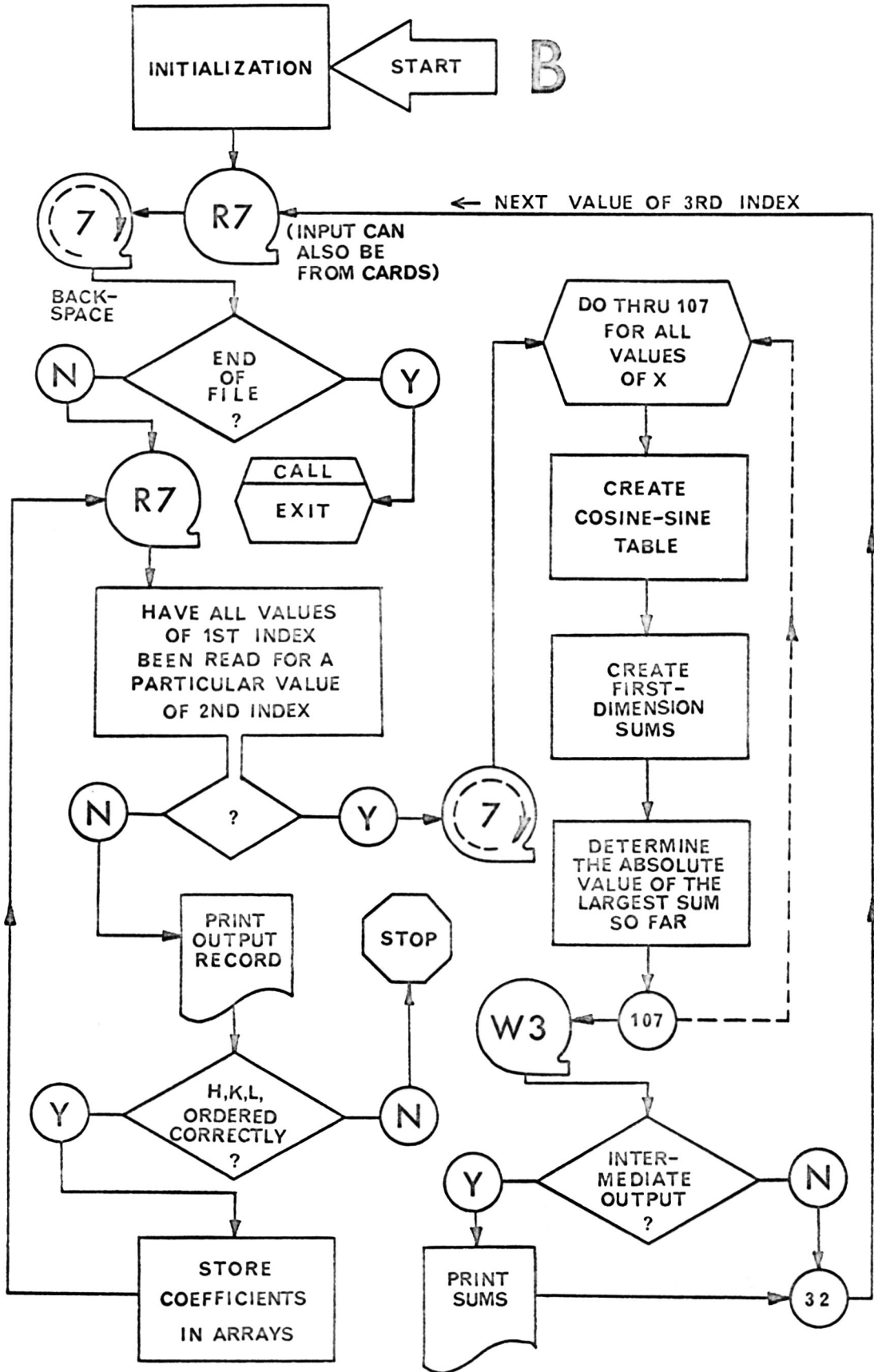
861 WRITE TAPE 3,NN2(1)
    IYY=1
862 DO 860 IY=2,MAXX22
    IF(NN2(IY))866,860,866
866 WRITE TAPE 3,NN2(IY)
    IYY=IYY+1
860 CONTINUE
C-----STATEMENTS THRU 870 ARE ANALOGOUS TO THE STATEMENTS FROM
C    IF(SENSE LIGHT 1)851,852 TO STATEMENT 850.
    IF(SENSE LIGHT 3)871,872
871 WRITE TAPE 3,NN3(1)
    IZZ=1
872 DO 870 IZ=2,MAXX33
    IF(NN3(IZ))876,870,876
876 WRITE TAPE3,NN3(IZ)
    IZZ=IZZ+1
870 CONTINUE
    REWIND 3
    WRITE TAPE 4,IXX,IYY,IZZ
C-----IF CARD OUTPUT IS DESIRED GO TO 880.
    IF(SENSE SWITCH 1)880,881
880 WRITE OUTPUT TAPE6,69,IXX,IYY,IZZ
    GO TO 882
881 WRITE OUTPUT TAPE6,70,IXX,IYY,IZZ
C-----IF CARD OUTPUT IS DESIRED EXECUTE 883 THRU 887.  OTHERWISE
C    EXECUTE 884 THRU 897.
882 IF(SENSE SWITCH 1)883,884
883 DO 885 IX=1,IXX
    READ TAPE 3,NN1(IX)
    WRITE TAPE4,NN1(IX)
885 WRITE OUTPUT TAPE6,67,NN1(IX)
    DO 886 IY=1,IYY
    READ TAPE3,NN2(IY)
    WRITE TAPE4,NN2(IY)
886 WRITE OUTPUT TAPE6,67,NN2(IY)
    DO 887 IZ=1,IZZ
    READ TAPE3,NN3(IZ)
    WRITE TAPE4,NN3(IZ)
887 WRITE OUTPUT TAPE6,67,NN3(IZ)
    GO TO 900
884 DO 895 IX=1,IXX
    READ TAPE3,NN1(IX)
    WRITE TAPE4,NN1(IX)
895 WRITE OUTPUT TAPE6,68,NN1(IX)
    DO 896 IY=1,IYY
    READ TAPE 3,NN2(IY)
    WRITE TAPE4,NN2(IY)
896 WRITE OUTPUT TAPE6,68,NN2(IY)
    DO 897 IZ=1,IZZ
    READ TAPE3,NN3(IZ)
    WRITE TAPE4,NN3(IZ)
897 WRITE OUTPUT TAPE6,68,NN3(IZ)
900 CONTINUE

```

```
C
C *****
C * END SORT OPERATION *
C *****
C
    REWIND 3
    REWIND 4
C-----TAPE 7 NOW CONTAINS THE COEFFICIENTS AND TAPE 4 CONTAINS THE
C    TOTAL NUMBER OF DIFFERENT VALUES OF EACH INDEX, AND LISTS OF
C    ALL OF THE DISTINCT INDICES.
    CALL EXIT
    STOP
    END
```

EXPLANATION OF PLATE XV

This plate shows the logical steps and flow of information within program link B. The diagram is the same for link B_{proj} .



EXPLANATION OF PLATE XVI

This plate (next 10 pages) is the FORTRAN II symbolic coding for program links B and B_{proj}.

PLATE XVI

102

BOP FOURIER B 08 08

C
C WRITTEN 3/14/64 HOLLIS
C MODIFIED JULY 20, 1964 TO ACCEPT OPTIONAL TAPE INPUT FROM
C FOURIER A.
C MODIFIED AUGUST 1, 1964 TO OPERATE WITHOUT NH TABLE.
C
C THIS PROGRAM IS TO BE PRECEDED BY FOURIER A AND FOLLOWED BY
C FOURIER C.
C MINX = MINIMUM VALUE OF X
C MAXX = MAXIMUM VALUE OF X
C INCX = INCREMENT OF X (120THS OF UNIT CELL)
C MINY = MINIMUM VALUE OF Y
C MAXY = MAXIMUM VALUE OF Y
C INCY = INCREMENT OF Y (120THS OF UNIT CELL)
C MINZ = MINIMUM VALUE OF Z
C MAXZ = MAXIMUM VALUE OF Z
C INCZ = INCREMENT OF Z (120THS OF UNIT CELL)
C -----NOTE... MINX, MAXX, MINY, ETC. BECOME MINX+1, MAXX+1,
C MINY+1, ETC., AFTER THE PROGRAM HAS BEGUN IN ORDER TO
C SATISFY DO LOOP REQUIREMENTS.
C MVALUE = A TABLE OF 150 COSINES, COVERING 1 1/4 CIRCLES. THIS
C DIVIDES THE CIRCLE INTO 120 PARTS, WITH ONE COSINE VALUE
C EVERY 3 DEGREES. SINE VALUES ARE PICKED OUT OF THE TABLE 90
C DEGREES AFTER EACH COSINE VALUE, OR 30 TABLE ENTRIES FORWARD.
C FOURIER COEFFICIENTS...
C NA1 = +A(+H,+K,+L) + A(-H,+K,+L) + A(+H,-K,+L) + A(+H,+K,-L)
C NA2 = -A(+H,+K,+L) - A(-H,+K,+L) + A(+H,-K,+L) + A(+H,+K,-L)
C NA3 = -A(+H,+K,+L) + A(-H,+K,+L) - A(+H,-K,+L) + A(+H,+K,-L)
C NA4 = -A(+H,+K,+L) + A(-H,+K,+L) + A(+H,-K,+L) - A(+H,+K,-L)
C NB1 = -B(+H,+K,+L) + B(-H,+K,+L) + B(+H,-K,+L) + B(+H,+K,-L)
C NB2 = +B(+H,+K,+L) - B(-H,+K,+L) + B(+H,-K,+L) + B(+H,+K,-L)
C NB3 = +B(+H,+K,+L) + B(-H,+K,+L) - B(+H,-K,+L) + B(+H,+K,-L)
C NB4 = +B(+H,+K,+L) + B(-H,+K,+L) + B(+H,-K,+L) - B(+H,+K,-L)
C THE FOURIER COEFFICIENTS ARE CALCULATED BY PROGRAM FOURIER A.
C NUMH = THE NO. OF DIFFERENT VALUES OF THE 1ST MILLER INDEX.
C NUMK = THE NO. OF DIFFERENT VALUES OF THE 2ND MILLER INDEX.
C NUML = THE NO. OF DIFFERENT VALUES OF THE 3RD MILLER INDEX.
C MAXSUM = ABSOLUTE VALUE OF THE LARGEST TERM COMPUTED.
C SENSE SWITCH 1 ON FOR PRINT OUT OF JSUM1,JSUM2,JSUM3,JSUM4,
C OFF TO IGNORE PRINT OUT.
C SENSE SWITCH 2 ON TO ACCEPT TAPE INPUT FROM FOURIER A.
C OFF TO ACCEPT CARD INPUT.
C
C THE ORDER OF THE CARDS AT OBJECT TIME IS AS FOLLOWS...
C
C (1) IDENTIFICATION CARD
C (2) SENSE SWITCH SETTINGS CARD (IF ONE).
C (3) OBJECT DECK FOURIER B.
C (4) A BLANK CARD.
C (5) CARD CONTAINING MINX,MAXX,...INCZ, PER FORMAT 15
C (6) THE MVALUE TABLE DECK (150 CARDS), PER FORMAT 16.
C IF SENSE SWITCH 2 IS ON, OMIT (7) THRU (12)

C INCLUDE (7) THRU (12) ONLY IF SENSE SWITCH 2 IS OFF.
 C (7) CARD CONTAINING NUMH, NUMK, NUML, PER FORMAT 17.
 C (8) DECK OF ALL DIFFERENT VALUES OF FIRST MILLER INDEX
 C PER FORMAT 18. (NUMH CARDS)
 C (9) DECK OF ALL DIFFERENT VALUES OF 2ND MILLER INDEX
 C PER FORMAT 18. (NUMK CARDS)
 C (10) DECK OF ALL DIFFERENT VALUES OF THIRD MILLER INDEX
 C PER FORMAT 18. (NUML CARDS)
 C (11) DECK OF MILLER INDICES AND FOURIER COEFFICIENTS,
 C PER FORMAT 1, ORDERED AS FOLLOWS...
 C (A) THE THIRD MILLER INDICES (COLS. 7-9) MUST
 C BE AN UNBROKEN ASCENDING SEQUENCE.
 C (B) THE SECOND MILLER INDICES (COLS. 4-6) MUST
 C BE AN ASCENDING SEQUENCE WITHIN EACH BLOCK
 C OF CONSTANT THIRD MILLER INDICES.
 C (C) THE FIRST MILLER INDICES (COLS. 1-3) MUST
 C BE AN ASCENDING SEQUENCE WITHIN EACH BLOCK
 C OF CONSTANT SECOND MILLER INDICES.
 C (12) A CARD WITH -1 PUNCHED IN COLS 5-6, AND -1 PUNCHED
 C IN COLS 8-9.
 C AT THE COMPLETION OF THIS PROGRAM, TAPE 3 WILL CONTAIN THE
 C FIRST DIMENSION SUMS AND TAPE 4 WILL CONTAIN DATA NECESSARY
 C FOR THE OPERATION OF FOURIER C.
 C

DIMENSION JSUM1(121),JSUM2(121),JSUM3(121),JSUM4(121)
 DIMENSION NH(100),NK(20),NL(20)
 DIMENSION NA1(100),NA2(100),NA3(100),NA4(100)
 DIMENSION NB1(100),NB2(100),NB3(100),NB4(100)
 DIMENSION NCH(100),NSH(100)
 DIMENSION MVALUE(150)
 C *****IMPORTANT*****IMPORTANT*****IMPORTANT*****IMPORTANT*****
 C * MVALUE, NK, AND NL MUST BE DIMENSIONED EXACTLY AS THEY *
 C * ARE DIMENSIONED IN PROGRAM FOURIER C. *
 C *****IMPORTANT*****IMPORTANT*****IMPORTANT*****IMPORTANT*****
 1 FORMAT(3I3,8(3X,I5),2X,I5)
 13 FORMAT(1X,3I3,8(3X,I5),2X,I5)
 14 FORMAT(3X,2I3)
 15 FORMAT(9(I3,3X))
 16 FORMAT(I6)
 17 FORMAT(3I3)
 18 FORMAT(I3)
 19 FORMAT(5(I4,3X))
 20 FORMAT(1X,14HMINIMUM X = ,I3/1X,14HMAXIMUM X = ,I3/
 1 1X,14HINCREMENT X = ,I3/1X,14HMINIMUM Y = ,I3/
 2 1X,14HMAXIMUM Y = ,I3/1X,14HINCREMENT Y = ,I3/
 3 1X,14HMINIMUM Z = ,I3/1X,14HMAXIMUM Z = ,I3/
 4 1X,14HINCREMENT Z = ,I3)
 21 FORMAT(1H1,35HQUANTITIES USED IN THIS CALCULATION//)
 22 FORMAT(1H0,19HINTERMEDIATE OUTPUT/1H0,3H MX,3X,9HJSUM1(MX),
 1 3X,9HJSUM2(MX),3X,9HJSUM3(MX),3X,9HJSUM4(MX),9X,3HNK1)
 23 FORMAT(1X,I3,I12,I12,I12,I12,I12)
 24 FORMAT(1H0,I12)
 25 FORMAT(1X,44HDATA CARDS OUT OF ORDER -- CORRECT AND RERUN)

```

        REWIND 3
        REWIND 4
        REWIND 7
        MAXSUM=0
C-----DEFINE RANGE TO BE COVERED, AND INCREMENTS
        READ INPUT TAPES,15,MINX,MAXX,INCX,MINY,MAXY,INCY,MINZ,MAXZ,
        1 INCZ
C-----READ COSINE TABLE
        READ INPUT TAPES,16,(MVALUE(M),M=1,150)
C-----IF TAPE INPUT IS DESIRED, TABLES ARE READ FROM TAPE 4.
C        OTHERWISE, INPUT IS FROM CARDS.
        IF(SENSE SWITCH 2)600,601
        600 READ TAPE 4,NUMH,NUMK,NUML
            DO 602 M1=1,NUMH
        602 READ TAPE 4, NH(M1)
            DO 603 M2=1,NUMK
        603 READ TAPE 4, NK(M2)
            DO 604 M3=1,NUML
        604 READ TAPE 4, NL(M3)
            REWIND 4
            GO TO 605
        601 READ INPUT TAPES,17,NUMH,NUMK,NUML
            READ INPUT TAPES,18,(NH(M1),M1=1,NUMH)
            READ INPUT TAPES,18,(NK(M2),M2=1,NUMK)
            READ INPUT TAPES,18,(NL(M3),M3=1,NUML)
        605 WRITE OUTPUT TAPE6,21
            WRITE OUTPUT TAPE6,20,MINX,MAXX,INCX,MINY,MAXY,INCY,MINZ,
            1 MAXZ,INCZ
C-----ADD UNITY TO RANGES.
        MINX=MINX+1
        MAXX=MAXX+1
        MINY=MINY+1
        MAXY=MAXY+1
        MINZ=MINZ+1
        MAXZ=MAXZ+1
        NCOUNT=0
C-----FOR TAPE INPUT GO TO 610, CARD INPUT GO TO 611.
C-----STATEMENT 32 IS THE STARTING POINT OF THE CYCLE OVER K.
        32 IF(SENSE SWITCH 2)610,611
C-610-READ A RECORD TO DETERMINE NK1,NL1.
        610 READ TAPE 7, NNN1,NK1,NL1,NNN2,NNN3,NNN4,NNN5,NNN6,NNN7,
        1 NNN8,NNN9,NNN10
            BACKSPACE 7
            GO TO 612
C-611-READ A CARD TO DETERMINE NK1, NL1.
        611 READ INPUT TAPES,14,NK1,NL1
            BACKSPACE 5
C-----IF NL1 IS NEGATIVE, THIS IS THE LAST RECORD.
        612 IF(NL1)33,35,35
            35 J=0
C-----FOR TAPE INPUT GO TO 613, CARD INPUT GO TO 614.
        34 IF(SENSE SWITCH 2)613,614
        613 READ TAPE7,MH,MK,ML,MA1,MA2,MA3,MA4,MB1,MB2,MB3,MB4,ICOUNT

```

```

        GO TO 615
    614 READ INPUT TAPES,1,MH,MK,ML,MA1,MA2,MA3,MA4,MB1,MB2,MB3,MB4,
        1 ICCOUNT
C-----IF MK CHANGES VALUE, ALL OF THE COEFFICIENTS FOR A GIVEN K
C        HAVE BEEN READ.
    615 IF(MK-NK1)31,30,31
C-----WRITE AN OUTPUT RECORD.
    30 WRITE OUTPUT TAPE6,13,MH,MK,ML,MA1,MA2,MA3,MA4,MB1,MB2,MB3,
        1 MB4,ICOUNT
C-----CHECK TO SEE IF CARDS ARE IN CORRECT ORDER.
        IF(ICOUNT-(NCOUNT+1))620,621,620
    620 TYPE 25
        WRITE OUTPUT TAPE6,25
        STOP 00005
    621 NCOUNT=ICOUNT
C-----REDEFINE NK1.
        NK1=MK
        J=J+1
C-----ASSIGN STORAGE LOCATIONS TO THE COEFFICIENTS.
        NH(J)=MH
        NA1(J)=MA1
        NA2(J)=MA2
        NA3(J)=MA3
        NA4(J)=MA4
        NB1(J)=MB1
        NB2(J)=MB2
        NB3(J)=MB3
        NB4(J)=MB4
        GO TO 34
    31 JMAX=J
C-----MK HAS CHANGED VALUE. BACKSPACE ONE RECORD TO PREPARE
C        FOR NEXT INPUT CYCLE.
        IF(SENSE SWITCH 2)700,701
    700 BACKSPACE 7
        GO TO 702
    701 BACKSPACE 5
C-----IF INTERMEDIATE OUTPUT IS DESIRED, PRINT COLUMN HEADINGS.
    702 IF(SENSE SWITCH 1)500,501
    500 WRITE OUTPUT TAPE6,22
C *****
C * BEGINNING OF DO LOOP OVER X. *
C *****
    501 DO 50 MX=MINX,MAXX,INCX
        NX=MX-1
C-----CALCULATE ARGUMENTS AND LOOK UP COSINES AND SINES NECESSARY
C        FOR THIS INPUT CYCLE.
        DO 10 J=1,JMAX
            NARG=NH(J)*NX
            NARG1=NARG/120
            NARG2=NARG-120*NARG1
            IF(NARG2)300,301,300
    301 NARG2=120
    300 NCH(J)=MVALUE(NARG2)

```

```

      10 NSH(J)=MVALUE(NARG2+30)
C-----TABLE LOOK UP COMPLETED.
C-----SET STORAGE LOCATIONS TO ZERO IN PREPARATION FOR SUMMING.
      JSUMT1=0
      JSUMT2=0
      JSUMT3=0
      JSUMT4=0
C *****
C *   THE SUMMATION OVER H BEGINS HERE *
C *****
      DO 107 J=1,JMAX
C-----REMCVE SUBSCRIPTS ON NCH AND NSH TO INCREASE SPEED.
      NC=NCH(J)
      NS=NSH(J)
      JT1=(NA1(J)*NC+NB2(J)*NS)/100
      JSUMT1=JSUMT1+JT1
      JT2=(NB3(J)*NC+NA4(J)*NS)/100
      JSUMT2=JSUMT2+JT2
      JT3=(NB4(J)*NC+NA3(J)*NS)/100
      JSUMT3=JSUMT3+JT3
      JT4=(NA2(J)*NC+NB1(J)*NS)/100
107 JSUMT4=JSUMT4+JT4
C *****
C *   THE SUMMATION OVER H ENDS HERE *
C *****
C-----THE ABSOLUTE VALUE OF THE LARGEST SUMMATION IS NOW
C   DETERMINED.
C-----JSUMT1,..., JSUMT4, ARE STORED IN ARRAYS.
      NN=XABSF(JSUMT1)
      IF(MAXSUM-NN)60,61,61
60 MAXSUM=NN
61 JSUM1(MX)=JSUMT1
      NN=XABSF(JSUMT2)
      IF(MAXSUM-NN)62,63,63
62 MAXSUM=NN
63 JSUM2(MX)=JSUMT2
      NN=XABSF(JSUMT3)
      IF(MAXSUM-NN)64,65,65
64 MAXSUM=NN
65 JSUM3(MX)=JSUMT3
      NN=XABSF(JSUMT4)
      IF(MAXSUM-NN)66,67,67
66 MAXSUM=NN
67 JSUM4(MX)=JSUMT4
C-----DETERMINATION OF MAXSUM ACCOMPLISHED.
      50 CONTINUE
C *****
C *   END OF DO LOOP CVER X. *
C *****
C-----FIRST INDEX SUMMATION HAS NOW BEEN COMPLETED FOR ALL VALUES
C   OF X, AND A PARTICULAR VALUE OF K. WRITE SUMS ON TAPE 3.
      WRITE TAPE3,(JSUM1(MX),JSUM2(MX),JSUM3(MX),JSUM4(MX),NK1,
1 MX=MINX,MAXX,INCX)

```

```
C-----IF INTERMEDIATE OUTPUT IS DESIRED, PRINT SUMS.
      IF(SENSE SWITCH 1)40,32
      40 WRITE OUTPUT TAPE6,23,(MX,JSUM1(MX),JSUM2(MX),JSUM3(MX),
      1 JSUM4(MX),NK1, MX=MINX,MAXX,INCX)
C-----GO TO 32 FOR DATA ASSOCIATED WITH THE NEXT VALUE OF K.
      GO TO 32
C-----THE DUMMY RECORD WRITTEN BY FOURIER A HAS BEEN READ. WRITE A
C      DUMMY RECORD ON TAPE 3 FOR FOURIER C.
      33 JSUMT1=0
      JSUMT2=0
      JSUMT3=0
      JSUMT4=0
      NK1=-1
      WRITE TAPE 3,(JSUMT1,JSUMT2,JSUMT3,JSUMT4,NK1,
      1 MX=MINX,MAXX,INCX)
      REWIND 3
      REWIND 4
      REWIND 7
C-----WRITE RANGES, COSINE TABLE, ETC., ON TAPE 4.
      WRITE TAPE 4,MINX,MAXX,INCX,MINY,MAXY,INCY,MINZ,MAXZ,INCZ,
      1 MVALUE,NUMH,NUMK,NUML,NK,NL,MAXSUM
      REWIND 4
      WRITE OUTPUT TAPE6,24,MAXSUM
      CALL EXIT
      STOP
      END
```

```

          BOP FOUR B PR    08    08
C ***** FOURIER B PROJECTION LINK *****
C WRITTEN 2/18/65 HOLLIS
C-----FOR COMMENTS ON VARIABLES AND THE ORDER OF THE CARDS AT
C OBJECT TIME, SEE PROGRAM FOURIER B.
  DIMENSION JSUM1(121),JSUM2(121)
  DIMENSION NH(100),NK(20),NL(20)
  DIMENSION NA1(100),NA2(100),NA3(100),NA4(100)
  DIMENSION NB1(100),NB2(100),NB3(100),NB4(100)
  DIMENSION NCH(100),NSH(100)
  DIMENSION MVALUE(150)
C *****IMPORTANT*****IMPORTANT*****IMPORTANT*****IMPORTANT*****
C * MVALUE, NK, AND NL MUST BE DIMENSIONED EXACTLY AS THEY *
C * ARE DIMENSIONED IN PROGRAM FOURIER C. *
C *****IMPORTANT*****IMPORTANT*****IMPORTANT*****IMPORTANT*****
  1 FORMAT(3I3,8(3X,I5),2X,I5)
 13 FORMAT(1X,3I3,8(3X,I5),2X,I5)
 14 FORMAT(3X,2I3)
 15 FORMAT(9(I3,3X))
 16 FORMAT(I6)
 17 FORMAT(3I3)
 18 FORMAT(I3)
 19 FORMAT(5(I4,3X))
 20 FORMAT(1X,14HMINIMUM X = ,I3/1X,14HMAXIMUM X = ,I3/
 1 1X,14HINCREMENT X = ,I3/1X,14HMINIMUM Y = ,I3/
 2 1X,14HMAXIMUM Y = ,I3/1X,14HINCREMENT Y = ,I3/
 3 1X,14HMINIMUM Z = ,I3/1X,14HMAXIMUM Z = ,I3/
 4 1X,14HINCREMENT Z = ,I3)
 21 FORMAT(1H1,35HQUANTITIES USED IN THIS CALCULATION//)
 22 FORMAT(1H0,19HINTERMEDIATE OUTPUT/1H0,3H MX,3X,9HJSUM1(MX),
 1 3X,9HJSUM2(MX),9X,3HNK1)
 23 FORMAT(1X,I3,I12,I12,I12)
 24 FORMAT(1H0,I12)
 25 FORMAT(1X,44HDATA CARDS OUT OF ORDER -- CORRECT AND RERUN)
  REWIND 3
  REWIND 4
  REWIND 7
  MAXSUM=0
C-----DEFINE RANGE TO BE COVERED, AND INCREMENTS
  READ INPUT TAPES,15,MINX,MAXX,INCX,MINY,MAXY,INCY,MINZ,MAXZ,
  1 INCZ
C-----READ COSINE TABLE
  READ INPUT TAPES,16,(MVALUE(M),M=1,150)
C-----IF TAPE INPUT IS DESIRED, TABLES ARE READ FROM TAPE 4.
C OTHERWISE, INPUT IS FROM CARDS.
  IF(SENSE SWITCH 2)600,601
 600 READ TAPE 4,NUMH,NUMK,NUML
  DO 602 M1=1,NUMH
 602 READ TAPE 4, NH(M1)
  DO 603 M2=1,NUMK
 603 READ TAPE 4, NK(M2)
  DO 604 M3=1,NUML
 604 READ TAPE 4, NL(M3)

```

```

REWIND 4
GO TO 605
601 READ INPUT TAPE5,17,NUMH,NUMK,NUML
    READ INPUT TAPE5,18,(NH(M1),M1=1,NUMH)
    READ INPUT TAPE5,18,(NK(M2),M2=1,NUMK)
    READ INPUT TAPE5,18,(NL(M3),M3=1,NUML)
605 WRITE OUTPUT TAPE6,21
    WRITE OUTPUT TAPE6,20,MINX,MAXX,INCX,MINY,MAXY,INCY,MINZ,
      1 MAXZ,INCZ
C-----ADD UNITY TO RANGES.
    MINX=MINX+1
    MAXX=MAXX+1
    MINY=MINY+1
    MAXY=MAXY+1
    MINZ=MINZ+1
    MAXZ=MAXZ+1
    NCOUNT=0
C-----FOR TAPE INPUT GO TO 610, CARD INPUT GO TO 611.
C-----STATEMENT 32 IS THE STARTING POINT OF THE CYCLE OVER K.
    32 IF(SENSE SWITCH 2)610,611
C-610-READ A RECORD TO DETERMINE NK1,NL1.
    610 READ TAPE 7, NNN1,NK1,NL1,NNN2,NNN3,NNN4,NNN5,NNN6,NNN7,
      1 NNN8,NNN9,NNN10
    BACKSPACE 7
    GO TO 612
C-611-READ A CARD TO DETERMINE NK1, NL1.
    611 READ INPUT TAPE5,14,NK1,NL1
    BACKSPACE 5
C-----IF NL1 IS NEGATIVE, THIS IS THE LAST RECORD.
    612 IF(NL1)33,35,35
      35 J=0
C-----FOR TAPE INPUT GO TO 613, CARD INPUT GO TO 614.
    34 IF(SENSE SWITCH 2)613,614
    613 READ TAPE7,MH,MK,ML,MA1,MA2,MA3,MA4,MB1,MB2,MB3,MB4,ICOUNT
      GO TO 615
    614 READ INPUT TAPE5,1,MH,MK,ML,MA1,MA2,MA3,MA4,MB1,MB2,MB3,MB4,
      1 ICOUNT
C-----IF MK CHANGES VALUE, ALL OF THE COEFFICIENTS FOR A GIVEN K
C    HAVE BEEN READ.
    615 IF(MK-NK1)31,30,31
C-----WRITE AN OUTPUT RECORD.
    30 WRITE OUTPUT TAPE6,13,MH,MK,ML,MA1,MA2,MA3,MA4,MB1,MB2,MB3,
      1 MB4,ICOUNT
C-----CHECK TO SEE IF CARDS ARE IN CORRECT ORDER.
    IF(ICOUNT-(NCOUNT+1))620,621,620
    620 TYPE 25
      WRITE OUTPUT TAPE6,25
      STOP 00005
    621 NCOUNT=ICOUNT
C-----REDEFINE NK1.
    NK1=MK
    J=J+1
C-----ASSIGN STORAGE LOCATIONS TO THE COEFFICIENTS.

```



```

NH(J)=MH
NA1(J)=MA1
NA2(J)=MA2
NA3(J)=MA3
NA4(J)=MA4
NB1(J)=MB1
NB2(J)=MB2
NB3(J)=MB3
NB4(J)=MB4
GO TO 34
31 JMAX=J
C-----MK HAS CHANGED VALUE. BACKSPACE ONE RECORD TO PREPARE
C FOR NEXT INPUT CYCLE.
IF(SENSE SWITCH 2)700,701
700 BACKSPACE 7
GO TO 702
701 BACKSPACE 5
C-----IF INTERMEDIATE OUTPUT IS DESIRED, PRINT COLUMN HEADINGS.
702 IF(SENSE SWITCH 1)500,501
500 WRITE OUTPUT TAPE6,22
C *****
C * BEGINNING OF DO LOOP OVER X. *
C *****
501 DO 50 MX=MINX,MAXX,INCX
NX=MX-1
C-----CALCULATE ARGUMENTS AND LOOK UP COSINES AND SINES NECESSARY
C FOR THIS INPUT CYCLE.
DO 10 J=1,JMAX
NARG=NH(J)*NX
NARG1=NARG/120
NARG2=NARG-120*NARG1
IF(NARG2)300,301,300
301 NARG2=120
300 NCH(J)=MVALUE(NARG2)
10 NSH(J)=MVALUE(NARG2+30)
C-----TABLE LOOK UP COMPLETED.
C-----SET STORAGE LOCATIONS TO ZERO IN PREPARATION FOR SUMMING.
JSUMT1=0
JSUMT2=0
C *****
C * THE SUMMATION OVER H BEGINS HERE *
C *****
DO 107 J=1,JMAX
C-----REMOVE SUBSCRIPTS ON NCH AND NSH TO INCREASE SPEED.
NC=NCH(J)
NS=NSH(J)
JT1=(NA1(J)*NC+NB2(J)*NS)/100
JSUMT1=JSUMT1+JT1
JT2=(NB3(J)*NC+NA4(J)*NS)/100
107 JSUMT2=JSUMT2+JT2
C *****
C * THE SUMMATION OVER H ENDS HERE *
C *****

```

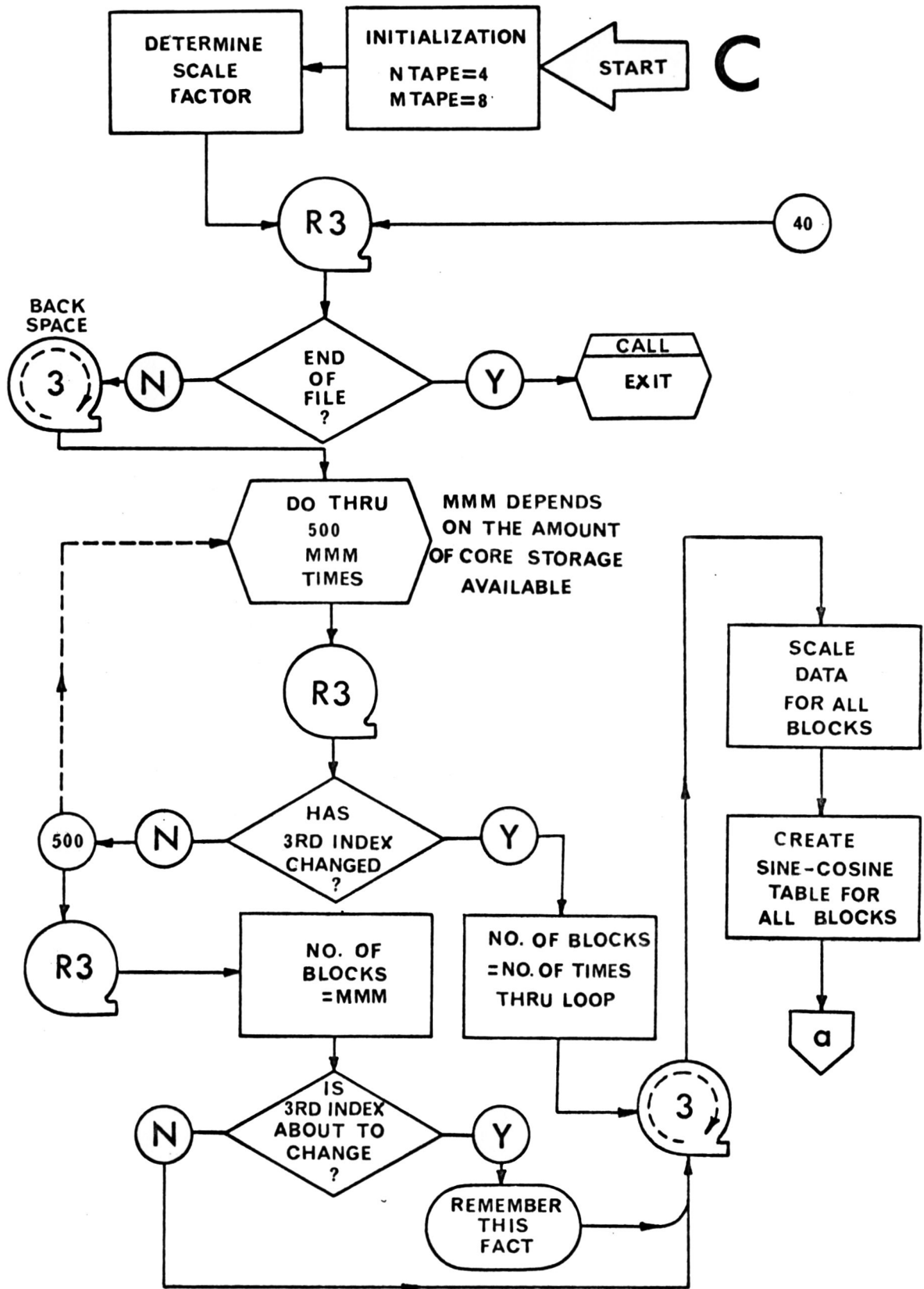
```

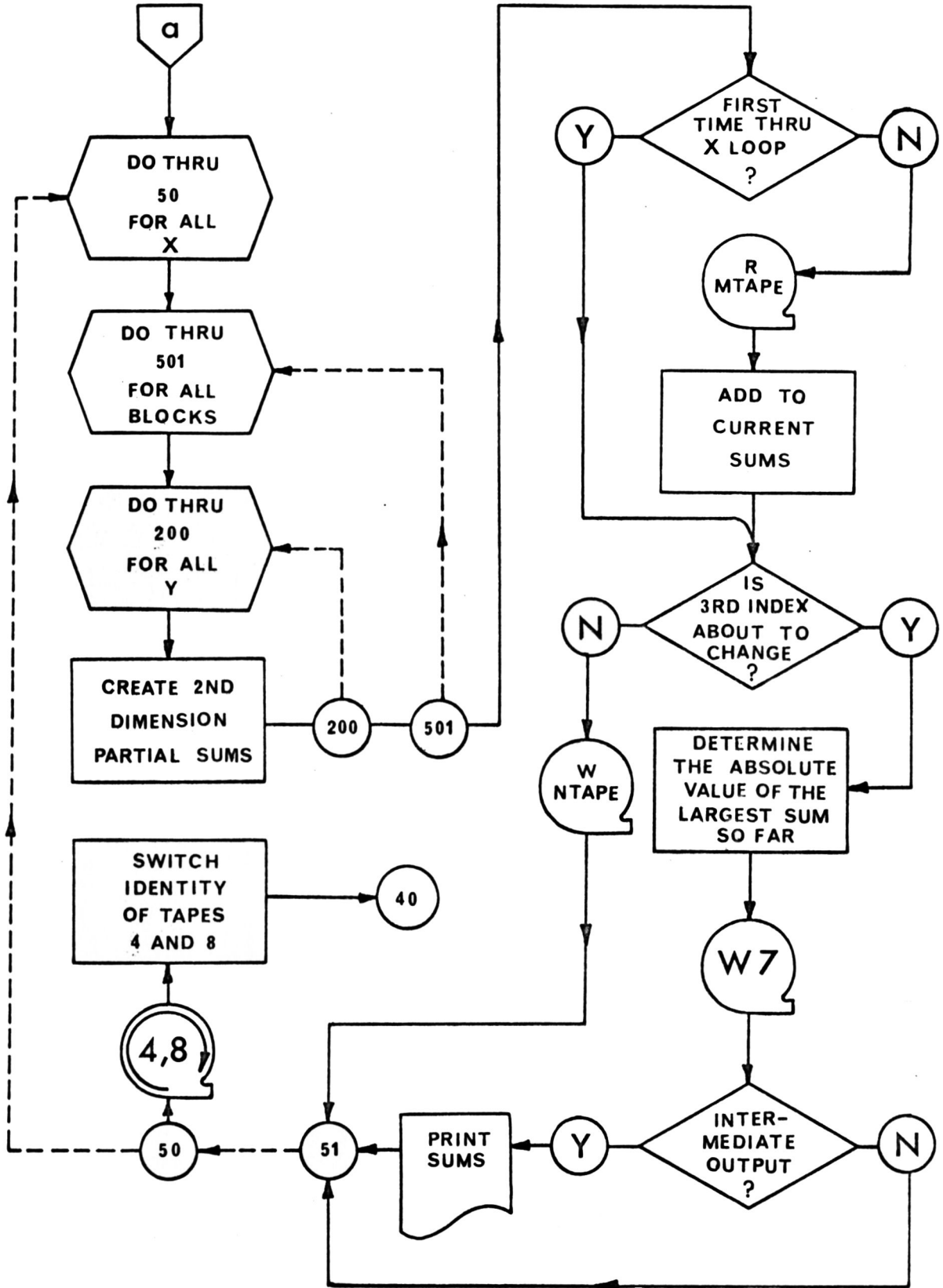
C-----THE ABSOLUTE VALUE OF THE LARGEST SUMMATION IS NOW
C   DETERMINED.
C-----JSUMT1,JSUMT2 ARE STORED IN ARRAYS.
      NN=XABSF(JSUMT1)
      IF(MAXSUM-NN)60,61,61
  60 MAXSUM=NN
  61 JSUM1(MX)=JSUMT1
      NN=XABSF(JSUMT2)
      IF(MAXSUM-NN)62,63,63
  62 MAXSUM=NN
  63 JSUM2(MX)=JSUMT2
C-----DETERMINATION OF MAXSUM ACCOMPLISHED.
  50 CONTINUE
C *****
C *   END OF DO LOOP OVER X.                               *
C *****
C-----FIRST INDEX SUMMATION HAS NOW BEEN COMPLETED FOR ALL VALUES
C   OF X, AND A PARTICULAR VALUE OF K. WRITE SUMS ON TAPE 3.
      WRITE TAPE3,(JSUM1(MX),JSUM2(MX),NK1,
  1 MX=MINX,MAXX,INCX)
C-----IF INTERMEDIATE OUTPUT IS DESIRED, PRINT SUMS.
      IF(SENSE SWITCH 1)40,32
  40 WRITE OUTPUT TAPE6,23,(MX,JSUM1(MX),JSUM2(MX),NK1,
  1 MX=MINX,MAXX,INCX)
C-----GO TO 32 FOR DATA ASSOCIATED WITH THE NEXT VALUE OF K.
      GO TO 32
C-----THE DUMMY RECORD WRITTEN BY FOURIER A HAS BEEN READ. WRITE A
C   DUMMY RECORD ON TAPE 3 FOR FOURIER C.
  33 JSUMT1=0
      JSUMT2=0
      NK1=-1
      WRITE TAPE 3,(JSUMT1,JSUMT2,NK1,
  1 MX=MINX,MAXX,INCX)
      REWIND 3
      REWIND 4
      REWIND 7
C-----WRITE RANGES, COSINE TABLE, ETC., ON TAPE 4.
      WRITE TAPE 4,MINX,MAXX,INCX,MINY,MAXY,INCY,MINZ,MAXZ,INCZ,
  1 MVALUE,NUMH,NUMK,NUML,NK,NL,MAXSUM
      REWIND 4
      WRITE OUTPUT TAPE6,24,MAXSUM
      CALL EXIT
      STOP
      END

```

EXPLANATION OF PLATE XVII

This plate (next two pages) shows the logical steps and flow of information within program link C. The diagram is the same for link CD_{proj}. The pentagonal boxes carry the program flow from page to page.





EXPLANATION OF PLATE XVIII

This plate (next 10 pages) is the FORTRAN II symbolic coding for program links C and CD_{proj}.

PLATE XVIII

116

```

C          BOP  FCURIER C    08    08
C ***** FOURIER C (KSUM) *****
C
C WRITTEN 3/14/64                                HOLLIS
C
C THIS PROGRAM IS TO BE PRECEDED BY FOURIER B AND FOLLOWED BY
C FOURIER D.
C MINX = MINIMUM VALUE OF X.
C MAXX = MAXIMUM VALUE OF X.
C INCX = INCREMENT OF X (120THS OF UNIT CELL)
C MINY = MINIMUM VALUE OF Y.
C MAXY = MAXIMUM VALUE OF Y.
C INCY = INCREMENT OF Y (120THS OF UNIT CELL)
C MINZ = MINIMUM VALUE OF Z.
C MAXZ = MAXIMUM VALUE OF Z.
C INCZ = INCREMENT OF Z (120THS OF UNIT CELL)
C -----NOTE... MINX, MAXX, MINY, ETC. BECOME MINX+1, MAXX+1,
C          MINY+1, ETC., AFTER THE PROGRAM HAS BEGUN IN ORDER TO
C          SATISFY DO LOOP REQUIREMENTS.
C MVALUE = A TABLE OF 150 COSINES, COVERING 1 1/4 CIRCLES. THIS
C DIVIDES THE CIRCLE INTO 120 PARTS, WITH ONE COSINE VALUE
C EVERY 3 DEGREES. SINE VALUES ARE PICKED OUT OF THE TABLE 90
C DEGREES AFTER EACH COSINE VALUE, OR 30 TABLE ENTRIES FORWARD.
C NUMH = THE NO. OF DIFFERENT VALUES OF THE 1ST MILLER INDEX.
C NUMK = THE NO. OF DIFFERENT VALUES OF THE 2ND MILLER INDEX.
C NUML = THE NO. OF DIFFERENT VALUES OF THE 3RD MILLER INDEX.
C MAXSUM = ABSOLUTE VALUE OF THE LARGEST TERM COMPUTED.
C
C -----SENSE SWITCH 2 OFF TO ACCEPT CARD INPUT.
C          ON TO ACCEPT TAPE INPUT.
C
C THE ORDER OF THE CARDS AT OBJECT TIME IS AS FOLLOWS...
C (1) IDENTIFICATION CARD
C (2) SENSE SWITCH SETTINGS CARD (IF ONE).
C (3) OBJECT DECK FOURIER C.
C (4) A BLANK CARD.
C IF SENSE SWITCH 2 IS ON, OMIT (5) THRU (10). INCLUDE (5)
C THRU (10) ONLY IF SENSE SWITCH 2 IS OFF.
C (5) CARD CONTAINING MINX, MAXX,...,INCZ, PER FORMAT 901.
C (6) THE MVALUE TABLE DECK (150 CARDS), PER FORMAT 902.
C (7) CARD CONTAINING NUMH, NUMK, NUML, PER FORMAT 903.
C (8) DECK OF ALL DIFFERENT VALUES OF SECOND MILLER INDEX
C PER FORMAT904. (NUMK CARDS)
C (9) DECK OF ALL DIFFERENT VALUES OF THIRD MILLER INDEX
C PER FORMAT 904. (NUML CARDS)
C (10) CARD CONTAINING MAXSUM PRINTED OUT BY FOURIER A,
C PER FORMAT 90C.
C AT THE COMPLETION OF THIS PROGRAM, TAPE 7 WILL CONTAIN THE
C SECCND DIMENSION SUMS AND TAPE 4 WILL CONTAIN DATA NECESSARY
C FOR THE OPERATION OF FOURIER D.
C
C -----THE SECOND SUBSCRIPT IN THE FOLLOWING TWO DIMENSION
C          STATEMENTS MAY BE CHANGED FOR COMPATABILITY WITH ANY SIZE

```

```

C      COMPUTER MEMORY.
      DIMENSION JSUM1(61,3),JSUM2(61,3),JSUM3(61,3),JSUM4(61,3)
      DIMENSION NCK(121,3),NSK(121,3)
      DIMENSION KPART1(121),KPART2(121),KSUM1(121),KSUM2(121)
      DIMENSION NK2(3)
      DIMENSION MVALUE(150)
      DIMENSION NK(20),NL(20)
C      *****IMPORTANT*****IMPORTANT*****IMPORTANT*****IMPORTANT*****
C      *   MVALUE, NK, AND NL MUST BE DIMENSIONED EXACTLY AS THEY *
C      *   ARE DIMENSIONED IN PROGRAM FOURIER B AND D.           *
C      *****IMPORTANT*****IMPORTANT*****IMPORTANT*****IMPORTANT*****
      1 FORMAT(1X,4I12)
      2 FORMAT(1H1,19HINTERMEDIATE OUTPUT//1X,10X,2HMX,10X,2HMY,3X,
      1 9HKSUM1(MY),3X,9HKSUM2(MY))
      3 FORMAT(11H $MAXSUM = ,I8)
900  FORMAT(I8)
901  FORMAT(9(I3,3X))
902  FORMAT(I6)
903  FORMAT(3I3)
904  FORMAT(I3)
      IF(SENSE SWITCH 2)14,13
      13 READ INPUT TAPES5,901,MINX,MAXX,INCX,MINY,MAXY,INCY,MINZ,
      1 MAXZ,INCZ
      MINX=MINX+1
      MAXX=MAXX+1
      MINY=MINY+1
      MAXY=MAXY+1
      MINZ=MINZ+1
      MAXZ=MAXZ+1
      READ INPUT TAPES5,902,(MVALUE(M),M=1,150)
      READ INPUT TAPES5,903,NUMH,NUMK,NUML
      READ INPUT TAPE 5,904,(NK(M2),M2=1,NUMK)
      READ INPUT TAPES5,904,(NL(M3),M3=1,NUML)
      READ INPUT TAPES5,900,MAXSUM
      GO TO 15
      14 REWIND 4
      READ TAPE 4,MINX,MAXX,INCX,MINY,MAXY,INCY,MINZ,MAXZ,INCZ,
      1 MVALUE,NUMH,NUMK,NUML,NK,NL,MAXSUM
      15 REWIND 4
C-----TAPES 4 AND 8 ARE GIVEN SYMBOLIC NAMES.
      NTAPE=4
      MTAPE=8
C-----START TO DETERMINE SCALING FACTOR TO BE USED ON ALL DATA.
      IF(MAXSUM-999999)89,89,90
      90 JSCALE=10000
      GO TO 100
      89 IF(MAXSUM-999999)91,91,92
      92 JSCALE=1000
      GO TO 100
      91 IF(MAXSUM-99999)93,93,94
      94 JSCALE=100
      GO TO 100
      93 IF(MAXSUM-9999)95,95,96

```



```

96 JSCALE=10
   GO TO 100
95 JSCALE=1
C-----SCALE FACTOR DETERMINED.
100 REWIND 3
    REWIND 7
    SENSE LIGHT 4
    MAXSUM=0
    MMM=3
C-----MMM MAY BE CHANGED FOR COMPATABILITY WITH ANY SIZE COMPUTER
C    MEMCRY.
    IF(SENSE SWITCH 1)150,40
150 WRITE OUTPUT TAPE6,2
    40 READ TAPE 3,(NN1,NN2,NN3,NN4,NK1,MX=MINX,MAXX,INCX)
    IF(NK1)99,85,85
    85 BACKSPACE 3
C-----A BLOCK OF 1ST DIMENSION SUMS ARE READ FOR EACH VALUE OF M.
C    TOTAL NUMBER OF BLOCKS IS LESS THAN OR EQUAL TO MMM.
    41 DO 500 M=1,MMM
        READ TAPE3,(JSUM1(MX,M),JSUM2(MX,M),JSUM3(MX,M),JSUM4(MX,M),
        1 NK2(M),MX=MINX,MAXX,INCX)
        IF(NK2(M)-NK1)28,30,30
    30 NK1=NK2(M)
    500 CONTINUE
C-----NORMAL DO LOOP EXIT HAS OCCURED. M IS UNDEFINED.
    MAXM=MMM
C-----ONE MORE BLOCK IS READ TO SEE IF L INDEX IS ABOUT TO CHANGE.
    READ TAPE3,(NN1,NN2,NN3,NN4,NK3,MX=MINX,MAXX,INCX)
    IF(NK3-NK1)350,31,31
    350 SENSE LIGHT 1
        GO TO 31
C-----ABNORMAL DO LOOP EXIT HAS OCCURED. M REMAINS DEFINED.
    28 MAXM=M-1
        SENSE LIGHT 1
    31 BACKSPACE 3
C-----SCALING OF ALL DATA OCCURS NOW.
    DO 20 M=1,MAXM
        DO 20 MX=MINX,MAXX,INCX
            JSUM1(MX,M)=JSUM1(MX,M)/JSCALE
            JSUM2(MX,M)=JSUM2(MX,M)/JSCALE
            JSUM3(MX,M)=JSUM3(MX,M)/JSCALE
    20 JSUM4(MX,M)=JSUM4(MX,M)/JSCALE
C-----SCALING ACCOMPLISHED.
C
C-----A TABLE OF SINES AND COSINES IS NOW PREPARED
C    FOR ALL DATA READ.
    DO 11 M=1,MAXM
        DO 11 MY=MINY,MAXY,INCY
            NY=MY-1
            NARG=NK2(M)*NY
            NARG1=NARG/120
            NARG2=NARG-120*NARG1
            IF(NARG2)400,401,400

```

```

401 NARG2=120
400 NCK(MY,M)=MVALUE(NARG2)
11 NSK(MY,M)=MVALUE(NARG2+30)
C-----TABLE PREPARATION ACCOMPLISHED.
C
C *****
C * BEGINNING OF DO LOOP OVER X *
C *****
DO 50 MX=MINX,MAXX,INCX
C-----K SUMMATION STORAGE LOCATIONS ARE NOW CLEARED.
DO 201 MY=MINY,MAXY,INCY
KSUM1(MY)=0
201 KSUM2(MY)=0
C-----CLEARING ACCOMPLISHED.
C *****
C * BEGINNING OF DO LOOP OVER M *
C *****
DO 501 M=1,MAXM
C-----SUBSCRIPTS ARE NOW REMOVED FOR EXTRA ZIP IN Y LOOP.
JSUMT1=JSUM1(MX,M)
JSUMT2=JSUM2(MX,M)
JSUMT3=JSUM3(MX,M)
JSUMT4=JSUM4(MX,M)
C *****
C * BEGINNING OF DO LOOP OVER Y *
C *****
DO 200 MY=MINY,MAXY,INCY
NC=NCK(MY,M)
NS=NSK(MY,M)
KT1=(JSUMT1*NC+JSUMT2*NS)/100
KSUM1(MY)=KSUM1(MY)+KT1
KT2=(JSUMT3*NC+JSUMT4*NS)/100
200 KSUM2(MY)=KSUM2(MY)+KT2
C *****
C * END OF DO LOOP OVER Y *
C *****
501 CONTINUE
C *****
C * END OF DO LOOP OVER M *
C *****
C-----CALCULATIONS FOR ALL DATA BLOCKS READ ARE NOW COMPLETE.
C THESE RESULTS ARE NOW EITHER WRITTEN ON TAPE FOR FURTHER USE
C BY THIS PROGRAM, COMBINED WITH EARLIER PARTIAL RESULTS AND
C WRITTEN FOR FURTHER USE, WRITTEN ON TAPE 7 FOR USE BY
C PROGRAM FOURIER D, OR COMBINED WITH EARLIER RESULTS AND
C WRITTEN ON TAPE 7 FOR USE BY FOURIER D.
IF(SENSE LIGHT 4)53,54
53 SENSE LIGHT 4
C-----LIGHT 4 WAS ON. TAPE MTAPE WILL NOT BE READ BECAUSE NOTHING
C HAS BEEN WRITTEN ON IT.
GO TO 302
C--54-LIGHT 4 WAS OFF. PARTIAL RESULTS ARE READ FROM TAPE MTAPE.
54 READ TAPEMTAPE,KPART1,KPART2

```

```

C-----THESE PARTIAL RESULTS ARE ADDED TO CURRENT SUMS.
      DO 70 MY=MINY,MAXY,INCY
          KSUM1(MY)=KSUM1(MY)+KPART1(MY)
      70 KSUM2(MY)=KSUM2(MY)+KPART2(MY)
C-----SUMMATION ACCOMPLISHED.
      302 IF(SENSE LIGHT 1)300,301
C-----INITIALIZATION FOR DUMPING ONTO TAPE 7 BEGINS.
C
C-----THE ABSOLUTE VALUE OF THE LARGEST SUMMATION
C      IS NOW DETERMINED.
      300 SENSE LIGHT 1
          DO 6 MY=MINY,MAXY,INCY
              NN=XABSF(KSUM1(MY))
              IF(MAXSUM-NN)60,61,61
          60 MAXSUM=NN
          61 NN=XABSF(KSUM2(MY))
              IF(MAXSUM-NN)62,6,6
          62 MAXSUM=NN
          6 CONTINUE
C-----DETERMINATION OF MAXSUM ACCOMPLISHED.
      WRITE TAPE 7,(KSUM1(MY),KSUM2(MY),MY=MINY,MAXY,INCY)
      IF(SENSE SWITCH 1)82,51
      82 WRITE OUTPUT TAPE6,1,(MX,MY,KSUM1(MY),KSUM2(MY),
          1 MY=MINY,MAXY,INCY)
      GO TO 51
C-301-LIGHT 1 WAS OFF. PARTIAL RESULTS ARE WRITTEN ON TAPE NTAPE.
      301 WRITE TAPE NTAPE,KSUM1,KSUM2
          51 CONTINUE
          50 CONTINUE
C *****
C *   END OF DO LOOP CVER X   *
C *****
      IF(SENSE LIGHT 1)290,291
      290 SENSE LIGHT 4
          GO TO 292
      291 IF(SENSE LIGHT 4)292,292
      292 REWIND 4
          REWIND 8
C-----THE IDENTITY OF TAPES NTAPE AND MTAPE ARE SWITCHED.
      NQ=NTAPE
      NTAPE=MTAPE
      MTAPE=NQ
      GO TO 40
      99 REWIND 3
          REWIND 4
          REWIND 7
          REWIND 8
      WRITE OUTPUT TAPE6,3,MAXSUM
C-----WRITE RANGES, COSINE TABLE, ETC., ON TAPE 4.
      WRITE TAPE 4,MINX,MAXX,INCX,MINY,MAXY,INCY,MINZ,MAXZ,INCZ,
          1 MVALUE,NUMH,NUMK,NUML,NL,MAXSUM
      REWIND 4
      CALL EXIT

```

```

          BOP FOUR CD PR 08 08
C ***** FOURIER CD PROJECTION LINK *****
C
C WRITTEN 2/18/65 HOLLIS
C
C THIS PROGRAM IS TO BE PRECEDED BY FOURIER B AND FOLLOWED BY
C FOURIER E.
C-----FOR COMMENTS ON VARIABLES AND THE ORDER OF THE CARDS
C AT OBJECT TIME SEE PROGRAM FOURIER C.
C AT THE COMPLETION OF THIS PROGRAM, TAPE 3 WILL CONTAIN THE
C SECOND DIMENSION SUMS AND TAPE 4 WILL CONTAIN DATA NECESSARY
C FOR THE OPERATION OF FOURIER E.
C
C-----THE SECOND SUBSCRIPT IN THE FOLLOWING TWO DIMENSION
C STATEMENTS MAY BE CHANGED FOR COMPATABILITY WITH ANY SIZE
C COMPUTER MEMORY.
DIMENSION JSUM1(61,3),JSUM2(61,3)
DIMENSION NCK(121,3),NSK(121,3)
DIMENSION KPART1(121),KSUM1(121)
DIMENSION NK2(3)
DIMENSION MVALUE(150)
DIMENSION NK(20),NL(20)
C *****IMPORTANT*****IMPORTANT*****IMPORTANT*****IMPORTANT*****
C * MVALUE, NK, AND NL MUST BE DIMENSIONED EXACTLY AS THEY *
C * ARE DIMENSIONED IN PROGRAM FOURIER B AND D. *
C *****IMPORTANT*****IMPORTANT*****IMPORTANT*****IMPORTANT*****
1 FORMAT(1X,3I12)
2 FORMAT(1H1,19HINTERMEDIATE OUTPUT//1X,10X,2HMX,10X,2HMY,3X,
1 9HKSUM1(MY))
3 FORMAT(1H0,9HMAXSUM = ,I12/1X,9HMINSUM = ,I12)
900 FORMAT(I8)
901 FORMAT(9(I3,3X))
902 FORMAT(I6)
903 FORMAT(3I3)
904 FORMAT(I3)
IF(SENSE SWITCH 2)14,13
13 READ INPUT TAPES,901,MINX,MAXX,INCX,MINY,MAXY,INCY,MINZ,
1 MAXZ,INCZ
MINX=MINX+1
MAXX=MAXX+1
MINY=MINY+1
MAXY=MAXY+1
MINZ=MINZ+1
MAXZ=MAXZ+1
READ INPUT TAPES,902,(MVALUE(M),M=1,150)
READ INPUT TAPES,903,NUMH,NUMK,NUML
READ INPUT TAPE 5,904,(NK(M2),M2=1,NUMK)
READ INPUT TAPES,904,(NL(M3),M3=1,NUML)
READ INPUT TAPES,900,MAXSUM
GO TO 15
14 REWIND 4
READ TAPE 4,MINX,MAXX,INCX,MINY,MAXY,INCY,MINZ,MAXZ,INCZ,
1 MVALUE,NUMH,NUMK,NUML,NK,NL,MAXSUM

```

```

15 REWIND 4
C-----TAPES 4 AND 8 ARE GIVEN SYMBOLIC NAMES.
      NTAPE=4
      MTAPE=8
C-----START TO DETERMINE SCALING FACTOR TO BE USED ON ALL DATA.
      IF(MAXSUM-9999999)89,89,90
90  JSCALE=10000
      GO TO 100
89  IF(MAXSUM-999999)91,91,92
92  JSCALE=1000
      GO TO 100
91  IF(MAXSUM-99999)93,93,94
94  JSCALE=100
      GO TO 100
93  IF(MAXSUM-9999)95,95,96
96  JSCALE=10
      GO TO 100
95  JSCALE=1
C-----SCALE FACTOR DETERMINED.
100 REWIND 3
      REWIND 7
      SENSE LIGHT 4
      MAXSUM=0
      MINSUM=0
      MMM=3
C-----MMM MAY BE CHANGED FOR COMPATABILITY WITH ANY SIZE COMPUTER
C      MEMORY.
      IF(SENSE SWITCH 1)150,40
150 WRITE OUTPUT TAPE6,2
40  READ TAPE 3,(NN1,NN2,NK1,MX=MINX,MAXX,INCX)
      IF(NK1)99,85,85
85  BACKSPACE 3
C-----A BLOCK OF 1ST DIMENSION SUMS ARE READ FOR EACH VALUE OF M.
C      TOTAL NUMBER OF BLOCKS IS LESS THAN OR EQUAL TO MMM.
41  DO 500 M=1,MMM
      READ TAPE3,(JSUM1(MX,M),JSUM2(MX,M),
1   NK2(M),MX=MINX,MAXX,INCX)
      IF(NK2(M)-NK1)28,30,30
30  NK1=NK2(M)
500 CONTINUE
C-----NORMAL DO LOOP EXIT HAS OCCURRED. M IS UNDEFINED.
      MAXM=MMM
C-----ONE MORE BLOCK IS READ TO SEE IF L INDEX IS ABOUT TO CHANGE.
      READ TAPE3,(NN1,NN2,NK3,MX=MINX,MAXX,INCX)
      IF(NK3-NK1)350,31,31
350 SENSE LIGHT 1
      GO TO 31
C-----ABNORMAL DO LOOP EXIT HAS OCCURED. M REMAINS DEFINED.
28  MAXM=M-1
      SENSE LIGHT 1
31  BACKSPACE 3
C-----SCALING OF ALL DATA OCCURS NOW.
      DO 20 M=1,MAXM

```

```

DO 20 MX=MINX,MAXX,INCX
  JSUM1(MX,M)=JSUM1(MX,M)/JSCALE
20 JSUM2(MX,M)=JSUM2(MX,M)/JSCALE
C-----SCALING ACCOMPLISHED.
C
C-----A TABLE OF SINES AND COSINES IS NOW PREPARED
C   FOR ALL DATA READ.
DO 11 M=1,MAXM
  DO 11 MY=MINY,MAXY,INCY
    NY=MY-1
    NARG=NK2(M)*NY
    NARG1=NARG/120
    NARG2=NARG-120*NARG1
    IF(NARG2)400,401,400
401 NARG2=120
400 NCK(MY,M)=MVALUE(NARG2)
  11 NSK(MY,M)=MVALUE(NARG2+30)
C-----TABLE PREPARATION ACCOMPLISHED.
C
C *****
C *   BEGINNING OF DO LOOP OVER X                               *
C *****
DO 50 MX=MINX,MAXX,INCX
C-----K SUMMATION STORAGE LOCATIONS ARE NOW CLEARED.
DO 201 MY=MINY,MAXY,INCY
  201 KSUM1(MY)=0
C-----CLEARING ACCOMPLISHED.
C *****
C *   BEGINNING OF DO LOOP OVER M                               *
C *****
DO 501 M=1,MAXM
C-----SUBSCRIPTS ARE NOW REMOVED FOR EXTRA ZIP IN Y LOOP.
  JSUMT1=JSUM1(MX,M)
  JSUMT2=JSUM2(MX,M)
C *****
C *   BEGINNING OF DO LOOP OVER Y                               *
C *****
DO 200 MY=MINY,MAXY,INCY
  NC=NCK(MY,M)
  NS=NSK(MY,M)
  KT1=(JSUMT1*NC+JSUMT2*NS)/100
  200 KSUM1(MY)=KSUM1(MY)+KT1
C *****
C *   END OF DO LOOP OVER Y                                     *
C *****
501 CONTINUE
C *****
C *   END OF DO LOOP OVER M                                     *
C *****
C-----CALCULATIONS FOR ALL DATA BLOCKS READ ARE NOW COMPLETE.
C   THESE RESULTS ARE NOW EITHER WRITTEN ON TAPE FOR FURTHER USE
C   BY THIS PROGRAM, COMBINED WITH EARLIER PARTIAL RESULTS AND
C   WRITTEN FOR FURTHER USE, WRITTEN ON TAPE 7 FOR USE BY

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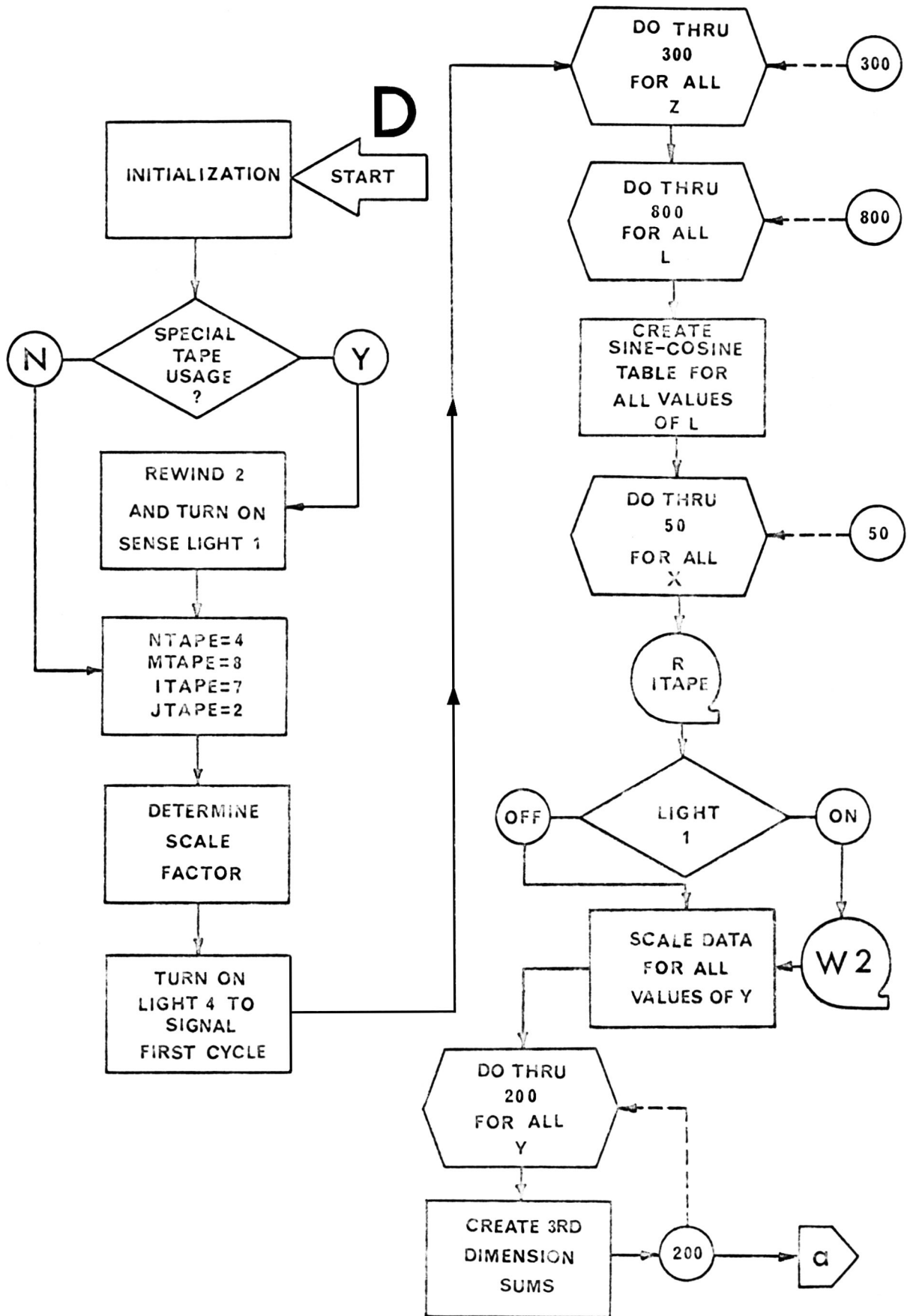
C      PROGRAM FOURIER D, OR COMBINED WITH EARLIER RESULTS AND
C      WRITTEN ON TAPE 7 FOR USE BY FOURIER E.
      IF(SENSE LIGHT 4)53,54
      53 SENSE LIGHT 4
C-----LIGHT 4 WAS ON. TAPE MTAPE WILL NOT BE READ BECAUSE NOTHING
C      HAS BEEN WRITTEN ON IT.
      GO TO 302
C--54-LIGHT 4 WAS OFF. PARTIAL RESULTS ARE READ FROM TAPE MTAPE.
      54 READ TAPE MTAPE,KPART1
C-----THESE PARTIAL RESULTS ARE ADDED TO CURRENT SUMS.
      DO 70 MY=MINY,MAXY,INCY
      70 KSUM1(MY)=KSUM1(MY)+KPART1(MY)
C-----SUMMATION ACCOMPLISHED.
      302 IF(SENSE LIGHT 1)300,301
C-----INITIALIZATION FOR DUMPING ONTO TAPE 7 BEGINS.
C
C-----THE ALGEBRAIC VALUES OF THE LARGEST AND SMALLEST SUMMATIONS
C      ARE NOW DETERMINED.
      300 SENSE LIGHT 1
      DO 6 MY=MINY,MAXY,INCY
      NN=KSUM1(MY)
      IF(MAXSUM-NN)60,61,61
      60 MAXSUM=NN
      61 IF(MINSUM-NN)6,62,62
      62 MINSUM=NN
      6 CONTINUE
C-----DETERMINATION OF MAXSUM,MINSUM ACCOMPLISHED.
      WRITE TAPE 7,(KSUM1(MY),MY=MINY,MAXY,INCY)
      IF(SENSE SWITCH 1)82,51
      82 WRITE OUTPUT TAPE6,1,(MX,MY,KSUM1(MY),
      1 MY=MINY,MAXY,INCY)
      GO TO 51
C-301-LIGHT 1 WAS OFF. PARTIAL RESULTS ARE WRITTEN ON TAPE NTAPE.
      301 WRITE TAPE NTAPE, KSUM1
      51 CONTINUE
      50 CONTINUE
C *****
C *   END OF DO LOOP OVER X   *
C *****
      IF(SENSE LIGHT 1)290,291
      290 SENSE LIGHT 4
      GO TO 292
      291 IF(SENSE LIGHT 4)292,292
      292 REWIND 4
      REWIND 8
C-----THE IDENTITY OF TAPES NTAPE AND MTAPE ARE SWITCHED.
      NQ=NTAPE
      NTAPE=MTAPE
      MTAPE=NQ
      GO TO 40
      99 REWIND 3
      REWIND 4
      REWIND 7

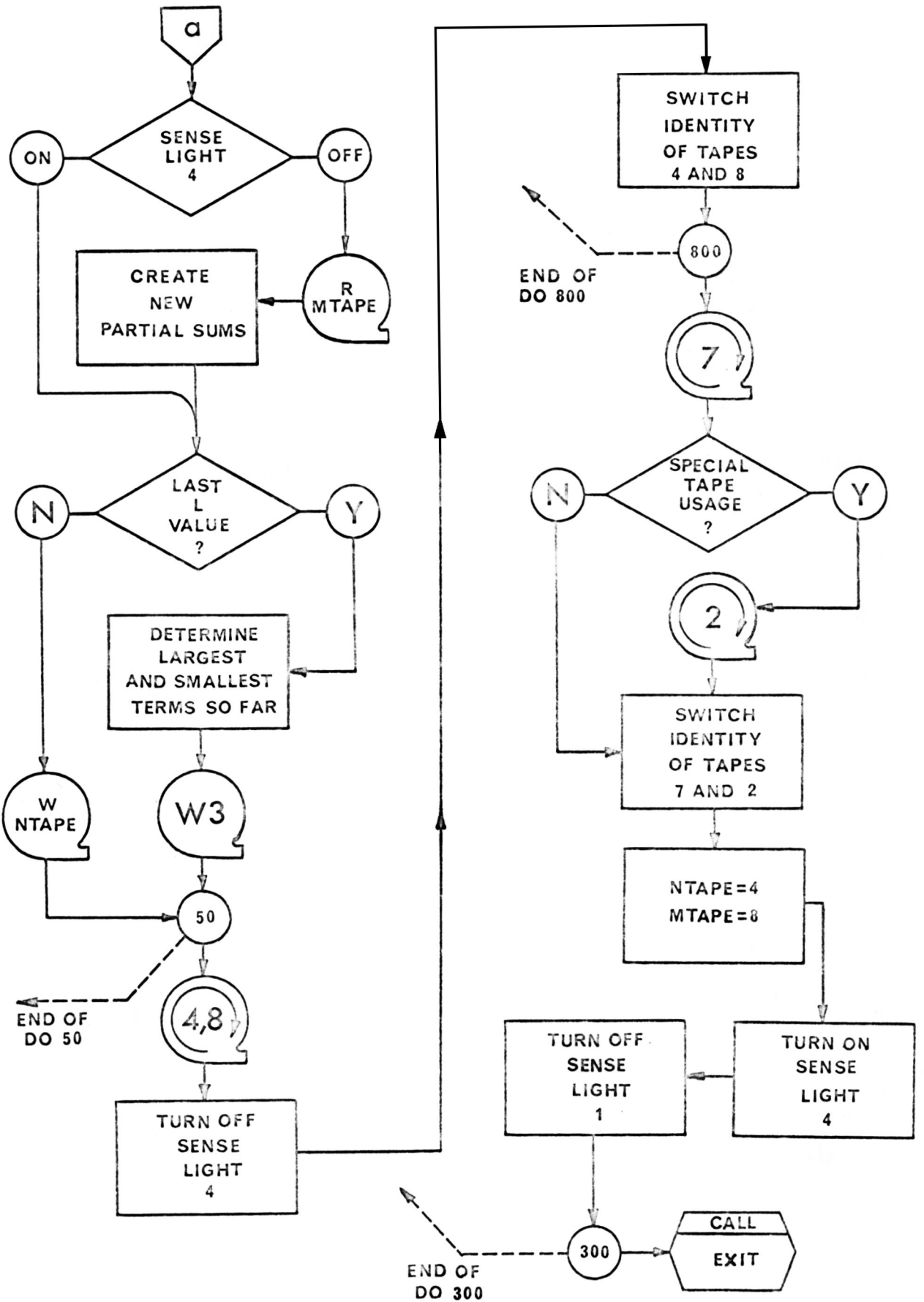
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```
      REWIND 8
C-----DEFINE TAPE UNIT TO BE USED BY FOURIER E.
      KTAPE=7
      WRITE OUTPUT TAPE6,3,MAXSUM,MINSUM
C-----WRITE RANGES, COSINE TABLE, ETC., ON TAPE 4.
      WRITE TAPE 4,MINX,MAXX,INCX,MINY,MAXY,INCY,MINZ,MAXZ,INCZ.
      1 MAXSUM,MINSUM,KTAPE
      REWIND 4
      CALL EXIT
      STOP
      END
```


EXPLANATION OF PLATE XIX

This plate (next two pages) shows the logical steps and flow of information within program link D. The pentagonal boxes carry the program flow from page to page.





EXPLANATION OF PLATE XX

This plate (next 5 pages) is the FORTRAN II symbolic coding for program link D.

PLATE XX

```

C ***** FOURIER D (LSUM) *****
C
C WRITTEN 3/14/64 HOLLIS
C
C THIS PROGRAM IS TO BE PRECEDED BY FOURIER C AND FOLLOWED BY
C FOURIER E.
C MINX = MINIMUM VALUE OF X.
C MAXX = MAXIMUM VALUE OF X.
C INCX = INCREMENT OF X (120THS OF UNIT CELL)
C MINY = MINIMUM VALUE OF Y.
C MAXY = MAXIMUM VALUE OF Y.
C INCY = INCREMENT OF Y (120THS OF UNIT CELL)
C MINZ = MINIMUM VALUE OF Z.
C MAXZ = MAXIMUM VALUE OF Z.
C INCZ = INCREMENT OF Z (120THS OF UNIT CELL)
C -----NOTE... MINX, MAXX, MINY, ETC. BECOME MINX+1, MAXX+1,
C MINY+1, ETC., AFTER THE PROGRAM HAS BEGUN IN ORDER TO
C SATISFY DO LOOP REQUIREMENTS.
C MVALUE = A TABLE OF 150 COSINES, COVERING 1 1/4 CIRCLES. THIS
C DIVIDES THE CIRCLE INTO 120 PARTS, WITH ONE COSINE VALUE
C EVERY 3 DEGREES. SINE VALUES ARE PICKED OUT OF THE TABLE 90
C DEGREES AFTER EACH COSINE VALUE, OR 30 TABLE ENTRIES FORWARD.
C NUMH = THE NO. OF DIFFERENT VALUES OF THE 1ST MILLER INDEX.
C NUMK = THE NO. OF DIFFERENT VALUES OF TH 2ND MILLER INDEX.
C NUML = THE NO. OF DIFFERENT VALUES OF THE 3RD MILLER INDEX.
C MAXSUM = VALUE OF LARGEST TERM COMPUTED.
C MINSUM = VALUE OF SMALLEST TERM COMPUTED.
C
C-----SENSE SWITCH 2 OFF FOR CARD INPUT.
C ON FOR TAPE INPUT.
C-----SENSE SWITCH 3 ON FOR SPECIAL TAPE USAGE FEATURE.
C THIS REQUIRES TAPE UNIT 2.
C OFF TO IGNORE SPECIAL TAPE FEATURE.
C
C THE ORDER OF THE CARDS AT OBJECT TIME IS AS FOLLOWS...
C (1) IDENTIFICATION CARD
C (2) SENSE SWITCH SETTINGS CARD (IF ONE).
C (3) OBJECT DECK FOURIER C.
C (4) A BLANK CARD.
C IF SENSE SWITCH 2 IS ON, OMIT (5) THRU (9). INCLUDE (5)
C THRU (9) ONLY IF SENSE SWITCH 2 IS OFF.
C (5) CARD CONTAINING MINX, MAXX,...INCX, PER FORMAT 901.
C NOTE... UNITY WILL BE ADDED TO MINX, MAXX, MINY,
C MAXY, MINZ, AND MAXZ.
C (6) MVALUE DECK (150 CARDS. PER FORMAT 902.
C (7) CARD CONTAINING NUMH, NUMK, NUML, PER FORMAT 903.
C (8)DECK OF ALL NL VALUES (IN ASCENDING ORDER),
C (NUML CARDS), PER FORMAT 904.
C (9) CARD CONTAINING MAXSUM FROM PROGRAM C PER FORMAT 900.
C
C AT THE COMPLETION OF THIS PROGRAM, TAPE 3 WILL CONTAIN THE
C THIRD DIMENSION SUMS AND TAPE 4 WILL CONTAIN DATA NECESSARY
C FOR THE OPERATION OF FOURIER E

```

```

C
  DIMENSION KSUM1(121),KSUM2(121)
  DIMENSION NL(20)
  DIMENSION NCL(121),NSL(121)
  DIMENSION MVALUE(150)
  DIMENSION LT1(121)
  DIMENSION LSUM1(121)
900 FORMAT(I8)
901 FORMAT(9(I3,3X))
902 FORMAT(I6)
903 FORMAT(3I3)
904 FORMAT(I3)
905 FORMAT(8HSECTION ,I3)
906 FORMAT(1H0,9HMAXSUM = ,I12/1X,9HMINSUM = ,I12)
C-----IF CARD INPUT IS DESIRED, GO TO 13. IF TAPE INPUT IS DESIRED
C      GO TO 14.
      IF(SENSE SWITCH 2)14,13
13 READ INPUT TAPE5,901,MINX,MAXX,INCX,MINY,MAXY,INCY,MINZ,
  1 MAXZ, INCZ
  MINX=MINX+1
  MAXX=MAXX+1
  MINY=MINY+1
  MAXY=MAXY+1
  MINZ=MINZ+1
  MAXZ=MAXZ+1
  READ INPUT TAPE5,902,(MVALUE(M),M=1,150)
  READ INPUT TAPE5,903,NUMH,NUMK,NUML
  READ INPUT TAPE5,904,(NL(M3),M3=1,NUML)
  READ INPUT TAPE5,900,MAXSUM
  GO TO 15
14 REWIND 4
  READ TAPE 4,MINX,MAXX,INCX,MINY,MAXY,INCY,MINZ,MAXZ,INCZ,
  1 MVALUE,NUMH,NUMK,NUML,NL,MAXSUM
15 REWIND 4
  IF(SENSE SWITCH 3)620,621
C-620-A SENSE LIGHT IS TURNED ON TO SIGNAL THE PROGRAM THAT THE
C   SPECIAL TAPE USAGE FEATURE IS IN EFFECT. TAPE 2 IS REWOUND.
620 REWIND 2
  SENSE LIGHT 1
C-621-TAPES 4, 8, 7, AND 2 ARE GIVEN SYMBOLIC NAMES.
621 NTAPE=4
  MTAPE=8
  ITAPE=7
  JTAPE=2
C-----START TO DETERMINE SCALING FACTOR TO BE USED ON ALL DATA.
  IF(MAXSUM-9999999)89,89,90
90 KSCALE=10000
  GO TO 100
89 IF(MAXSUM-999999)91,91,92
92 KSCALE=1000
  GO TO 100
91 IF(MAXSUM-99999)93,93,94
94 KSCALE=100

```

```

      GO TO 100
      93 IF(MAXSUM-9999)95,95,96
      96 KSCALE=10
      GO TO 100
      95 KSCALE=1
C-100-SCALE FACTOR DETERMINED.
      100 REWIND 3
      REWIND 7
C-----TURN ON SENSE LIGHT 4 TO SIGNAL PROGRAM THAT THIS IS
C      THE FIRST CYCLE.
      SENSE LIGHT 4
      MAXSUM=0
      MINSUM=0
C *****
C *   BEGINNING OF DO LOOP OVER Z                               *
C *****
      DO 300 MZ=MINZ,MAXZ,INCZ
      NZ=MZ-1
      TYPE 905,NZ
C *****
C *   BEGINNING OF DO LOOP OVER L                               *
C *****
      DO 800 M3=1,NUML
C-----CALCULATE ARGUMENT AND LOOK UP COSINE AND SINE VALUE FOR
C      CURRENT VALUE OF L.
      NARG=NL(M3)*NZ
      NARG1=NARG/120
      NARG2=NARG-120*NARG1
      IF(NARG2)400,401,400
      401 NARG2=120
      400 NC=MVALUE(NARG2)
      NS=MVALUE(NARG2+30)
C-----TABLE LOOK UP ACCOMPLISHED.
C *****
C *   BEGINNING OF DO LOOP OVER X                               *
C *****
      DO 50 MX=MINX,MAXX,INCX
      40 READ TAPE ITAPE,(KSUM1(MY),KSUM2(MY),MY=MINY,MAXY,INCY)
C-----IF LIGHT 1 IS ON, GENERATE A DUPLICATE TAPE.
      IF(SENSE LIGHT 1)622,623
      622 SENSE LIGHT 1
      WRITE TAPE 2,(KSUM1(MY),KSUM2(MY),MY=MINY,MAXY,INCY)
      623 CONTINUE
C-----SCALE DATA.
      DO 20 MY=MINY,MAXY,INCY
      KSUM1(MY)=KSUM1(MY)/KSCALE
      20 KSUM2(MY)=KSUM2(MY)/KSCALE
C-----SCALING ACCOMPLISHED.
C *****
C *   BEGINNING OF DO LOOP OVER Y                               *
C *****
      DO 200 MY=MINY,MAXY,INCY
      200 LT1(MY)=(KSUM1(MY)*NC+KSUM2(MY)*NS)/100

```

```

C *****
C *   END OF DO LOOP OVER Y                               *
C *****
C-----IF THIS IS THE FIRST CYCLE GO TO 53.  OTHERWISE GO TO 54.
      IF(SENSE LIGHT 4)53,54
      53 SENSE LIGHT 4
      DO 660 MY=MINY,MAXY,INCY
      660 LSUM1(MY)=LT1(MY)
      GO TO 653
C--54-READ PARTIAL SUMS FROM TAPE MTAPE.
      54 READ TAPE MTAPE,LSUM1
C-----CREATE NEW PARTIAL SUMS.
      DO 70 MY=MINY,MAXY,INCY
      70 LSUM1(MY)=LSUM1(MY)+LT1(MY)
      653 IF(M3-NUML)600,601,601
C-601-THE SUMMATION OVER L HAS BEEN COMPLETED.
C-----THE ALGEBRAIC VALUES OF THE LARGEST AND SMALLEST SUMMATIONS
C      ARE NOW DETERMINED.
      601 DO 36 MY=MINY,MAXY,INCY
      NN=LSUM1(MY)
      IF(MAXSUM-NN)360,37,37
      360 MAXSUM=NN
      37 IF(MINSUM-NN)36,36,361
      361 MINSUM=NN
      36 CONTINUE
C-----DETERMINATION OF MAXSUM, MINSUM ACCOMPLISHED.
C-----WRITE FINAL SUMS ON TAPE 3.
      WRITE TAPE 3,(LSUM1(MY),MY=MINY,MAXY,INCY)
      GO TO 50
C-600-WRITE PARTIAL SUMS ON TAPE NTAPE.
      600 WRITE TAPE NTAPE,LSUM1
      50 CONTINUE
C *****
C *   END OF DO LOOP OVER X                               *
C *****
      REWIND 4
      REWIND 8
C-----TURN OFF SENSE LIGHT 4 BY INTERROGATING IT.
      IF(SENSE LIGHT 4)55,55
C-----SWITCH THE IDENTITY OF TAPES NTAPE AND MTAPE. (TAPES 4 AND 8,
C      OR TAPES 8 AND 4).
      55 NQ=NTAPE
      NTAPE=MTAPE
      MTAPE=NQ
      800 CONTINUE
C *****
C *   END OF DO LOOP OVER L                               *
C *****
      REWIND 7
      IF(SENSE SWITCH 3)630,631
C-630-SPECIAL TAPE 2 HAS BEEN CREATED.
      630 REWIND 2
C-----SWITCH THE IDENTITY OF TAPES ITAPE AND JTAPE. (TAPES 7 AND 2,
C      OR TAPES 2 AND 7).
      NQ=ITAPE

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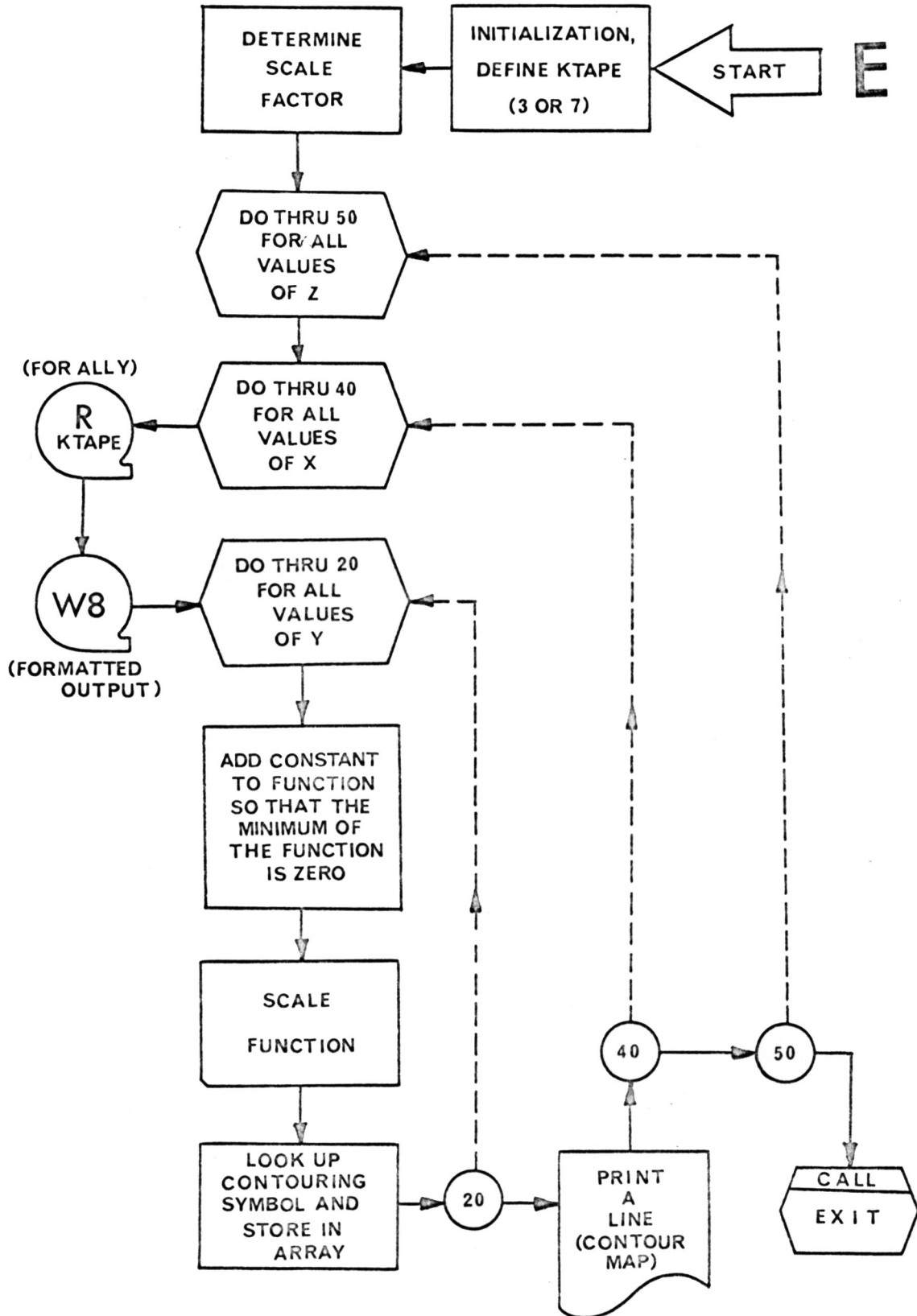
        ITAPE=JTAPE
        JTAPE=NQ
C-631-DEFINE NTAPE AND MTAPE
        631 NTAPE=4
           MTAPE=8
C-----TURN ON SENSE LIGHT 4 TO SIGNAL THE BEGINNING OF A NEW CYCLE.
C      (NEW VALUE OF Z).
           SENSE LIGHT 4
C-----TURN OFF SENSE LIGHT 1 BY INTERROGATING IT. THIS PREVENTS
C      THE PROGRAM FROM CREATING A NEW FILE ON TAPE 2.
           IF(SENSE LIGHT 1)801,801
           801 CONTINUE
           300 CONTINUE
C *****
C *      END OF DO LOOP OVER Z
C *****
C-----DEFINE KTAPE FOR FOURIER E.
           KTAPE=3
C-----WRITE RANGES, MAXSUM, MINSUM, KTAPE ON TAPE 4 FOR FOURIER E.
           WRITE TAPE 4,MINX,MAXX,INCX,MINY,MAXY,INCY,MINZ,MAXZ,INCZ,
           1 MAXSUM,MINSUM,KTAPE
           REWIND 4
           WRITE OUTPUT TAPE6,906,MAXSUM,MINSUM
           REWIND 3
           CALL EXIT
           STOP
           END

```

EXPLANATION OF PLATE XXI

This plate shows the logical steps and flow of information within program link E.

PLATE XXI



EXPLANATION OF PLATE XXII

This plate (next 3 pages) is the FORTRAN II symbolic coding for program link E.

PLATE XXII

BOP FCURE 08 08

***** FOURIER E *****

WRITTEN 3/14/64

HOLLIS

MINX = MINIMUM VALUE OF X.

MAXX = MAXIMUM VALUE OF X.

INCX = INCREMENT OF X (120THS OF UNIT CELL)

MINY = MINIMUM VALUE OF Y.

MAXY = MAXIMUM VALUE OF Y.

INCY = INCREMENT OF Y (120THS OF UNIT CELL)

MINZ = MINIMUM VALUE OF Z.

MAXZ = MAXIMUM VALUE OF Z.

IN CZ = INCREMENT OF Z (120THS OF UNIT CELL)

-----NOTE... MINX, MAXX, MINY, ETC. BECOME MINX+1, MAXX+1,
MINY+1, ETC., AFTER THE PROGRAM HAS BEGUN IN ORDER TO
SATISFY DO LOOP REQUIREMENTS.

MAXSUM = VALUE OF LARGEST TERM COMPUTED.

MINSUM = VALUE OF SMALLEST TERM COMPUTED.

-----SENSE SWITCH 3 ON FOR DOUBLE SPACING ACROSS PAGE.

OFF FOR SINGLE SPACING.

-----SENSE SWITCH 4 ON FOR DOUBLE SPACING DOWN PAGE.

OFF FOR SINGLE SPACING.

-----SENSE SWITCH 2 OFF FOR CARD INPUT OF PARAMETERS.

ON FOR TAPE INPUT FROM FOURIER D. (UNIT 4).

THE ORDER OF THE CARDS AT OBJECT TIME IS AS FOLLOWS...

(1) IDENTIFICATION CARD.

(2) SENSE SWITCH SETTINGS CARD. (IF ONE).

(3) OBJECT DECK FOURIER E.

(4) A BLANK CARD.

IF SENSE SWITCH 2 IS ON, OMIT (5) AND (6). INCLUDE (5) AND
(6) ONLY IF SENSE SWITCH 2 IS OFF.

(5) CARD CONTAINING MINX, MAXX, ..., INCZ,
PER FORMAT 207.

(6) CARD CONTAINING MAXSUM, MINSUM, PER FORMAT 208.

(7) CARD CONTAINING PLOTTING CHARACTERS, PER FORMAT 2.

AT THE COMPLETION OF THIS PROGRAM, TAPE 8 WILL CONTAIN A
LISTING OF THE NUMERICAL OUTPUT IN FORMATTED FORM. THE
CONTOUR MAPS ARE WRITTEN ON THE STANDARD OUTPUT UNIT.

DIMENSION LSUM1(121)

DIMENSION NFIG(121)

DIMENSION NCHAR(50)

1 FORMAT(1H0,10I12/1X,10I12/1X,10I12/1X,10I12/1X,10I12/1X,10I12/
1 1X,10I12/1X,10I12/1X,10I12/1X,10I12/1X,10I12/1X,10I12/1X,10I12/1X,112)

2 FORMAT(45A1)

3 FORMAT(5X,121A1)

4 FORMAT(1H1,12HSECTION Z = ,I3//)

6 FORMAT(2H \$)

7 FORMAT(1X,38HTHE MAXIMUM OF THE ENTIRE FUNCTION IS ,I9/

```

1 1X,38HTHE MINIMUM OF THE ENTIRE FUNCTION IS ,I9/
2 1X,30HTHE CONTCUR SCALING FACTOR IS ,I6)
8 FORMAT(2H15,12HSECTION Z = ,I3//)
9 FORMAT(12HSECTION Z = ,I3)
200 FCRMAT(5X,60(A1,1X),A1)
206 FCRMAT(1H )
207 FCRMAT(9(I3,3X))
208 FCRMAT(2I12)
C IF CARD INPUT, GO TC 205, IF TAPE INPUT, GO TO 210.
IF(SENSE SWITCH 2)210,205
210 REWIND 4
READ TAPE 4,MINX,MAXX,INCX,MINY,MAXY,INCY,MINZ,MAXZ,INCZ,
1 MAXSUM,MINSUM,KTAPE
REWIND 4
GO TO 209
205 READ INPUT TAPES,207,MINX,MAXX,INCX,MINY,MAXY,INCY,MINZ,
1 MAXZ,INCZ
MINX=MINX+1
MAXX=MAXX+1
MINY=MINY+1
MAXY=MAXY+1
MINZ=MINZ+1
MAXZ=MAXZ+1
READ INPUT TAPES,208,MAXSUM,MINSUM
KTAPE=3
209 REWIND KTAPE
REWIND 8
C-----DETERMINE SCALE FACTOR FOR CONTOUR MAPS.
MSCALE=(MAXSUM-MINSUM)/45+1
WRITE OUTPUT TAPE6,7,MAXSUM,MINSUM,MSCALE
WRITE OUTPUT TAPE 8,7,MAXSUM,MINSUM,MSCALE
C-----READ CONTOURING CHARACTER FIELD.
READ INPUT TAPES,2,(NCHAR(I),I=1,45)
C *****
C * BEGINNING OF DO LOOP OVER Z *
C *****
DO 50 MZ=MINZ,MAXZ,INCZ
NZ=MZ-1
WRITE OUTPUT TAPE6,4,NZ
WRITE OUTPUT TAPE 8,4,NZ
TYPE 9, NZ
C *****
C * BEGINNING OF DO LOOP OVER X *
C *****
DO 40 MX=MINX,MAXX,INCX
READ TAPE KTAPE,(LSUM1(MY),MY=MINY,MAXY,INCY)
WRITE OUTPUT TAPE8,1,(LSUM1(MY),MY=MINY,MAXY,INCY)
DO 20 MY=MINY,MAXY,INCY
C-----SUBTRACT MINSUM FROM ALL VALUES SO THAT THE MINIMUM VALUE OF
C THE ENTIRE FUNCTION IS ZERO.
LSUM1(MY)=LSUM1(MY)-MINSUM
C-----DIVIDE BY MSCALE SO THAT ALL VALUES OF THE FUNCTION LIE FROM
C 0 TO 44.

```

```

      LSUMT1=LSUM1(MY)/MSCALE
C-----LOOK UP THE CONTOURING CHARACTER ASSOCIATED WITH THE VALUE
C OF THE FUNCTION.
      20 NFIG(MY)=NCHAR(LSUMT1+1)
      IF(SENSE SWITCH 3)1C0,1C1
      100 WRITE OUTPUT TAPE6,200,(NFIG(MY),MY=MINY,MAXY,INCY)
      GO TO 203
      101 WRITE OUTPUT TAPE6,3,(NFIG(MY),MY=MINY,MAXY,INCY)
      203 IF(SENSE SWITCH 4)2C4,4C
      204 WRITE OUTPUT TAPE6,206
      40 CONTINUE
C *****
C *   END OF DO LOOP OVER X                                     *
C *****
      50 CONTINUE
C *****
C *   END OF DO LOOP OVER Z                                     *
C *****
      END FILE 8
      END FILE 8
      REWIND KTAPE
      REWIND 4
      CALL EXIT
      STOP
      END

```

APPENDIX II

Along with the Fourier calculation, perhaps the next most important calculation performed by the crystallographer is the calculation of structure factors. The structure factor is given by

$$F_{hkl} = \sum_{n=1}^N f_n(hkl) \exp 2\pi i (hx_n + ky_n + lz_n), \quad (65)$$

where $f_n(hkl)$ is the atomic scattering factor for the n^{th} atom, N is the number of atoms in the unit cell, and x_n, y_n, z_n are the coordinates of the n^{th} atom. With this equation, one can calculate the scattering from a postulated structure consisting of a collection of atoms of known type and position in the unit cell. The program described here calculates F_{hkl} values and the residual R given by

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}. \quad (66)$$

The program is completely general and there is no limitation to the quantity of input data.

Input to the program consists of a table of observed structure factors, a table of atomic scattering factors for each atom type and each set of h, k, l , values; and the types and atomic coordinates of the atoms.

Plate XXIII shows the program listing. This listing is intended to be self-explanatory.

EXPLANATION OF PLATE XXIII

This plate (next 3 pages) shows the FORTRAN II coding for the structure factor program.

PLATE XXIII

```

C      **** STRUCTURE FACTOR PROGRAM ****
C
C      WRITTEN 11/22/63                      HOLLIS
C      MODIFIED 11/25/63 (DECOU HISTAMINE FORMATS)
C      MODIFIED 1/4/64 (IGNORE PRINT OUTS, STRUCTURE NUMBER DELETED)
C      MODIFIED 12/10/64 1410-PR-155
C      F = STRUCTURE FACTOR = F(H,K,L)
C      FO = OBSERVED STRUCTURE FACTOR
C      A = REAL PART OF F, B = IMAG. PART OF F
C      ASF(I,J)=ATOMIC SCATTERING FACTOR CORRESPONDING
C      TO ATOM TYPE J=1,2,...ECT., AND THE ITH REFLECTION
C      JJ(K) = TYPE OF ATOM (JJ = 1,2,3,4,5,OR 6)
C      MILLER INDICES NH = H, NK = K, NL = L
C      X(K), Y(K), Z(K) = COORDINATES OF KTH ATOM
C      R = RESIDUAL FACTOR
C      IREM = REMAINING F(H,K,L) BEYOND AN INTEGRAL MULTIPLE OF 100
C      KMAX = MAX VALUE OF K = TOTAL NO. OF COORDINATES CONSIDERED
C      LMAX = NUMBER OF BLOCKS OF 100 F(H,K,L)
C      IMAX = MAX VALUE OF I = NUMBER OF F(H,K,L) IN EACH CALCULATION
C      NTOTAL = TOTAL NUMBER OF FO(H,K,L)
C      SENSE1 = 0 FOR NON-CENTROSYM STRUCTURE, 1 FOR CENTROSYM
C      SENSE2 = 0 FOR DELETION OF F PRINT OUT, 1 FOR PRINT OUT OF F
C
C
C      THE ORDER OF THE DATA CARDS IS AS FOLLOWS....
C      (1)      CARD CONTAINING SENSE1 AND SENSE2 PER FORMAT 702
C      (2)      CARD CONTAINING NTOTAL PER FORMAT 21
C      (3)
C              (A) IF LMAX=0 , DECK OF H,K,L, OBSERVED F VALUES PER
C                  FORMAT 1 FOLLOWED BY DECK OF ATOMIC SCATTERING
C                  FACTORS PER FORMAT 2 (H,K,L ORDERED LIKE F)
C              (B) IF LMAX IS GREATER THAN 0 , ALTERNATE DECKS OF
C                  100 H,K,L AND 100 A S F
C      (4)      AS MANY SETS OF DATA AS DESIRED, ORDERED AS FOLLOWS...
C              (A)  ALPHAMERIC IDENTIFICATION CARD, WITH AN
C                  IDENTIFYING MESSAGE IN COLS 2-79. COLUMN
C                  80 MUST BE BLANK
C              (B)  CARD CONTAINING KMAX PER FORMAT 21
C              (C)  THE DECK OF COORDINATES, WITH ONE POINT
C                  PER CARD AS PER FORMAT 4 BELOW
C      (5)      A CARD WITH A 1 PUNCH IN COLUMN 80
C
C
C      INTEGER SENSE 1,SENSE2
C      DIMENSION ASF(100,6),NH(100),NK(100),NL(100),FO(100),FO1(100),
C      1F(100),A(100),B(100),X(50),Y(50),Z(50),JJ(50)
C      1 FORMAT(3I3,2X,E9.3)
C      2 FORMAT (3I3,1X,F6.4,4X,F6.4,4X,F6.4,4X,F6.4,14X,F6.4,4X,F6.4)
C      3 FORMAT(I4)
C      4 FORMAT(3(F5.3,2X),I2)
C      18 FORMAT(26H CENTROSYMMETRIC STRUCTURE )
C      19 FORMAT(4HKTHE,I3,16H COORDINATES ARE/4X,1HX,6X,1HY,6X,1HZ,3X,
C      1 4HTYPE/(1X,F5.3,2X,F5.3,2X,F5.3,2X,I2))
C      21 FORMAT(I4)
C      22 FORMAT(30H NON-CENTROSYMMETRIC STRUCTURE)

```

```

23 FORMAT(32H AND CENTROSYMMETRIC EQUIVALENTS)
24 FORMAT(1X,8HASF CARD,3I3,1X,15HIS OUT OF ORDER)
32 FORMAT(1HK,2X,1HH,2X,1HK,2X,1HL,5X,10HOBSERVED F,3X,6HCALC F/
1 (1X,3I3,2F12.3))
34 FORMAT(1HK,2X,1HH,2X,1HK,2X,1HL,5X,10HOBSERVED F,4X,5HMOD F,9X,
1 1HA,11X,1HB/(1X,3I3,4F12.3))
35 FORMAT(13HLRESIDUAL R =,F6.4,5X,6HNUM = ,F10.4,5X,6HDEN = ,F10.4)
42 FORMAT(17H ARITHMETIC ERROR)
700 FORMAT(1X,78H
1
, I1)
701 FORMAT(2H1 )
702 FORMAT(2I1)
SUM2=0.
READ(1,702)SENSE1,SENSE2
READ(1,21)NTOTAL
LMAX=NTOTAL/100
L1=LMAX+1
IREM=NTOTAL-LMAX*100
IF(LMAX.EQ.0)GO TO 72
70 REWIND 6
IMAX=100
GO TO 160
72 IMAX=IREM
160 DO 71 L=1,L1
READ(1,1)(NH(I),NK(I),NL(I),FO(I),I=1,IMAX)
DO906I=1,IMAX
SUM2=SUM2+FO(I)
READ(1,2) MH,MK,ML,(ASF(I,J),J=1,6)
IF(NH(I)-MH)901,902,901
902 IF(NK(I)-MK)901,904,901
904 IF(NL(I)-ML)901,906,901
901 WRITE(3,24)MH,MK,ML
STOP
906 CONTINUE
IF(LMAX.EQ.0)GO TO 151
150 WRITE(6) (NH(I),NK(I),NL(I),FO(I),I=1,IMAX)
WRITE(6) ((ASF(I,J),J=1,6),I=1,IMAX)
151 IF(L.GE.LMAX)IMAX=IREM
71 CONTINUE
153 IF(LMAX)152,77,152
152 REWIND 6
IMAX=100
77 READ(1,700)NOMORE
IF(NOMORE.NE.0)GO TO 45
READ(1,21)KMAX
WRITE(3,701)
WRITE(3,700)NOMORE
READ(1,4)(X(K),Y(K),Z(K),JJ(K),K=1,KMAX)
IF(SENSE1.EQ.0)GO TO 17
WRITE(3,18)
WRITE(3,19)KMAX,(X(K),Y(K),Z(K),JJ(K),K=1,KMAX)
WRITE(3,23)
GO TO 125
17 WRITE(3,22)
WRITE(3,19)KMAX,(X(K),Y(K),Z(K),JJ(K),K=1,KMAX)

```

```

125 SUM1=0.
    DO 79 L=1,L1
      IF(LMAX.EQ.0)GO TO 76
      READ(6) (NH(I),NK(I),NL(I),FO(I),I=1,IMAX)
      READ(6) ((ASF(I,J),J=1,6),I=1,IMAX)
76 DO 7 I=1,IMAX
    A(I)=0.
    B(I)=0.
    F(I)=0.
    CH=NH(I)
    CK=NK(I)
    CL=NL(I)
    DO 7 K=1,KMAX
      PHI=6.2832*(CH*X(K)+CK*Y(K)+CL*Z(K))
      J=JJ(K)
      ASFF=ASF(I,J)
      IF(SENSE1.EQ.0)GO TO 6
      F(I)=F(I)+2.*ASFF*CCS(PHI)
      GO TO 7
6 A(I)=A(I)+ASFF*COS(PHI)
  B(I)=B(I)+ASFF*SIN(PHI)
  F(I)=SQRT(A(I)**2+B(I)**2)
7 CONTINUE
  IF(SENSE2.EQ.0)GO TO 88
  IF(SENSE1.EQ.0)GO TO 87
  WRITE(3,32)(NH(I),NK(I),NL(I),FO(I),F(I),I=1,IMAX)
  GO TO 88
87 WRITE(3,34)(NH(I),NK(I),NL(I),FO(I),F(I),A(I),B(I),I=1,IMAX)
88 DO 26 I=1,IMAX
26 SUM1=SUM1+ABS(FO(I)-ABS(F(I)))
  IF(L.LT.LMAX)GO TO 79
90 IMAX=IREM
79 CONTINUE
  R=SUM1/SUM2
  WRITE(3,35)R,SUM1,SUM2
  CALL OVERFL(NUTTY)
  IF(NUTTY.EQ.1)WRITE(3,42)
  CALL DVCHK(NUTTI)
  IF(NUTTI.EQ.1)WRITE(3,42)
  GO TO 153
45 IF(LMAX.EQ.0)STOP
  REWIND 6
  STOP
  END

```

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AN INVESTIGATION OF THE CRYSTAL STRUCTURE
OF SODIUM HYPONITRITE

by

RALPH LEROY HOLLIS, JR.

B. S., Kansas State University, 1964

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Physics

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1965

The valence states between nitrogen and oxygen have been studied by many chemists as well as physicists. The structures of nitrogen oxides have been studied in recent years, yet there are many things that are still unknown. For the case of the $\text{N}_2\text{O}_2^{--}$ ion, investigations by infrared and Raman Spectroscopic methods in the vapor and liquid phases indicated the trans-configuration. On the other hand preliminary X-ray studies of some $\text{N}_2\text{O}_2^{--}$ compounds indicated the cis-configuration. It was therefore important to determine the structure of the $\text{N}_2\text{O}_2^{--}$ ion using the mathematical techniques of X-ray diffraction. Data in the form of structure factors had been prepared by S. C. Chang for sodium hyponitrite, and these were used to obtain a tentative structure.

Crystalline sodium hyponitrite has a monoclinic cell with space group $\text{P}2_1/\text{b}$. The cell parameters were determined to be

$$a = 7.32 \pm 0.03 \text{ \AA}$$

$$b = 17.10 \pm 0.07 \text{ \AA}$$

$$c = 6.01 \pm 0.02 \text{ \AA}$$

$$\alpha = 90^\circ$$

$$\beta = 90^\circ$$

$$\gamma = 107.5 \pm .04^\circ .$$

The Patterson projection was computed as well as the three-dimensional Patterson function. Peak height interpretation was conducted in order to predict the heights of Patterson peaks due to atom foldings. Unitary structure factors were calculated and the inequalities of Harker and Kasper were

applied. Because there were few large unitary structure factors, these inequalities could not be used. The symbolic addition procedure of Karle and Hauptman was applied, but absence of sufficient data for the 1 Miller index prevented the success of this method. The Harker section for $P2_1/b$ was calculated. Clues were obtained from the Harker section and Patterson projection which enabled trial structures to be postulated. R values were computed and a structure was selected for refinement. Refinement stopped at $R = .3179$.

The molecular form was found to be of trans-structure with three waters of hydration. Atomic coordinates obtained to date are given as follows:

	x	y	z
Na ₁	.823	.068	---
Na ₂	.057	.098	---
O ₁	.651	.167	---
O ₂	.245	.000	---
N ₁	.542	.091	---
N ₂	.357	.071	---
W ₁	.350	.195	---
W ₂	.248	.263	---
W ₃	.090	.250	---

Investigation of the convergence process indicated that one or more waters were probably misplaced or missing. Thus the structure obtained remains tentative until further work can be done.

During the work it was necessary to develop a large number of computer programs. A fast two- and three-dimensional Fourier-Patterson Program with a high degree of flexibility was written. Minimum machine requirements

included 40,000 decimal digits of core storage, and at least four magnetic tape units in addition to those units required for input, output, and the system monitor. A card-to-magnetic tape unit and a tape-to-printer unit were required peripheral equipment. The program was written in FORTRAN II symbolic language and could therefore be run on many medium and large scale computers. High speed operation was obtained by using the Beevers-Lipson factorization procedure, table look-up for sines and cosines, and integer arithmetic throughout. The use of magnetic tape was governed by the amount of core storage available; the running time could be optimized for a particular problem by suitable choice of a parameter within the program. Any number of X-ray reflections could be included subject to the requirement that no Miller index exceeded 99. The full unit cell could be calculated in a single run without restrictions, or any portion of the unit cell could be calculated separately. In addition, the program was segmented into five links, each of which could be run independently if desired. Link A sorted the input data and calculated the coefficients for the Beevers-Lipson factorization. Links B, C, and D performed summations over the first, second and third Miller indices, respectively. Link E created contour maps and numerical listings of the results. Link D could be by-passed if a projection were calculated. The grid interval could be $1/120$, $1/60$, $1/40$, $1/30$, $1/20$, or $1/15$ of the unit cell, and could be different for each direction.

A program was also written to calculate structure factors.