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PROTON MAGNETIC RESONANCE IN  
SINGLE CRYSTALS OF SODIUM  
THIOSULFATE PENTAHYDRATE

Thesis for the Degree of M. S.

MICHIGAN STATE COLLEGE

Hugh Galt, Jr.

1955

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PROTON MAGNETIC RESONANCE  
IN SINGLE CRYSTALS OF  
SODIUM THIOSULFATE PENTAHYDRATE

by

Hugh Galt, Jr.

A THESIS

Submitted to the School of Graduate Studies of Michigan

State College of Agriculture and Applied Science

in partial fulfillment of the requirements

for the degree of

MASTER OF SCIENCE

Department of Physics

1955

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Hugh Galt, Jr.



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AN ABSTRACT

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This thesis reports an investigation of sodium thiosulfate pentahydrate to determine the positions of the hydrogen atoms of the waters of hydration in the unit cell of the crystal. The crystals were investigated by the proton magnetic resonance method developed by Pake<sup>1</sup>. The dipole-dipole interaction of the proton pairs produces a doublet whose separation is anisotropic. The crystals were grown by slow rotation of a seed crystal in a slowly evaporating aqueous solution. The doublet separations were recorded from the resonance signals as the crystal was rotated in the magnetic field. The angular position of the maximum value of the doublet separation indicates the position of the p-p vector whose dipole-dipole interaction produces the signal.

The hydrogen atoms were assumed to lay on the chemical bonds of the atoms of the compound so that they would form the bonds  $O-H \cdots O$ , and  $O-H \cdots S$ .

Crystallographic data indicates that the unit cell is tetramolecular and thus possesses twenty waters of hydration. The angle between each p-p vector and the magnetic field was calculated by trigonometry with the assumption that the distances of the two protons from the oxygen atom of the water were equal. These calculations indicated that there are twenty non-equivalent waters of hydration in a unit cell.

Comparing the experimental results with the assumed positions indicated that ten of the p-p vectors were located as assumed. Experimental evidence indicated four p-p vector positions that did not agree with any of the assumed

locations. The maximum value of the inter-proton distance, as calculated from the values of the maximum doublet separations, was 1.46 Å.

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1. Pake, G. E., Journal Chem. Phys., 16 327 (1948).

TAB

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## I. INTRODUCTION

Recently proton magnetic resonance has been adapted to an investigation of hydrated crystalline compounds in the hope that more might be learned about the position of the hydrogen atoms of the waters of hydration in the crystal. The ordinary methods of crystallography employing the X-ray and electron diffraction techniques fail to locate the hydrogens because of their small scattering cross section. The proton resonance technique was first employed by G. E. Pake<sup>1</sup>. By means of this resonance method he located the hydrogens' positions in single crystals of gypsum. Since then other crystals have been studied<sup>2,3,4</sup>.

In these previous studies the number of waters of hydration in a unit cell of the crystal under investigation ranged from two to eight. However, the investigators in each instance were fortunate that the total number of non-equivalent p-p orientations, the line joining the two protons of each water molecule, never exceeded two.

This raises the interesting question as to whether the proton resonance technique can be used in an investigation of hydrated crystals with a fairly large number of non-equivalent waters of hydration in a unit cell. There are a great many such compounds and an investigation of one of these might prove helpful in outlining a general program to be employed in further work. This thesis deals with an investigation of such a crystal. The crystal undertaken for study was that of sodium thiosulfate pentahydrate, or hypo.

## II. CRYSTALLOGRAPHY OF SODIUM THIOSULFATE PENTAHYDRATE

### A. Morphology

The morphology of sodium thiosulfate pentahydrate has been studied by Groth<sup>5</sup>. He describes a single crystal as being monoclinic and prismatic with the axial ratio,

$$a : b : c = 0.3503 : 1 : 0.2745; \text{ and } \beta = 103^{\circ} 58'$$

Figure (1) shows a rough sketch of the crystal from Groth's data.

### B. X-Ray Analysis

A crystallographic study of hypo, as the compound will be referred to hereafter, has been made by Taylor and Beevers<sup>6</sup>. They substantiate Groth's morphological results and assign a class  $P2_1/c$  to the crystal. They describe a unit cell of the crystal as being tetramolecular. This means a unit cell of the crystal contains twenty molecules of water, their being five waters per molecule of hypo. The complete unit cell, from Taylor and Beevers' paper, is pictured in figure (2). Data from this figure was used to construct a three dimensional model of the unit cell (see figure 3). The tops of the dowels in the model represent some of the atoms of the unit cell. The sodium atoms were neglected because they do not enter into any consideration of proton positions. The white thread corresponds to the chemical bonds as indicated in Taylor and Beevers' paper. The black thread represents the hypothesized p-p orientations under assumptions to be defined later.

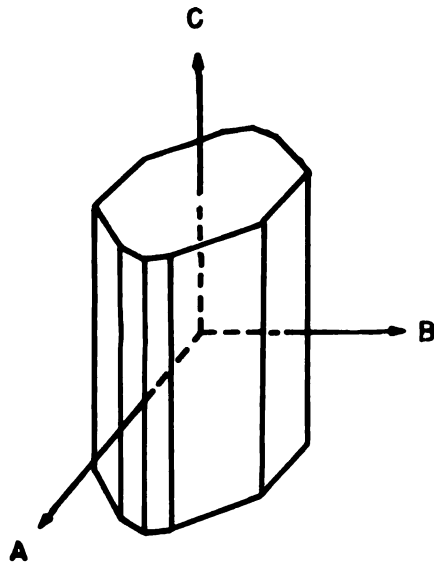


Figure 1. Sketch of single crystal of sodium thiosulfate pentahydrate.

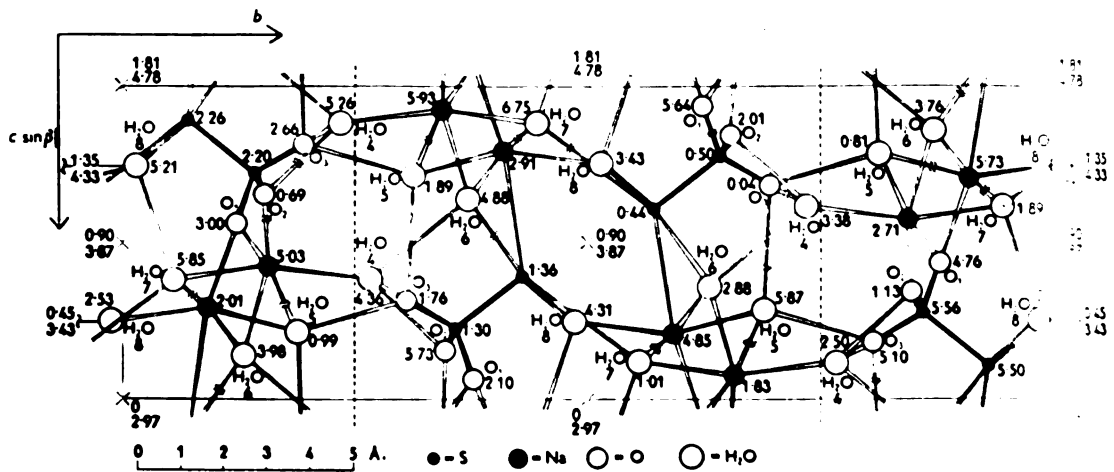


Figure 2. The unit cell of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ . The heights of the atoms are shown in Angstrom units above a standard plane perpendicular to the a axis.



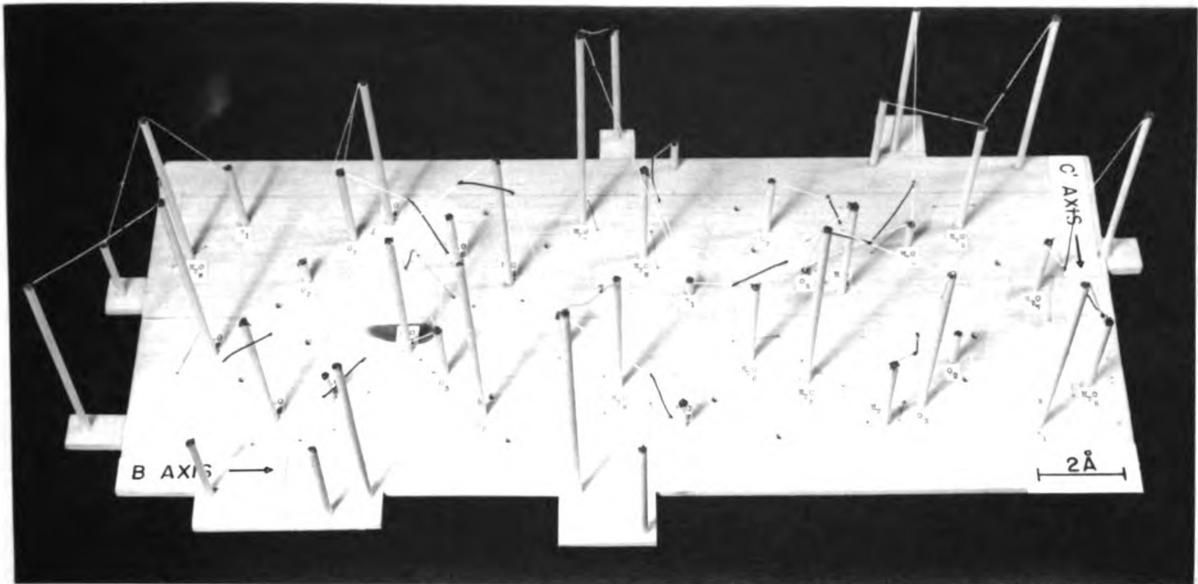


Figure 3. Photograph of three-dimensional scale model of a unit cell for hypo.

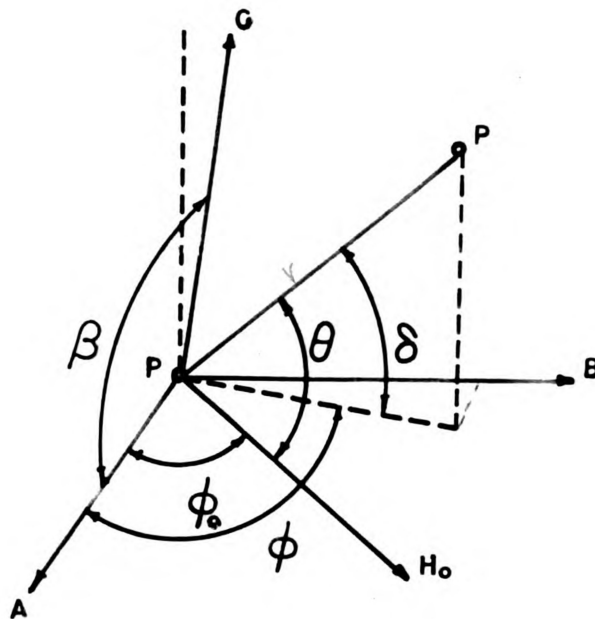


Figure 4. Diagram defining various angles relating  $H_o$  direction to crystal axes and the p-p vector in a water molecule of hypo.

### III. THEORY

#### A. p-p Interaction

If we assume the proton pair associated with a water molecule is an isolated pair, then at resonance they should yield a doublet whose separation is given by<sup>1</sup>

$$\Delta h = (H - H_0) = \pm \alpha (3 \cos^2 \Theta - 1), \quad (1)$$

where  $H_0$  is the resonance magnetic field in the absence of the p-p interaction,

$$\alpha = 3/2 \mu r^{-3}, \quad (2)$$

$\Theta$  is the angle between the p-p vector and the magnetic field vector, and  $r$  is the inter-proton distance. Since we shall always consider the total separation between the doublet, equation (1) may be rewritten

$$\Delta h = \alpha' (3 \cos^2 \Theta - 1), \quad (3)$$

$$\alpha' = 3 \mu r^{-3}. \quad (4)$$

The angle  $\Theta$  may be related to the angle of inclination  $\delta$  and the angle of rotation  $\Phi$  (see figure 4) by computing the dot product of the magnetic and p-p vectors so that

$$\cos \Theta = \cos \delta \cos (\Phi - \Phi_0). \quad (5)$$

Substitute this into equation (3) and,

$$\Delta h = \alpha' [3 \cos^2 \delta \cos^2 (\Phi - \Phi_0) - 1], \quad (6)$$

$\Phi$  is the angular orientation of the magnetic field vector with the p-p vectors' projections in the plane of rotation.  $\delta$  and  $\Phi_0$  are constant angles for each p-p vector.

A significant change can be made in equation (6) that will greatly assist the investigator. We know,

$$\Delta h \equiv [3 \cos^2 \delta \cos^2 (\varphi - \varphi_0) - 1]. \quad (7)$$

Say

$$\cos^2 \Phi = \cos^2 (\varphi - \varphi_0). \quad (8)$$

Now

$$\cos^2 \Phi \equiv \frac{1}{2} (1 + \cos 2\Phi). \quad (9)$$

Substitute this identity into equation (7). Then

$$\Delta h \equiv 3 \cos^2 \delta \left[ \frac{1}{2} (1 + \cos 2\Phi) \right] - 1,$$

Or

$$\Delta h \equiv \beta + \gamma \cos 2\Phi, \quad (10)$$

where

$$\beta = 3/2 \cos^2 \delta - 1, \quad (11)$$

and

$$\gamma = 3/2 \cos^2 \delta, \quad (12)$$

so that

$$\beta = \gamma - 1. \quad (13)$$

There are three possibilities for values of  $\beta$ . If  $\beta$  is positive, then  $\delta > 1$  and equation (10) gives the solid curve illustrated in figure (5).

If  $\beta = 0$ , then  $\gamma = 1$  and the dotted curve of figure (5) is the result.

The inverted section of the curve is a result of only considering the absolute values. If  $\beta$  is negative then  $\delta < 1$  and the dashed curve illustrated in the figure is the result. The curve is seen in the positive quadrant since only absolute values are considered.

Consider the particular case of  $\beta$  negative. This means  $\delta < 1$ , so that

$$3/2 \cos^2 \delta < 1. \quad (14)$$

Solve this inequality, restricting the solution to the first quadrant, and it follows that  $\delta > 35.3^\circ$ . This means those p-p vectors whose angle with

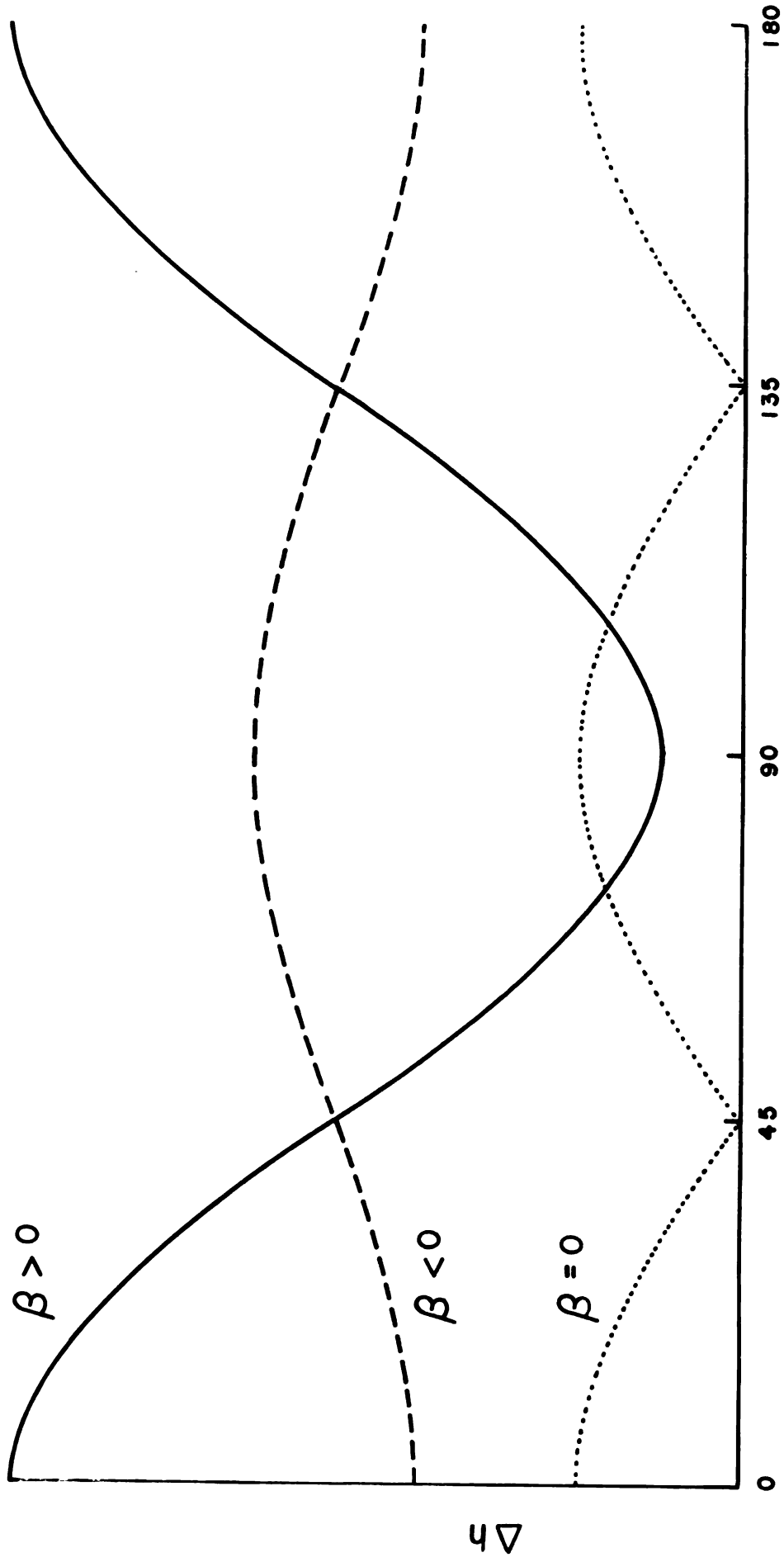


FIGURE 5. RELATIONSHIPS BETWEEN  $\Delta h$  AND  $\Phi$  FOR DIFFERENT VALUES OF  $\beta$ .

the plane of rotation is greater than  $35.3^\circ$  contribute a doublet whose separation is very small. Conversely, any p-p vector with an angle  $\delta < 35.3^\circ$  may give a doublet whose separation is large.

## B. Proton Location

To simplify calculations the protons belonging to the waters of hydration were assumed to lie on straight line bonds joining the atoms of the hypo crystal. If we adopt this criterion and assume the chemical bonds illustrated in Taylor and Beevers are correct then the protons form the following types of bonds;  $O - H \cdots O$ , and  $O - H \cdots S$ . The bonds for the protons of each water molecule were arbitrarily chosen. In some cases the choice of bonds was easy since the oxygen of the water molecule was bound to the sodium atoms and to two other oxygen atoms of the sulfate group. Then the only choice for the proton position is on the  $O - O$  bond. However, for other waters the choice was not as restricted. Then the most likely bond was chosen. There is no certain knowledge which indicates that the protons must lie on these bonds. Indeed, it is possible that the  $O - H$  bond is warped away from the straight line bond. Furthermore we may postulate that the protons undergo a rotation, either free or hindered, and never remain stationary, thus continually changing the p-p orientation for a water molecule. The resonance signal obtained from such molecules will be a single line. This is due to the p-p vector having a random orientation and so giving a resonance signal not unlike that of a liquid. If the  $O - H$  bonds are warped then maximum line separations will occur at angular orientations that do not coincide with the expected angles.

The  $O - H$  bond distance for each proton was taken to be the same in calculat-

ing the angles  $\delta$  and  $\varphi_0$ . These angles were determined by inserting the values of the space coordinates of the atoms whose bonds contained the protons into equations (15) and (16).

$$\tan \varphi_0 = \frac{[(y_2 - y) A - (y_1 - y) B]}{[(x_2 - x) A - (x_1 - x) B]}, \quad (15)$$

$$\cot \delta \cos \varphi_0 = \frac{[(x_2 - x) A - (x_1 - x) B]}{[(z_2 - z) A - (z_1 - z) B]}, \quad (16)$$

where

$$A = [(x_1 - x)^2 + (y_1 - y)^2 + (z_1 - z)^2]^{\frac{1}{2}},$$

and

$$B = [(x_2 - x)^2 + (y_2 - y)^2 + (z_2 - z)^2]^{\frac{1}{2}}.$$

Table (1) is a list of the angles calculated in such a manner. The angles are for each p-p vector in regard to crystal rotation about the a axis. To identify each p-p vector the following notation was adopted. Each vector is associated with a water molecule. The unit cell is divided into four molecular sections and each section assigned a Roman numeral. Thus the notation 7II refers to the p-p vector associated with water molecule  $H_2O_7$  in the second molecular section.

The result of the calculations is that there are twenty non-equivalent p-p directions, or a unique direction for each water of the unit cell. If this is true one should observe twenty pairs of lines in the proton resonance signal. These twenty lines should each be uniquely anisotropic in that they will reach a maximum and minimum in doublet separations at certain angular orientations of the crystal with the magnetic field. Also their separations will not all be the same, but will depend on the p-p orientations with the plane of rotation.

Water Molecule	$\delta$	$\phi_0$	Water Molecule	$\delta$	$\phi_0$
4I	-19° 43'	162° 09'	4II	69° 35'	36° 41'
5I	- 9 06	142 20	5II	-12 04	35 20
6I	40 37	93 06	6II	-32 00	99 11
7I	- 4 27	162 27	7II	-12 13	8 22
8I	-42 02	177 33	8II	58 12	7 57
4III	-38 26	41 05	4IV	-69 26	143 14
5III	27 31	51 36	5IV	41 53	131 39
6III	37 44	93 47	6IV	40 14	92 54
7III	22 12	22 50	7IV	43 17	161 56
8III	-12 08	5 55	8IV	-42 32	178 16

Table 1. Angles of orientation for the p-p vectors in regard to crystal rotation about the a axis with  $0^\circ = c'$  axis.

a Axis	r (A)	b Axis	r (A)	c' Axis	r (A)
0°	1.46	0°	1.44		
60°	1.41	100°	1.44	60°	1.48
130°	1.43	150°	1.44	95°	1.43
				125°	1.46

Table 2. Angular positions of maximum splitting and values of inter-proton distance.

#### IV. EXPERIMENTAL PROCEDURE

##### A. Crystal Growth

The single crystals of hypo were grown by slow rotation of a seed crystal in a slowly evaporating super-saturated aqueous solution of hypo, maintained at room temperature. The time required for growth to the necessary size of approximately 2 cm. in length and 1 cm. in diameter was between two and four days. The seed crystal was grown in about two or three hours by pouring a small amount of the super-saturated solution into an evaporating dish to produce rapid evaporation. A close watch was maintained on the solution and when the first crystals began to form the more promising ones were separated from the rest. This was done so that only single crystals would grow rather than twins as was the usual case if the solution were left to its own accord. When the crystals had attained a size convenient for their attachment to ordinary household thread they were removed from the dish. Duco cement was used to glue the seeds to the thread. Duco cement gives a proton resonance signal, a single line, however the small quantity used in the crystal was not expected to affect the hypo signal appreciably. The seeds were lowered into the slowly evaporating bath and when they had grown to the desired size removed and the thread cut. After ascertaining the crystal axes by visual observation and comparison with Groth's data (see figure 1) they were glued, again using Duco cement, to a small section of dowel.

Three crystals were grown in this manner and each was attached to a wood dowel so that the crystal could be conveniently rotated about one of its crystallographic axes. A separate crystal was used for each axis; a, b, and c' (the c' axis is the  $c \sin \theta$  axis of Taylor and Beever's data).



While mentioning the signal obtained from Duco cement it should also be noted that wood gives a proton resonance signal. However, here again the signal was not of a large enough magnitude and was neglected. When this wood influence was first noted a spare crystal was attached to a piece of foam glass, the foam glass was first tested for proton resonance with negative results, and the resonance signal still contained a strong central line.

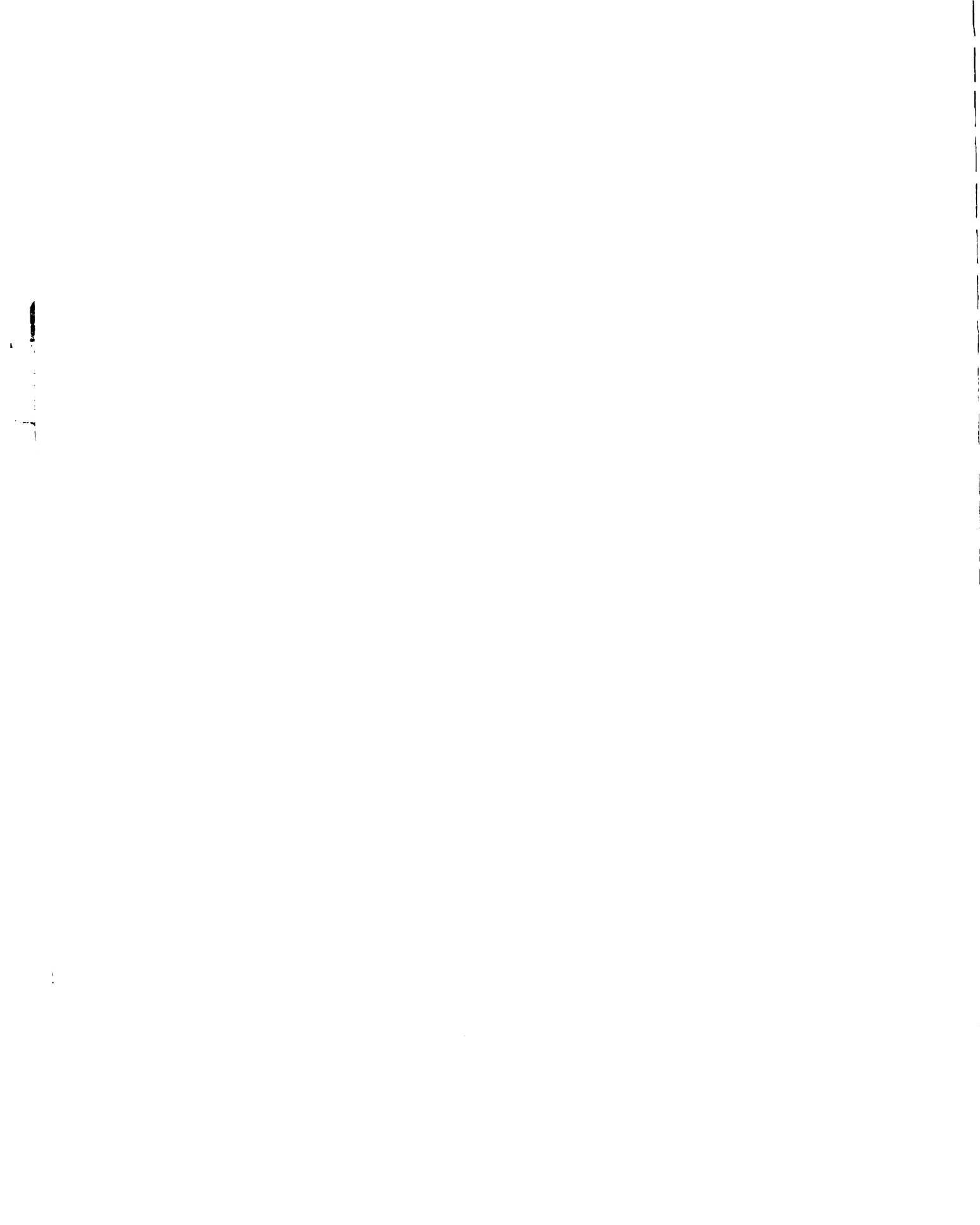
When the crystals were not being used they were stored in a sealed glass tube containing a small wad of cotton soaked in hypo solution. This was done to maintain an atmosphere that would prevent evaporation of the waters of hydration. As a precaution to prevent evaporation during prolonged exposure to air the crystals were sprayed with a thin coating of Krylon (duPont acrylic spray).

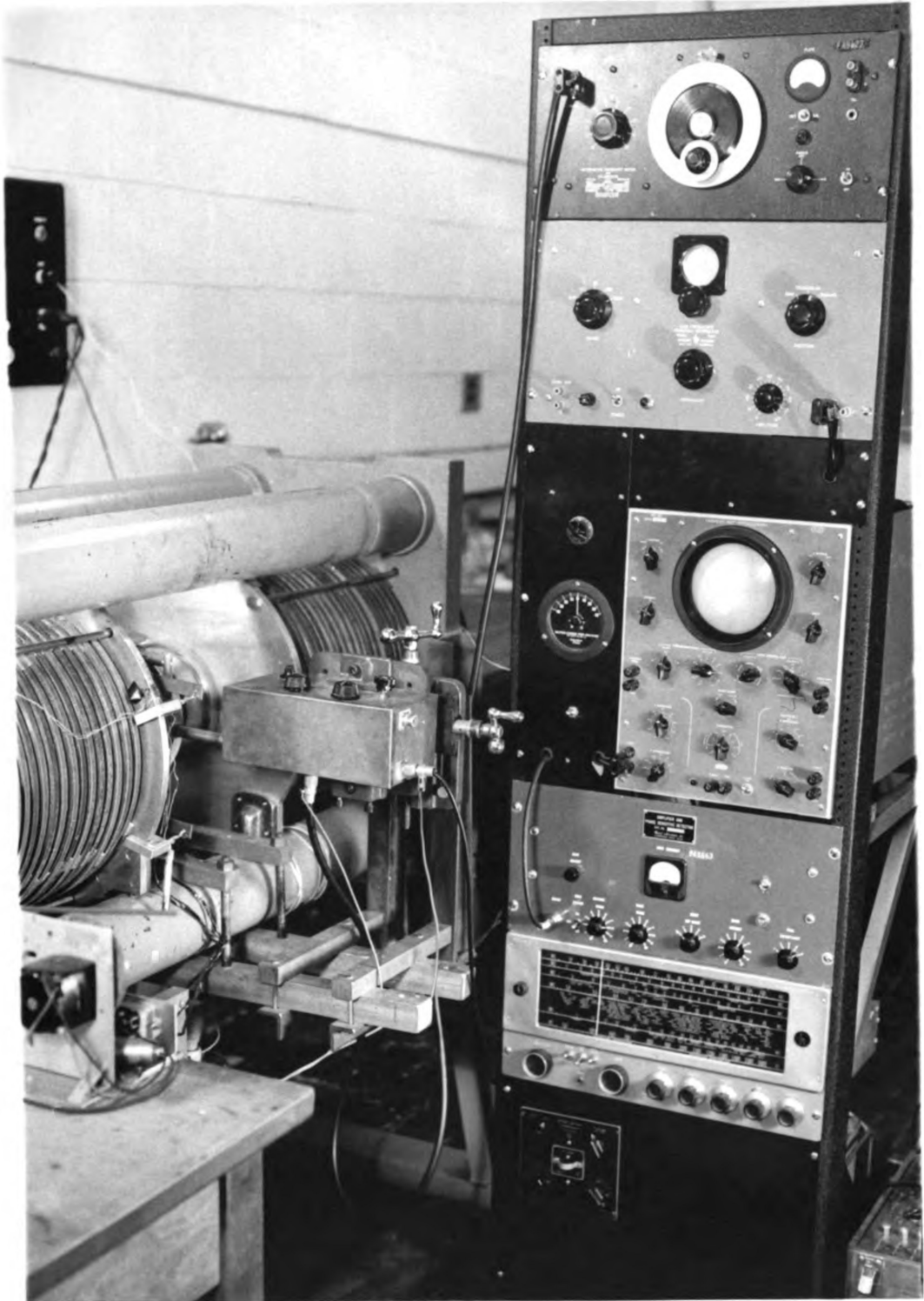
It might be remarked in passing that the growth of the hypo crystals was quite irregular in that they would grow in one instance and fail in what was supposed a like instance. Several different methods were tried before the rather standard process of slow evaporation and rotation was used. Some of these methods were; fast evaporation at room temperature of a super-saturated aqueous solution, and controlled temperature decrease with no evaporation. In the latter attempt the seed crystal was immersed in a super-saturated bath at a temperature of about  $42^{\circ}$  C. and the temperature slowly lowered about three degrees a day. One crystal was grown in this manner, however further attempts failed.

## B. Apparatus

The radio-frequency bridge method devised by Bloembergen, Purcell, and Pound<sup>7</sup> was used to detect the proton resonance signal. The apparatus is essentially the same as that described by Jain<sup>8</sup> (see figure 7). A block diagram of the apparatus is shown in figure (8). The lock-in amplifier was used with a 280 cycle modulating field of low amplitude. In order to provide a slow sweep of the resonance line a separate coil was mounted on one of the pole pieces of the magnet. This coil supplied an additional field parallel to the original magnetic field,  $H_0$ . In order to produce a nearly linear sweep a constant speed motor varied the position of a rheostat contact by means of a gear driven rack and pinion.

The shaft of the crystal holder was turned down from an aluminum rod approximately five inches in length and one-half inch in diameter. Mounted on one end of the shaft was a circular plate on which two five inch celluloid protractors were glued so as to make a complete 360 degree scale. On the other end of the shaft a Teflon rod (duPont fluorine-substituted poly-ethylene) was fastened. The rod was notched at the free end so that the dowel holding the crystal might be inserted. The entire holder was held in a vertical position between the pole faces of the magnet (see figure 9). A pointer was fashioned from some brass rods and attached to the magnet supports so that the relative angular positions of the crystal with the magnetic field could be read from the protractors.





**Figure 7. Photograph of Nuclear Resonance Apparatus.**

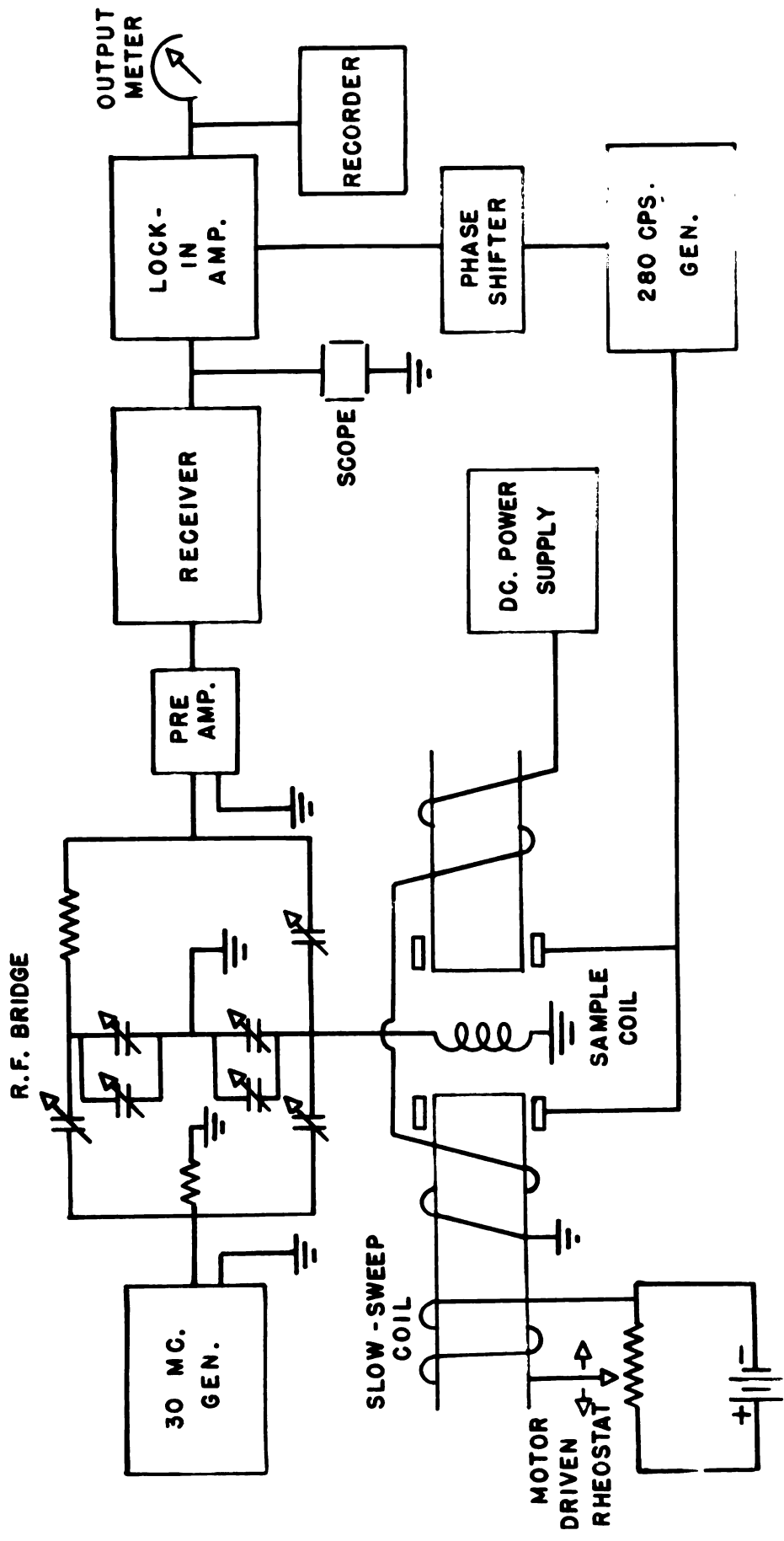
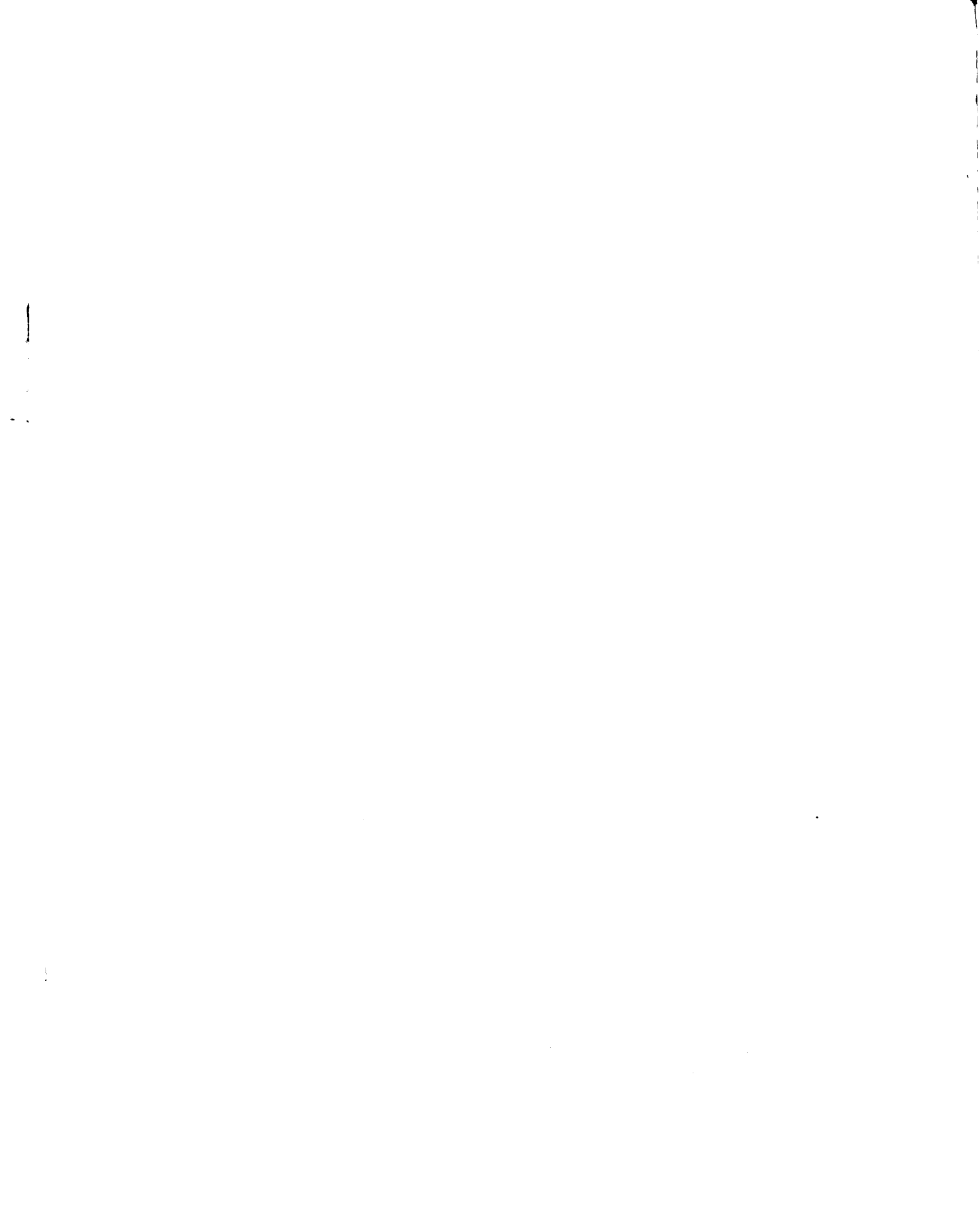
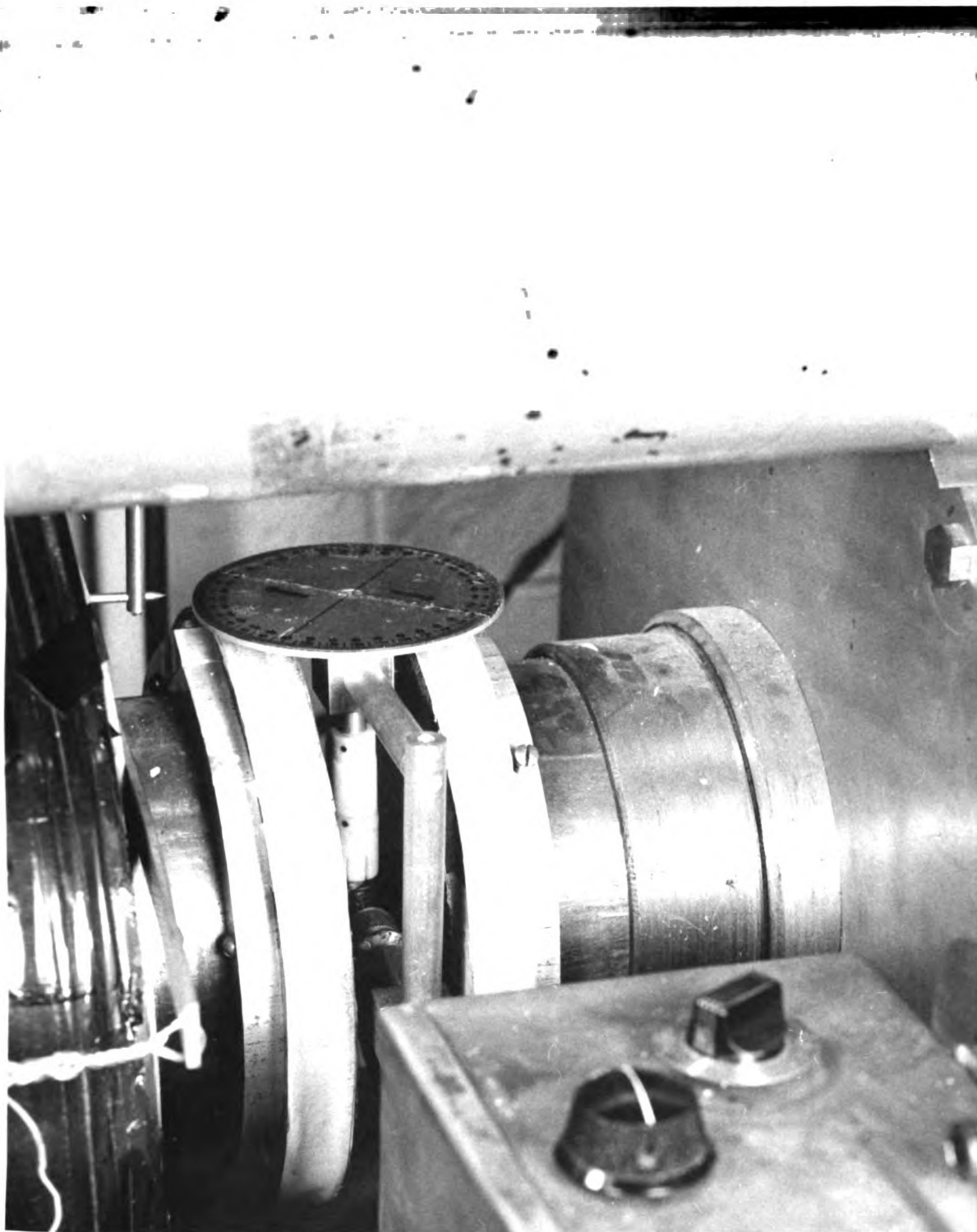


FIGURE 8. BLOCK DIAGRAM OF APPARATUS.





**Figure 9.** Photograph showing sample holder in position between the pole-faces of the magnet.





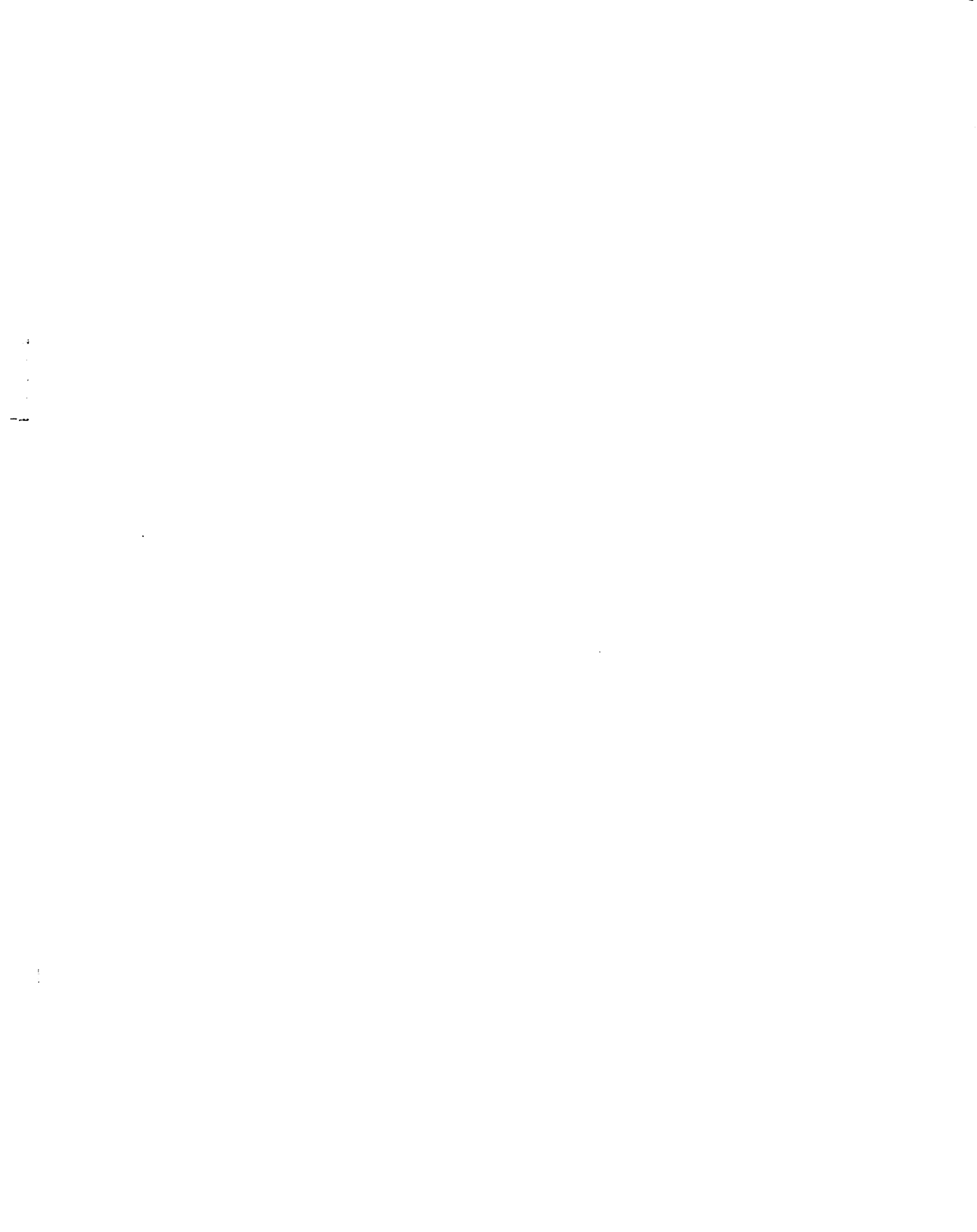
### C. Method of Recording the Signal

The separate crystals were placed in the coil and rotated in a clockwise direction perpendicular to the magnetic field. In each instance the crystal was oriented in the holder so that one of the crystal axes corresponded to the pre-defined zero degree mark on the holder.

The output of the lock-in amplifier is proportional to the slope of the resonance curve. This output was connected to a Millivac Sanborn chart recorder. From the recorder a trace of the derivative of the resonance curve was obtained. This derivative of the signal was taken for every ten degrees as the crystal was rotated through 180 degrees. Four derivative traces were recorded at each angle so that any non-linearity in the sweep might be averaged out. Samples of these traces at various angles appear for rotation about the a, b, and c' axes in figure (10). Photographs of the signal as seen on the oscilloscope were made by a Polaroid Land camera (see figure 11). The photographs were used as a check on the line width measurements obtained from the derivative curves.

Visual measurements were made of the line separations from the signal as it appeared on the oscilloscope. These measurements were made for each axial rotation through a full 360 degrees, at ten degree intervals. This was done for a general check on the shape of the doublet separation curves and to assure the observer that the curves repeated themselves in 180 degrees.

The reason for using the derivative trace of the signal was two-fold. First; higher accuracy was attained in the separation measurements. In the visual



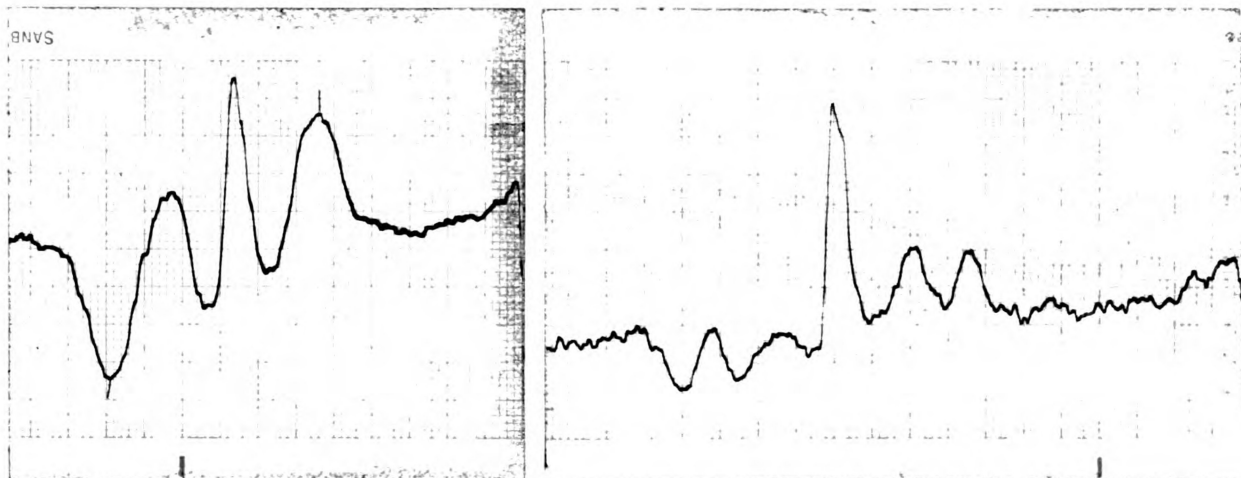


Figure 10. Samples of the derivative traces of the proton resonance signal from single crystals of hypo.



Figure 11. Photographs of the proton resonance signal from single crystals of hypo.

observations very rough estimates had to be made of the positions of the doublet because of the weakness of the signal and the large amount of noise. Second; the derivative apparatus had a much higher resolving power and therefore was able to detect more lines than by visual means. In one instance seven lines were detected with the derivative apparatus while only five lines could be seen on the oscilloscope.

The line separation is measured in gauss as is customary. The variable rheostat was calibrated by measuring the time required for the rheostat to run through a complete signal. This value was divided into the value of the modulating magnetic field,  $H_m$ . Its value was obtained from a previous calibration of the modulating voltage done in the manner described by Jain<sup>8</sup>. The quotient of this division is the number of gauss per second that the rheostat sweeps through as it is varied. The recorder tape is known to move at a constant speed of 2.5 squares per second. So by dividing this value into the previous quotient the final result is the number of gauss per square for a particular modulating and rheostat voltage. By multiplying this value by the number of squares between the signal peaks of the derivative the doublet separation in gauss is obtained.

## V. ANALYSIS OF RESULTS

### A. Experimental Results

The experimental values of the doublet separations as a function of the angle of rotation about the three crystal axes are shown in figures (12), (13), and (14). The solid lines through the experimental points represent theoretical curves with shapes corresponding to equation (10). The dotted lines through the points are hypothetical curves based on experimental evidence. Because of a definite broadening of the doublet components of the signal at particular angles the curves were assumed to intersect as indicated at the several points.

The resonance signals that appear may in some cases result from the superposition of two or more proton pairs that have very nearly the same orientation. The strong central line that appears in the signals (see figures 10 and 11) is probably due to a superposition of several narrow doublets and/or a result of rotating proton groups as previously described. Because of the confused situation which exists in the central portion of the line the doublet separation of a given proton pair can be traced only for those angles for which the separation is large. Therefore we will consider only components with large separations, thus the angle  $\delta$  for all the p-p orientations listed is less than  $35.3^\circ$ .

The angle  $\theta_0$  for the p-p vectors obtained from an investigation of figures (12), (13), and (14) is listed in table (2). The angles listed under the a axis are for a clockwise rotation about that axis with  $0^\circ$  corresponding to the c axis. The angles listed under the b and c' axes are for clockwise rotations about these axes with  $0^\circ$  corresponding to the c' and a axis respectively.



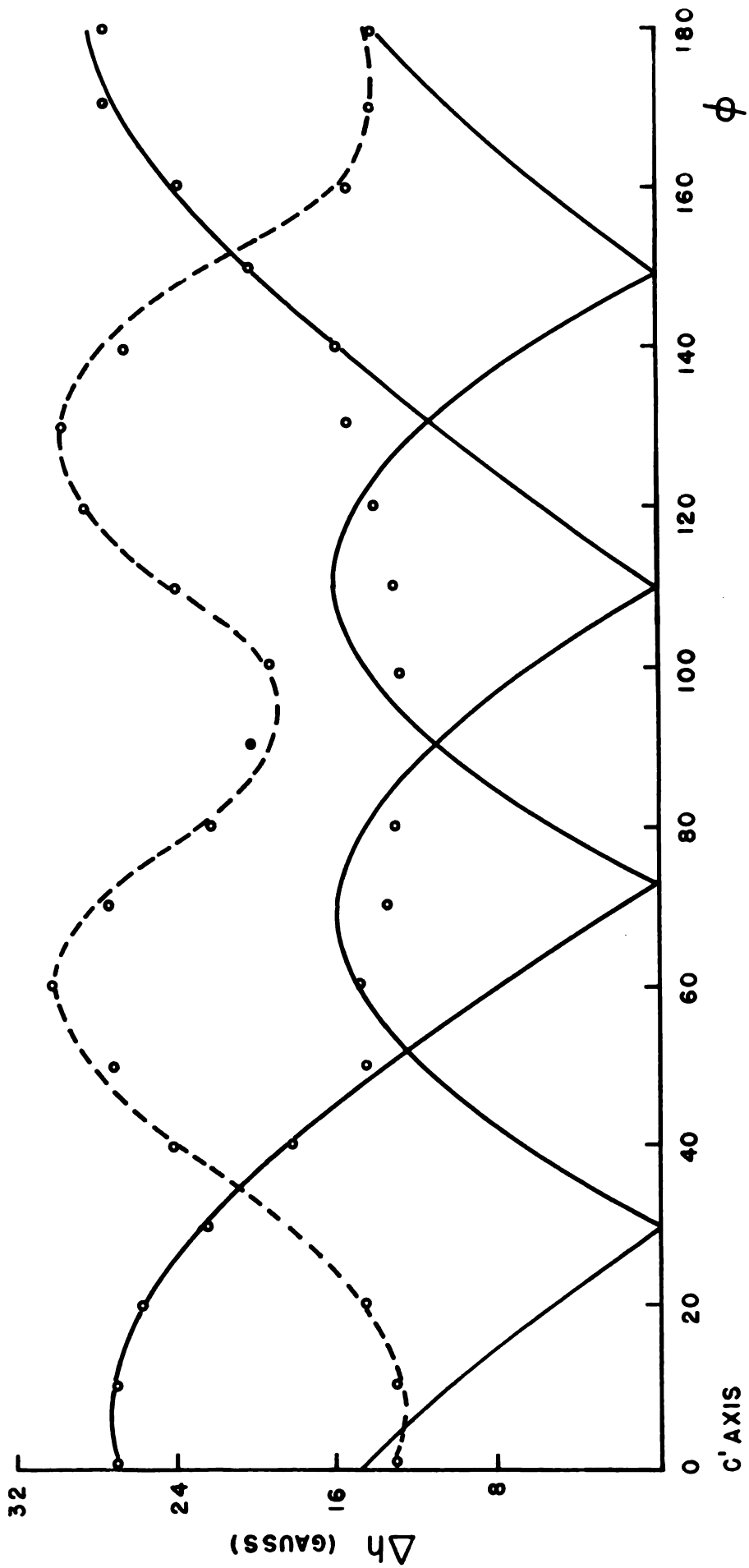


FIGURE 12. DOUBLET SEPARATION AS A FUNCTION OF THE ANGLE OF ROTATION ABOUT THE A AXIS.

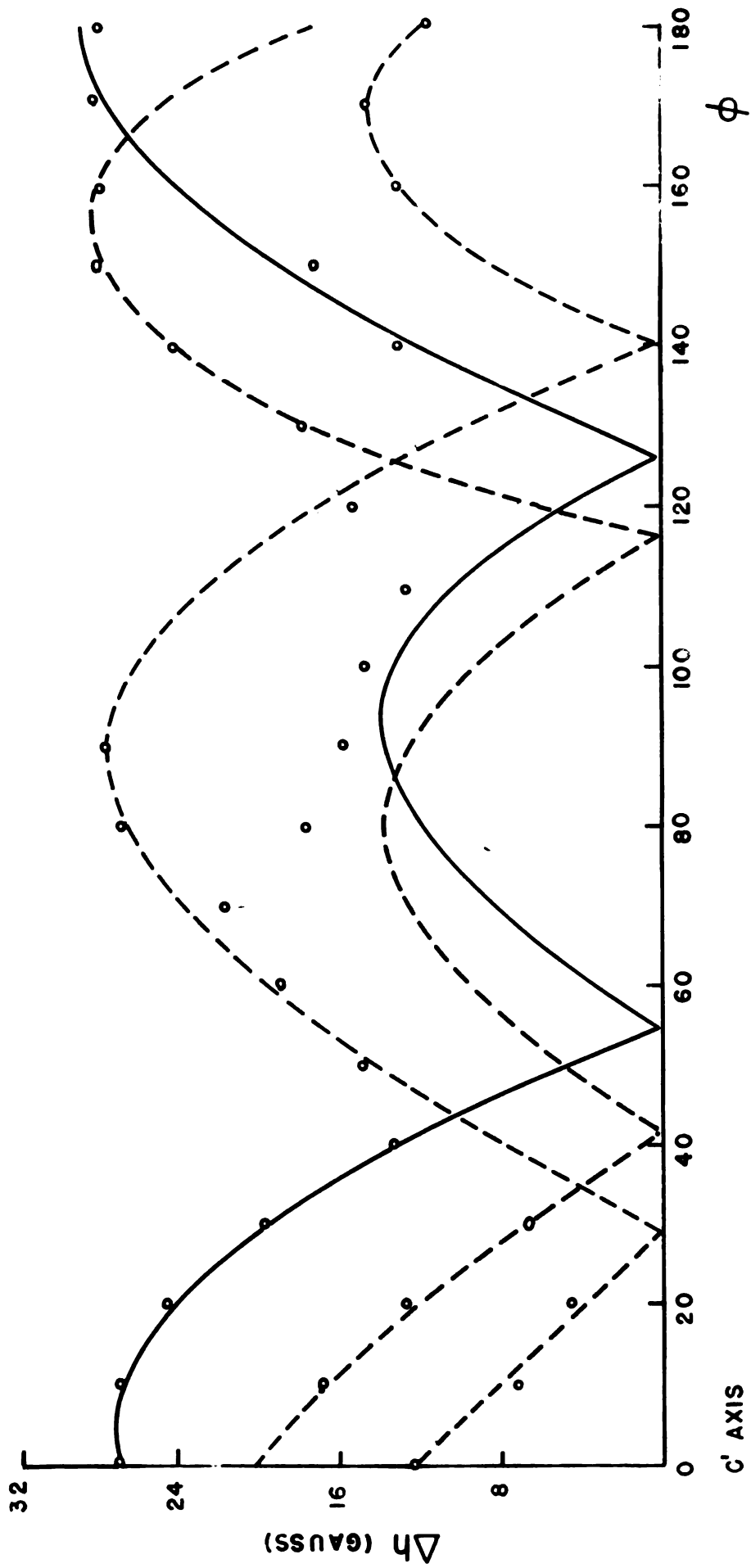


FIGURE 13. DOUBLET SEPARATION AS A FUNCTION OF THE ANGLE OF ROTATION ABOUT THE B AXIS.



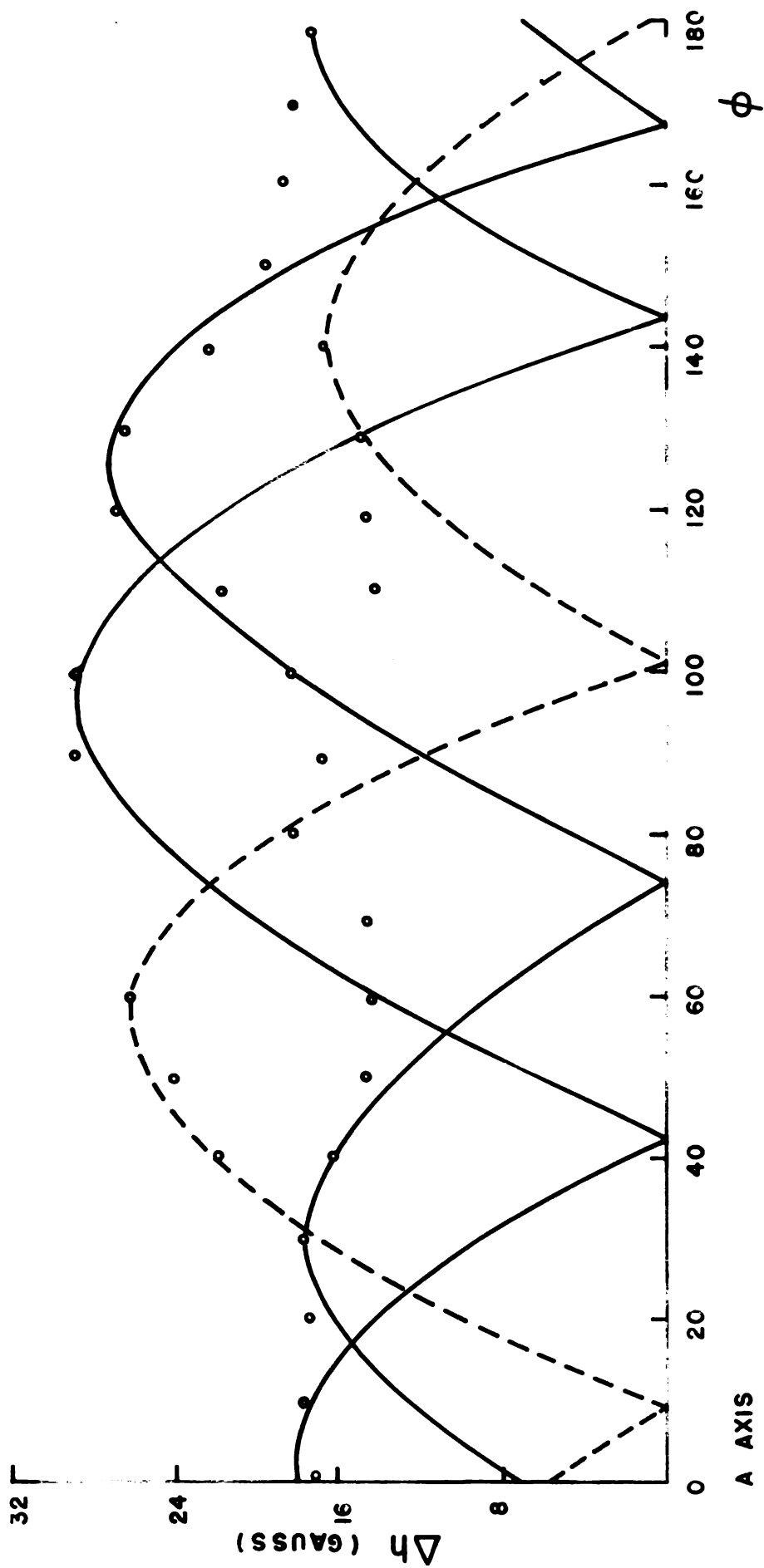


FIGURE 14. DOUBLET SEPARATION AS A FUNCTION OF THE ANGLE OF ROTATION ABOUT THE C' AXIS.



The  $\alpha_0$  angle listed above the double line of table (2), when read across for the a and b axes, probably refers to the same p-p vector which was detected in the two rotations. The angles below the double line refer to p-p vectors that seem to appear only in rotation about a particular axis.

The values of the inter-proton distance (r) for each particular proton pair are also listed in table (2). At maximum splitting the term  $(3\cos^2\theta - 1)$  in equation (3) approaches two since  $\theta$  approaches  $0^\circ$ . Then equation (3) becomes,

$$\Delta h = 6 \mu r^{-3}.$$

The value of  $6 \mu$  is known,  $84.6 \text{ gauss } \text{A}^3$ , and  $\Delta h$  may be determined from the experimental work. The value of r obtained from this equation represents the upper limit since in determining it we have assumed the maximum splitting.

The error in the determination of the angles  $\theta$  and  $\alpha_0$  is probably on the order of  $10^\circ$ . Most of this arises from errors in orienting the crystal. The error in the maximum value of the separation is perhaps 5% since the derivative curves were repeated four times and an average used. The value of r, as a result, is probably accurate to within 2% error.

## B. Discussion

An attempt to relate the experimental p-p orientations (see table 2) with the assumed orientations (see table 1, and figure 3) was made with the following results. The doublet whose maximum separation occurs at  $0^\circ$  in the a and b axis rotations may result from the p-p interaction of the proton pairs of the following waters; 4I, 7I, 7II, 7III, and 8III. The doublet whose maximum splitt-

ing occurs at  $130^\circ$  in a axis rotation may be due to the proton pair of the 5IV water molecule. The waters; 6I, 6III, and 6IV may give the doublet whose maximum separation is at  $95^\circ$  in the c' axis rotation. The doublet whose maximum splitting occurs at  $125^\circ$  in c' axis rotation may have resulted from the protons of the 6II water molecule.

The experimental results which indicate maximum splitting at  $60^\circ$  in the a axis,  $100^\circ$  and  $150^\circ$  in the b axis, and  $60^\circ$  in the rotation about the c' axis cannot be correlated with any of the assumed positions of the p-p vectors. This is perhaps the most important result of the work for it indicates that either the crystallographic data is incorrect or that the basic picture of the way in which the protons are located on the lines joining the water oxygens to the nearest electronegative atoms is in error.

Some of the water molecules were not listed because the assumed positions of the proton pairs for these waters was such that they laid within the shaded area shown in figure (15) and therefore theoretically gave no detectable signal. This shaded portion of the figure is that area not covered by rotation of the sample about the three crystal axes because of the previous assumption of considering only those p-p orientations whose angle  $\delta$  is less than  $35.3^\circ$  as being detectable in the proton resonance signal. In order to detect any possible p-p orientations within this area a rotation in the (110) plane and also in the ( $\bar{1}\bar{1}0$ ) plane would have to be made.

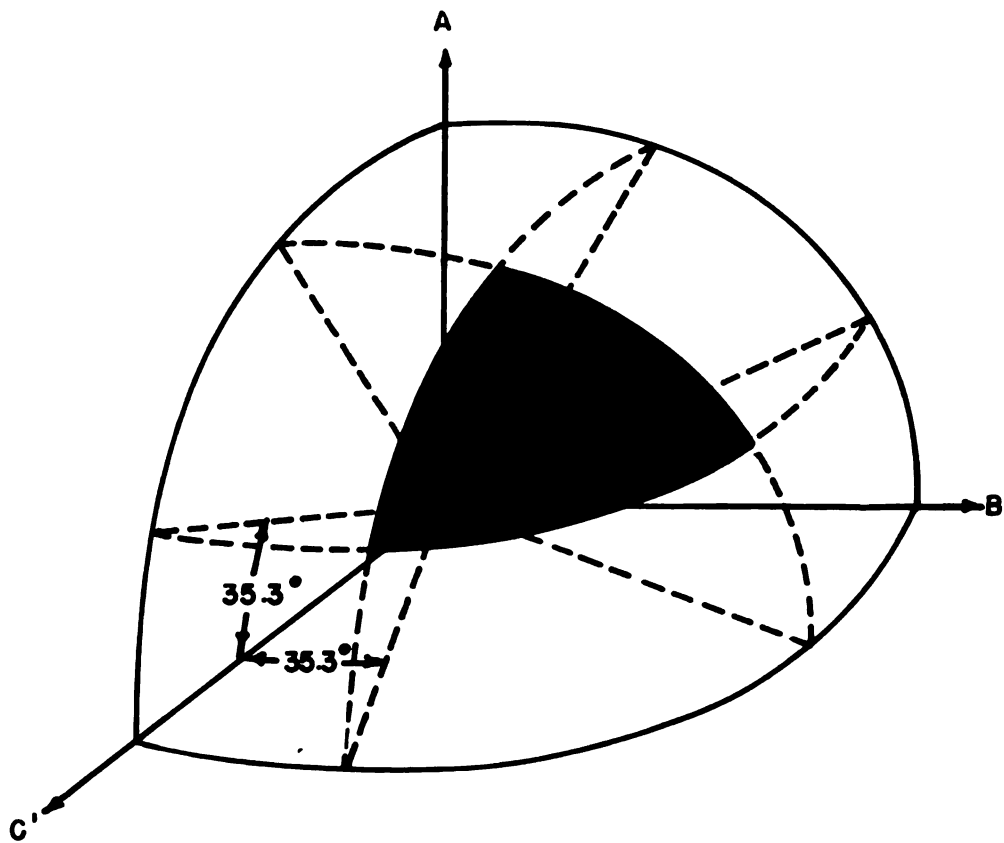


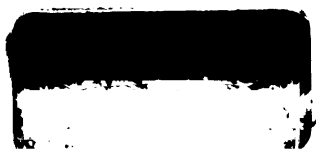
Figure 15. The shaded section shows that portion of the crystal volume which is probably not explored by rotation about the a, b, and c' axes.

### C. Summary

Although an attempt to locate a large number of non-equivalent waters of hydration by the proton resonance method may appear to be a rather ambitious project the results of the present problem indicate that with sufficient work it is quite feasible.

## REFERENCES

1. Pake, G. E., *Journal Chem. Phys.*, 16 327 (1948).
2. Soutiff, M. and Ayant, Y., *Journal Chim. Phys.*, 50 C107-C109 (1953).
3. Kakuichi, Shono, Komatau, and Kigoshi, *Journal Phys. Soc. Japan*, 7 102 (1952).
4. Spence, R. D. Paper soon to be published.
5. Groth, P. H., Chemische Krystallographie, 2 670 (1906-1919).
6. Taylor, P. G. and Beevers, C. A., *Acta Cryst.*, 5 341 (1952).
7. Bloembergen, Purcell, and Pound, *Phys. Rev.*, 73 679 (1948).
8. Jain, P. L., Proton Resonance in Nematic Liquid Crystals, PhD. Thesis, Michigan State College (1954)





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