

AN INVESTIGATION OF THE CRYSTAL STRUCTURE  
OF ANHYDROUS LITHIUM ACETATE

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Master of Science

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by  
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## ABSTRACT

An investigation of the crystal structure of anhydrous lithium acetate was undertaken, using X-Ray diffraction methods. The material studied, although very hygroscopic, was shown to be anhydrous by density measurements combined with unit cell dimensions. Unit cell dimensions were determined from precession photographs using Cu K $\alpha$  radiation. Values obtained were:

$$a = 9.29 \text{ \AA}$$

$$\alpha = 101^{\circ} 0'$$

$$b = 12.33 \text{ \AA}$$

$$\beta = 100^{\circ} 19'$$

$$c = 6.80 \text{ \AA}$$

$$\gamma = 105^{\circ} 5'$$

The density was determined by the flotation method:  $d = 1.23 \text{ gm./cm.}^3$

The number of molecules per unit cell,  $Z$ , was thus shown to be 8. The presence of a centre of symmetry was indicated by a statistical method, and the space group was thus deduced as  $P \bar{1}$ .

Intensity data were collected from precession photographs using molybdenum radiation for each of the  $hk0$ ,  $0kl$ , and  $h0l$  zones. Lorentz and polarization correction factors were applied, and the observed structure factors were then put on an absolute scale using Wilson's method. By an associated method, the temperature factor was determined as  $B = 2.0 \text{ \AA}^2$ .

Patterson syntheses were performed for each of the  $hk0$ ,  $0kl$ , and  $h0l$  zones, using  $F^2$  coefficients modified by a sharpening function. A structure was postulated, from our interpretation of the Patterson syntheses, and three successive cycles of Fourier syntheses and structure factor calculations were performed. Lack of agreement between the observed and calculated structure factors indicated that the structures proposed were not correct, and suggested that the only method likely to succeed in solving the structure was a complete three-dimensional Patterson synthesis.

Programs for two-dimensional Fourier Synthesis and for Structure Factor calculations were written for the Bendix G-15D computer using the interpretive routine Intercom 1000. The Fourier Synthesis program proved to be too slow to be useful, but the Structure Factor program was quite satisfactory.

## CHAPTER I

### INTRODUCTION

The author became interested in crystal-structure analysis while working in the X-Ray Diffraction laboratory of the Division of Pure Chemistry at the National Research Council during the summers of 1957 and 1958. When the present problem was brought to her attention, it was decided to undertake it as an M.Sc. thesis project.

#### PURPOSE OF THE INVESTIGATION.

The present investigation was undertaken in the hope of providing crystallographic evidence to either support or refute spectroscopic evidence for the existence of intermolecular lithium bonding. This phenomenon was postulated by Rodionov et al. (1958) on the basis of a study of the infra-red spectra of a number of lithium alkyl, lithium aryl, and lithium alkoxide compounds. Certain frequency shifts led them to suspect the existence of both  $-C \dots Li$   $-C$  and  $-O \dots Li$   $-O-$  bonds, but they reported that the  $-O \dots Li$   $-O-$  bond was considerably stronger than its carbon counterpart. These results are to be expected if an analogy is made to the well-known phenomenon of hydrogen bonding, where bond strength increases with the electronegativity of the anion concerned. It is surprising, however, that a cation as large as lithium should be able to participate to any appreciable extent in intermolecular bond formation. It has been generally maintained that only a naked proton, as is the hydrogen ion, could approach anions closely enough to provide the large force of attraction necessary for intermolecular bonding.

In compounds where such Li bonds exist, (if they do), they should be obser-

vable as shorter than normal intermolecular distances. The existence of abnormally short intermolecular bond distances involving Li could be readily tested by an accurate crystal structure analysis of some compound in which intermolecular lithium bonds might be expected to occur.

#### SELECTION OF THE COMPOUND

The first problem, therefore, was to pick some suitable compound for a detailed structure analysis. It is well known that potassium hydrogen fluoride shows the strongest hydrogen bond yet observed (Robertson, 1953) if the shortness of the bond is taken as the criterion of strength. By analogy, a compound with the formula  $\text{KFLiF}$  would be expected to show the strongest possible intermolecular lithium bond. Unfortunately, the stability of this compound was disproved by studies of the phase diagram of the system  $\text{KF} - \text{LiF}$  by Bergman and Dergunov (1941) and by Bergman and Pavlenko (1944). The lithium compounds studied by Rodionov et al. (1958) were non-crystalline at room temperature, and were therefore unsuitable for the present investigation. Lithium acetate was finally selected as a suitable compound for the following reasons: 1) its parent acid, acetic acid, shows relatively strong hydrogen bonding; acetic acid occurs as the dimer  $(\text{HC}_2\text{H}_3\text{O}_2)_2$  in the gaseous state; 2) lithium acetate is crystalline at room temperature; and 3) it can be easily obtained. The usual form of lithium acetate is the dihydrate, but we decided that the anhydrous compound, if it exists, would be more suitable for the present purpose since crystal-chemical considerations suggest that in the dihydrate, lithium would tend to surround itself with water molecules rather than participate in intermolecular bonds. Shortly after we made this decision, Amirthalingam and Padmanabhan (1958) published a brief account of their work on the crystal structure of lithium acetate dihydrate. No evidence of intermolecular lithium bonding could be inferred from their work, in



fact, the intermolecular distances were on the whole, larger than those usually observed.

#### THE X-RAY DIFFRACTION TECHNIQUE

Historically speaking, the X-Ray diffraction technique of structure analysis extends back to 1912, when von Laue discovered the diffraction of X-Rays by crystals. Since then, a great many crystal structures have been solved, and a great deal of detailed information has been deduced on bond lengths and angles and on atomic configurations in such groups as the silicates and the aromatic organic compounds. Enormous progress has also been made in developing the mathematical and computational methods necessary for structure analysis, especially since the advent of high-speed electronic digital computers. The feature which makes the X-Ray method incapable of easy application to all structure problems is that, despite these developments, a stage of trial and error generally is encountered during the analysis; in most cases the experimental data do not provide sufficient information to work out the structure directly. Use of the more recent methods speeds up the trial-and-error process, and may sometimes offer valuable clues as to the correct structure, but unfortunately many of the most generally fruitful methods were inapplicable to this problem. The X-Ray diffraction technique does, however, eventually provide information as to the exact electron distribution in a compound (if the crystal structure can be solved) which is not obtainable by any other method, and it was just such information which was required in the present problem.

## CHAPTER II

### EXPERIMENTAL METHODS

#### TREATMENT OF CRYSTALS

For a structure determination, one of the first requirements is a supply of suitable single crystals. One hundred grams of "anhydrous lithium acetate" were purchased from the Fabian Chemical Company (Montreal). This material consists of a fine hygroscopic powder with which is mixed a relatively few tiny, colorless crystals, which are less hygroscopic than the powder. These crystals were found by sifting fairly large quantities of the material through a series of sieves, or alternatively, by hand-picking the crystals under a binocular microscope. An attempt was made to prepare some purified single crystals of anhydrous lithium acetate by recrystallization of a few of the tiny crystals from absolute ethanol; large euhedral, colorless, non-hygroscopic plates resulted, but unfortunately a chemical analysis of these showed them to be lithium acetate dihydrate.\* An X-Ray powder photograph of this compound (crystallized from absolute ethanol) is shown in Figure 1. Some of the tiny hygroscopic crystals from the commercial chemical were also powdered and immediately sealed in a tiny glass capillary. A powder photograph of this compound is shown in Figure 2. The two photographs are seen to be unmistakably different; none of the strong lines are common to both photographs. Therefore, the original material must have undergone some change during recrystallization. From the name by which the product was sold "anhydrous lithium acetate", and from the hygroscopic nature of the original material, we concluded that the change was, in fact, hydration. No mention is made in the standard works (Structure Re-

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\* We are indebted to Mr. H. Seguin, of the National Research Council for performing this analysis.

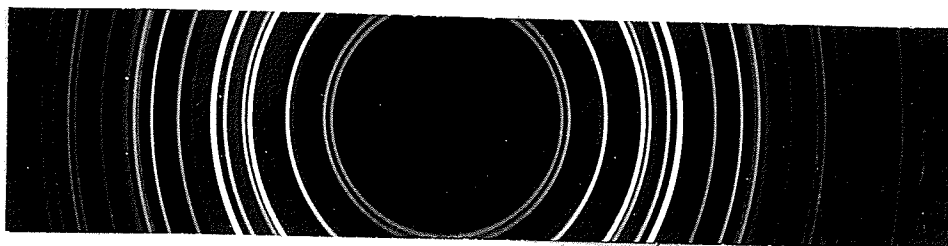


Figure 1

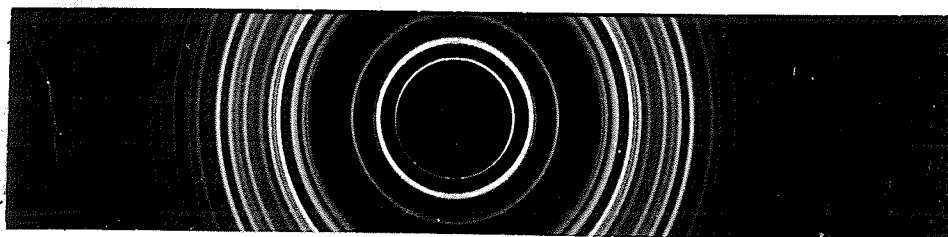


Figure 2



Figure 3

Figures 1,2,3 - X-Ray Powder Photographs of Lithium Acetate, Cu  
Radiation, Ni filter, 2 mm =  $1^\circ$  e.  
Figure 1 - Dihydrate form.                      Figure 2 - Anhydrous form.  
Figure 3 - Mixture of Dihydrate and Anhydrous forms.

ports (1913 - 52), Chemical Rubber Handbook (1959), etc.,) of the compound anhydrous lithium acetate.

In an effort to assure that the crystal studied would be anhydrous, some of the original crystals were subjected to heating at  $110^{\circ}\text{C}$ . for periods of up to six hours. Such treatment served only to make them much more susceptible to hydration than before heating; even after being allowed to cool in vacuum, they dissolved extremely rapidly in water of hydration as soon as they were exposed to air. Similar results were observed after storing a few crystals in a  $\text{P}_2\text{O}_5$  dessicator. These observations suggest to us that perhaps a very thin layer of the dihydrate had formed a protective coating around a nucleus of crystalline anhydrous lithium acetate. Such a protective layer would be decomposed on heating or drying, and thus the resultant unprotected material would show a much greater tendency to become hydrated than the original crystals. Some of the heat-treated material was powdered and sealed in a glass capillary as rapidly as possible after being removed from vacuum. A powder photograph of this sample is shown in Figure 3. This picture shows some lines from each of the two previous photographs, and the sample is therefore assumed to be a mixture of the dihydrate and the anhydrous form.

Additional evidence showing the likelihood that the original crystals were anhydrous is presented and discussed in the next chapter. It should be pointed out that neither a very thin crystalline layer nor a relatively thick non-crystalline layer surrounding a crystalline nucleus would have any noticeable effect on the X-Ray photograph of the substance studied. Therefore, the crystals studied were coated with a waterproof material to prevent hydration during the experiments. Both Krylon, a plastic waterproof spray, and transparent nail polish were used at different times, with equal success. With either of these coatings, a crystal did not deteriorate for about two weeks, whereas it became unusable within

an hour (after being taken from the tightly closed sample bottle) if unprotected.

In the initial stages of this work, any transparent single crystals which appeared to be of suitable size were mounted on a glass fiber about 0.01 cm. in diameter, protectively coated, and used for taking X-Ray diffraction photographs. Using a binocular microscope, crystals were mounted on glass rods using a drop of Duco or Household cement mixed with isopropyl alcohol. This mixture became tacky and then hardened in about 30 seconds. Crystals were selected, and if necessary, cut with a razor blade, so as to be not larger than 0.03 cm. in each dimension.

Sieves, used for sifting the powder, provided crystals having dimensions between 0.06 cm. and 0.015 cm.

A further criterion as to whether any crystal should be considered suitable for study was its behaviour under the polarizing microscope. If the crystal showed complete extinction four times in one complete revolution of the stage of the microscope, it was assumed to be untwinned and therefore suitable. The extinction positions were also used to help orient the crystals; generally crystals were mounted so that the glass fiber axis was approximately parallel or perpendicular to an extinction direction. The glass fibres were inserted in small brass pins, using beeswax as an adhesive. These pins then fitted interchangeably into the adjustable heads of the single-crystal X-Ray cameras.

#### SINGLE-CRYSTAL X-RAY DIFFRACTION PHOTOGRAPHS.

In X-Ray crystallography, we are concerned with the diffraction of X-Rays by the electrons of the atoms; since crystals consist of groups of atoms which are repeated indefinitely in three dimensions, quite complex interference patterns are produced. Although von Laue derived the first set of mathematical

relationships describing this phenomenon, the most generally used equation is that of W.L. Bragg (1913):  $2d \sin \theta = n\lambda$ , where  $d$  is the perpendicular distance between successive parallel atomic planes in the crystal in Angstrom units,  $\theta$  is the Bragg or glancing angle (Bragg considering X-Rays to be "reflected" by sets of parallel atomic planes); " $n$ " is an integer denoting the order of reflection and  $\lambda$  is the wavelength of the X-radiation in Å units.

While the concept of sets of parallel atomic planes of various interplanar spacings is extremely useful in most of the more common X-Ray powder work which is used mainly to identify compounds by comparison with standard diffraction patterns, a somewhat different concept is more useful in single-crystal work which is used for structure analysis. This latter concept is called the reciprocal lattice, and is derived from the direct lattice by drawing normals to all the sets of parallel planes from an arbitrary origin. Then along the normals are plotted points whose distances from the origin are reciprocals of the interplanar spacings of the sets of planes concerned. The points thus located constitute a three-dimensional lattice in which each lattice point represents an entire set of parallel atomic planes of the direct lattice.

X-Ray diffraction photographs were taken with Buerger's Precession camera using either copper or molybdenum radiation. This ingenious instrument, shown in Figure 4, permits unusually easy interpretation of its photographs because they are undistorted representations of portions of the reciprocal lattice. A typical precession photograph is shown in Figure 9. It will be noticed that each strong reflection is accompanied by two weaker reflections near it on a line joining the reflection to the centre of the picture. These two reflections are due to the diffraction of small amounts of radiation of wavelengths slightly less than the predominant wavelength. The faint lines emanating from the centre of the picture are also due to diffraction of small amounts of radiation of continu-

ous wavelength. The blank area in the centre of the photograph is due to a metal trap which absorbs the direct (undiffracted) X-Ray beam which would otherwise cause serious fogging on the film. The photograph shown is of a well-aligned crystal; the central horizontal line is parallel to the line joining the two fiducial marks near the outer edges of the film, and the central horizontal line is a diameter of the circle of reflections recorded.

Figure 4.  
The Buerger Precession Camera



Figures 5 - 9 show some of the stages in aligning a crystal on a precession camera. Adjustments to bring a crystal into proper alignment are made with the aid of small adjusting screws to two mutually perpendicular rockers on the camera head. By means of them, the axis along which a crystal was originally mounted can be tilted as much as  $20^{\circ}$  in any direction. Figures 5 - 8 show the process of aligning a crystal so that a main reciprocal lattice row corresponds to the axis of rotation. In each of these photographs arrows show the position of the row chosen. Corrections to the rockers are determined by measuring the number of degrees between the reciprocal lattice row and the line joining the fiducial spots

Figure 5.

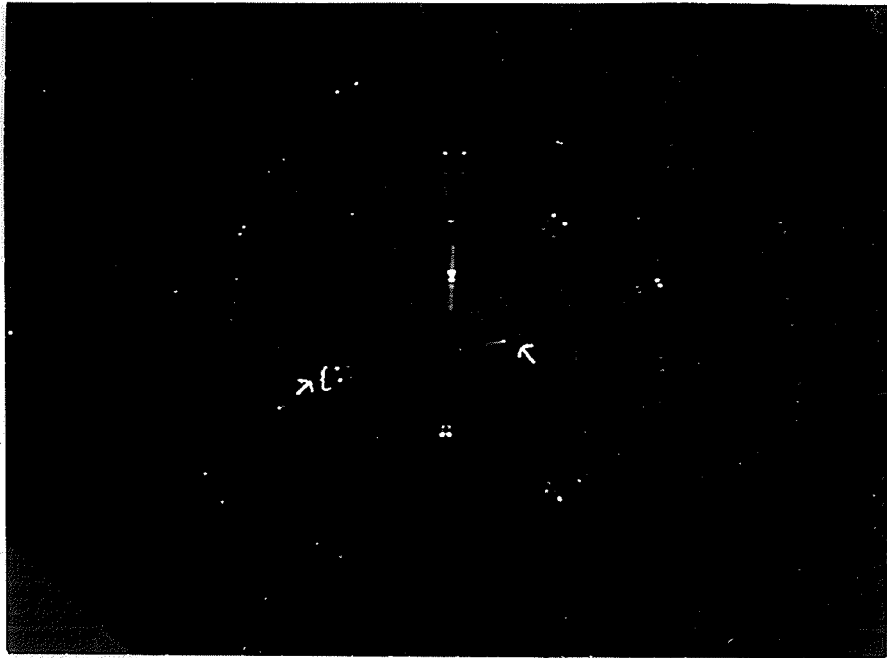


Figure 6.



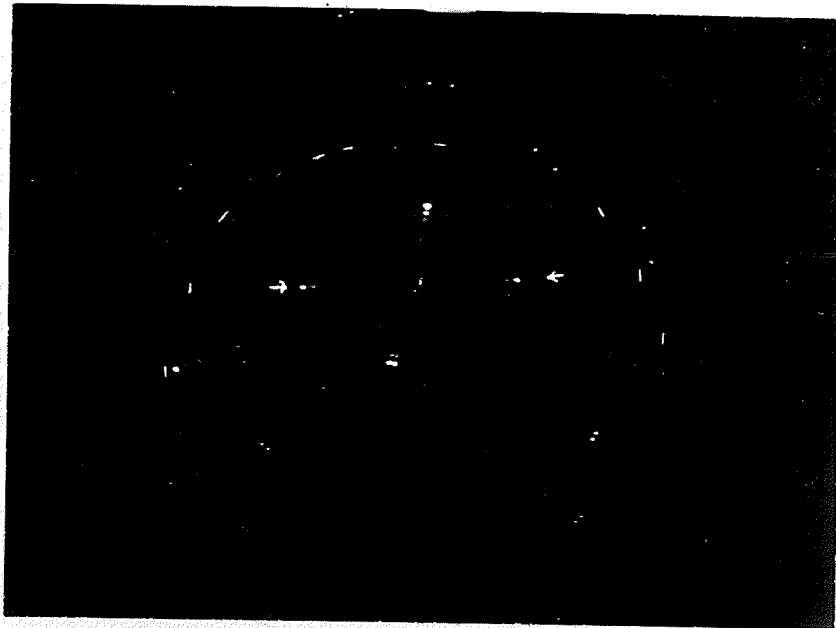
Figures 5,6 - X-Ray Precession Photographs of Anhydrous  
Lithium Acetate - Successive Stages in Alignment.



Figure 7.



Figure 8.



Figures 7,8 - X-Ray Precession Photographs of Anhydrous Lithium Acetate - Successive Stages in Alignment.

which are parallel to the axis of rotation. For each of these photographs one of the rockers was parallel to the film; the correction was therefore made to that rocker. Corrections can also be made by measuring the differences in length between the two ends of the row (measured from the centre of the photograph), and reading the appropriate correction directly in degrees from an orientation error chart (Von der Heyde, 1959). Correction is made to the rocker so as to bring the side of the crystal corresponding to the shorter end of the row towards the incident beam of X-Rays. In Figures 5 and 6, one end of the row is noticeably doubled, and in Figure 7 it is slightly doubled. The doubling is a result of inaccurate alignment of the row with respect to the rocker which is perpendicular to the film. This effect is corrected by taking successive exposures with each rocker alternately parallel and perpendicular to the film. Generally, at least four exposures are needed to bring a reciprocal lattice row into proper alignment, assuming that a main reciprocal row (with reflections close to the centre of the photograph) is visible on the initial picture. If such a row is visible but inclined from the horizontal at an angle greater than  $20^{\circ}$ , the crystal has to be remounted to bring the row closer to the horizontal. In Figure 8 the row is seen to be fairly well aligned with respect to the two rockers, although small corrections had still to be made to them.

Once the crystal has been adjusted for rotation about a reciprocal lattice row, it is necessary to find a main non-reciprocal axis perpendicular to the axis of rotation, about which to precess the crystal. To find such a direct lattice row one generally must rotate the crystal in successive exposures until a satisfactory picture is obtained; this procedure has to be used except in a few fortuitous situations and is time-consuming and frustrating. In more favorable cases, where a suitable direct row is not far from the normal to the film (as in Figure 8) more direct methods may be used. One of these involves picking out undoubled streaks

such as those marked in Figure 8, and from them the general orientation of the circle of reflections. In this case the difference in length of the two parts of the vertical axis is measured, and the angular correction is applied around the axis of rotation. In Figure 8, the circle is centred somewhat below the line joining the fiducial spots, and therefore the crystal was rotated (by  $5^{\circ}$ ) so as to bring the top half of the crystal forward (toward the incident radiation). In Figure 9, the crystal is satisfactorily aligned with respect to both the axis of rotation and the axis of precession. The same orientation error chart as previously mentioned may be used to find the appropriate correction for bringing a crystal axis into coincidence with the axis of precession. Figure 10 shows a similar photograph, but taken with molybdenum radiation rather than copper. As a result of the shorter wavelength, the  $\sin \theta$  values for all reflections are considerably less, bringing the reflections closer to the centre of the photograph in Figure 10 than in Figure 9.

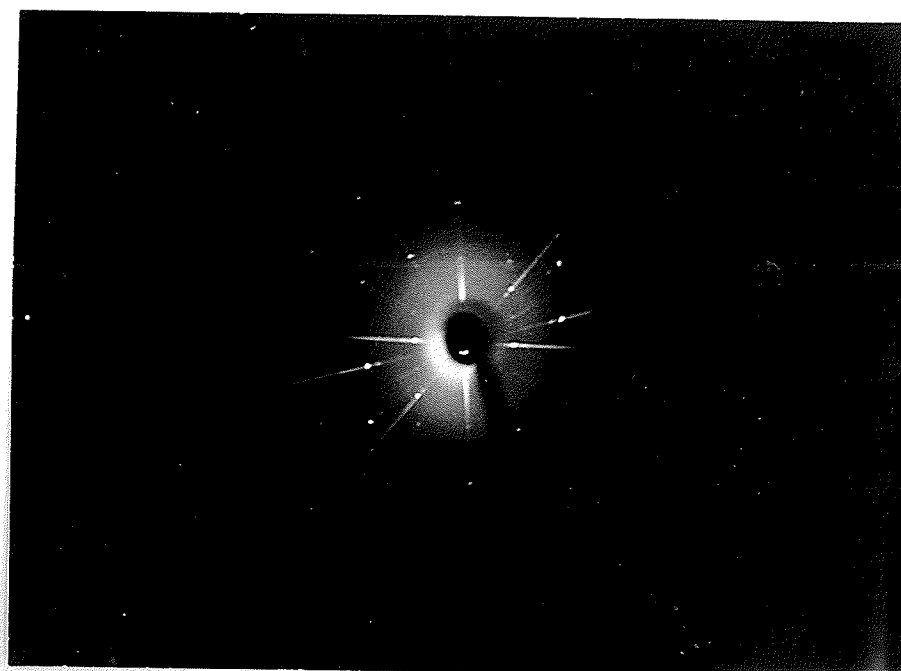
In Figures 9 and 10, a so-called "layer line screen" was placed so as to permit recording of only one layer of the reciprocal lattice, thus omitting all the doubled reflections due to other layers in previous photos.

Figures 11 and 12 illustrate a second method of aligning a crystal axis with the axis of precession, presuming the crystal is properly aligned with respect to the axis of rotation. These are called "cone axis" photographs and they are taken with the film placed in the slot usually used for the layer-line screen rather than in the normal film holder. In Figure 12, a properly aligned crystal had been used which gave reflections which were arranged in a circular pattern, whereas in Figure 11, the reflections do not lie exactly on circles and represent an error in orientation of  $45'$ . To make corrections to an inaccurately-set crystal by the use of cone-axis photos is largely a matter of trial and error, but on the other hand, this method is more sensitive to errors than the first method. Because of these conside-

Figure 9.



Figure 10.



Figures 9, 10 -X-Ray Precession Photographs of Anhydrous Lithium Acetate - Precession about the a axis - Figure 9. Cu Radiation, Figure 10. Mo Radiation.

Figure 11.

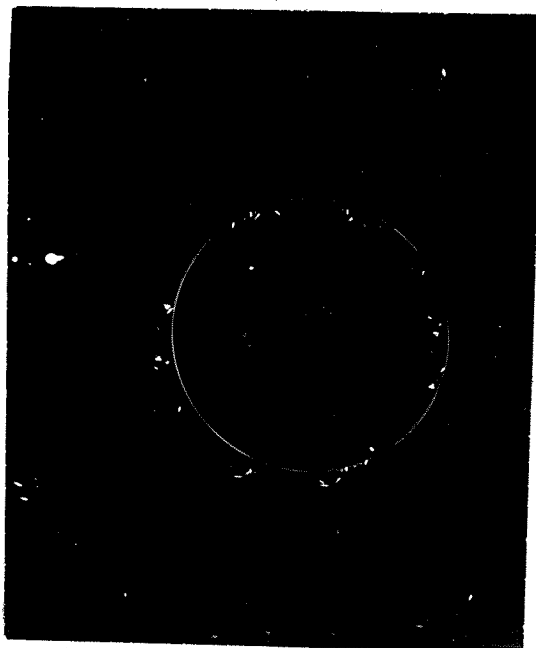
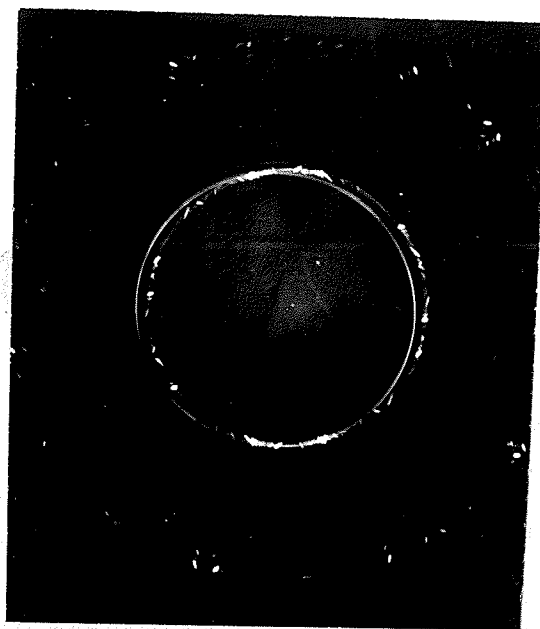


Figure 12.



Figures 11,12 -Cone Axis Photographs of Anhydrous Lithium Acetate-  
Settings.  $\mu = 20^\circ$ ,  $s = 50$  mm. - Figure 11. Precessing  
about the a axis. Figure 12. Precessing about the  
b axis.

rations, cone axis photographs are usually taken only when the crystal is approximately aligned, and hence only small corrections are required.

Accurate orientation of a crystal is an absolute necessity if the intensities of the reflections are to have any significance, and also if the unit cell dimensions are to be deduced accurately.

## CHAPTER III

### UNIT CELL DIMENSIONS AND INTENSITY DATA

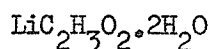
#### UNIT CELL DIMENSIONS

Before any attempt can be made to find the atomic positions in a crystal, the dimensions and symmetry of the smallest repeat unit, the unit cell, are required. These may be obtained from photographs of a properly-oriented single crystal, using such cameras as Buerger's Precession instrument. Unit cell dimensions and the symmetry of the diffraction pattern were also used in this investigation as a check on the identity of successive crystal fragments. The dihydrate has orthorhombic symmetry, whereas the material used in this study is triclinic.

The cell dimensions of the dihydrate measured by the author from precession photos are unmistakably different from those of the triclinic form. However, the cell dimensions of the dihydrate could well be studied further; serious discrepancies exist between the values determined by various investigators. Table I lists the two sets of cell dimensions of the dihydrate now published as well as those of the author.

TABLE I.

Unit Cell Dimensions (in Å. units) of



a	b	c	Source
12.80	11.63	7.43	International Critical Tables I, 345 (1933) (original source Becker and Jancke 1921).
6.86	11.49	6.59	Amirthalingam and Padmanabhan (1958)
13.16	11.64	6.62	Author's values

While the discrepancies are obviously serious, the agreement is better than

might be thought. The "a" unit of A. and P. should possibly be doubled; such an error could occur through an incorrect choice of unit cell. If this were done, the discrepancies would still generally be beyond the limits of experimental error, but might be ascribed to distortion of the cell due to varying degrees of hydration. The cell dimensions from the International Critical Tables were obtained from powder photographs; the sample may have been anhydrous, with a wrong interpretation of the powder photograph.

In determining unit cell dimensions, an appropriate reciprocal cell is first chosen and then the reciprocal lattice dimensions measured. Donnay (and Nowacki, 1954) lists various rules to be followed in choosing unit cells; adopting his convention, (the standard one in practice) the shortest reciprocal lattice unit was called  $b^*$ , the longest unit  $c^*$ , and the intermediate-length unit  $a^*$ . Also,  $\alpha^*$ ,  $\beta^*$ ,  $\gamma^*$  were all chosen to be acute angles. The  $a^*$  unit is proportional to the distance between two successive reflections along the corresponding  $X^*$  reciprocal axis. In the precession method, the absolute value of  $a^*$  is obtained by measuring the distance in cm. and then correcting by a magnification factor,  $\frac{1}{F}$ , usually  $= \frac{1}{6}$  (cm.<sup>-1</sup>).

Values thus obtained for crystals of the anhydrous material are:

$$a^* = 0.1772$$

$$b^* = 0.1338$$

$$c^* = 0.2380$$

Since the crystal has triclinic symmetry, the three interaxial angles for the reciprocal lattice,  $\alpha^*$ ,  $\beta^*$ ,  $\gamma^*$  must also be determined. Two of these were measured directly from pictures of two of the principal planes of the reciprocal lattice; the third was calculated from the angle of turn between the two crystal positions for the two pictures which was, in fact, the direct cell angle  $\alpha$ . The reciprocal angles obtained are:

$$\alpha^* = 75^\circ 32'$$

$$\beta^* = 76^\circ 2'$$

$$\gamma^* = 72^\circ 15'$$

From the reciprocal lattice dimensions, direct cell dimensions were calcu-



lated using the following formulae.

$$a = \frac{\lambda b^*c^* \sin \alpha^*}{V^*} = 9.29 \text{ \AA}$$

$$b = \frac{\lambda a^*c^* \sin \beta^*}{V^*} = 12.33 \text{ \AA}$$

$$c = \frac{\lambda a^*b^* \sin \gamma^*}{V^*} = 6.80 \text{ \AA}$$

$$\alpha = 101^\circ 0' \text{ (meas.)}$$

$$\beta = \cos^{-1} \left( \frac{\cos \alpha^* \cos \gamma^* - \cos \beta^*}{\sin \alpha^* \sin \gamma^*} \right) = 100^\circ 19'$$

$$\gamma = \cos^{-1} \left( \frac{\cos \alpha^* \cos \beta^* - \cos \gamma^*}{\sin \alpha^* \sin \beta^*} \right) = 105^\circ 5'$$

Where  $V^* = a^*b^*c^* \sin \alpha \sin \beta^* \sin \gamma^* = .005119$ .

The volume of the unit cell was then calculated:

$$V = \frac{\lambda^3}{V^*} = 716.1 \text{ \AA}^3$$

The density of a lithium acetate crystal was determined by the "floating crystal" method. A crystal is added to a mixture of suitable liquids and the density of the liquid adjusted until the crystal neither floats nor sinks but remains motionless. Ethylene chloride ( $d = 1.256$ ) and ethylidene chloride ( $d = 1.174$ ) were chosen as the pair of miscible liquids since they dissolve lithium acetate only slowly. The density of this liquid was then determined using a Westphal balance.

It was found that most of the crystals studied had specific gravities in the range 1.225 - 1.230 while a few had greater specific gravities. After some preliminary work, only those crystals which had specific gravities approximately in this range were used for further study, since it was assumed that crystals with specific gravities greater than the maximum value of the range were likely to be

partially hydrated. (The specific gravity of lithium acetate dihydrate is reported (A. and P.) as 1.30).

From the measured density,  $d$  (in gm./cm.<sup>3</sup>), the volume of the unit cell,  $V$  (in cm.<sup>3</sup>), Avagadro's number,  $N$ , and the molecular weight,  $M$  (in grams/mole) of the substance studied, the number of molecules,  $Z$ , per unit cell can be calculated. Since  $Z$  must, of logical necessity, be an integer, this relationship provides a check on the accuracy of the various measurements and on the validity of the assumptions made. If the assumption is made that the molecular weight,  $M$ , corresponds to anhydrous lithium acetate, then

$$Z = \frac{V \times d \times N}{M} = \frac{716.1 \times 10^{-24} \times 1.227 \times 6.023 \times 10^{23}}{65.96} = 8.04$$

If the formula of the compound is assumed to be  $\text{LiC}_2\text{H}_3\text{O}_2 \cdot 1/2 \text{H}_2\text{O}$  then  $M = 74.97$  and  $Z = 7.08$  whereas if the formula is assumed to be  $\text{LiC}_2\text{H}_3\text{O}_2 \cdot \text{H}_2\text{O}$ , then  $M = 83.98$  and  $Z = 6.33$ . The latter possibility is extremely unlikely because of the large divergence of  $Z$  from an integral value. Symmetry requirements demand that  $Z$  be an even integer and this rules out the second formula. Error in the volume of the unit cell is probably not larger than 1%, and error in the density measurements is probably not more than 1% also. Thus the assumption that the compound studied has the anhydrous formula is shown to be very probably correct. Since the presence of four or eight water molecules per unit cell would be disclosed more or less automatically in the course of a successful structure analysis, the outcome of the investigation would not be seriously imperiled if the assumption that the compound is anhydrous were incorrect.

In summary, we may say that the evidence is strong that the compound under investigation is anhydrous lithium acetate, and that the crystals are characterized by the following constants:

$$a = 9.29 \text{ \AA}, \quad b = 12.33 \text{ \AA}, \quad c = 6.80 \text{ \AA}, \quad \alpha = 101^\circ 0', \quad \beta = 100^\circ 19'$$

$$\gamma = 105^{\circ}5', \quad V = 716.1 \text{ \AA}^3, \quad d_{\text{meas.}} = 1.227, \quad Z = 8(\text{LiC}_2\text{H}_3\text{O}_2),$$

$$d_{\text{calc.}} = 1.220$$

#### COLLECTION OF INTENSITY DATA

X-Ray photographs for intensity measurements were taken with unfiltered Mo radiation, using Buerger's Precession camera and the method of multiple exposures. The crystals used for these photographs had been accurately aligned, as previously described, so that one set of photographs was obtained for each of the three zero levels of the reciprocal lattice -  $hk0$ ,  $h0l$ , and  $0kl$ . Settings used were:  $\bar{\mu} = 30^{\circ}$ ,  $r = 20 \text{ mm}$ ,  $s = 34.5 \text{ mm}$ . Knowing the unit cell dimensions, one could index these photographs extremely easily;  $h$ ,  $k$  and  $l$  indices could be assigned to the various reflections by mere inspection of a given photograph. Figure 10 shows a typical photograph suitable for intensity measurements. These measurements were made by visual comparison with a calibrated intensity strip, prepared from the same crystal. Since only a narrow range of intensities could be accurately measured from a single film, about eight exposures of varying (accurately-timed) duration were taken for each of the three zones. By knowing the various time factors, reflections from all films could be put on the same relative scale. In practice the stronger reflections on one film were measured also on the next weaker film. By this means, some correlation between films could be achieved independently of the time factors, and each reflection was measured at least twice. The average of at least two measurements was accepted as the final intensity. Intensities were recorded in the range 1 - 650 (on a relative scale).

The intensities were corrected for Lorentz and polarization factors by a graphical method: the films were superimposed on charts reproduced from Waser (1951) and the corrections (the reciprocals of the Lorentz and polarization fac-

tors) were read off directly for each reflection. Absorption corrections were not made since molybdenum radiation (which is very penetrating) had been used.

When the measured intensity,  $I$ , has been corrected for Lorentz and polarization factors, as well as absorption and primary and secondary extinction effects (all of which proved negligible in this problem), the resulting quantity is the square of the structure factor,  $F^2$ . To distinguish this experimentally observed structure factor from that which is calculated later, the former is called  $F_o$  and the latter  $F_c$ .

CHAPTER IV  
SPACE GROUP, ABSOLUTE SCALE AND TEMPERATURE  
FACTOR DETERMINATION

DETERMINATION OF THE SPACE GROUP

As mentioned above the X-Ray pictures showed that our crystal has triclinic symmetry. In this system only two space groups are possible:  $P1$  and  $\bar{P}1$ . The presence or absence of a centre of symmetry ( $\bar{1}$ ) may be indicated by testing for the piezoelectric effect, but since we do not have an instrument for making this test, we used the statistical method of Howells, Phillips and Rogers (1950) instead. In this method, all the intensities (corrected for Lorentz and polarization factors) are divided into groups according to their  $\sin \theta$  values. In order to have enough reflections in each group for the theory to be valid, only two groups were used for each of the three zones:  $\sin \theta = 0.2 - 0.3$  and  $\sin \theta = 0.3 - 0.4$  for  $(hk0)$  and  $(0kl)$ , and  $\sin \theta = 0.25 - 0.45$  and  $\sin \theta = 0.45 - 0.65$  for  $(h0l)$ . These ranges were chosen to omit very low  $\theta$  values to which the theory does not apply, and to include approximately the same number of reflections in each group. Experimentally observed reflections did not occur much beyond  $\sin \theta = 0.5$  with  $Mo K\alpha$  radiation.

For each group, the average intensity was calculated, and the fractions  $N(Z)$  of reflections found whose intensities were equal to or less than a fraction  $Z$  of the group average. From theoretical considerations Howells et al. showed that the fractions  $N(Z)$  are given by the function  $N(Z) = 1 - \exp(-Z)$  for a non-centrosymmetric crystal and by the function  $N(Z) = \text{erf}(1/2 Z)^{1/2}$  for a centrosymmetric crystal, where "erf" is a complicated error function for which values have been tabulated. By plotting the calculated values of  $N(Z)$  against  $Z$  and comparing the result with the two theoretically derived curves, a centre

of symmetry was found to be present in the anhydrous lithium acetate structure. Figures 13, 14 and 15 show the various curves. The space group is therefore determined unambiguously as  $\overline{P1}$ .

#### DETERMINATION OF THE ABSOLUTE SCALE.

To simplify the interpretation of electron density maps and to facilitate comparison between observed and calculated structure factors, it is desirable to have the observed structure factors on the same scale as the calculated structure factors, the absolute scale. To accomplish this, a scaling factor was determined using Wilson's method (1942). This method also gives an estimate of the temperature factor constant,  $B$ , whose magnitude is determined by the amount of thermal vibration of the atoms.

In this method, the reflections from all three zones are divided into groups on the basis of their  $\sin e$  values. Ranges chosen for these groups were  $\frac{\sin^2 e}{\lambda^2} = 0.03 - 0.07, 0.07 - 0.13, 0.13 - 0.21$  and  $0.21 - 0.30$ . These represented mean values of  $\frac{\sin e}{\lambda} = 0.2, 0.3, 0.4$  and  $0.5$ . For each group the mean corrected intensity ( $= \langle F_o^2 \rangle$ ) and  $\sum_n f_n^2$  were calculated:  $\sum_n f_n^2$  represents the sum of the squares of the scattering factors corresponding to  $\frac{(\sin e)}{\lambda}$  for each atom in the unit cell,  $f_n$  values being read from tables (ex. Internationale Tabellen, 1935).

The ratios  $\sum_n f_n^2 / \langle F_o^2 \rangle$  were calculated and called  $c$ . Then  $\log c$  was plotted against  $\frac{\sin^2 e}{\lambda^2}$  and the intercept at  $\sin e = 0$ ,  $\log c_o$ , gave  $c_o$ , the scaling factor. Figure 16 shows the graph of  $\log c$  vs.  $\frac{\sin^2 e}{\lambda^2}$ ;  $c_o$  was found to be 17.4. Accordingly, all the  $F^2$  relative values were multiplied by 17.4 to put them on an absolute scale. Later calculations showed that the scaling factor,  $c_o$ , was more accurate than usually expected from this method; recalculations of the scale factor showed differences of the order of 5% (with respect to  $\sqrt{c_o}$ ) for two zones

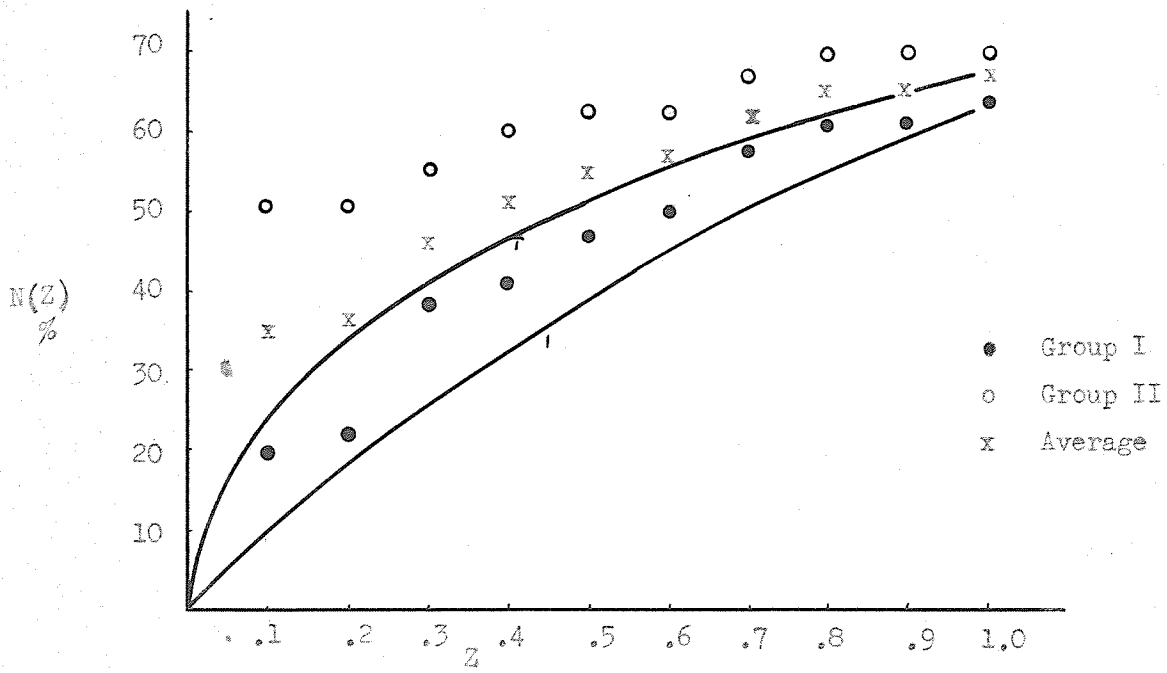


Figure 13. Statistical Test for  $\bar{I}$  - hkO Data

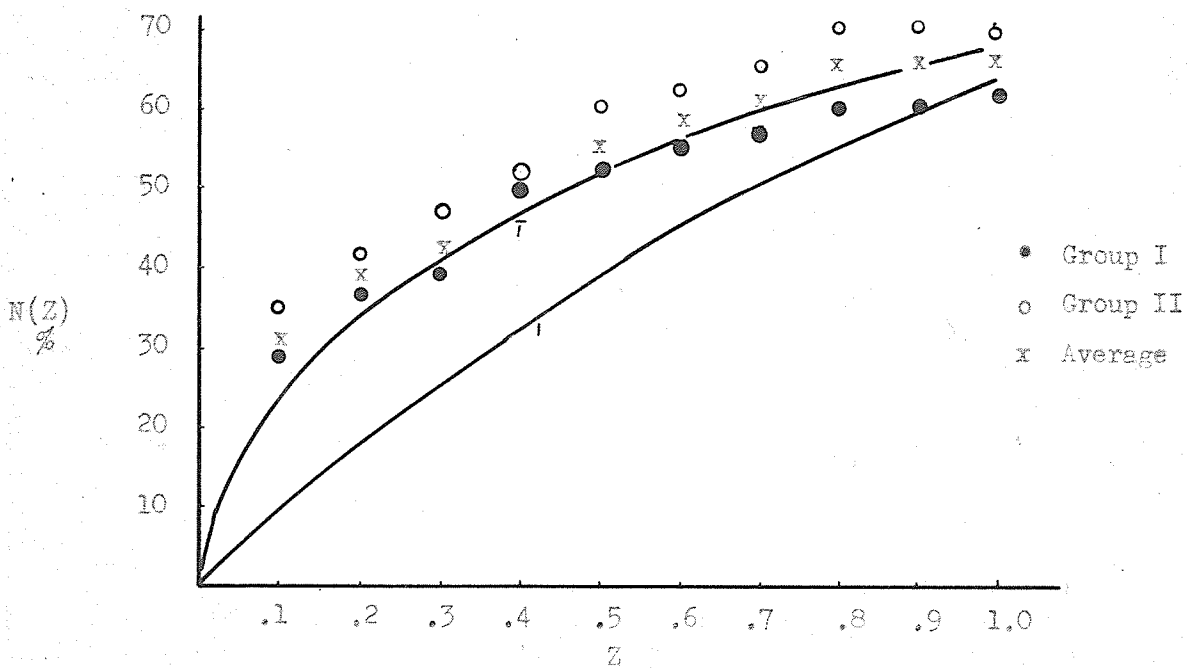


Figure 14. Statistical Test for  $\bar{I}$  - Okl Data

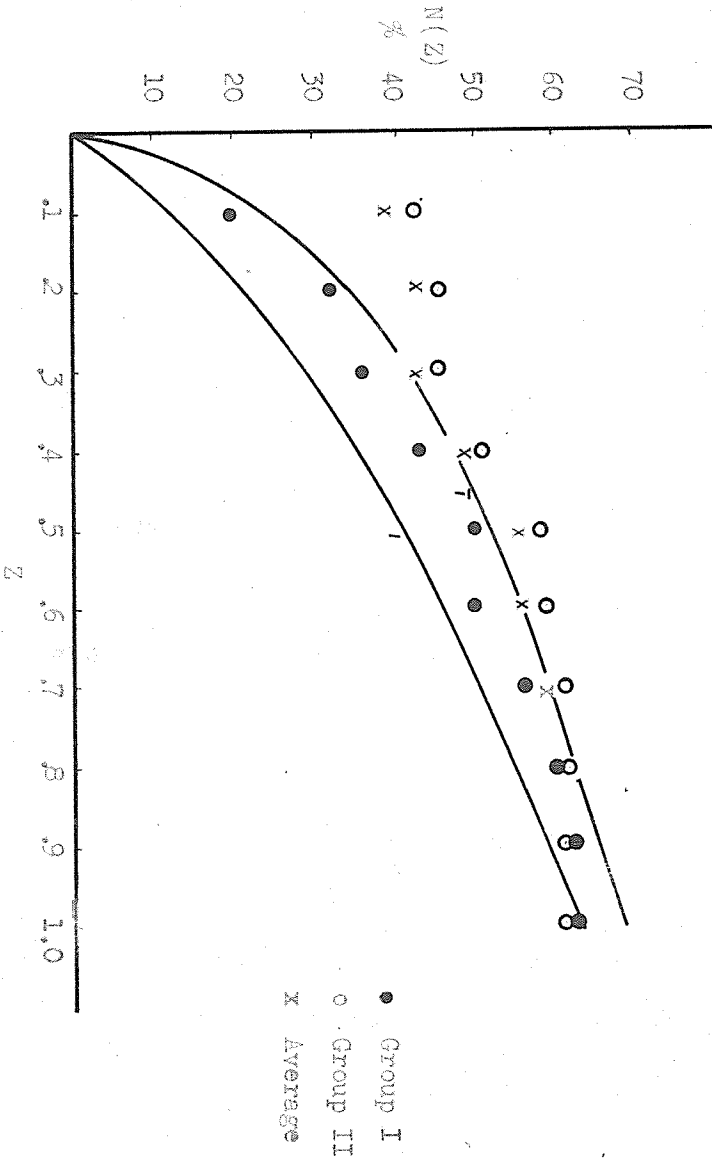


Figure 15. Statistical Test for  $\bar{I}$  - h01 Data



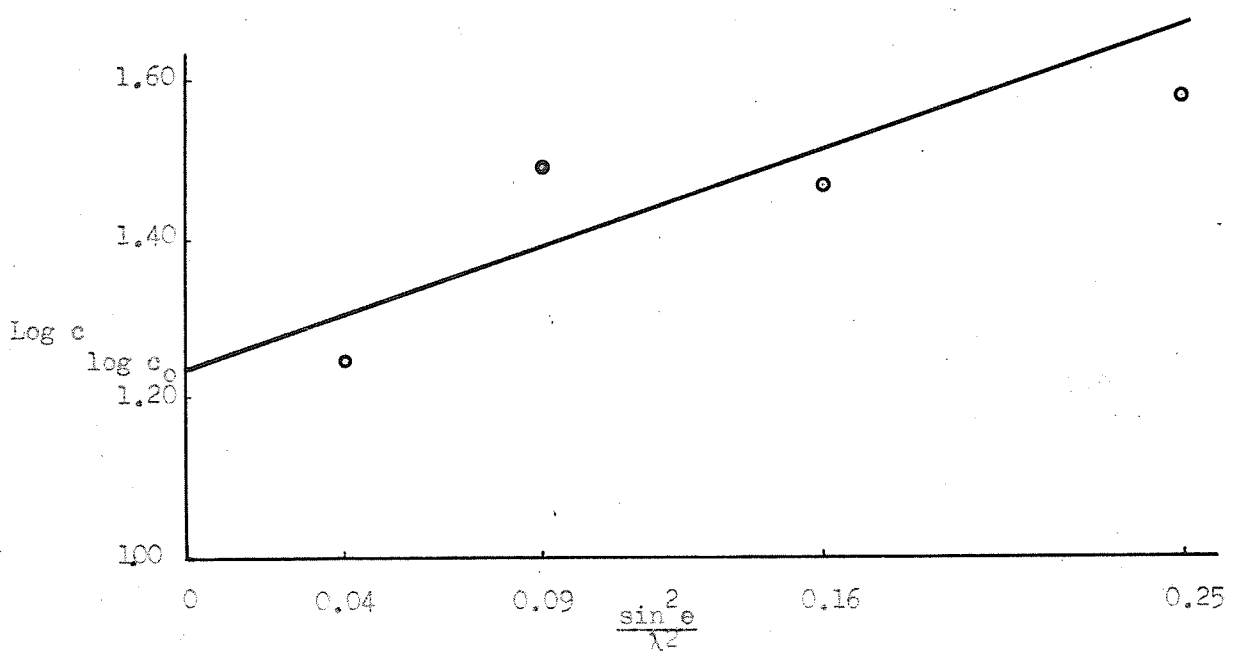


Figure 16. Determination of Absolute Scale

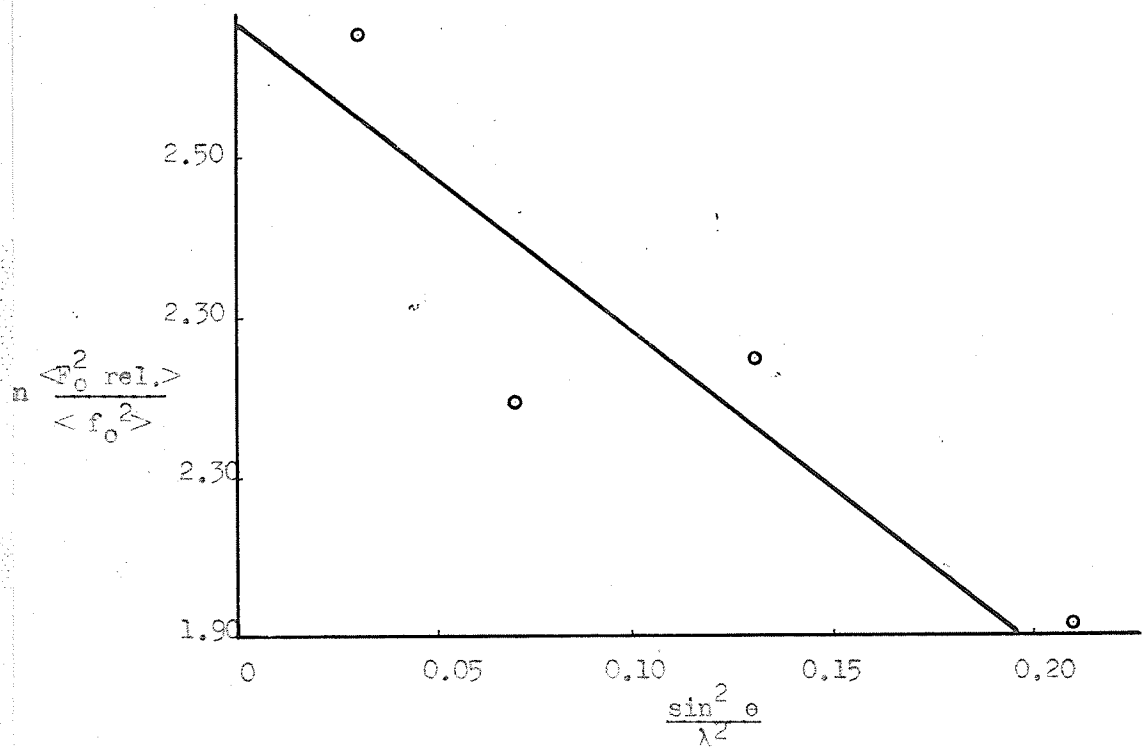


Figure 17. Determination of Temperature Factor Constant

and of 15% for one zone, while the method is usually considered accurate only to about 20%.

#### DETERMINATION OF THE TEMPERATURE FACTOR CONSTANT

Since the formula for calculating Structure Factors contains a temperature factor, the temperature factor constant must be known in advance of the calculations. To find the temperature factor constant, B, the same groups of intensities with respect to  $\frac{\sin^2 \theta}{\lambda^2}$  were used as for the scaling factor. The mean value of I ( $= \langle F_o^2 \rangle$ ) for each group was used as before, but instead of  $\sum_n f_n^2$ ,  $\langle f_n^2 \rangle$  was calculated using the same tables as mentioned previously. For both calculations, the contributions of the very light lithium and hydrogen atoms were ignored. The contributions of the carbon and oxygen atoms were weighted in the proportions 1:1 for calculating the mean.

The natural logarithms of the ratios  $\frac{\langle F_o^2 \rangle}{\langle f_n^2 \rangle}$  were plotted against their corresponding values of  $\frac{\sin^2 \theta}{\lambda^2}$ ; the slope of the graph gave  $-2B$ .

Figure 17 shows the graph of  $\ln \frac{\langle F_o^2 \rangle}{\langle f_n^2 \rangle}$  vs.  $\frac{\sin^2 \theta}{\lambda^2}$ . The value obtained was  $B = 2.0 \text{ \AA}^2$ .

## CHAPTER V

### STRUCTURE FACTORS AND THE ELECTRON - DENSITY DISTRIBUTION

In a structure analysis, the validity of any proposed structure is tested by comparing many structure factors calculated for this structure,  $F_c$ , with the corresponding observed structure factors,  $F_o$ . The structure factor,  $F_c$ , is calculated from the expression

$$F_{hkl} = \sum_i f_{oi} \cdot \exp\left(\frac{B \sin^2 \theta}{\lambda^2}\right) \cdot \exp(2\pi i(hx_i + ky_i + lz_i))$$

which simplifies for structures containing a center of symmetry (which is chosen as the origin of the coordinate system):

$$F_{hkl} = \sum_i f_{oi} \cdot \exp\left(-\frac{B \sin^2 \theta}{\lambda^2}\right) \cdot \cos 2\pi(hx_i + ky_i + lz_i).$$

For zero levels in the reciprocal lattice, a further simplification results, and formulae are of the type

$$F_{hk0} = 2 \sum_i f_{oi} \cdot \exp\left(-\frac{B \sin^2 \theta}{\lambda^2}\right) \cdot \cos 2\pi(hx_i + ky_i).$$

The symbols have the following meanings:  $f_{oi}$  is the scattering factor for the  $i$ 'th atom, and is a known function of  $\theta$ , the Bragg angle, approaching the atomic number of the atom at low values of  $\theta$ ;  $B$  (in  $\text{\AA}^2$ ) is called the temperature factor constant, and is obtained as described above;  $\lambda$  is the wave-length in  $\text{\AA}$ . of the radiation used to record the data;  $h, k, l$  are integers and are the numbers of units into which a given set of lattice planes divides the three unit distances  $a, b, c$ ;  $x_i, y_i, z_i$  are the atomic coordinates of the  $i$ 'th atom expressed as fractions of  $a, b,$  and  $c$  lengths respectively.

In general, the reason one cannot solve a crystal structure directly is because each structure factor has a phase as well as an amplitude or magnitude and only the magnitude,  $F$ , may be determined experimentally. In centrosym-

metric cases, the phase problem simplifies to assigning a positive or negative sign to each structure factor, but except in special cases, this must be determined initially by a trial-and-error procedure. The reason for our interest in the magnitude and phase of each of the structure factors is that the electron density  $\rho$  at any point  $x, y, z$  in the unit cell may be expressed as

$$\rho(x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_{l=-\infty}^{+\infty} F(hkl) \exp(-2\pi i(hx + ky + lz))$$

where  $V$  is the volume of the unit cell, and the other symbols have been previously defined. Thus to determine the electron density distribution over the whole unit cell, or in other words, to solve the structure, the required information includes the magnitude and phase of each of the structure factors,  $F_{hkl}$ . The expression giving the electron density distribution is known as a Fourier series summation or synthesis.

It is experimentally impossible to observe even the magnitudes of structure factors whose indices exceed a certain limit. This limit is governed by the Bragg equation  $\frac{2d}{n} \sin \theta = \lambda$ . If it is realized that the indices  $h, k, l$  are implicit functions of  $\sin \theta$ , and that  $\sin \theta$  cannot be greater than unity, then it follows that the limits on  $h, k$  and  $l$  are governed by the wave-length of the radiation used. For this reason it is desirable to use molybdenum radiation which has a very short wave-length and permits the experimental observations of about three times as many structure factors as copper radiation, that most commonly used. Actually, this restriction is not as important as might be thought; the magnitude of the structure factors drops fairly quickly with increasing indices, other factors being constant, and so the Fourier summation is not greatly affected by omission of all structure factors past a certain limit. For all but the most accurate work, the use of copper radiation generally permits the observation of sufficient structure factors to solve the structure.

## THE PATTERSON FUNCTION

The Patterson function of an electron density distribution is defined mathematically as

$$P(u, v, w) = \int_0^1 \int_0^1 \int_0^1 \rho(x, y, z) \rho(x+u, y+v, z+w) V dx dy dz$$

and may be represented by the Fourier series

$$P(u, v, w) = \frac{1}{V} \sum_h \sum_k \sum_l |F(h, k, l)|^2 e^{-2\pi i(hu + kv + lw)}$$

where  $u, v, w$  are fractions of the unit cell dimensions and the other symbols have been defined previously. It should be noted that the Patterson function involves  $|F_0|^2$ , which is measurable rather than  $F_0$ , the Fourier type of coefficient.

It may be seen from the definition of the Patterson function that if some electron-density distribution shows maxima at the points  $(x, y, z)$  and  $(x + u, y + v, z + w)$ , then the Patterson function will show a maximum at the point  $(u, v, w)$ .

Patterson (1934, 1935) and others have developed these ideas very fully to show how a Patterson function, plotted for all points  $0 < u, v, w < 1$ , gives information about the interatomic vectors in a structure. Basically, a Patterson map gives a picture of the interatomic vectors in a structure, all of these being placed with their origins at the same point. In cases where there are only a few atoms per unit cell a Patterson map may be fairly easily interpreted to give the electron-density distribution. However, in all but the simplest cases, a Patterson map is not easily interpreted. Many of the Patterson peaks may overlap (especially if a two-dimensional map is used), since the number of peaks increases with the square of the number of atoms. For this reason, the coefficients  $|F_0|^2$  are often modified by "sharpening" functions which sharpen the Patterson peaks and therefore help eliminate overlapping. Such functions, however, often have the effect of distorting the Patterson maps, and must therefore be used with discretion.

In this investigation the modification function used was (Lipson and Cochran, 1953)

$$M(s) = \left(\frac{1}{f}\right)^2 \exp\left(-\frac{\pi}{p} s^2\right)$$

where  $s = \frac{\sin \theta}{\lambda}$  and  $\hat{f} = \hat{f}_0 \exp\left(-B \frac{\sin^2 \theta}{\lambda^2}\right)$ ;  $\hat{f}_0$  is called the "unitary scattering factor" and is a function of  $\frac{\sin \theta}{\lambda}$ . B had been determined to be  $2.0 \text{ \AA}^2$  and p was chosen\* to be 6.0. A table of values of M(s) was calculated for  $0 < s < 2$ , and a curve drawn of M(s) vs. s. The value of s was calculated for each reflection, and the appropriate value of M(s) was read from the curve. Each of the reflections then had its  $F_0^2$  value (on absolute scale) multiplied by the appropriate M(s) value.

The resulting values, which are called  $F^2_{\text{mod}}$ , were then used as coefficients in Patterson syntheses, one synthesis being performed for each zone of reflections. The calculations were done with the aid of a Bendix G-15D computer. Computational aspects of the problem are discussed in the following chapter.

Because the sharpening function had a maximum at  $\sin \theta$  of approximately 0.45, and because the limit of the observed structure factors was at about  $\sin \theta = 0.55$  there was a large termination-of-series effect which created large negative values at some points in the Patterson map. A less drastic modification curve could have been used, but while this would have lessened the termination-of-series errors and hence created fewer negative values, it would also have had a lesser sharpening effect on the positive peaks.

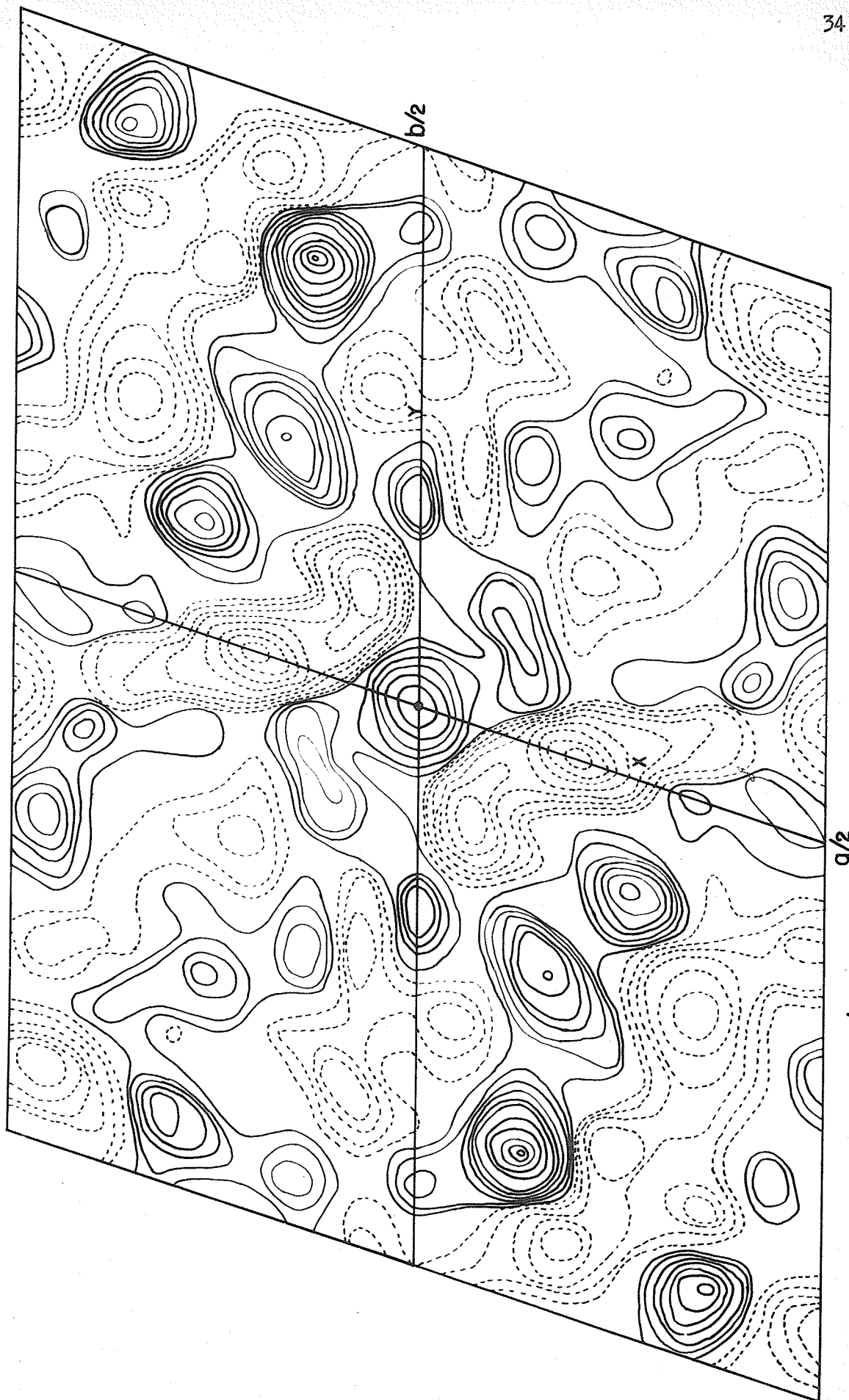
\* This value for p was chosen on the advice of Dr. J. Trotter of the National Research Council.

The calculated values of  $P(u,v,w)$  were plotted on grids and the resulting Patterson maps were then contoured. From two of these three maps, shown in Figures 18 and 19, a plausible structure was proposed. This is shown in Figures 20 and 21. The third map showed too much overlapping to be interpreted. This structure accounted for the bigger peaks in the Patterson maps, and seemed reasonable from a crystal-chemical point of view. In proposing this structure, the acetate group was thought of as planar and as having trigonal symmetry; this assumption was reasonable on the basis of previous acetate structures which all showed planar acetate groups and bond angles close to  $120^\circ$  (for example, the structures of  $\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$  done by Niekerk and Schoening (1953)).

Hydrogen atoms were ignored throughout the investigation. For the first structure, carbon and oxygen atoms were both treated as having the scattering power of nitrogen. No attempt was ever made to assign positions to the lithium atoms.

Table II gives the fractional atomic coordinates of each of the structurally independent atoms in the various structures proposed (neglecting the lithium and hydrogen atoms). The atoms are labelled only with respect to their acetate groups, and no continuity in naming the atoms was attempted since we made drastic changes in our successively proposed structures. Figures 20 and 21 show projections of our first proposed structure along the a and c axes.

PATTERSON SYNTHESIS (hko)

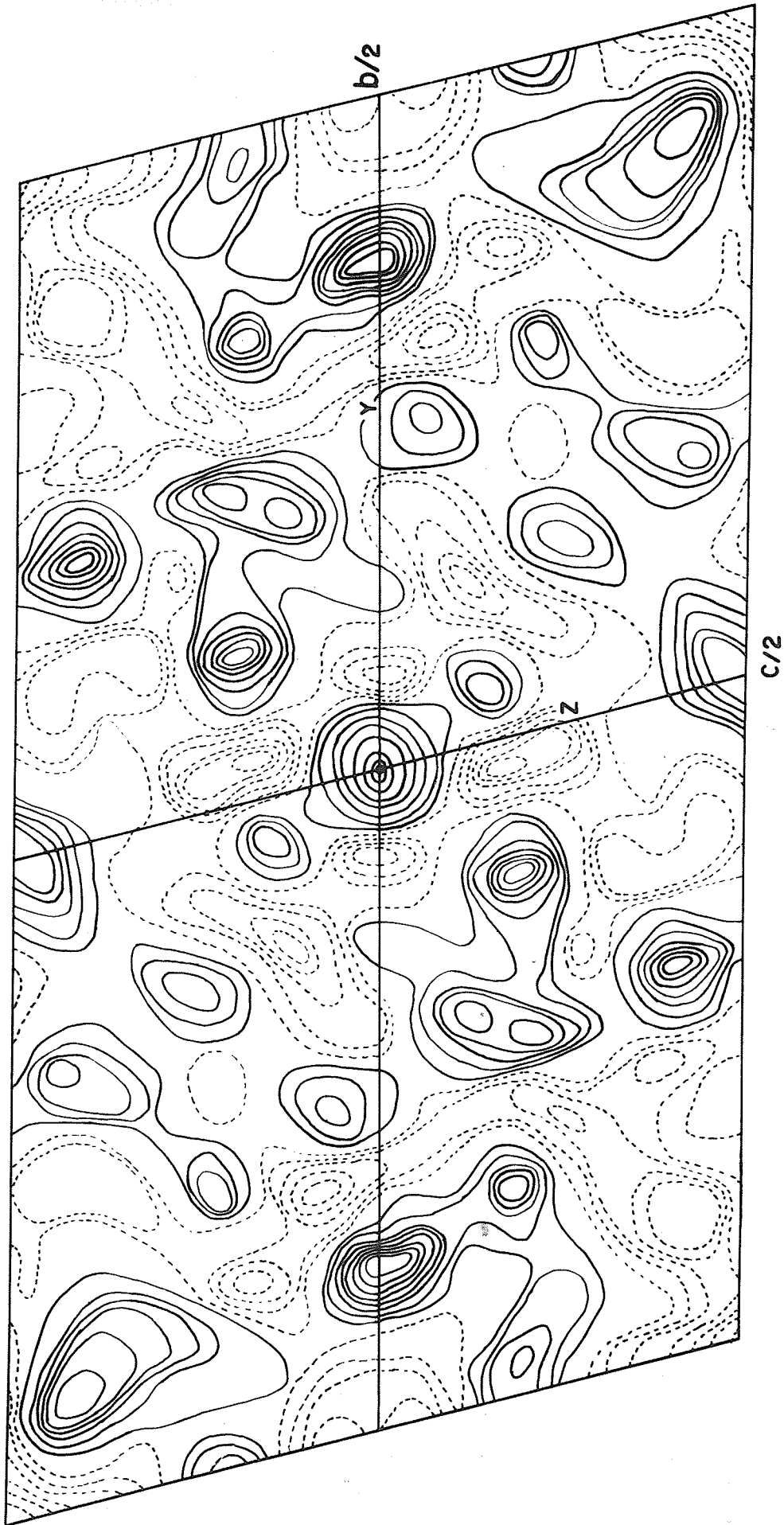


contour lines at  $20e^2/A^2$

Figure 18.



PATTERSON SYNTHESIS (OKI)

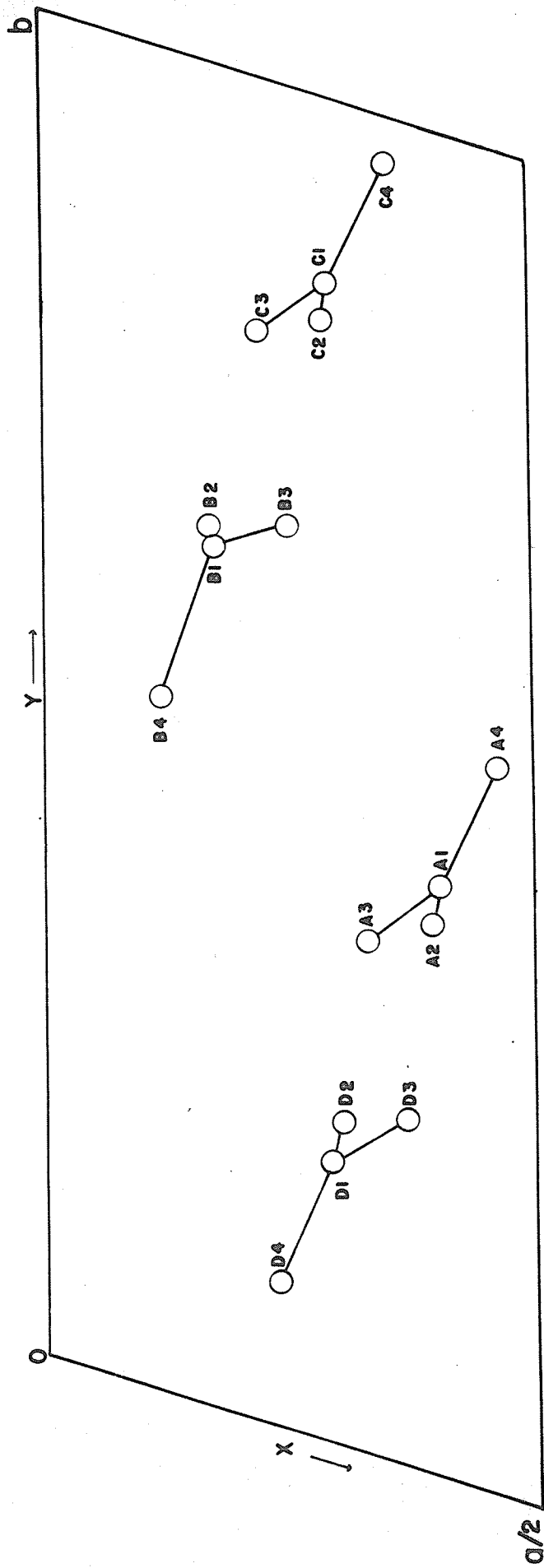


contour lines at  $20 \text{ el.}^2/\text{\AA}^2$

0  $\overline{\hspace{1cm}}$   $\text{\AA}$

Figure 19.

# STRUCTURE I. X-Y PROJECTION



0 1 Å  
Figure 20

STRUCTURE I. Y-Z PROJECTION

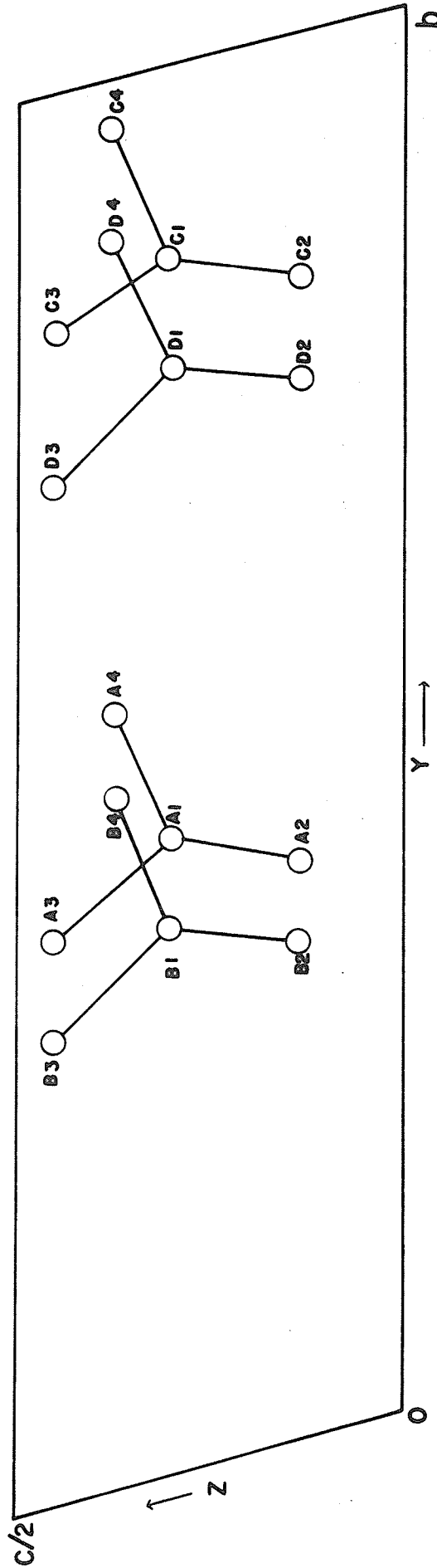


Figure 21.

TABLE II

	Set I			Set II		
	X	Y	Z	X	Y	Z
A <sub>1</sub>	.40	.43	.29	.30	.22	.69
A <sub>2</sub>	.39	.40	.13	.23	.14	.69
A <sub>3</sub>	.32	.37	.44	.30	.24	.86
A <sub>4</sub>	.45	.53	.37	.33	.31	.54
B <sub>1</sub>	.83	.37	.29	.48	.10	.16
B <sub>2</sub>	.82	.34	.13	.43	.01	.03
B <sub>3</sub>	.75	.32	.44	.42	.08	.37
B <sub>4</sub>	.88	.47	.37	.54	.17	.16
C <sub>1</sub>	.29	.87	.29	.39	.42	.30
C <sub>2</sub>	.28	.84	.13	.37	.39	.15
C <sub>3</sub>	.22	.81	.44	.30	.36	.45
C <sub>4</sub>	.34	.97	.37	.42	.52	.36
D <sub>1</sub>	.72	.80	.29	.19	.62	.30
D <sub>2</sub>	.71	.76	.13	.10	.54	.36
D <sub>3</sub>	.65	.74	.44	.17	.63	.49
D <sub>4</sub>	.78	.89	.37	.28	.65	.13
	Set III			Set IV		
	X	Y	Z	X	Y	Z
A <sub>1</sub>	.131	-.017	.359	.055	-.142	.419
A <sub>2</sub>	.200	-.083	.314	.197	-.100	.314
A <sub>3</sub>	.055	-.033	.478	.066	-.017	.478
A <sub>4</sub>	.186	.100	.389	-.044	-.208	.531
B <sub>1</sub>	.339	.383	.299	.410	.425	.194
B <sub>2</sub>	.317	.304	.448	.306	.429	.389
B <sub>3</sub>	.427	.417	.164	.536	.500	.120
B <sub>4</sub>	.290	.442	.374	.449	.333	.105
C <sub>1</sub>	.191	.667	.314	.219	.717	.433
C <sub>2</sub>	.246	.650	.433	.142	.775	.523
C <sub>3</sub>	.274	.700	.149	.350	.683	.247

	X	Y	Z		X	Y	Z
C <sub>4</sub>	.131	.592	.179		.131	.625	.516
D <sub>1</sub>	.460	.087	.179		.465	.083	.179
D <sub>2</sub>	.405	.091	.269		.399	.083	.381
D <sub>3</sub>	.416	.000	.015		.416	-.017	.030
D <sub>4</sub>	.525	.142	.164		.569	.192	.149

## CHAPTER VI

### COMPUTATIONAL ASPECTS

From the foregoing discussions, the reader will have deduced that structure analysis is a field of research in which good computing facilities are essential. During the first forty years of X-Ray structure analysis work, Fourier (and Patterson) syntheses were generally performed with the aid of Beavers-Lipson strips and desk calculators, a procedure so tedious as to eliminate the possibility of determining any very large or complex structures. (Beavers - Lipson strips contain values of  $A \cos 2\pi X$  or  $A \sin 2\pi X$  at intervals of  $\frac{1}{120}$  for the range  $0 \leq x \leq \frac{1}{4}$ , for integral values of  $A$  in the range  $0 < A \leq 100$ , and for  $A = 200, 300 \dots 900$ ). Around 1950 the scope of possible problems was greatly extended as electronic digital computers began to make their appearance.

The first (modified) Patterson synthesis, the  $hk0$  zone, done during this investigation was carried out using the Beavers-Lipson strips and a desk calculator. However, since these calculations took approximately three weeks, it was decided to program the problem for the University's Bendix G-15D computer. The Interpretive Routine, Intercom 1000 (single precision), was chosen as the coding system to simplify programming as much as possible. Appendix I describes with explanatory details, the Fourier Synthesis program that was written. (A working knowledge of Intercom 1000 on the part of the reader is assumed). The first Patterson synthesis (for the  $(hk0)$  zone) was recalculated, using this program, as a program test run. Patterson syntheses for the other two zones,  $(0kl)$  and  $(h0l)$ , were then computed. Because of the very long computation time (between 60 and 80 hours) required for each of the syntheses and the scarcity of available time on the computer, an effort was made to prepare a much faster pro-

gram. The POGO (Program Optimizer for G-15 Operation) coding system was used. This system is much less commonly used than Intercom 1000, perhaps because of increased difficulty in programming. To the best of the author's knowledge, the only previous attempt to use POGO at this University was by M. Ito during the summer of 1959. This first attempt was not successful due to errors in the University's copy of the POGO tapes. The author encountered the same errors and spent a great deal of time trying to overcome them. However, the POGO program for Fourier synthesis was never run successfully at the University, and hence no description of this program is included in this thesis. Subsequent examination of the program by members of the staff of Computing Devices of Canada (Canadian agents for the Bendix Computer) confirmed that the program was correctly written, and hence could be used successfully if a corrected POGO system were available. Estimated running time for the "POGO-ized" program was between 6 and 10 hours.

A program was also prepared, using Intercom 1000, to compute Structure Factors as defined in Chapter III. Appendix II contains a description of this program. Computation time was sufficiently short (about one minute per Structure Factor) that there was no need to try to optimize this program.

Because of the slowness of the Intercom Fourier program, and the lack of success with the POGO version of this program, a copy of a Fourier Synthesis program for the IBM 650 computer, which was known to be very efficient and completely free from errors, was obtained through the great kindness of Dr. F.R. Ahmed of the National Research Council in Ottawa. Computing time per synthesis was approximately one hour for this program. The marked decrease in operating time relative to the Bendix programs may be attributed both to more sophisticated programming and to the increased speed of the 650 computer. A number of time-saving programming devices, such as table look-ups, which

were used in the program for the "650", could not be used in the Bendix programs because of restrictions imposed by the coding systems. If the author had realized initially the problems which she would later encounter with Intercom and POGO, she would likely have tried to write the program in the basic Bendix machine language, despite its complexity. Advantage could thus have been taken of more efficient and powerful commands, and a much faster program made up.

Due to an unfortunate breakdown later in this investigation, of the Bendix computer, on which Structure Factors were being calculated, it became virtually necessary to ask Dr. Ahmed for his Structure Factor program for the IBM 650 computer, this in addition to the previously requested Fourier Synthesis program. Through his help and the cooperation of Prof. Germain this program was also put into operation.

#### ATTEMPTS TO DETERMINE THE CRYSTAL STRUCTURE

When a set of atomic coordinates had been derived from a study of the Patterson maps and from crystal-chemical considerations, they were tested by computing  $F$  values for each of the experimentally observed reflections, using the Bendix program (Appendix II). It was obvious from the large discrepancies between the calculated ( $F_c$ ) and the observed ( $F_o$ ) values that this set of coordinates did not represent the correct structure. However, it was decided that the proposed structure was sufficiently reasonable that many of the phases calculated on that basis should be correct. (In this case, phases were represented only by plus or minus signs). Accordingly, the sign of each of the  $F_c$ 's, calculated from the first set of coordinates, was attached to its corresponding  $F_o$  value, and a Fourier Synthesis computed for each of the (hk0), (0kl) and (h0l) zones. The resulting electron-density values were plotted on



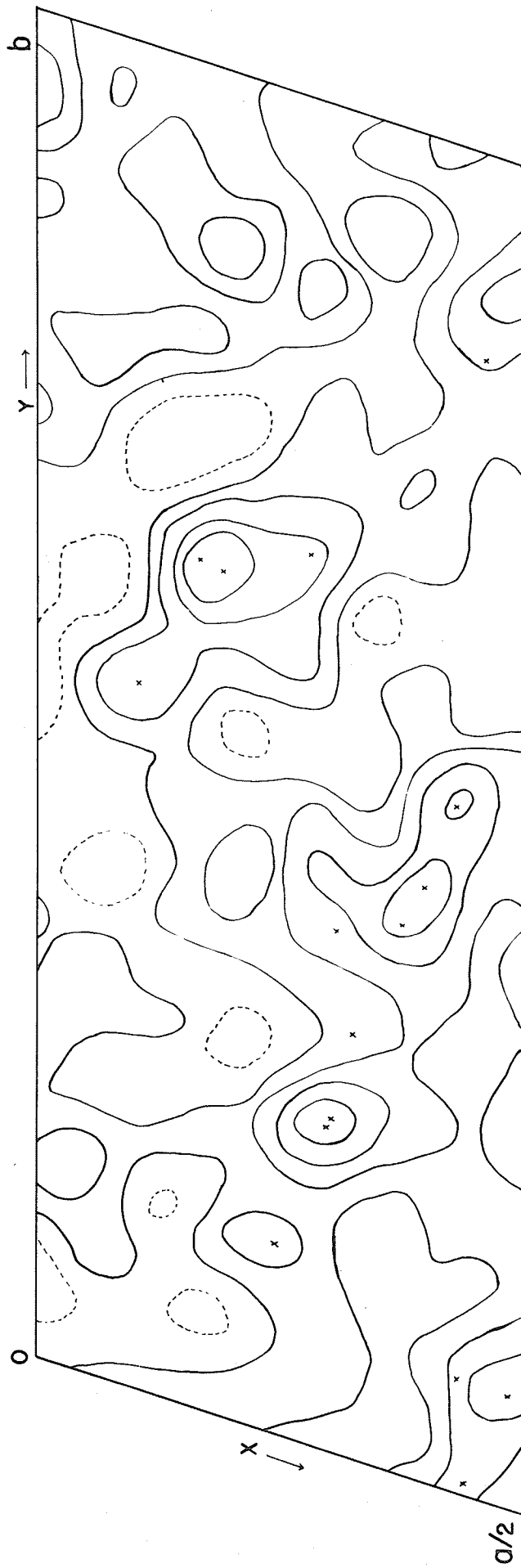
a grid, as for Patterson results, where the grids were drawn on a scale 4 cm. = 1 Å. The grid lines were drawn at intervals of  $\frac{1}{60}$ th of the longer a and b axes, and  $\frac{1}{30}$ th of the shorter c axis, since these were the intervals chosen for computation. When all the electron-density values had been plotted on the grid, contour lines were sketched in at intervals of 2 electrons/Å<sup>2</sup>. The resulting Fourier maps showed projections of the electron-density distribution (resulting from the proposed phases) viewed along the a, b, and c crystal axes.

From a study of the first set of Fourier projections a new set of atomic coordinates was derived. Projections of the electron density along the a and c axes are shown in Figures 22 and 23. In proposing a second set of atomic coordinates, the acetate groups were positioned as units and then the individual atoms were placed by rotating and tilting the acetate groups so as to best fit the contoured peaks. An effort was made not to distort the acetate groups any more than the minimum necessary to fit atoms to peaks of electron density.

Table II lists the various sets of atomic coordinates, expressed as fractions of the unit cell lengths. Set I represents the structure proposed from the Patterson syntheses, while sets II, III and IV represent the structures postulated after study of the first, second and third sets of Fourier maps respectively. All atoms belonging to one acetate group are lettered the same, but not much continuity exists between sets with respect to lettering or numbering, aside from the fact that the central carbon atom in an acetate group was always numbered one.

From the set of atomic coordinates derived from the first Fourier maps, another set of Structure Factors was calculated, this time using the program for the IBM computer. More input data were necessary for this program than for the

FOURIER SYNTHESIS I. (hko)



0  $\overline{\hspace{1cm}}$  1 Å

Figure 22.

The (hk0) and (0kl) projections (along the c and a axes respectively) are shown in Figures 24 and 25. A third set of atomic coordinates was derived from a study of these: the (h0l) projection, as usual, showed too much overlapping to be of use. The third set of coordinates is listed in Table II. From them, a third set of structure factors was calculated. The R factors were now .53, .59 and .54. As before, the sign of each  $F_c$  value was attached to the corresponding  $F_o$  and a third set of Fourier syntheses calculated. From these a fourth set of atomic coordinates was derived, and structure factors calculated. The final R factors were .58, .66 and .65 for the (hk0), (0kl) and (h0l) reflections respectively. Final coordinates are listed in Table II, and Figures 26 and 27 show projections of the final proposed structure along the c and a axes. Table III lists the values of  $F_o$  derived from experimental measurements.

It may be seen from examining the R factors that the crystal structure of anhydrous lithium acetate has not been solved, although it seems unlikely that the correct structure could be completely different from those proposed; the R factors are, after all, close to .50. However, it is equally obvious that the two-dimensional methods used are inadequate to solve this structure. Quite possibly a three-dimensional Patterson synthesis would offer sufficient information to subsequently solve the structure.

FOURIER SYNTHESIS 2. (hk0)

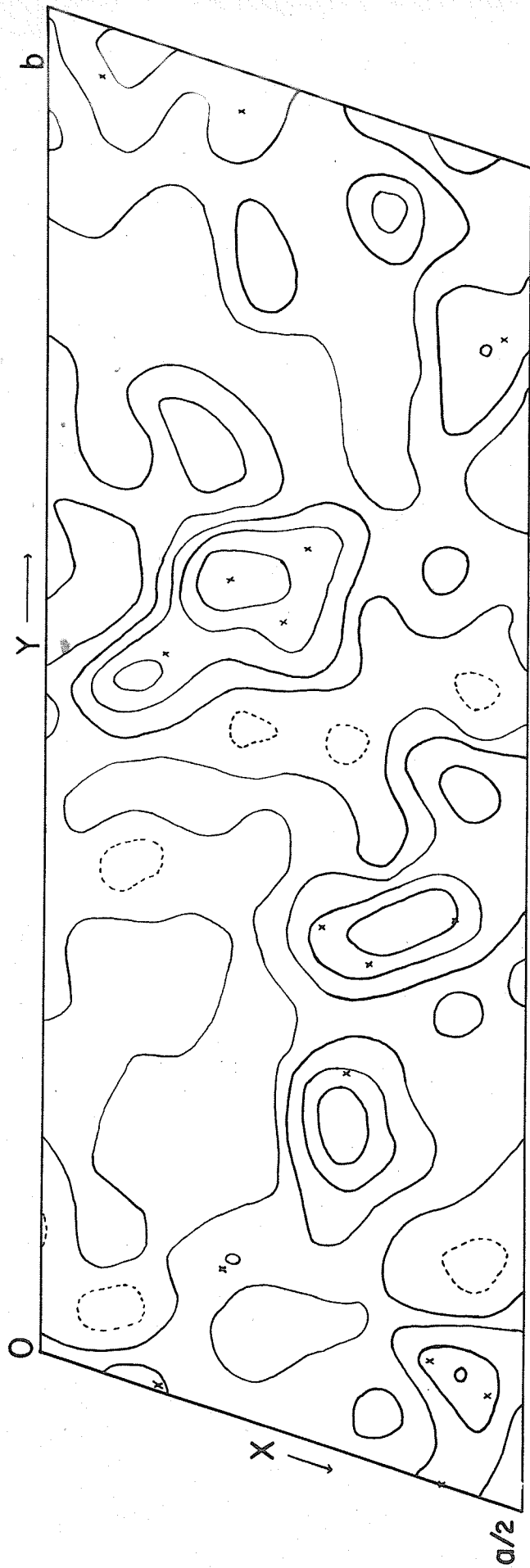
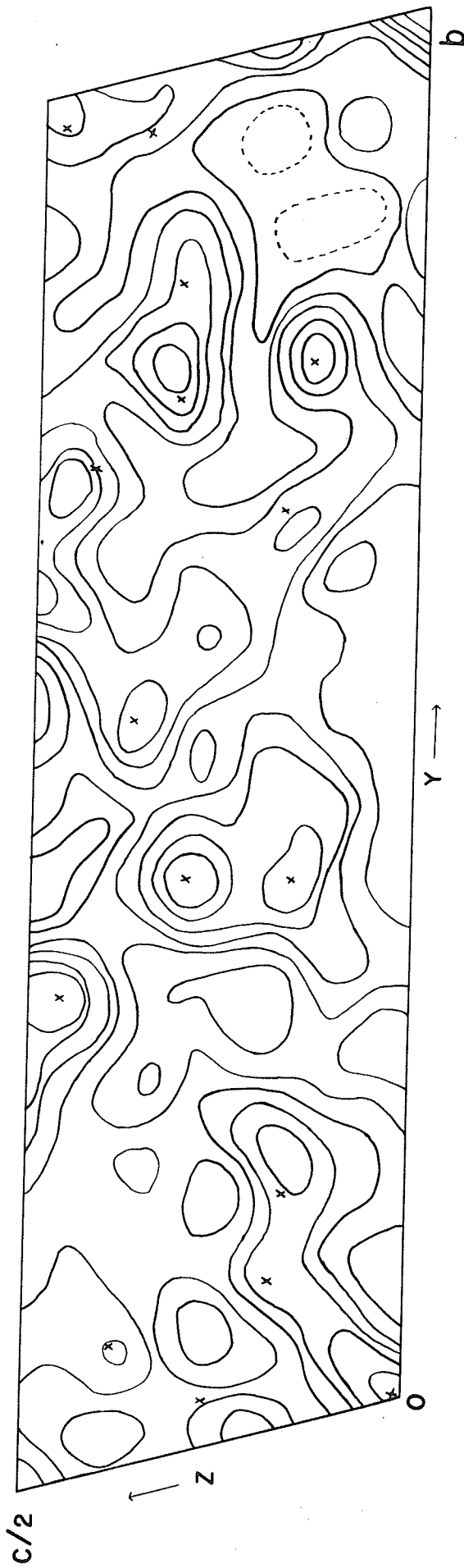


Figure 24.

FOURIER SYNTHESIS 2. (OKI)



0 1 Å

Figure 25.

# STRUCTURE 4. X-Y PROJECTION

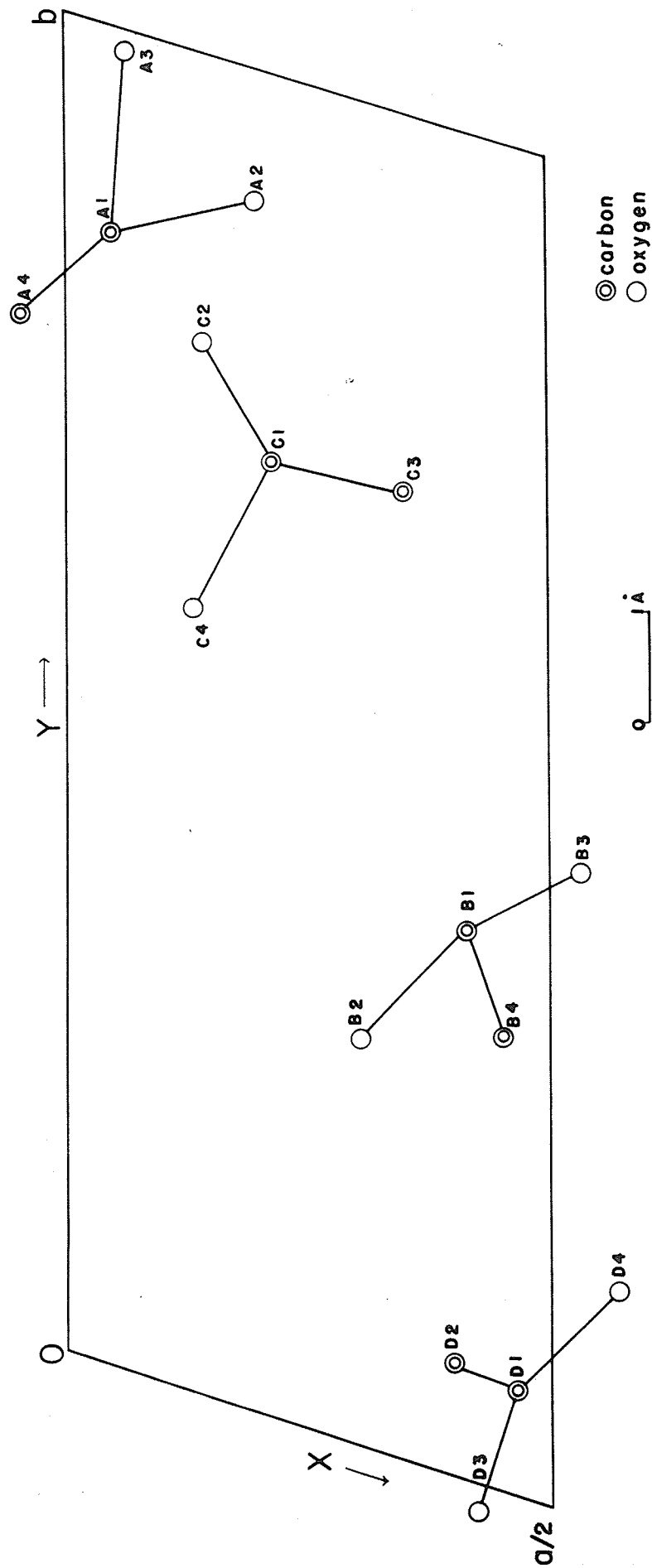


Figure 26.

STRUCTURE 4. Y-Z PROJECTION

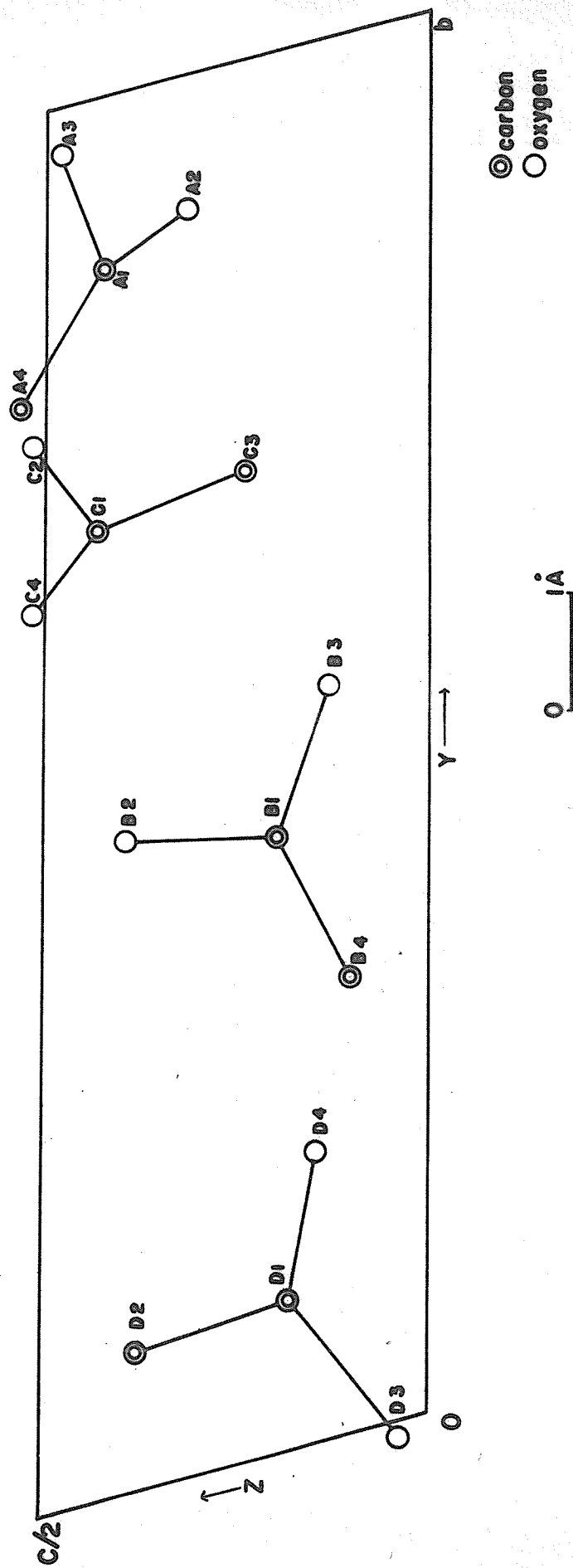


Figure 27.

TABLE III

## OBSERVED STRUCTURE FACTORS

h	k	0	F <sub>o</sub>	h	k	0	F <sub>o</sub>
1	0	0	38.5	$\bar{1}$	5	0	21.2
2	0	0	5.5	$\bar{1}$	6	0	u
3	0	0	u	$\bar{1}$	7	0	9.3
4	0	0	8.0	2	1	0	42.1
5	0	0	7.5	2	2	0	7.5
6	0	0	13.1	2	3	0	u
7	0	0	17.7	2	4	0	7.7
8	0	0	11.3	2	5	0	7.7
9	0	0	9.8	2	6	0	24.6
0	1	0	19.9	2	7	0	4.9
0	2	0	u	2	8	0	3.7
0	3	0	9.6	$\bar{2}$	1	0	5.8
0	4	0	u	$\bar{2}$	2	0	23.0
0	5	0	13.7	$\bar{2}$	3	0	36.7
0	6	0	u	$\bar{2}$	4	0	25.0
0	7	0	u	$\bar{2}$	5	0	39.4
0	8	0	8.4	$\bar{2}$	6	0	13.4
0	9	0	10.9	$\bar{2}$	7	0	15.3
0	10	0	5.5	$\bar{2}$	8	0	11.4
1	1	0	4.4	$\bar{2}$	9	0	3.5
1	2	0	19.2	$\bar{2}$	10	0	11.2
1	3	0	u	$\bar{2}$	11	0	u
1	4	0	2.6	$\bar{2}$	12	0	8.1
1	5	0	6.5	3	1	0	7.7
1	6	0	16.3	3	2	0	7.1
1	7	0	5.8	3	3	0	8.0
1	8	0	3.5	3	4	0	u
$\bar{1}$	1	0	19.4	3	5	0	u
$\bar{1}$	2	0	5.8	3	6	0	7.9
$\bar{1}$	3	0	5.3	3	7	0	18.9
$\bar{1}$	4	0	9.7	3	8	0	u

u = unobserved



h	k	0	F <sub>0</sub>	h	k	0	F <sub>0</sub>
3	9	0	10.5	4	12	0	u
3	1	0	u	4	13	0	5.9
3	2	0	51.5	5	1	0	10.3
3	3	0	18.0	5	2	0	4.9
3	4	0	15.9	5	3	0	7.2
3	5	0	14.3	5	4	0	u
3	6	0	7.2	5	5	0	8.5
3	7	0	16.7	5	1	0	14.5
3	8	0	4.8	5	2	0	5.6
3	9	0	18.0	5	3	0	10.7
3	10	0	9.1	5	4	0	11.3
3	11	0	10.3	5	5	0	9.3
3	12	0	11.4	5	6	0	8.9
4	1	0	14.1	5	7	0	7.0
4	2	0	u	5	8	0	u
4	3	0	8.2	5	9	0	u
4	4	0	10.5	5	10	0	6.9
4	5	0	6.3	6	1	0	u
4	6	0	5.3	6	2	0	11.9
4	7	0	u	6	3	0	u
4	8	0	u	6	4	0	u
4	9	0	9.2	6	5	0	14.9
4	1	0	23.8	6	6	0	5.8
4	2	0	9.6	6	1	0	u
4	3	0	u	6	2	0	u
4	4	0	20.9	6	3	0	8.7
4	5	0	5.3	6	4	0	15.4
4	6	0	8.4	6	5	0	u
4	7	0	10.9	6	6	0	11.9
4	8	0	u	6	7	0	u
4	9	0	u	6	8	0	u
4	10	0	7.5	6	9	0	7.7
4	11	0	u	6	10	0	u

h	k	0	F <sub>0</sub>
6	11	0	u
6	12	0	5.8
7	1	0	7.8
7	2	0	u
7	3	0	4.0
7	1	0	10.7
7	2	0	u
7	3	0	3.8
7	4	0	u
7	5	0	7.5
7	6	0	3.8
7	7	0	u
7	8	0	6.7
8	1	0	4.0
8	2	0	u
8	1	0	5.6
8	2	0	u
8	3	0	u
8	4	0	5.6
8	5	0	7.9
8	6	0	u
8	7	0	6.9
9	1	0	7.0
9	2	0	u
9	3	0	u
9	4	0	8.0
9	5	0	u
9	6	0	7.0
9	7	0	4.1
9	8	0	u
9	9	0	u
9	10	0	u
9	11	0	u
9	12	0	4.0
10	9	0	5.6

h	k	0	F <sub>0</sub>
10	10	0	6.9
10	11	0	u
10	12	0	4.9

0	k	l	F <sub>o</sub>	0	k	l	F <sub>o</sub>
0	0	1	34.9	0	1	2	2.7
0	0	2	u	0	2	2	23.0
0	0	3	11.0	0	3	2	11.2
0	0	4	14.0	0	4	2	18.7
0	0	5	19.0	0	5	2	31.5
0	0	6	6.9	0	6	2	16.6
0	0	7	8.1	0	7	2	15.7
0	1	0	27.4	0	8	2	14.2
0	2	0	u	0	9	2	7.7
0	3	0	11.0	0	10	2	5.6
0	4	0	u	0	11	2	9.2
0	5	0	37.8	0	1̄	2	51.9
0	6	0	u	0	2̄	2	u
0	7	0	u	0	3̄	2	46.5
0	8	0	8.4	0	4̄	2	18.8
0	9	0	14.9	0	5̄	2	17.5
0	10	0	6.6	0	6̄	2	19.6
0	1	1	4.9	0	1̄1̄	2	14.5
0	2	1	u	0	1	3	u
0	3	1	31.2	0	2	3	u
0	4	1	11.8	0	3	3	25.2
0	5	1	9.4	0	4	3	u
0	6	1	u	0	5	3	23.4
0	7	1	4.8	0	6	3	5.1
0	8	1	9.1	0	7	3	3.7
0	9	1	8.2	0	8	3	13.4
0	10	1	u	0	1̄	3	11.8
0	11	1	u	0	2̄	3	21.9
0	12	1	9.2	0	3̄	3	u
0	1̄	1	6.9	0	4̄	3	3.2
0	2̄	1	33.0	0	5̄	3	15.4
0	3̄	1	17.9	0	6̄	3	3.5
0	4̄	1	4.4	0	7̄	3	16.2
0	5̄	1	6.6	0	8̄	3	18.0
0	6̄	1	5.9				

0	k	1	F <sub>0</sub>	0	k	1	F <sub>0</sub>
0	9	3	u	0	7	5	10.5
0	10	3	u	0	8	5	u
0	11	3	13.5	0	9	5	9.2
0	1	4	11.2	0	10	5	10.9
0	2	4	12.9	0	1	6	4.0
0	3	4	10.2	0	2	6	5.6
0	4	4	5.3	0	8	6	10.4
0	5	4	3.7	0	1	6	9.8
0	6	4	5.5	0	2	6	12.0
0	7	4	6.8	0	3	6	15.4
0	1	4	7.0	0	4	6	8.0
0	2	4	8.6	0	5	6	7.0
0	3	4	21.7	0	6	6	11.5
0	4	4	u	0	7	6	9.2
0	5	4	10.2	0	8	6	5.8
0	6	4	8.3	0	9	6	8.1
0	7	4	19.3	0	10	6	9.8
0	8	4	25.4	0	1	7	u
0	9	4	6.9	0	2	7	10.5
0	1	5	u	0	3	7	u
0	2	5	11.6	0	4	7	u
0	3	5	5.5	0	5	7	8.8
0	4	5	u	0	6	7	3.7
0	5	5	u	0	7	7	u
0	6	5	u	0	8	7	5.6
0	7	5	4.1	0	1	7	5.6
0	8	5	8.2	0	2	7	u
0	9	5	7.1	0	3	7	u
0	1	5	u	0	4	7	9.8
0	2	5	5.5	0	5	7	7.9
0	3	5	6.6	0	6	7	u
0	4	5	u	0	7	7	6.9
0	5	5	u				
0	6	5	14.1				

h	0	1	F <sub>0</sub>
0	0	1	32.1
0	0	2	u
0	0	3	12.2
0	0	4	14.8
0	0	5	18.5
0	0	6	u
0	0	7	8.1
1	0	0	36.5
2	0	0	5.5
3	0	0	u
4	0	0	9.6
5	0	0	6.8
6	0	0	17.5
7	0	0	21.6
8	0	0	16.9
9	0	0	9.0
1	0	1	u
2	0	1	24.7
3	0	1	18.3
4	0	1	u
5	0	1	u
6	0	1	12.8
7	0	1	11.4
1	0	1	u
2	0	1	12.5
3	0	1	11.0
4	0	1	5.5
5	0	1	11.0
6	0	1	7.6
1	0	2	44.3
2	0	2	10.7
3	0	2	5.3
4	0	2	47.3
5	0	2	16.1
6	0	2	23.2

h	0	1	F <sub>0</sub>
7	0	2	29.3
1	0	2	29.4
2	0	2	58.5
3	0	2	36.8
4	0	2	29.3
5	0	2	35.4
6	0	2	35.6
1	0	3	8.4
2	0	3	39.1
3	0	3	26.3
4	0	3	24.7
5	0	3	9.4
6	0	3	u
7	0	3	u
8	0	3	u
9	0	3	13.9
1	0	3	35.2
2	0	3	10.5
3	0	3	15.3
4	0	3	10.8
5	0	3	20.9
1	0	4	17.1
1	0	4	6.9
2	0	4	u
3	0	4	u
4	0	4	7.4
5	0	4	u
6	0	4	12.9
7	0	4	22.7
1	0	5	u
2	0	5	u
3	0	5	5.6
4	0	5	10.6
1	0	5	11.3
2	0	5	11.2

h	0	1	F <sub>0</sub>
3	0	5	14.5
4	0	5	9.2
5	0	5	5.5
6	0	5	u
7	0	5	8.9
1	0	6	5.6
1	0	6	u
2	0	6	u
3	0	6	5.6
4	0	6	8.9
5	0	6	u
6	0	6	9.0
1	0	7	7.0
2	0	7	5.8
3	0	7	9.8

## SUMMARY AND CONCLUSIONS

An unsuccessful attempt has been made to determine the crystal structure of anhydrous lithium acetate. Crystals were obtained to which it seemed reasonable to assign the formula  $\text{LiC}_2\text{H}_3\text{O}_2$ . Reasons for assuming the anhydrous nature of this compound were: a) its extremely hygroscopic nature and tendency to become  $\text{LiC}_2\text{H}_3\text{O}_2 \cdot 2\text{H}_2\text{O}$ , and b) density measurements combined with unit cell dimensions which jointly indicated the formula to be  $\text{LiC}_2\text{H}_3\text{O}_2$ . Unit cell dimensions were determined using Buerger's Precession camera and  $\text{CuK}\alpha$  radiation. Values obtained were:

$$\begin{array}{ll} a = 9.29 \text{ \AA} & \alpha = 101^\circ 0' \\ b = 12.33 \text{ \AA} & \beta = 100^\circ 19' \\ c = 6.80 \text{ \AA} & \gamma = 105^\circ 5' \end{array}$$

The density was determined to be  $1.23 \frac{\text{gm}}{\text{cm}^3}$  using the flotation method, and hence it was shown that  $Z = 8$ . A centre of symmetry was shown to be present by a statistical method; the space group was therefore deduced as  $P\bar{1}$ .

Intensity data were collected for each of the (hk0), (0kl) and (h0l) zones using the Precession camera and unfiltered Mo radiation. The appropriate Lorentz and polarization correction factors were applied. Observed structure factors were put on an absolute scale by Wilson's method; by an associated method the temperature factor constant was determined as  $B = 2.0 \text{ \AA}^2$ .

Patterson syntheses were performed using  $F^2$  coefficients modified by a sharpening function. One synthesis was performed for each of the (hk0), (0kl) and (h0l) projections. A structure was postulated on the basis of the Patterson maps and structure factors then calculated. Using the signs from these structure factors and the magnitudes of the observed structure factors, Fourier syntheses were calculated, and a revised structure postulated. The cycle:

structure factors  $\longrightarrow$  Fourier syntheses  $\longrightarrow$  structure  $\longrightarrow$  structure factors  
was repeated three times, with no appreciable improvement of the agreement between observed and calculated structure factors. The problem was then abandoned, so far as two-dimensional methods were concerned. The possibility remains that a three-dimensional study might solve the problem.



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## APPENDIX I

A Two-Dimensional Fourier Synthesis Program for the  
Bendix G-15D Computer

## INTRODUCTION

A two-dimensional Fourier synthesis program was prepared in order to carry out one of the two lengthy calculations necessary in a crystal structure determination. The interpretive routine, Intercom 1000s, for the Bendix G-15D computer, was used to simplify the programming.

## PROBLEM STATEMENT

Given a set of structure factors of the type  $\pm F(h, k)$ , to evaluate, for a large number of points  $x, y$ , the function

$$B(x, y) = \frac{1}{A} \sum_h \sum_k F(h, k) \cos 2\pi (hx + ky)$$

in which  $B$  is the electron density in  $e/\text{\AA}^2$

$x, y$  are fractions of the unit cell edges,  $a, b$ , usually taken at intervals of  $1/30, 1/60$  or  $1/120$ ,

$A$  is the area of the  $xy$  projection in  $\text{\AA}^2$ , and

$F(h, k)$  is the observed structure factor of the X-ray reflection with the Miller indices  $h, k$ .

In this program the function is calculated for  $x$  and  $y$  intervals of  $1/30$  over the ranges  $0 \leq x \leq 31/60$  and  $0 \leq y \leq 61/60$ , and for  $h$  and  $k$  limits of  $0 \leq h \leq 10$  and  $-15 < k < 15$ .

## COMPUTATIONAL APPROACH

See Flow Diagram.

The double summation is performed for each successive pair of  $x$  and  $y$

values, with immediate type-out in floating-point. Computation proceeds by holding  $y$  constant, varying  $x$ , then incrementing  $y$ , holding it constant, varying  $x$ .  $Y$  is typed out in floating-point after each incrementation. The  $y$  value is distinguished from  $B(x,y)$  only by being the last in a set of 17 type-outs, and by being followed by 3 carriage returns.

The double summation is calculated using the Intercom 1000s cosine subroutine, and checking each  $F(h,k)$  value for non-zero magnitude. If  $F(h,k)$  is zero, computation of the corresponding cosine term is omitted, saving an appreciable amount of time. During computation of the sum,  $k$  is varied from minimum  $k$  to maximum  $k$  for each value of  $h$ . Modification of data addresses is carried out by means of an index register; the index register limit is 399, but data use is terminated by tests of  $k$  and  $h$  successively before this limit is reached.

#### DATA INPUT AND OUTPUT

See Storage Layout Sheet.

It is essential to choose minimum  $x = 0$ , since one location, 1052, is used both for minimum  $x$  and as a source of zeros throughout the program. If the program were modified so as to use some other convenient location as a source of zeros, this restriction would no longer be necessary.

$F(h,k)$  values are entered as integers in fixed - or floating-point notation in the order  $F(\text{min. } h, \text{min. } k) \dots F(\text{min. } h, \text{max. } k), F(\text{min. } h+1, \text{min. } k) \dots F(\text{min. } h+1, \text{max. } k) \dots F(\text{max. } h, \text{max. } k)$ . Experimentally unobserved data must be entered as zero; great care must be taken to avoid getting out of sequence, since correspondence of  $F(h,k)$  and the actual  $h$  and  $k$  values is maintained only by the correct location of  $F(h,k)$ .

If a very large number of  $F(h,k)$  values must be used, one could rearrange the storage layout, putting  $F(h,k)$  in channels 11 - 18, and storing the program and cosine subroutine in any two of channels 7 - 9.

In general, however, the computation time (about 70 hours) required for about 300  $F(h,k)$  values completely excludes the possibility of using a larger set of data. This computation time implies that the intervals for both  $x$  and  $y$  are only  $1/30$ .

Output of  $B(x,y)$  and  $y$  values is arranged in lines of 8 type-outs in floating-point, with 3 carriage returns separating each set of type-outs; each set of 17 type-outs corresponds to one  $y$  value. A tab space = 11 was used to ensure that 8 type-outs occurred within one page-width.

If it is desired to compute  $B$  values for the  $x$ - $z$  projection, the locations formerly assigned to  $h$  and  $x$  will now contain  $l$  and  $z$ , while  $k$  and  $y$  will be replaced by  $h$  and  $x$ . If the  $y$ - $z$  projection is desired,  $k$  and  $y$  locations will be unaffected while  $h$  and  $x$  are replaced by  $l$  and  $z$ . The area factor  $A$ , will be different for each projection.

#### OPERATING INSTRUCTIONS

1. Read Intercom 1000 s into the memory.
2. Read the cosine subroutine from the Intercom 1000s magazine into the memory - channel 11.
3. Type the program into channel 12.
4. Have tapes punched of the program and subroutine (channels 11 and 12) if desired for future use.
5. Type the  $F(h,k)$  values into channels 7 - 10, taking great care to keep them in their proper sequence.
6. Type the constants into channel 10 as outlined in the storage layout.
7. It is a good policy to have tapes punched at this stage of the  $F(h,k)$  values and constants for use in case of interrupted computation.

8. Ensure that the typewriter has tab space = 11 across the entire page-width, and reset the margins if necessary.
9. Begin automatic computation at location 1200.

#### REFERENCE

See Intercom 1000s Manual.

## Storage Layout

## Permanent Storage

Data  $\pm F(0, \text{min. } k)$  0700  
 .. .  
 .. .  
 $\pm F(0, \text{max. } k)$  .  
 $\pm F(1, \text{min. } k)$  .  
 .. .  
 .. .  
 $\pm F(1, \text{max. } k)$  .  
 .. .  
 .. .  
 .. .  
 .. .  
 $\pm F(\text{max. } h, \text{max. } k)$  .  
 .. 1050

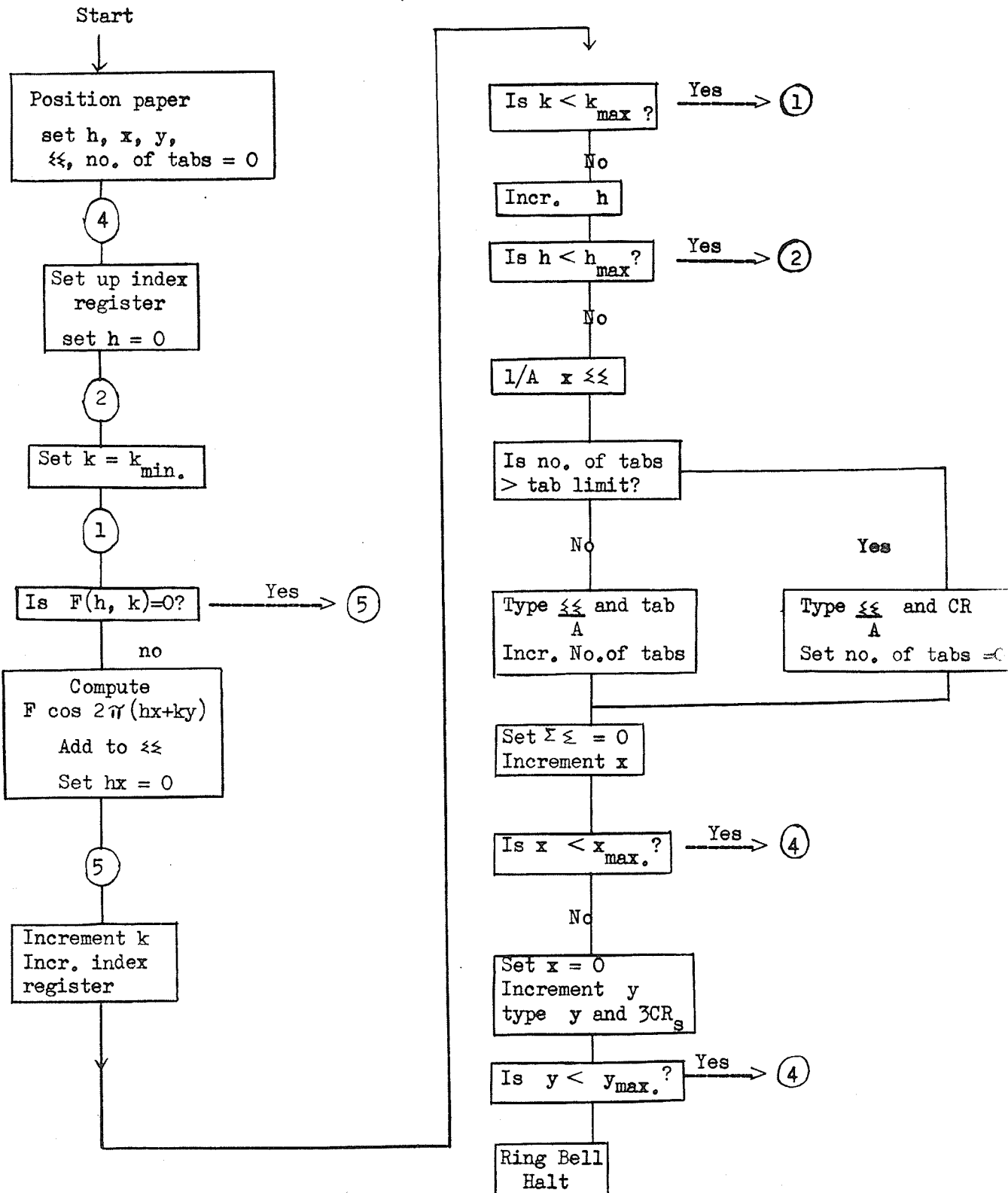
## Active Storage

$h = 1065$   
 $k = 1066$   
 $x = 1067$   
 $y = 1068$   
 $hx = 1069$   
 $\sum \sum F(h,k) \cos 2\pi (hx+ky) = 1070$   
 $h \quad k$   
 no. of tabs = 1071

## Constants

$\pi = 3.1416$  1051  
 min.  $x = 0.00$  1052  
 min.  $y = .00$  1053  
 $\Delta x, \Delta y = .033333$  1054  
 max.  $x = .51600$  1055  
 max.  $y = 1.01600$  1056  
 max.  $h =$  1057  
 min.  $k =$  1058  
 max.  $k =$  1059  
 $1/A =$  1062  
 tab limit = 6.5 1063  
 1,00000 1064  
 zero check = 0.01 1073

FOURIER SYNTHESIS





INTERCOM 1000

PROBLEM FOURIER SYNTHESIS				Prepared by: C. Saunderson	
Computation of $\sum_{h,k} F(h,k) \cos 2\pi(hx + ky)$				Date: 12: 1: 60	Page 1 of 4
LOC	K	OP CODE	A D I D R	(A)	Notes
1200		30	00 05		Position paper
01		42	10 52		(1052) 0 $\xrightarrow{+}$ $A_c$
02		49	10 65		store in 1065 (h
03		49	10 70		" " 1070 ( $\leq\leq$
04		49	10 71		" " 1071 ( tabs
05		49	10 67		" " 1067 ( x
06		49	10 68		" " 1068 ( y
07	4	73	00 00		set $CB_4 = 0000$ <span style="float:right">← 4</span>
08	4	74	01 00		" $CD_4 = 0100$
09	4	75	03 00		" $CL_4 = 0300$
1210	4	70	00 00		" $WB_4 = 00$
11	4	71	00 01		" $WD_4 = 01$
12	4	72	00 99		" $WL_4 = 99$
13		42	10 52		(1052) 0 $\xrightarrow{+}$ $A_c$
14		49	10 65		store in 1065 (h
15		42	10 58		(1058) min. k $\xrightarrow{+}$ $A_c$ <span style="float:right">← 2</span>
16		49	10 66		store in 1066 (k
17	4	45	07 00		1(0700)11F1 $\xrightarrow{+}$ $A_c$ <span style="float:right">← 1</span>
18		41	10 73		(1073) 0,01 $\xrightarrow{-}$ A
19		22	12 34		If A < 0, go to $\xrightarrow{>}$ <span style="float:right">5</span>
1220		42	10 65		(1065) h $\xrightarrow{+}$ $A_c$
21		44	10 67		(1067) x $\xrightarrow{-}$ A
22		49	10 69		store in 1069 (h,x
23		42	10 66		(1066) k $\xrightarrow{+}$ $A_c$
24		44	10 68		(1068) y $\xrightarrow{-}$ A

INTERCOM 1000

<b>PROBLEM</b> FOURIER SYNTHESIS	Prepared by: C. Saunderson
Date: 12: 1: 60	Page 2 of 4

LOC	K	OP CODE	A	D	DR	(A)	Notes
1225		43	10		69		(1069) $hx \rightarrow A$
26		44	10		51		(1051) $\pi \rightarrow A$
27		43	21		01		$A \rightarrow A$
28		08	11		26		compute cosine
29	4	44	07		00		(0700)F $\rightarrow A$
1230		43	10		70		(1070) $\rightarrow A$
31		49	10		70		store in 1070
32		42	10		52		(1052) $0 \rightarrow A_c$
33		49	10		69		store in 1069 (h,x
34		42	10		66		(1066) $k \rightarrow A_c$ <span style="float:right">← 5</span>
35		43	10		64		(1064) $1 \rightarrow A$
36		49	10		66		store in 1066
37	4	76	12		40		increment $WB_A$ and go to >
38	4	77	12		39		increment $CB_A$ and go to >
39	4	70	00		00		reset $WB_A = 00$ ←
1240		42	10		66		(1066) $k \rightarrow A_c$ ←
41		41	10		59		(1059) max. $k \rightarrow A$
42		22	12		17		If $A < 0$ , go to > <span style="float:right">1</span>
43		42	10		65		(1065) $h \rightarrow A_c$
44		43	10		64		(1064) $1 \rightarrow A$
45		49	10		65		store in 1065
46		41	10		57		(1057) max. $h \rightarrow A$
47		22	12		15		If $A < 0$ , go to > <span style="float:right">2</span>
48		42	10		70		(1070) $\rightarrow A_c$
49		44	10		62		(1062) $1/A \rightarrow A$

INTERCOM 1000

PROBLEM FOURIER SYNTHESIS	Prepared by: C. Saunderson
Date: 12 : 1 : 60	Page 3 of 4

LOC	K	OP CODE	A	D	DR	(A)	Notes
1250		49	10		70		store in 1070
51		42	10		63		(1063) tab.lim. $\pm \rightarrow A$
52		41	10		71		(1071) no. of tabs $\rightarrow A$
53		22	12		59		If $A < 0$ , go to $>$ <span style="float:right; border: 1px solid black; padding: 2px;">3</span>
54		32	10		70		type (1070) and tab
55		42	10		71		(1071) no. of tabs $\pm \rightarrow A$
56		43	10		64		(1064) 1 $\pm \rightarrow A$
57		49	10		71		store in 1071
58		29	12		62		go to $>$
59		34	10		70		type (1070) and CR $\leftarrow$ <span style="float:right; border: 1px solid black; padding: 2px;">3</span>
1260		42	10		52		(1052) 0 $\pm \rightarrow A_c$
61		49	10		71		store in 1071
62		42	10		52		(1052) 0 $\pm \rightarrow A_c$ $\leftarrow$
63		49	10		70		store in 1070
64		42	10		67		(1067) x $\pm \rightarrow A_c$
65		43	10		54		(1054) 2/60 $\pm \rightarrow A$
66		49	10		67		store in 1067
67		41	10		55		(1055) max. x $\rightarrow A$
68		22	12		07		If $A < 0$ , go to $>$ <span style="float:right; border: 1px solid black; padding: 2px;">4</span>
69		42	10		52		(1052) min. x $\pm \rightarrow A_c$
1270		49	10		67		store in 1067
71		42	10		68		(1068) y $\pm \rightarrow A_c$
72		43	10		54		(1054) 2/60 $\pm \rightarrow A$
73		49	10		68		store in 1068
74		34	10		68		type (1068) and CR



## APPENDIX II

## Structure Factor Computation

## INTRODUCTION

A program was prepared to compute crystallographic structure factors from two-dimensional atomic coordinates using the interpretive routine Intercom 1000s for the Bendix computer.

## PROBLEM STATEMENT

Crystallographic structure factors of the type  $F(hk0)$ , for the most general centrosymmetric plane group, which is the one required in the present problem, may be represented by the relation

$$F(hk0) = 2 \sum_i f_{o_i} e^{-\frac{B_t \sin^2 \theta}{\lambda^2}} \cos 2\pi (hx_i + ky_i)$$

where  $f_{o_i}$  represents the atomic scattering factor of the  $i$ 'th atom,  $B_t$  is known as the temperature factor constant,  $h$  and  $k$  are known as Miller indices and have integral values, and  $x_i, y_i$  are atomic coordinates, having fractional values  $0 \leq x_i, y_i < 1$ .  $\sin \theta$ , a function of  $h$  and  $k$ , according to the Bragg equation, may be experimentally measured, and  $\lambda$  is the wavelength of the X-radiation used. In this problem,  $h$  and  $k$  were in the range  $0 \leq h < 10, -13 \leq k < 13$ . The value of  $f_{o_i}$ , the atomic scattering factor, may be computed using the formula developed by Vand, Eiland and Pepinsky (1957):

$$f_{o_i} = A_i e^{-a_i \sin^2 \theta} + B_i e^{-b_i \sin^2 \theta}$$

where  $A_i, a_i, B_i, b_i$  are constants of known value for each atom of different atomic number.

## COMPUTATIONAL APPROACH

See Flow Diagram.

This program was initially planned as a fairly generalized method of calculating structure factors for the centrosymmetric plane group  $p2$ . At the time, however, it was realized that considerable simplification and saving of time could be achieved by taking into account the special conditions existing in the early stages of this problem. For example, it was decided that because of their similar atomic numbers, initially we could treat oxygen and carbon atoms as having equal atomic scattering factors; we, therefore utilized the scattering constants of the nitrogen atom for these two atoms. Also, because of the low atomic number of lithium, the lithium atoms could not be expected to make any sizable contributions to the electron density distribution, so they were ignored. Thus only one scattering factor had to be calculated for each value of  $h$  and  $k$ . Provision was made in the original coding for future treatment of atoms of varying atomic number; to eliminate confusion the superfluous commands are omitted here. The more elaborate version of the program was not used due to the break-down of the Bendix computer at the stage where a more elegant program would have become necessary.

Additional time was saved by having the computation carried out only for structure factors which were experimentally observed. Arbitrarily,  $\frac{\sin e}{\lambda}$  was entered as zero if  $F(h,k)$  was experimentally unobserved. Therefore to indicate when computation should be omitted, the corresponding value of  $\frac{\sin e}{\lambda}$  was tested for zero value; a non-zero value of  $\frac{\sin e}{\lambda}$  meant that the structure factor had been experimentally observed, and therefore, that computation should be carried out for that pair of  $h$  and  $k$  values.

The Intercom 1000s exponential and cosine subroutines were used when appropriate, as were index registers.

#### DATA INPUT AND OUTPUT

See Storage Layout.

Input data include a complete set of  $\frac{\sin e}{\lambda}$  values corresponding to the limits of h and k, with unobserved values being entered as zero, in channels seven to nine inclusive. Atomic coordinates  $x_i, y_i$  are entered in pairs in channel ten (with  $x_i$  in even-numbered locations) using three significant digits. Constants are also entered in channel ten, as outlined in the storage layout sheet. The cosine and exponential subroutines are entered in channels eleven and twelve respectively, while the program proper occupies channel thirteen. Channel ten also supplies temporary storage locations. Data may be typed in using either fixed or floating-point notation.

Output data consist of  $F(hk0)$  values typed out in floating-point and, periodically, the value of h after incrementation, typed out in fixed-point notation. The same general format was used as in the Fourier Synthesis program; a tab space of eleven was chosen to permit eight type-outs in floating-point per row.  $F(hk0)$  values may be identified only by knowledge of the order of  $\frac{\sin e}{\lambda}$  values typed in; care must be taken to correlate the  $F(hk0)$  values with their respective h and k indices, especially within each group of values with common h index. Negative values of k are treated first, then positive values are used. The values of h typed out periodically are easily identified, both by being separated from the preceding and succeeding type-outs by carriage returns, and by being typed out in fixed-point notation.

#### GENERAL OBSERVATIONS

If it is desired to compute another zone of structure factors, using atomic coordinates from a different projection, the Miller index which varies least (for that zone) is chosen as "h" while the index which varies most frequently is denoted as "k". Thus, for the (0kl) zone the k index varies most frequently and remains in its previous position, while the l index now occupies those loca-

tions used by h for the (hk0) zone;  $y_i$ ,  $z_i$  are the atomic coordinates used ( $z_i$  in even-numbered locations). A different set of  $\frac{\sin e}{\lambda}$  values must naturally be used for each zone, and the limits of "h" and "k" must be reset accordingly. For the (h0l) zone, h replaces "k" and l replaces "h"; coordinates  $z_i$ ,  $x_i$  are used ( $z_i$  in even-numbered locations).

Computation time is approximately one minute per non-zero  $F(hk0)$  value.

#### OPERATING INSTRUCTIONS

1. Read Intercom 1000s into the memory.
2. Read the cosine and exponential subroutines from the Intercom 1000s magazine into channels 11 and 12 respectively.
3. Type the program into channel 13.
4. Have tapes punched of channels 11 - 13 if desired for future use.
5. Type  $\frac{\sin e}{\lambda}$  values into channels 7 - 9, carefully maintaining their proper sequence.
6. Type the atomic coordinates and constants into channel 10 as outlined in the storage layout sheet.
7. Have tapes punched of channels 7 - 10 for use in case of interrupted computation.
8. Set the margins and check that the tab space is eleven.
9. Begin automatic computation at location 1300.

#### REFERENCES

- Intercom 1000 Single Precision Manual.
- Vand, V., Eiland, P.F., and Pepinsky, R. (1957): Analytical Representation of Atomic Scattering Factors, Acta Cryst. 10, 303.



## Storage Layout

## Permanent Storage

## Active Storage

## Data

sin e (min.h, min.k)	0700
.	.
.	.
sin e (min.h, max.k)	.
.	.
.	.
.	.
sin e (max.h, max.k)	.
.	0999
$x_i, y_i$	1000
( $x_i$ in even locations)	.
.	.
.	1031

h =	1075
k =	1076
hx =	1077
$\Sigma \cos$ =	1078
$f_0 \Sigma \cos$ =	1079
$(\sin^2 e) / \lambda^2$ =	1080
$Ae^{-a \sin^2 e}$ =	1081
$f_0$ =	1082
no. of tabs =	1085
F(h,k) =	1087

Program	1300
---------	------

## Constants

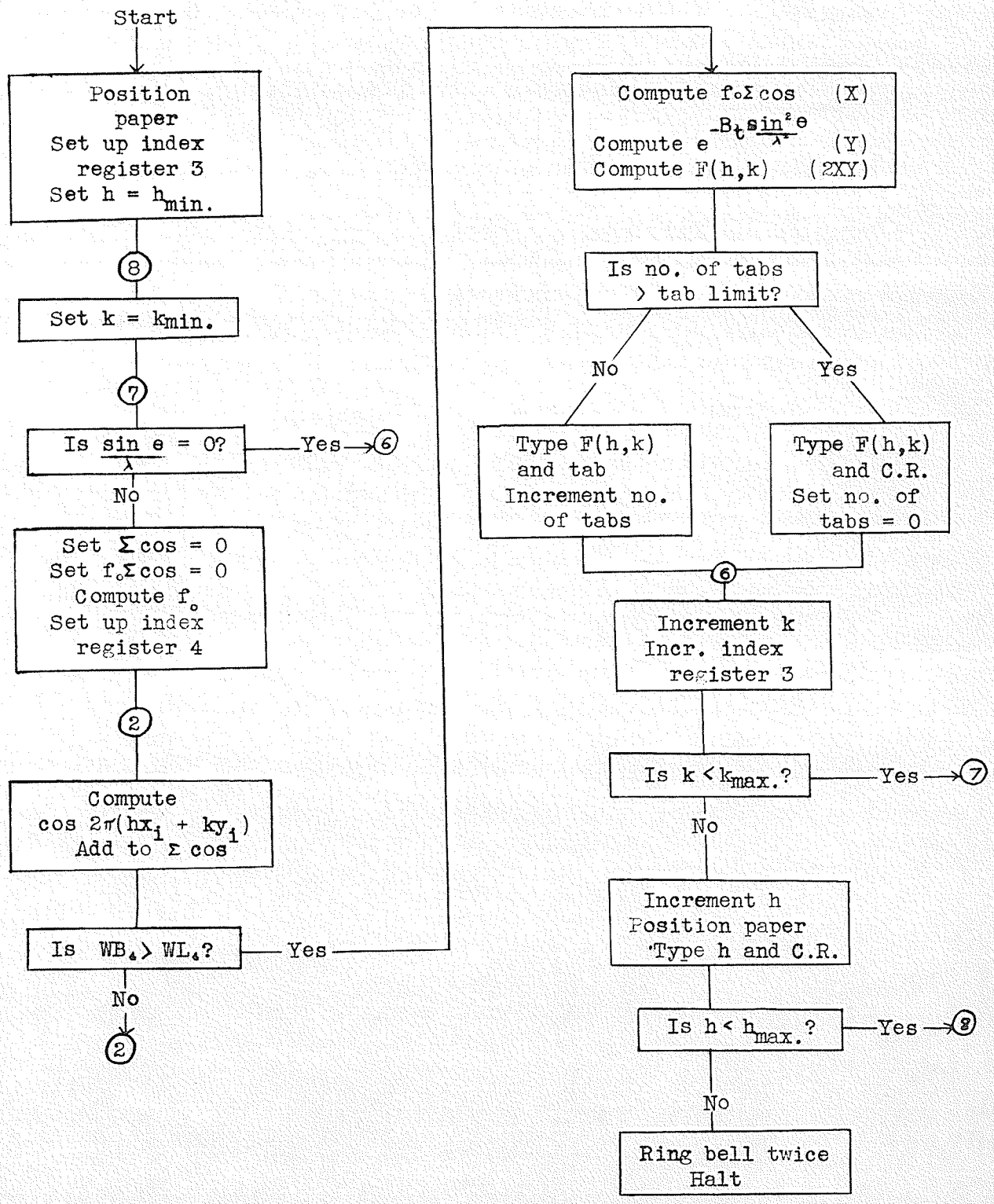
min. h= 0	1051
max. h= 10.5	1052
min. k= -13.	1053
max. k= 10.5	1054
$\pi = 3.1416$	1055
tab limit = 6.5	1056
1.000	1057
A = 2.528	1058
a = $-0.444\lambda^2$	1059
= -1.042	
B = 4.472	1060
b = $-7.47\lambda^2$	1061
= -17.70	
0.000	1072
-1.000	1073
0.00001	1088

## Subroutines

cosine	1100
$e^x$	1200

STRUCTURE FACTOR COMPUTATION

FLOW DIAGRAM



INTERCOM 1000

PROBLEM STRUCTURE FACTORS

$$F(h, k) = 2 \sum_i f_{oi} e^{-B \sin^2 \theta} \cos 2\pi(hx_i + ky_i)$$

$$f_o = A e^{-a \sin^2 \theta} + B e^{-b \sin^2 \theta}$$

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LOC	K	OP CODE	A	D	R	(A)	Notes
1300		30	00	02			Position paper
01	3	70	00	00			WB <sub>3</sub> = 00
02	3	71	00	01			WD <sub>3</sub> = 01
03	3	72	00	99			WL <sub>3</sub> = 99 IR #3
04	3	73	00	00			CB <sub>3</sub> = 0000
05	3	74	01	00			CD <sub>3</sub> = 0100
06	3	75	02	00			CL <sub>3</sub> = 0200
07		42	10	51			(1051) h <sub>min</sub> $\xrightarrow{+}$ Ac
08		49	10	75			store in 1075
09		42	10	53			(1053) K <sub>min</sub> $\xrightarrow{+}$ Ac ←
1310		49	10	76			store in 1076
11	3	42	07	00			(0700) $\frac{\sin \theta}{\lambda} \xrightarrow{+}$ Ac ←
12		41	10	88			(1088) 10 <sup>-5</sup> $\xrightarrow{-}$ A
13		22	13	67			If A < 0, go to >
14		42	10	72			(1072) 0 $\xrightarrow{+}$ Ac
15		49	10	78			store in 1078 (Σ cos)
16		49	10	79			store in 1079 (Σ f <sub>o</sub> cos)
17	3	42	07	00			(0700) $\frac{\sin \theta}{\lambda} \xrightarrow{+}$ Ac
18		44	21	01			A $\xrightarrow{x}$ A
19		49	10	80			store in 1080 ( $\frac{\sin^2 \theta}{\lambda^2}$ )
1320		44	10	59			(1059) a <sub>1</sub> $\xrightarrow{x}$ A
21		08	12	22			e <sup>x</sup> subroutine
22		44	10	58			(1058) A <sub>1</sub> $\xrightarrow{x}$ A
23		49	10	81			store in 1081 (A e <sup>-a, sin<sup>2</sup> θ</sup> )
24		42	10	80			(1080) $\frac{\sin^2 \theta}{\lambda^2} \xrightarrow{+}$ Ac

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INTERCOM 1000

PROBLEM STRUCTURE FACTORS	Prepared by: C.Saunderson
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LOC	K	OP CODE	A	D	DR	(A)	Notes
1325		44	10		61		(1061) $b_1 \xrightarrow{x} A$
26		08	12		22		$e^x$ subroutine
27		44	10		60		(1060) $B_1 \xrightarrow{x} A$
28		43	10		81		(1081) $Ae^x \xrightarrow{+} A$
29		49	10		82		store in 1082 (fo
1330	4	70	00		00		WB <sub>4</sub> = 00
31	4	71	00		02		WD <sub>4</sub> = 02
32	4	72	00		30		WL <sub>4</sub> = 30
33		42	10		72		(1072) $0 \xrightarrow{+} Ac$
34		49	10		78		store in 1078 ( $\int \cos$
35		42	10		75		(1075) $h \xrightarrow{+} Ac$ ← <span style="border: 1px solid black; padding: 2px;">2</span>
36	4	44	10		00		(1000) $x_i \xrightarrow{x} A$
37		49	10		77		store in 1077 ( $hx_j$
38		42	10		76		(1076) $K \xrightarrow{+} Ac$
39	4	44	10		01		(1001) $y_j \xrightarrow{x} A$
1340		43	10		77		(1077) $hx_j \xrightarrow{+} A$
41		44	10		55		(1055) $\pi \xrightarrow{x} A$
42		43	21		01		$A \xrightarrow{+} A$
43		08	11		26		cosine subroutine
44		43	10		78		(1078) $\Sigma \cos \xrightarrow{+} A$
45		49	10		78		store in 1078 ( $\Sigma \cos$
46	4	76	13		35		Incr. WB <sub>4</sub> and go to → <span style="border: 1px solid black; padding: 2px;">2</span>
47		44	10		82		(1082) fo $\xrightarrow{x} A$
48		49	10		79		store in 1079 (fo $\Sigma \cos$
49		42	10		80		(1080) $\frac{\sin^2 \theta}{\lambda^2} \xrightarrow{+} Ac$

INTERCOM 1000

PROBLEM					Prepared by: C. Saunderson	
STRUCTURE FACTORS					Date: 25:11:59	Page 3 of 4
LOC	K	OP CODE	A D	DR	(A)	Notes
1350		43	21	01		A $\xrightarrow{+}$ A ( $\frac{\text{mult}}{B=2}$ by
51		44	10	73		(1073) - 1 $\xrightarrow{x}$ A
52		08	12	22		e <sup>x</sup> subroutine
53		44	10	79		(1079) fo $\Sigma \cos \frac{x}{2}$ A
54		43	21	01		A $\xrightarrow{+}$ A
55		49	10	87		store in 1087 ( F (hk)
56		42	10	56		(1056) tab limit $\xrightarrow{+}$ Ac
57		41	10	85		(1085) no.of tabs $\xrightarrow{+}$ A
58		22	13	64		If A < 0, go to $\xrightarrow{>}$
59		32	10	87		Type (1087) and tab.( fl.pt.)
1360		42	10	85		(1085) no.of tabs. $\xrightarrow{+}$ Ac
61		43	10	57		(1057) 1 $\xrightarrow{+}$ A
62		49	10	85		store in 1085
63		29	13	67		go to $\xrightarrow{>}$
64		34	10	87		Type 1087 and CR $\xleftarrow{<}$
65		42	10	72		(1072) 0 $\xrightarrow{+}$ Ac
66		49	10	85		store in 1085 (no.of tabs
67		42	10	76		(1076) K $\xrightarrow{+}$ Ac $\xleftarrow{<}$
68		43	10	57		(1057) 1 $\xrightarrow{+}$ A
69		49	10	76		store in 1076 (K
1370	3	76	13	73		Incr.WB <sub>3</sub> and go to $\xrightarrow{>}$
71	3	77	13	72		Incr.CB <sub>3</sub> and go to $\xrightarrow{>}$
72	3	70	00	00		Reset WB <sub>3</sub> =00 $\xleftarrow{<}$
73		42	10	76		(1076) K $\xrightarrow{+}$ Ac $\xleftarrow{<}$
74		41	10	54		(1054) K <sub>max</sub> $\xrightarrow{+}$ A

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INTERCOM 1000

PROBLEM STRUCTURE FACTORS	Prepared by: C. Saunderson
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LOC	K	OP CODE	A	D	I	R	(A)	Notes
1375		22	13	11				If A < 0, go to >
76		42	10	75				(1075) h $\xrightarrow{+}$ Ac
77		43	10	57				(1057) 1 $\xrightarrow{+}$ A
78		49	10	75				store in 1075 (h
79		30	00	101				position paper
1380		38	10	75				Type h and CR
81		40	10	52				(1052) max. h $\xrightarrow{-}$ Ac
82		43	10	75				(1075) h $\xrightarrow{+}$ A
83		22	13	09				If A < 0, go to >
84		63	00	100				) Ring bell twice
85		63	00	00				
86		67	00	00				

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