A BUTRON DIVERAUTION STUDY OF NATEOLITE

## A NEUTRON DIFFRACTION STUDY OF

## HATROLITE

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## A Thesic

Dubmitted to the Faculty of Graduate Studies in partial Fulfilment of the Requirements for the Degree Doctor of Fhilosophy

> NeWester University Nay 1963

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THE DIFFRACTOMETER



DOTOR OF PHILODOLAY (1965)

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A newly constructed neutron diffractometer is described in detail. Several experiments were conducted to or sine the observatoristics of the instrument, and to propare the instrument for the collection of data for a crystal structure determination.

## ADRIAO, LADGRUNATIS

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#### Chapter I

#### Introduction

#### A. Neutron Diffraction

Neutron diffraction experiments were first performed over 25 years ago. Elsasser suggested in 1936 that neutrons could be diffracted by solids, and this was demonstrated experimentally in the same year by Halband and Preisverk, and Mitchell and Powers, using radium-beryllium neutron sources. These early experiments proved that noutrons were diffracted by solids, but did not give quantitative data since the available neutron sources were of very low intensity.

Since intense neutron beams have become available from nuclear reactors, the properties of neutrons have been extensively used to study the solid state. The equivalent wavelength for low energy neutrons is given by de Broglie's equation

(1)

## $\lambda = h/mv$

where h is Planck's constant,

m is the mass of the neutrons,

and v is the velocity of the neutrons. Diffraction effects are produced when the wavelength is of the same magnitude as the atomic dimensions (i.e., of the order of 1 %). Nost of the neutrons in a reactor are in thermal equilibrium with the moderator at a temperature T. These

Figure 1:1

...

Diagrammatic arrangement of the neutron diffractometer and its associated equipment.



thermal neutrons have a Maxwellian distribution of velocities with a root-mean square velocity given by the equation

 $\frac{1}{2} = \frac{3}{2} \text{ k P}$ From equations 1 and 2, 1t follows that (2)

$$\lambda^2 = h^2 / 3 m k T$$
 (3)

For  $T = 40^{\circ}$ C, the wavelength is equal to 1.45 A which is of the desired magnitude.

A beam of neutrons can be obtained from a reactor by means of a port through the reactor shield (see Figure 1.1). The energy distribution of the neutrons emerging from the collimator will be a slightly modified Hammellian distribution since proportionately more neutrons of high energy will emerge (Eacon and Thewlis, 1949). The general nature of the neutron spectrum is illustrated in Figure 1:2.



Figure 1:2. Wavelength Spectrum of the Neutrons emerging from a Reactor (Bacon, 1955)

In order to obtain well resolved diffraction peaks from a crystal sample, it is necessary to limit the range of wavelengths of the incident neutrons to a narrow band. This band may be selected from the wide range of wavelengths available by diffracting the neutrons from a large single crystal, the monochromator. Only those neutrons which satisfy the Bragg equation

### $n\lambda = 2$ d sin 3

will be diffracted through an angle 2 3, where n is the order of the reflection, d is the interplanar spacing of the crystallographic planes, and 3 is the angle between the incident beam and the reflecting plane. Normally the wavelength band is centered to the high energy side of the peak of the distribution functions as illustrated in Figure 1:2, so that the  $\lambda/2$ component of the diffracted beam is small. The monochromatic beam is then ready for diffraction studies.

Nost of what we know about the spatial arrangement of atoms in a crystal has been determined using X-ray diffraction. The equipment required for X-ray studies is much more compact than a neutron diffractometer and the intensity of the beam from a typical X-ray generator is many times greater than the neutron beam from the most powerful nuclear reactor. For these reasons, neutron diffraction is only used to complement the data which can be obtained using X-ray diffraction. X-rays are scattered by electrons so that the picture which one

obtains from X-ray diffraction is that of the electron density within the crystal with the atoms appearing as rather diffuse peaks. In the case of neutrons, there are two important scattering interactions. The first is a short-range interaction with the atomic nuclei, and the second is an interaction between the magnetic moment of the neutron and electrons which have unpaired spins. Thus the neutrons "see" the static nuclei, and, in the case of paramagnetic ions, a few of the electrons in the outer chells. This latter interaction has led to the use of neutron diffraction to study the magnetic structures of certain materials such as the arrangement of atomic magnetic moments in ferromagnetic and antiferromagnetic crystals.

Soutron diffraction is also important in solid state research due to the fact that atoms have different scattering amplitudes for h-rays and neutrons. A-ray scattering amplitudes are approximately proportional to the atomic numbers except in the vicinity of a critical absorption edge. On the other band, neutron scattering amplitudes vary considerably from element to element, and even from isotope to isotope. The general trend of the contering amplitudes can be given in terms of the nuclear radius, but the existence of strong resonances associated with the contering models greatly effects the magnitudes and the phases of the scattering amplitudes. This difference in the nature of the scattering amplitudes. This

amplitudes (i.e., those which are adjacent in the periodic table), for example, manganess and iron. Another case in which the difference in scattering amplitude is an advantage is in the location of light atoms, in particular, hydrogen in the presence of heavy atoms. X-ray diffraction techniques can aclded locate the single electron associated with the hydrogen atom dince the effect of the hydrogen electron is likely to be lost in the background of experimental uncertainties. The neutron background of experimental uncertainties. The neutron background of experimental uncertainties. The other hand, is of the same order of magnitude as that of most other nuclei, so that it is possible to determine the position of the hydrogen atoms with good recursoy. Such information is invaluable in any study of the unique role played by hydrogen in the structure of matter.

Heutrons can also be used to study the vibrational spectrum of stokes in a crystal. With X-rays, the energy changes, arising from interactions with lattice vibrations are negligible in comparison with the energy of the X-ray photons, but with thermal soutrons, the energy changes may be comparable to the energy of the neutrons. A study of these energy changes leads to information about the vibrational modes of the orystal lattice.

B Zeolives

Hatrolite, the crystal studied in this thesin, is a meaber of the geolite family. The crystals in this family

are formed from silicon-oxygen and aluminum-oxygen tetrahedra which are linked together by sharing ouggen atoms to form an open framework structure containing interconnected cavities. The aluminum tetrahedra have a net negative charge which is balanced by loosely bound positive ions in the cavities.

Meetites originated in hot, water-bearing lawes. Meat of the minerals in the laws crystallized out of solution as feldeper, which is also made up of silicon-exygen and aluminus-exygen tetrahedra, but with a less open framework. Formation of the zeolites took place in the dilute solution which was left, and they crystallized in such a way as to leave room for some of the water in their cavities.

Three main types of seelite framework occur. These are: 1. three-dimensional frameworks made up by linking the tetrihedra into four-and cix - membered rings which are joined to form a robust structure in three dimensions.

2. lasinar frameworks which are made up of closely knit cheets of tetrahedra

3. fibrous frameworks containing chains of tetrahedra which are loosely cross-linked to each other.

Interest in reolites arises from their ion exchange, dehydration, and molecular-sieve properties. The positive ions in the channels may be exchanged for others merely by soaking the crystal in a solution of the appropriate selt. Thus a codium-containing reolite will soften hard water by exchanging

the codium for orleans. The enter schooles contained in the atructure can also more through the channels in the orystal. If the water is driven off by heating the crystal, a slight shrinkage of the crystal will result, but the basic framework structure results intact. Therefore the veter can be readsorbed when the crystal is cooled. Other molecules can also be adsorbed by the realite. This adsorption is selective, being dependent on the dismeter of the channels in the crystal. For example, estane molecules may pees easily through the structure when larger molecules such as iso-octane cannot enter the crystal. Since the dismeter of the channels can be changed by verying the temperature, or by exchanging the positive ions thich particley block the channels, realities can be effectively used as moleculer-sieves.

Early work on the realities was carried out in the 1930's, but they have been noglected since them. Current interest in the molecular-sieve and ention-eachings reporties has led to a re-examination and extension of the work on these erystals. In the last three years, K-ray studies of three crystals which are typical of the three types of realite frequents have been reported. These are

1. Shabisite - robust structure in three dimensions

(Pang, 1961 and balth, 1962)

2. Hullipsite - laminar framework

(Steinfink, 1962)

3. Introlate - fibrous framework

(Neier, 1960 and Pang, 1961)

9.

A complete list of carlier references is given by Fang (1961). G matrolite

The structure of natrolite, Ma<sub>2</sub>Al<sub>2</sub>Ji<sub>3</sub>O<sub>10</sub>.2U<sub>2</sub>O, was first proposed by Fauling (1930). The silicon-oxygen and aluminum-oxygen tetrahedra are linked together to form chains parallel to the e axis as shown in Figures 1:3 and 1:4. Taylor, Hock and Jackson (1933) determined the approximate location of all the atoms in the structure except the hydrogens, and Heier (1960) subsequently determined the accurate locations for these same atoms. The orystallographic data for natrolite are summarised on page 13.

Two different systems of channels are found in natrolite. The channels purallel to the c axis shown in Figure 1:4 have a minimum free diameter of 2.08 Å, and the channels provided by the openings between neighbouring chains shown in Figure 1:3 have a minimum diameter of 2.60 Å. The dehydration and cation exchange phenomena can be attributed to diffusion along the latter system of channels.

Bohydration studies on natrolite have been carried out by Hey (1932), Milligan and Weiser (1937), Kolyumi and Miriyama (1953), Beng (1955) and Yukhnevich et al. (1961). These studies indicated that the water is fixed in the structure at room temperature. As the temperature of the crystal is



Figure 1:3. The chains in natrolite. The lower SiO<sub>4</sub> tetrahedra of a chain are linked to the upper AlO<sub>4</sub> tetrahedra (shaded) of neighbouring chains (after Meier, 1960).



Figure 1:4. (001) projection of the natrolite structure. The repeat distances are a/2 and b/2 in this projection. The AlO4 tetrahedra have been shaded (after Meier, 1960).

increased, the safer welcoulds are evolved as liketisted in Figure 1:5. This welch has versus temperature curve the obtained from an experiment conducted in our lateratory, and is essentially the same up the one obtained by long (1955).



Figure 1:5. Water loss versus temperature curve for natrolite. Fun; (1961) attempted to solve the structure of dehydrated natrollte vithout success.

In view of the interact in the debydration when enon, and because the value moleculo is fired in the structure at room tenperature, it and decided to locate the hydrogen atoms in the water molecule using neutron diffraction. Communic studies walk: molecule applied resonance techniques were also undertaken to many the social and clusters sites (letch and lennington, 1962) and to exclusion the dynamics of the tatter molecule at different temperatures (letch and Cant, 1962). Crystallogra, his bata for Natrolite

Porsula MagAlgilgO10 .2120

Unit coll

-orthorhombic

-contains 8 formula units

Cell dimensions (Meier, 1960)

 $a = 16.30 \pm 0.01$  $b = 18.63 \pm 0.01$  $a = 6.60 \pm 0.02$ 

Space Group Car - Fdd2

#### Chapter II

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#### ADURES SUG

### A Production of a Concehrozatic Seam

An ideal source of neutrons for neutron diffraction atudies would produce an intense, monochromatic, parallel beam of neutrons with a wavelength of the same order of magnitude as the distance of measuration of the atoms in a crystal. A beam of neutrons with approximately these characteristics can be produced using a nuclear reactor. Nost of the high energy neutrons produced in a reactor are alonged down to thereal energies by making many collisions with a moderator. These thermal neutrons have a Disvellian distribution of velocities, and fortunately, the mean velocity corresponds to a mayologith of the desired magnitude.

A beak of neutrons and gramm rays is removed from the relator through an air column, or collimator, directed at the core. Neutrons in a marrow emergy range are differented from the collimated beam by a large single crystal, the monochromator, and the neutrons and gramm rays remaining in the undeflected beam are absorbed in a concrete shield. The deflected beam is suitable for differention studies. <u>Collimator</u> (see figure 2:1)

The collimator assembly is held in one of the reactor beam orts, and provides an open passage for neutrons from the core of the reactor to the external face of the





SCALE |"=16"

FIGURE 2.1

# HORIZONTAL SECTION OF BEAMPORT AND COLLIMATOR ASSEMBLY

shielding wall. Hear the core, a 3' foot long steel funnel of 1' degrees convergence allows the optimum number of neutrons to enter the collimator. This latter portion of the assembly is 1 inch tide by f inch high, and extends for 6 feet through the centre of a steel tube. These dimensions limit the horizontal divergence of the emerging beam to 1.600%. A reduced divergence of either 0.780 or 0.520 can be obtained by inserting one or two 0.018" steel slate into grooves in the collimator. Streaming of neutrons along the surface of the collimator is prevented by a step from 4 to 6 inches in diameter. The whole assembly is supported along the axis of the beam port by steel rings, and alignment between the funnel and collimator is maintained by two steel dowels.

The beam port is directed towards the centre of the reactor core and approaches to within a few inches of the core. The diameter of the aluminum tube which lines the beam port increases in steps from 4 to 10 inches. The 4 inch diameter near the core allows the high gamma ray flux to be attenuated in the region surrounding the funnel, without creating cooling problems. Additional reduction in the gamma ray flux and adequate discipation of heat is provided

<sup>II</sup>The horizontal divergence is equal to  $2\beta$  where  $\beta$  is the angle given by the ratio of the collimator width to the collimator length.

-----

by the two steel shielding pluge nearest the core. At the emit end of the beam port, a one foot long lead plug was placed to absorb low angle **Y**-rays that are scattered near the end of the collimator. The remaining shielding plugs consist of aluminum cans filled with barytes concrete. The beam port emit is covered by a balf-inch steel plate which poscesses an aperture with a shutter to provide a nearly leak-tight closure in the event of serious water leakage into the beam port. This shutter can be controlled from the top of the external shielding blocks (see figure 2:2). <u>Monochromating Grant</u>

Neutrons of a wide energy spectrum emerge from the collimator, and are incident on the monochromating crystal. Those neutrons thich satisfy Bragg's law for the particular orientation of the crystal will be reflected, while the majority pass through the crystal and are caltured in the external shield. The monochromating crystal is a single crystal of corper about 14 inches wide by 5 inches in length (see figure 2:3). The surface of the crystal is cut at approximately 6 degrees to the (111) plane to increase the intensity of the diffracted beam by reducing its width (see Fankuchen, 1937). Accurate adjustment of the crystal, with three degrees of freedom, can be made from outside the external shield (see figures 2:2 and 2:4). Two of the degrees of freedom, rotation about and translation along the axis of



Figure 2:2. Monochromator Controls (in box) and Shutter Control (cable in background)



Figure 2:3. Monochromator and Exit Tube





Figure 2:4 (a)

19a.

the collimator, allow the secondary beam to be aligned with the exit tube which is set into the external shield. The third adjustment, rotation about the vertical axis, allows the monochromator to be so oriented that neutrons of the appropriate wavelength pass down the exit tube. This tube can be placed in one of two positions making angles of  $22^{\circ}$  and  $30^{\circ}$ with the main beam so that the secondary monochromatic beam can be chosen with a wavelength of 0.80 Å or 1.08 Å.

The external shield consists of four barytes concrete class stacked one on top of the other. The second sleb from the bottom is at the height of the beam port, and has a 2' x 2' x 2' cavity at the point where the beam emerges from the collimator. This cavity contains the monochromator which is surrounded by blocks of boric weid in paraffin to attenuate feat neutrons and absorb the slow neutrons which are not reflected down the exit tube by the monochrometor. In the path of the main beam, the concrete shield is five feet thick and should be adecuate for a collimator aperature much larger than the one described, and for a reactor power of 5 megawatts. The thickness of the shielding at the sides of the monochromator cavity is less than the calculated recuired value, but this region will be blocked by the external shielding material around the exits of the adjacent beam ports.

<u>xit Tube</u> (see figure 2:5)

The secondary beam diffracted by the monochromator passes through a steel exit tube set into one of the two stopped holder tubes in the external shield. The oper ture in the exit tube is eccentric so that, by rotating the exit tube in its holder, its height can be accurately aligned to match that of the collimator. The exit tube which is not in use is blocked by a steel encased concrete plug. <u>I The Diffractometer and Accordated Control Circuits</u>

The crystal under study is mounted in the neutron band on an are system on the axis of the diffractometer, a modified General Electric BFG X-ray spectrogeniometer.<sup>1</sup> Orystal planes are adjusted to a reflecting position using the are system, and by rotating them about the axis of the diffractometer using the crystal orienter<sup>2</sup> located below the are system. Neutrons diffracted by the crystal are detected by a BF<sub>3</sub> counter<sup>3</sup> mounted on the rotatable arm of the diffractometer. Hormally the movements of the counter and crystal are coupled to rotate in a horizontal plane about the same axis, the counter rotating at twice the speed of the crystal so that all neutrons diffracted by a particular set of parallel planes are detected.

provision is made for operating the diffractometer in

luce Allendix A for description of modifications She Albendiz B for description of crystal orienter Dec Appendix C for description of SF, counter



5

## EXIT TUBE ASSEMBLY Figure 2.5

•



SECTION AA Scale  $\frac{1}{2}$ "=1"

In automatic mode. Heutrons emerging from the exit tube are monitored by a fission counter<sup>H</sup> and the output from this counter is used to control the operation of the diffractometer. Fulses from the fission counter and the BF counter are fed through the systems shown in figure 2:6, and the outputs of the systems are recorded on both scalars and a two-pan recorder, the latter providing a visual check on the operation of the diffractometer.

Then a preset number of counts is reached in the fission counter system, a tripper pulse from the preset scalar stope the printing scalar and causes the total number of counts recorded on the scalar to be printed by a digital recorder. At the same time, the BF3 counter is advanced to a new position. A pulse from the printing scalar resets both scalars to zero, and counting recommences. At predetermined positions of the BF3 counter, a total is printed, corresponding to the integrated count accumulated since the last total was printed. At the end of a scan, the crystal orienter repositions the crystal and a new scan commence. The following variables in this process can be controlled by the operator:

1. The length of time s ont at each step in terms of integrated neutron flux recorded by the fission counter.

2. The tidth of each step. (1 to 6 minutes of arc of counter movement)

Muse Appendix D for description of fission counter.



CONTROL AND MEASURING CIRUIT


S FOR THE DIFFRACTOMETER FIGURE 2.6

3. The total number of degrees included in the soan of a diffraction beak, and the direction of soan.

a can be as a second as a second

4. The orientation of the crystal about the axis of the diffractometer. Seventeen orientations of the crystal can be set on the orienter in advance.

#### rogrammer

Data is collected automatically under the control of a programmer condisting of two components, a rotary relay and a crystal orienter (see figure 2:7 for circuit diagram). The rotary relay consists basically of two microswitches which can be closed independently when the table of the programmer is in any one of 180 possible positions. The relay advances one position at the end of every } degree scan of the BF, counter, and at preselected positions, the microswitches are closed. One of the switches operates the total key of the digital recorder, and the other operates the crystal orienter, and reverses the direction in which the diffractometer scans. The crystal orienter locates the crystal in one of seventeen preselected orientations about the axis of the diffractometer, in preparation for a scan, and, operating in conjunction with the rotary relay, it permits the diffractometer to operate in a completely automatic mode for extended periods.

## ligure 2:7

Control Lanel and Associated Circuits

Function of Components:

-----

A- rotary relay advance

E- crystal orienter on - off

C- diffractoseter on - off

D- rogrammer on - off

- reverse diffractometer drive (manual)

F- programor

6- ratchet relay to reverse diffractometer drive

H- crystal orienter advance (manual)

I- choice of continuous or step scan

J- colenoid to overate crystal orienter

K- drive motor for crystal orienter

1- limit awitches

- arive motor for diffractometer

I- step sean control solenoid.



# CONTROL PANEL AND ASSOCIATED CIRCUITS STEP SCAN CONTROL CIRCUIT SEE FIGURE A.I 0 ł B G H A ! NOO LX Μ 000 1000 <del>م</del>يرا. -16 2600

#### CHAPTER III

#### Testing of A perstus

This chapter describes the experiments which were performed to study the characteristics of the neutron diffractometer, and to prepare the equipment for the collection of data. First, we will consider the properties of the monochromatic been emerging from the exit tube. Experiments were performed to maximize the number of neutrons in the beam, to examine the distribution of neutrons in the beam, to determine the wavelength  $\lambda$  of the neutrons, and to determine the second order contamination of the beam (i.e., the percentage of neutrons with a wavelength  $\lambda/2$ ).

Once the monochromator was placed in position, the intensity of the monochromatic beam could be adjusted using two of the degrees of freedom of the monochromator. Freliminary experiments showed that the third degree of freedom, translational motion 2, had no effect on the intensity as long as the crystal remained in the beam.  $\Theta$  and  $\chi$  were adjusted as shown in figure 3:1, using the fiscion counter as a detector. There was little coulding between the two degrees of freedom and the maximum intensity was relatively insensitive to changes in  $\chi$ , being constant over a range of 20'.  $\chi$  was set in the middle of this range, and the complete monochrometor rooking curve shown in figure 3:2 was made. Note the lack of

## Figure 3:1

## Aligning of Monochromator

Several scans of the type shown in curve A were made for different values of  $\chi$ . The maximum counting rate in each case occurred for = 13.30. Curve B shows the variation of the maximum counting rate as a function of  $\chi$ .

7



-----

28 0



symmetry to this curve. This is likely due to the lineage structure which can appear in large crystals grown from the melt (Meiss, Hastings and Corliss, 1951). A fibrous structure aligned in the direction of growth occurs with the verious lineage regions, differing in orientation by as such as 30 minutes.

The flux distribution in the beam was examined using the Fr counter. To make these measurements, the BFr counter and its mounting cradle were removed from the arm of the diffractometer, and remounted so that the counter could be soved across the beam while its axis remained parallel to the direction of the bass. Vertical adjustment of the counter vas ande with the mounting cradle. These two degrees of freedom permitted the counter to be moved through a large portion of the bank. A series of scans was made with the counter limited by a 2mm. diemeter allt, to give the flux distribution curves shown in figure 3:3. In addition, the central seen x-x was repeated with a loss. x loss., and a loss. x loss. allt placed at the mouth of the exit tube (see figure 3:4). The average flux through the loam. x loam. slit is 5 x 104 neutrons/cm.<sup>2</sup>/sec. for a reactor power of 1 megawatt. This value was obtained using the calculated officiency of the fission counter (0.13).

The average wavelength of the neutron beam was determined by locating the maxima of the diffraction peaks for four

## Figure 3:3

et es al la com

....

Flux distribution in the beam emerging from the exit tube. The contours indicate relative values only.





### Figure 3:4

## Flux Distribution with Slits

. .

The accompanying surves give the flux distribution along the central scan  $-\infty$  shown in Figure 3.3. Surve A is the distribution with no plit at the mouth of the exit tube, curve B is the distribution with a 15 mm. x 15 mm. slit, and curve C is the distribution with a 10 mm. x 10 mm. slit. The maximum counting rate is opprovidetely the same in all three curves.



# Flux Distribution with Slits

520

orders of the (100) reflection from a quartz sample placed on the diffractometer. These measurements gave the value  $\lambda$ =1.087 ± 0.001 A. The  $\lambda$ /2 contamination of the beam was checked using the (200) reflection from a NaGl crystal. The ratio of the intensity of the  $\lambda$ /2 peak to that of the  $\lambda$  peak was less than 0.4%.

## SF3 Counter and Associated Electronics

The geometry of a BF3 counter causes the efficiency to vary considerably across the face of the counter. In order to determine the most efficient portion of the BF3 counter, a beam of neutrons 2000s. In diameter was directed along the counter parallel to its axis. Three scans were made across the beam to give the efficiency curves as shown in figure 3:5. For subsequent measurements, the slit in front of the counter was adjusted so that neutrons entered the most sensitive portion of the counter.

A series of experiments was conducted to determine the best settings for the preapplifier, applifier, discriminator and high voltage. The results of these experiments are summarized in figure 3:6. From these surves, the final settings were shown to give the maximum counting rate with good discrimination spainst background noise. Bubsequent shocks on the operation of the system were made by testing to see that the peak in the energy spectrum occurred at the same threshold level as shown in figure 3:6. The continuously variable H.T. applied

## Figure 3:5

# Efficiency of BFg Counter 1

The variations in the efficiency of the  $BF_3$ counter across the face of the counter were measured in the manner described in the text. The sensitivity of the counter is almost constant in the area enclosed by the contour marked 10, except for the region surrounding the wire which note as the anode of the counter. In this region the efficiency of the counter drops to near zero.

# EFFICIENCY OF BF<sub>3</sub> COUNTER # 1 (VIEWED FROM FRONT)



SCALE 5"=1"

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### Figure 3:6

## Spectra fros sta Counter 1

The accompanying spectra were determined using a single channel analyzer. In each case, the gain was adjusted so that the maximum counting rate occured for a threshold level of approximately 7.65.

At voltages lower than 1700 volto, there is poor separation of background pulses and pulses resulting from neutron induced reactions. At high voltages, over 2000 volts, the range of pulse energies increases and the counting rate decreases. A final operating voltage of 1000 volts was chosen.



to the counter allows the gain to be accurately adjusted if necessary.

Fulses from the BF3 counter system were examined using an oscilloscope. These pulses had a rise time of 2 microseconds, and a total duration of 10 microseconds.



If these pulses are replaced by equivalent square pulses of 8 microseconds duration, then the probability of two pulses occuring at the same time is given by Poisson's formula  $r = nt \exp(-nt)$  where n is the number of pulses per second, and t is the time duration of the pulse. Ordinarily the maximum counting rate for a diffraction peak does not exceed 10,000 counts per minute corresponding to  $P = 1.33 \times 10^{-3}$  so coincidence losses can be neglected.

## Fission Counter and Associated Electronics

The variables in the fission counter system are limited to the presablifier and discriminator settings since it is necessary to use the maximum gain of the amplifier (2400x) to obtain suitable sized pulses (approximately 10 volts high). The precaplifier was set to give the maximum counting rate, and the discriminator was set as indicated in figure 3:7.

## Figure 3:7

## Spectrum of Fission Counter

The number of counts recorded per unit time by the fission counter system was noted as the discriminator setting was raised from 0 to 60 (curve marked integrated count). The change in counting rate for every change of 5 in the discriminator setting was used to obtain the energy distribution of pulses recorded by the system (curve marked  $\Delta C$ ).



DISCRIMINATOR SETTING

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#### Chapter IV

Preparation of Crystals and Collection of Data Beleating and Shaping a Crystel

Grystals of natrolite were selected from a group of large terminated crystals from Aroy, Langesundofjiore, Horway. The samples had well developed (110) frees, and grew preferentially in the [001] direction. On the basis of the m-ray results and predicted hydrogen atom positions, it was expected that the hydrogen atoms should be well resolved in the (001) and (110) projections, so erystals were propared to give data for these projections.

hereflections from several uncut crystals were examined on the diffractometer to compare the quality of the crystals and to obtain an estimate of the extinction correction (see the discussion of secondary extinction later in this chapter). A crystal was selected which gave intence reflections without producing a large amount of ertinction. This sample was polished by hand to form a cylinder 4.5 mms. in diameter by 20 mms. In length. An attempt was made to increase the mosaic spread of the crystal by dipping it in liquid air, but no change in the intensities of the diffraction peaks could be observed.

Only one large crystal was evailable which was suitable for collecting data for the (110) projection.

The (110) face of this sample was comented to a metal rod for mounting in a lathe, and the crystal was out with an "Airbrasive" unit to form a cylinder 4mms. In diameter by 7.5 mms. in length.

### Aliming the Grystal

The crystal to be examined was mounted on an arc system so that the axes of rotation of the arc crossed near the centre of the crystal (which required the use of an aluminum spacer in the case of the shorter crystal). As a preliminary adjustment, the axis of the natrolite crystal was optically aligned with the axis of the diffractometer. Once a diffraction beak had been located, the axis of the crystal was accurately aligned by moving each are through several degrees until the position was found which maximized the counting rate. Alignment is simplified if the axis of rotation of one of the two ares is varellel to the normal to the reflecting plane so that only the second are effects the intensity of the peak (neglecting end and extinction effects). With less favourable orientations, there will be coupling between the effects of the two ares and the p-setting which makes aligning the crystel more difficult (/ is the angle giving the orientation of the crystal about the axis of the diffractometer). In this case, it is necessary to observe four coulvalent peaks located approximately 90° apart, and to

systematically very all three coupled variables until the marinum intensity for each of the peaks is obtained.

Figure 4:1 shows the scans used to align the large are with natrolite sample 22. The axis of rotation of the small are made an angle of loss than 5 degrees with the normal to the reflecting plane so that coupling between the two area and the A-setting was almost negligible.

## Rainstion of one chapps

The shape of a diffraction peak is determined by the geometry of the diffractometer and by the characteristics of the monochromator and the crystal under study. A detailed conclustion of the peak shapes will yield an estimate of the mostic spreads of the two crystals, and more important, it will aid in choosing the angle viewed by the analyzing counter (i.e., the angle subtended by the analyzing counter slit at the crystal sample).

## Calculated cal Sha es

Neutrons emerging from a collimator 1" wide by 72" long with non-reflecting walls would have an angular distribution function of triangular shape with a total width  $24=1.6^{\circ}$  as shown in figure 4:2. Since the angle of divergence of the collimating system is of the same order of magnitude as the critical angle for total reflection (  $a_{\circ} = 0.17^{\circ}$  for iron), the distribution function is modified as shown. For simplicity in making calculations, the



FIGURE 4.1



HORIZONTAL DISTRIBUTION OF NEUTRONS FROM COLLIMATOR



SIMPLIFIED DISTRIBUTION FUNCTION USED IN CALCULATIONS

1

resulting distribution function is approximated by a rectangular function of full width,  $2 \propto_{m} = \propto_{0} + \propto_{m}' = 0.97$ .

The monic a read of the monochromating crystal can be estimated from the rocking curve shown in figure 3:2. Using a rectangular distribution function for the collimated neutrons, Willis (1960) showed that the half width at half height of the rocking curve h is approximately equal to 1.177 where  $\eta_{f_2}$  is the standard deviation of the Gaussian distribution function describing the angular distribution of the mossic blocks in the crystal. From figure 3:2,  $2H_1 = 37^2$  so that  $\eta \approx 16^4$ .

Willis also gives expressions for the shape of the double reflection curve as a function of the angular position of the second crystal. His calculations have been extended to give the shape of the diffraction peaks from the second crystal as represented in a 20 versus  $\beta$  plot.

Reutrons reflected from the monochromator have an

angle of incidence  $\theta = \theta_B + \alpha + \Delta + \beta$  where  $\theta_B$  is the sean brack angle,  $\alpha$  is the angle between the axis of the collisator and the path of the neutron under consideration,  $\Delta$ is the orientation of the reflecting sosaic block relative to the mean orientation of the blocks, and  $\beta$  is the angle defining the mean orientation of the mosaic blocks relative to  $\theta_B$ .  $\alpha$  is limited to  $\pm \alpha_n$ , and  $\Delta$  is limited to  $\pm \eta$ . Let 28 represent a small deviation from the mean  $2\theta_B$ 

28=20+2B+X and let  $\lambda_{o}$  be the mean wavelength corresponding to  $e_{B}$  $\lambda = 2 d \sin \theta$ = 2 d sin  $(\partial_n + \Delta + \beta + \alpha)$ = 2 d sin ( $e_{a} + 8 + \alpha/2$ ) =  $\lambda_0$  + 2 d 8 cos  $\Theta_B$  + 2 d  $\frac{\alpha}{2}$  cos  $\Theta_B$ =  $\lambda_0(1 + \delta \cot \Theta_B + \alpha/2 \cot \Theta_B)$ 8 and & are assumed to be small. Using  $\delta'$ ,  $\Delta'$ ,  $\Theta_{B}'$  and  $\beta'$  for the second crystal Angle of incluence =  $e_{a}' + 2\delta' + \Delta' + \beta'$ Angle of diffraction = 200 + 28+28' . Brass angle =  $\partial_{B}' + \delta' + \delta' =$  angle of incidence  $\therefore \delta' = (\Delta + \beta) + (\Delta' + \beta') + \alpha/2$  $\beta' = \delta' - (\Delta - \beta) - \Delta' - \alpha/2$ Also  $\lambda = \lambda_0 \{ 1 + (\delta + \alpha/2) \operatorname{cot} \Theta_0 \} = 2 \operatorname{d'sin} (\Theta_0 + \delta + \delta')$ = 2 { 1 + 8 + 8' cot 0; } :  $(\delta + \alpha/2) = \delta + \delta'$  or  $\delta' = \delta (z-1) + (\alpha/2) K$ where k = cot dg /oot da Also  $\delta' = \Delta' + \beta' + \delta'$  $\beta' = \delta(k-2) - \Delta' + (\alpha/2) k$ X is limited to  $\pm (|\mathcal{N}| + |\alpha_{1/2}|)$ 8' is limited to  $\pm \{|\eta(k-1)| + |\alpha_m/2(2k-1)|\}$  $\beta'$  is limited to  $\pm \{|\eta(k-2)| + |\eta'| + |\alpha_m(k-1)|\}$ 8'-B' is limited to  $\pm \{|\eta| + |\eta'| + |\alpha_m/2|\}$ 

These relationships give calculated peak shapes as illustrated

CACULATED PEAK SHAPES



### in flgure 4:3.

### Experimental eat sha es

Several scans with different #-settings were ande through each of three intense peaks to obtain the results shown in figure 4:4. For these scans, the aperature of the analyzing counter was limited by a marrow clit, 1 as. in width.

A fit of the expression for  $\mathbf{X}' - \mathbf{\beta}'$  to the experimentally determined peak shape gives a reasonable value for the measure spread ( $\mathbf{\eta} = 11^{\circ}$ ), but this may be regarded as fortuitous since the expressions for  $\mathbf{X}'$  and  $\mathbf{\beta}'$  do not give values for  $\mathbf{\eta}$  and  $\mathbf{\alpha}_{\mathbf{m}}$  which agree with the values given earlier. The lack of constitutive agreement is not surprising since no necessarily has been taken of the exact shape of the collimated beam and of the fact that the monochromator only subtends a limited angle at the second crystal.

The minimum width required for the slit which limits the opening to the analyzing counter can be obtained directly from the experimental peak shapes. It is simply the width of the peak parallel to the 20 axis.

## dennurement of the Intensities of the Diffraction Peaks

The intensity of each diffraction peak was obtained by step scanning through each peak and the surrounding background. The contribution of the incoherently scattered neutrons to the integrated intensity of the peak was obtained from the average background count, and subtracted from the



measured intensity. All equivalent reflections vero measured to give an average value for the intensity.

Data for the (001) projection were collected out to an angle of  $2\theta = 120^{\circ}$ , a total of 160 reflections. 105 reflections out to an angle of  $2\theta = 140^{\circ}$  were measured for the (110) projection. In order to make a correction for changes in the efficiency of the instrument which occurred during the several months required to collect the data, a standard peak was measured at the beginning of each automatic run.

#### Alecantion Correction

Y

The effective absorption in a crystal is made up of the components, true absorption, and incoherent scattering. The absorption cross-sections of the atoms found in netrelite are very shall, so that the effect of true absorption can be neglected. Incoherent scattering is mainly due to the hydrogen nuclei with an incoherent scattering cross-section of 26 barns for the neutron energy used. The absorption coefficient is  $\mu_{\mu} = (6 N \rho) / M.W.$ 

where  $6 = \text{oreas-section per molecule in ev.}^2$ 

N = Avogadre's number

 $\rho$  = anaple density - 2.2 gas/sc. for natrolite

 $M_{\rm W}$  = Holocular weight of the sample material For natrolite,  $M_{\rm g} = 0.37$  cm<sup>-1</sup>. The corresponding absorption correction obtained from the International Tablec for -rayGrystallography Volume II has a maximum value of 1.5%. To correction for elegrption was applied since the average correction is small compared to the standard deviation of the data. Neglect of this correction will reduce the testerature permuters by a very such amount, but should have no effect on the positional parameters.

#### Extinction

Then a been of neutrons passes through a crystel at the proper angle for Bragg reflection to take place, there will be a continual interchange of energy between the primary and accordery beams. In a perfect crystel there will be a phase-leg of 180° between the primary and twice reflectod beam travelling in the direction of the primary beam which leads to a reduction in the amplitude of the primary beam which leads to a reduction in the amplitude of the primary beam. In a crystal made up of module blocks, the blocks near the surface of the crystal will partially shield the lower blocks oriented in the same direction, but each block centers independently. The reduction in the intensity of a beam due to scherent scattering in a perfect crystal or single module block is termed primary extinction, and the reduction in intensity due to coherent scattering in a module crystal is termed scandary extinction.

The effect of crystal chaps on rescalary estinction that been treated by Mamilton (1957), and is reviewed here for the ease of a cylindrical crystal.

If a Cartesian co-ordinate system is defined with

n parallel to the incident beam and a parallel to the diffracted beam, then

> $\partial P_{\mu} / \partial n = -(\mu + 6) P_{\mu} + 6 P_{\sigma} = \gamma P_{\mu} + 6 P_{\sigma}$  $\partial P_{\sigma} / \partial n = -(\mu + 6) P_{\sigma} + 6 P_{\mu} = \gamma P_{\sigma} + 6 P_{\mu}$

where  $P_{o}$  = power per unit area of primary beau at the point (n.m)

 $F_{\rm H}$  = power per unit area in diffracted beas at the point (m,m)

M = linear coefficient of true absorption

= ; : (Ae)

 $J = (\lambda^3 F_c^2 / V_c^2 \sin 20) \, cm^{-1}$  for equatorial reflections  $V_c = unit$  cell volume

 $\lambda$  = wavelength of neutrons

 $W(A \Theta) =$  distribution function for mosale blocks in terms of  $\Delta \Theta$ , the deviation of a mosale block from the mean Bragg angle  $\Theta$ 

F = amplitude of the diffracted beam from a unit cell of a crystal assuming an incident beam of unit intensity

Boundary Conditions:

 $P_{a} = P_{0}^{o}$  along the surface of incidence

 $F_{\rm H}$  = 0 along the surface opposite the surface of emergence of the differented beam

A secondary extinction coefficient is defined as  $E_a = R^{\Theta} / QV_A$  where  $R^{\Theta} =$  the integrated intensity obtained experimentally for the rotating-crystal method.

The differential eductions given above are difficult to solve in general, but the approximate expression  $B_s = \exp(-6.6D/3\pi)$  can be obtained for the special case  $2\theta = 0^{\circ}$  or  $180^{\circ}$  and  $\mu = 0$ . D is the diameter of the crystal. The error obtained by using this expression is less than 25 for 6D < 0.2 and less than 55 for 6D < 0.4. Humarical integration at other angles showed that the extinction coefficients of reflections at different stags angles vary by only about 35 for 6D = 0.50 (corresponding to an  $B_s$  of approximately 0.7).

### Determination of Stinction Correction

Six hk0 reflections were measured accurately using both the large crystal from which the data for the (001) projection was obtained, and a second crystal of smaller diameter which was assumed to produce no secondary extinction. This second crystal was 1 mm. in diameter by 10 mms. in length. No attempt was made to shape the small crystal so it was not a perfect cylinder.

The ratio of the intensities of the diffraction peaks measured with the two orystels is given in Table I. (These ratios were plotted versus the intensity measured using the large crystal (see Figure 4:5), and the curve  $h_s = \exp(-1.03 \times 10^{-6} \text{ I})$  was fitted to the points. The extinction correction  $1/E_s$  is plotted versus I in Figure 4.75.


h	ls.	1	28	I z 19-3*	Ratio <u>larse</u> small
626 28 60 46	4 6 0 19 14	0 0 0 0 0	24.08 42.35 25.35 27.46 36.35 27.46 36.35	20.9 38.2 57.2 02.5 117.0 135.0	$21.1 \pm 0.6$ $20.1 \pm 0.3$ $20.1 \pm 0.3$ $10.2 \pm 0.3$ $18.6 \pm 0.3$ $10.2 \pm 0.2$

Table I. Natio of the Intendities of Meflections second with a large and small crystal

\*I is the intensity measured using the large crystal

The extinction correction for the second projection who determined by comparing the intensities of the reflections which are common to the two projections. Table II gives the ratio of the corrected intensities from the (001) projection to the uncorrected intensities from the (110) projection. No systematic variation of these ratios with intensity can be observed, so it was concluded that there was a negligible smount of extinction with the second crystal.

The method of obtaining an extinction correction described above can not be regarded as totally satisfactory since it is based on the assumption that there is no extinction with the small crystal. This assumption could be tested by comparing corresponding peaks from several different sizes of orystal, but this would be very time consuming. In future, it is hoped that extinction corrections can be determined more satisfactorily by varying the path length of the neutrons in the crystal under study using a three circle geniometer (Willic, 1961).

h	le	1	T = 1.0 <sup>-3</sup> #	Batio	
2	2	0	99	3.02	
4	L.	0	19	1.89	
5	6	0	58	1.81	
3	8	Ĵ	36	1.83	
10	1.0	0	117	1.85	
12	12	0	6	1.64	
16	16	0	70	1.87	

Table II. Actio of the Intensities of the Reflections which are common to the (001) and (110) projections

. .

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\* I is the corrected intensity measured with the large crystal used for the (001) projection

This is the ratio of the corrected intensities from the (001) projection to the uncorrected intensities from the (110) projection.

### Chapter /

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Analysis of the Structure

Assuming that the intensity of the incident been is unity, the structure factor or amplitude of the diffracted beam from a unit cell of a crystal is given by the expression

 $P(hkl) = \xi T_r b_r \exp 2 \pi i (hx_r + ty_r + lz_r)$  (1) where hkl = the Miller indices of the reflecting plane

b. = the southering length of the r th atom

x, y, s, = the positional parameters of the r th atom expressed as fractions of the corresponding cell dimensions

> ", = a factor introduced by the thermal solion of the atols

If the action of the atoms is isotropia

 $T_r = \exp\left(-E_r \sin^2\theta/\lambda^2\right)$ 

where B, is the temperature factor of the r th atom  $B_r = 8 \pi u_r^2$  where  $u_r^2$  is the mean scuare displacement of the r th atom in the direction of the scattered vector (see for example, James 1948, Gh.5). The density of the scattering material at a point (X, X, X) within a unit cell may be expressed in terms of the structure factors as follows:

 $\rho(XYZ) = \frac{1}{V_c} \leq \leq \leq F(hkL) \exp\left[-2 \pi I (hk+kY+LZ)\right]$  (2) where V<sub>c</sub> is the volume of the unit cell. Thus if the structure factors are known, one can solve the crystal structure through the use of the above equation.

However, in a diffraction experiment, one measures the integrated intensity of the reflections rather than the structure factors. For the case where the crystal is rotated through a reflecting position, the integrated intensity or number of neutrons scattered in the Bragg reflection is related to the structure factors by

 $M^{2} = (I_{0}\lambda^{3} \sqrt{2}V |F|^{2}) / \omega \sin 2\theta$ where  $I_{0} =$  the incident intensity (3)

. W = number of unit cells per unit volume

 $\omega$  = the angular velocity of rotation

V = volume of specimen

Extinction and absorption effects have been neglected. Since the structure factor enters the expression for the integrated intensity as the square of its aggitude, one can determine its magnitude out not its phase. This is the essential problem in solving a crystal structure.

It is usually more convenient to work in two dimensions then in three during the initial stages of a structure analycls. For the (001) projection, ecuations 1 and 2 can be written

$$\mathbb{P}(\mathbf{h};\mathbf{0}) = \xi \mathbb{T}_{\mathbf{r}} \mathbb{P}_{\mathbf{r}} \exp (2\pi \mathbf{i} \langle \mathbf{h} | \mathbf{r}_{\mathbf{r}} + \mathbf{K} \mathbf{y}_{\mathbf{r}} \rangle$$
(4)

$$\rho(XY) = \frac{1}{A} \leqslant \leqslant F(ik0) \exp 2\Pi I(iA + KI)$$
(5)

where A is the area of the unit cell in projection. If the projection has a centre of symmetry, the above expressions can be further simplified to

$$P(hk0) = \xi T_{r} b_{r} \cos 2\pi (hx_{r} + ky_{r})$$
 (6)

 $\rho(AL) = \frac{1}{A} \underset{k}{\leq} \underset{k}{\leq} P(hk0) \cos 2\pi (hk + KL)$ (7)

The structure factors in this case have no imaginary part and the problem of determining their phases is reduced to the problem of determining their signs (+ or -).

### The difference synthesis

If the physes of the structure factors were morn, it tould be possible to obtain a projection of the crystal structure using constion 5 with the observed structure factors Po, and hence to obtain the positional parameters of the atoms diroctly. In practice, the usefulness of this method is limited by the false detail arising from diffraction rings which appear around individual atoms when only a finite number of terms is taken in the Fourier series. This effect is analogous to the one observed when an object is viewed through a alcroscope with a finite aperature. The image of a point course will appear as a spot of finite width surrounded by a number of diffraction rings of decreasing intensity and amolitudes which are alternately negative and positive. This filse detail can be reauced through the use of the difference synthesis. Suppose we replace F (hts) is equation 5 with the aliferenois 2 (1kc) between the observed structure factors and calculated structure factors based on a model of the crystal structure. Is the model does not contain all of the atoms in the structure, then the resulting synthesis of  $\rho(xy)$ 

will show only those store which were not included. Dince both a number of store and their associated diffraction rings do not ap ear in the projection, the remaining store are better resolved and lose distorted than they would be in a couplete Fourier synthesis. Afterence syntheses are particularily useful for locating store with low scattering power, or for removing the distortion due to overlap of atoms in projection.

The difference synthesis also provides a sensitive setted for refining the positional and thersal parameters of the atoms. If our model contains all of the atoms, then the difference synthesis represents the difference in centuring density between the true structure and our model, and changes can be made in the parameters to reduce this residual sectoring density.

### Lealing and Tearrature Frators

No effort was ande to obtain the absolute values of the integrated intensities of the diffraction peaks, so that only the relative magnitudes of the structure factors were known from the experimental data. These observed structure factors were scaled to the calculated structure factors for the difference syntheses by sultiplying  $P_0$  by X, where  $X = \xi |F_0|/\xi |F_0|$ . If the average inductor factor 2 is incorrect, or has initially been taken equal to zoro, then the above method of scaling will only give goes agreement between the structure factors for medium angle perfections. The ratio

of  $F_0$  to  $F_c$  will either increase or decrease systematically with  $\theta$ , depending on whether B is high or low. Since the effect of thermal motion on the structure factors is given by  $T_r = \exp(-B_r \sin^2\theta/\chi^2)$ , the correction to be applied to B can be obtained from

K  $|F_0| = |F_0| \exp(-\Delta B \sin^2\theta/\lambda^2)$ or  $|n(K |F_0|/|F_0|) = -\Delta B \sin^2\theta/\lambda^2$ If  $|h(K|F_0|/|F_c|)$  is plotted against  $\sin^2\theta/\lambda^2$ , the slope of the graph will give the required correction to B. Individual temperature factors  $B_r$  can be determined from the residue left in the difference synthesis about the point where the r th atom is located. This residue is compared with the differences between calculated peak shapes obtained using the appropriate scattering length and different values of the temperature factor.

#### Least Squares Refinement

The difference synthesis is a good heuristic technique of refinement since the effect of parameter changes can be followed closely, but the method is cumbersome in three dimensions and takes no account of the differing accuracies of the observed structure factors. If the  $F_0$ 's are normally distributed about their true values, then the best atomic parameters are those which minimize  $R' = \underset{k \in I}{\leq} W(hkl) (F_0 - F_c)^2 \underset{k \in I}{\leq} W\Delta^2$ where the weight w is inversely proportional to the square of the probable error of the corresponding  $F_0$ . Let  $u_1$ ,  $u_2$ ,  $--u_n$ 

be the n parameters occuring in F, whose values are to be determined. When H' is a minimum  $\partial R'/\partial u_j = O(j=1, 2, -n)$ . The parameters must be chosen to satisfy these n conditions. Suppose we start with a set of trial parameters close to the correct set but differing from them by the amounts  $\epsilon_j$ . We can define  $\Delta(u_j + \epsilon_j) = F_c (u_j + \epsilon_j) - F_c (u_j)$  $= \frac{1}{2} \frac{\partial F_c}{\partial u_j} \epsilon_j$ where  $\partial F_c / \partial u_j = \partial F_c (u_j + \epsilon_j) / \partial u_j \approx \partial F_c (u_j) / \partial u_j$ Therefore  $R^1 = \sum_{k=1}^{n} w \{\Delta u_j - \Delta (u_j + \epsilon_j)\}^2$ and  $\frac{\partial R'}{\partial u_j} = 0 = 2 \sum_{k=1}^{n} w \{\Delta (u_j) - \Delta (u_j + \epsilon_j)\}^2$ or  $\sum_{k=1}^{n} w (hki) \{\Delta - \frac{1}{2} \frac{\partial F_c}{\partial u_j} \epsilon_j\}^{\frac{1}{2}} \delta F_c / \partial u_i = 0$ 

From these n simultaneous equations, the values of gen be calculated. Since n is often of the order of 100, a large digital computer is needed to solve the equations.

### Refinement of (001) Projection of Natrolite

The (001) projection of natrolite has a centre of symmetry and belongs to the plane group pgg. In this projection, a! = a/2 and b! = b/2, and application of the symmetry operators reduces the structure factors to the form

 $A = 4 \cos 2\pi h \times \cos 2\pi h y$  B=0 h + h = 2h

 $A = -4 \sin 2\pi h x \sin 2\pi k y = 3 = 0$  h + k = 2n + 1where  $A' = \xi T_{+} b_{+}A$  and  $B' = \xi T_{+} b_{+}B$  are the real and imaginary components of the structure factors. Also the Fourier transforms of the structure factors becomes

 $\rho (XY) = \frac{1}{A_{c}} \left[ F(00) + 2 \left\{ \sum_{h=1}^{h=2n} \mathbb{P}(h0) \cos 2\pi hX + \sum_{k=2n}^{k=2n} \mathbb{P}(0K) \cos 2\pi kY \right\} \\
+ 4 \sum_{h=2k}^{n} F(hK) \cos 2\pi hX \cos 2\pi kY - 4 \sum_{k=2k}^{n} F(hK) \sin 2\pi hX \sin 2\pi kY \right]$ 

Structure factors and  $\rho(XYO)$  were calculated using the Bendix G15D computer.

Refinement of the projection was conducted in the manner described previously. Figure 5:1 shows the initial difference synthesis with the two hydrogen atoms clearly shown by two large negative peaks. The reliability index given by  $R = \frac{\leq |F_0 - F_1|}{\leq |F_0|} = 26.0\%$  at this stage. Beflections whose intensities were not significantly greater than the background intensity were neglected. In Table 1 are listed the parameters used in this and subsequent syntheses. For second synthesis, a hydrogen atom was placed in the model structure at the vosition indicated by the larger negative peak(see Figure 5:2). Since the temperature factor chosen for this atom was too low. a positive peak remained when the hydrogen abon was subtracted out. Adjustments to other temperature factors were made as indicated in Table 1. The second hydrogen atom was included in the model used to obtain the third synthesis shown in Figure 5:3. Further adjustment of the inalviquel and overall temperature factors gave the final difference synthesis shown in Figure 5:4. The reliability index at this stage in the refinement was 8.2 . The signs associated with the calculated structure factors were applied to the observed structure factors to obtain the Fourier synthesis shown in Figure 5:5. A difference synthesis chowing only the hydrogen atoms is given in Figure 5:6.

# Table 1. caralleters from refinement of (001) projection . outtional reprineters

All Difference Syntheses Least Squares

-		See pelangelik to be a second see a free as a free see and	J.	11	
Ĩ	2 <sup>3</sup> 21	0 0	0 0	C O	
31 <b>I</b>	¥2 ¥2	• 306 • 422	• 3076 • 4211	· 3076 · 4211	
A1.	X 3 3	.075 .187	.0748 .1374	.0746	
r	×11 V 14	.045 .137	.0460 .1364	.0461 .1364	
с¤ ,	135	• 1.41 • 365	• 3640	.1405	
СШ.	×6 V6	.197 .069	.1962 .9697	.1962 .0697	
° IV	37	•413 • 305	•4131 •3057	•4131 •3058	
0 X	×9 ¥8	• 360 • <sup>1</sup> 454	• 360 3 • 4 5 4 9	• 360 3 • 4550	
C VI	Xo Xo	.113	•1126 •3774	.1126 •3776	
No.	A <sup>70</sup>	.442 .061	.4446	.4447 .0611	
11	×11 y11	.103 <sup>*</sup> .286	.1020 .2902	.1023 .2905	
H2	¥12 ¥12	• 200 <sup>†</sup> • 370	• 2029 • 3753	• 20 33 • 3768	~
100.001010.004	A REAL PROPERTY AND A REAL PROPERTY.	and wat open printing a place and sub-th and sub-the sub-	the set of	10 11 10 10 10 10 10 10 10 10 10 10 10 1	

#  $n_1$  the not included until the third difference synthesis  $T = H_2$  the not included until the second difference synthesis

	Lifferenc	e synthesis		least bu	uares
Figure 5:1 R = 26.0%	Figure 5:2 R= 23.7%	Figure 5:3 R= 15.1%	rigure 5:4 5= 8.2%	1 E=7.7%	LI R=7.6%
 1.0	1.0	1.0 0.9	0.9	0.48 0.64	0.51
1.0	1.1	3.0	0.8	0.75	0.60 1.40
1.3	1.3	1.2	0.8	0.43	0.42
1.3	1.2	1.2	0.9	0.76	0.74
1.3	1.3	1.3	1.3	1.72	1.76
· • ·		1.5	3.0	3.11	3.00

Table 1 (continued)

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lefinement of the (001) rejection (continuea)

ligure 5:3. All stous inclused in model structure.

Figure 5:4. Final alfforence synthesis.





and the second

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### Figure 5:5

Fourier Synthesis of (001) Projection

(contours are double the interval of those in the previous

figures)



Liguro 5:6

(051) irejection of ag and hg

• \

(contours at same interval as in Figure 5:5)



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end as belgeved asy soliterian To noiree(one (011) and sancture milb fitte lies line claimenes a Te noiree(ore (010)

This projection has plane group symmetry can. The new coordinates N<sub>2</sub>K can be determined from the old coordinates z<sub>2</sub>V, z using the

1(000) Enternovarie shots red  $X = X = \cos x = \sqrt{2}$   $X = X = \cos x = \sqrt{2}$ 

For atoms surrounding ( ....):

X\_a' = a'/2 + xa cosa - ybsina

 $Z = Z + \frac{1}{4}$ 

General positions:

# $x y z \rightarrow X_{+} Z \qquad 4 - x, 4 + y, 4 + z \rightarrow 2 - X_{-}, 4 + z$ $\overline{x}\overline{y}\overline{z} \rightarrow \overline{X}_{+} Z \qquad 4 + x, 4 - y, 4 + z \rightarrow 2 + X_{-}, 4 + z$

Note that each atom appears twice in this projection.

Application of the symmetry operators in this projection reduces the structure factors to the form

P.	5	4	808	2 Th	X	006	2712	7	h + l = 2m
В	=	4	000	$2\pi h$	X	əin	2T1Z	5	1 + 4 - 2.1
Δ	=	-	= 0						h + l = 2n + 1

and the Fourier transform of the structure factors becomes  $\rho(XZ) = \frac{1}{A_c} \left[ F(00) + 2\{\tilde{\xi}^{h} | F(n0) | \cos 2\pi h_X + \tilde{\xi}^{g} | A(01) \cos 2\pi l_Z + B(01) \sin 2\pi l_Z) \right] \\
+ 4 \tilde{\xi}^{h} \tilde{\xi}^{g} (A(hl) \cos 2\pi h_X^{g} \cos 2\pi l_Z + B(hl) \cos 2\pi l_X \sin 2\pi l_Z) \right]$ 

Programs were written for the Bendix 015D computer to calculate both of these series as well as to calculate the quantities:  $F_c = \sqrt{A'^2 + B'^2}$ ,  $A_o = A_c \frac{F_o}{F_c}$ ,  $B_o = B_c \frac{F_o}{F_c}$ ,  $F_o - F_c$ ,  $A_o - A_c$ ,  $B_o - B_c$ 

The atomic coordinates in the monoclinic cell were calculated from Meier's X-ray results for all the atoms except the hydrogens, and are listed in Table 2, along with the parameters for other sycles. These calculated parameters along with the temperature factors obtained from the final difference synthesis for the (110) projection were used as the input for the first difference synthesis. The positions of the hydrogen atoms are not well defined in this projection as can be seen from Figure 5:7. For the second synthesis, the 3 coordinates of the hydrogens were calculated from the results of the other projection and the 2 coordinates were average values taken from the two pair of hydrogen atoms. Hydrogen atoms one and three, and two and four should be separated by c/4. Refinement of the temperature factors was carried out in two further syntheses, the last of which is shown in Figure 5:8. The final reliability index was 9.0%, not including reflections for which  $F_0 \approx 0$ .

An attempt to complete the refinement of the parameters using the least-squares program was unsuccessful owing to the large amount of overlap between the atoms.

### Three Dimensional Analysis

As the final stage in the analysis, the data for the two projections was combined and a three dimensional leastsquares refinement was carried out. x and y coordinates from the least-squares refinement of the (001) projection and z coordinates from the (110) projection were used as the input for the first cycle of refinement in three dimension. The second cycle of refinement reduced H to 7.7, and produced no oignificant changes in the parameters. The final parameters and their standard deviations calculated from the least-squares totals are listed in Table 3 along with the final parameters obtained by Meier. These parameters were used to calculate

-	-	8	0	and the second s			in the second
81,	z1 z1	0 0	0 0	0 m	211 211	.1332 .4997	•1.343 •4967
51 1	×2 22	•5 •25	• 50 • 25	() <sub>III</sub> t	×12 =12	.0640 .2497	. 0653 .2467
11 11	N C C	.0530 .3681	.0504 •3720	0 IA	×13	.0537	.0601 .4719
31 <sub>11</sub> 1	2/1	.1356 .1181	.1356 .1220	0,141	ж <u>14</u> 214	.1411 .2166	1393 2219
<u>A1</u>	25	.0560 •3619	.0547 .3620	0 <b>v</b>	215	.4071 • 3660	.4072 .3828
AL I	26	• 3638 • 1219	• 3693 • 1120	0 <sub>4</sub> 1	716 16	.0473 .1360	.0398 .1328
0	x7 z7	.4090 •3594	.4095 • 3595	0 <mark>vi</mark>	×17 z17	·2457 •1085	·2433 1045
01 +	z8 z8	•4544 •2094	.4563 .1095	0 <sub>v1</sub> '	×1.5 218	• 3671 • 3585	• 3711 • 3545
0 <mark>1</mark> 1	Z <sub>2</sub>	.1120	.1073 • 3454	in	219 219	.1903 .3620	1951 3658
0 <sub>Ш</sub> т	210 210 210	.2472 .1011	•2505 •095時	Sa I	×20 *20	.2487	.2437 .1158

Table 2. Lar deters from refinement of (110) projection

a - Farameters calculated from x-ray results (Meler, 1960) b - Farameters calculated from final neutron results Table 2 (continued)

Comparison of hydrogen atom coordinates obtained from difference synthesis #1, and from final three dimensional least-squares refinement.

		Difference	Synthesis	Lengt Lourves	
II,	X 21 Z 21	.1945 .0433		.1940 .0282	
Hn	Z 21 Z 21	.2850 .1700		•2881 •17 <sup>2</sup> 0	
8 m	X 23 Z 23	.4065 .2933		.4304 .2782	
H IN	X 14 Z 14	.4150 .4200		•4 <u>181</u> • <sup>1</sup> 22120	

Table 2 (continued) Thermal parameters 3 (in  $2^{2}$ )

	D. S. # 1	D. 3. / 2	5. 3. 7 3	D. D. # 4	Final 3-0. L.S.
31,	0.9		0.8 0.8	1.0 0.9	0.47
51 <sub>11</sub>	0.7		0.5	0.7 0.5	0.59
A1.	0.8		0.5	0.7	0 <b>. 50</b>
01	1.4		1.0 0.9	1.0 0.7	1.07
0.	0.8		0.6	0.6	0.30
0	0.9		0.9 0.9	1.2 1.1	0.90
0.14	0.9		0.7	1.0 0.8	0.89
0,	1.1		1.2	1.2 1.2	1.08
0.41	2.0		2.3 2.3	2 3 2 3	1.78
Na	1.1		1.2 0.8	1.5 0.8	1.12
1.1		3:2	2.7	2.9	2.83
1.2		3.2	2.5	2.7	
Н3		2.8	1.9	1.8	3.73
1. L4		2.8	2.3	2.3	

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F1 juro 5:7

Difference Jynthesia (1

2%.

(110) Trojection

Contours represent relative neutron scottering density only.



### Migune 5:8

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bifference Synthesis 22

### (110) irojection

(rentours are at the same interval as in Figure 5:7)





The second secon

150

## Figure 5:9 Fourier Synthesis (110) Irojection

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(contours are at ten times the interval of Figure 5:6)





final  $P_0$ 's which are listed in Table 4 along with the observed structure factors. Theses from the final structure factors were applied to the observed structure factors for the (110)projection to obtain the Fourier projections shown in Figure 5:9. The final Fourier projection for the (001) projection will be almost identical with the projection shown in Figure 5:5 since only two structure factors of small magnitude have final signs which are different from those used to calculate  $\rho(XX)$  for the projection.

# Table 3. Final . arqueters

I

Atoa	Final at (with of	ioule com Iondard de	olnates viations	) val- ueg in 2	Gorresp given by	onding son Nieier (1	ordinates 1960)	B Val- uese in 22
-		7	2		Z	- in-	7	
$1_{1}$	)	0	)	0.47	0	Ō	G	1.07
Di.	0.1542 (0.0004)	0.2111 (0.0003)	0.6220 (0.0025)	0.59	0.1532	0.2112	0.6181 (0.0010)	1.00
43	0.0373 (0.6004)	0_ <u>094</u> 4; (0_0004)	0.6120 (0.0024)	0.50	0.0376 (0.0002)	0.0936 (0.0002)	0.6119 (0.0011)	1.12
C.	0.0230 (0.0003)	0.0633 (0.0003)	0.3595 (0.0024)	1.07	0.0227	0.0683 (0.0004)	0.8594 (0.0024)	1.61
e <sub>n</sub>	(0.0703) (0.0003)	0.1821 (0.)002)	0.5954 (0.0023)	0.30	0.0704 (0.0004)	0.1824 (0.0003)	0.6011 (0.0023)	1.10
0m	0.0980 (0.0003)	0.0351 (0.0002)	0.4967 (0.0023)	0.90	0.0986 (0.0004)	0.0346 (0.0004)	0.4997 (0.0020)	1.55
0 <sub>IV</sub>	0.2066 (0.0003)	0.1530 (0.0003)	0.7219 (0.0023)	0.89	0 <b>.2063</b> (0.0002)	0.1526 (0.0004)	0.7166 (0.0022)	1.24
0.	0.1804 (0.0003)	0-2275 (0-0003)	0.0828 (0.0022)	1.08	0.1799 (0.0002)	0.2272 (0.0004)	0.3860 (0.0920)	1.83
011	0.0562 (0.0004)	0 1894 (0 0004)	0.1045 (0.0025)	1.78	0.0564 (0.0005)	0.1893 (0.0004)	0.1085 (0.0058)	2.50
Ur,	0.2216 (0.0004)	0.0311 (0.0004)	0.6250 (0.0037)	1.12	0.2208 (0.0003)	0.0305	0.6120 (0.0016)	2.00
H	0.0513	0.1443 (0.0006)	0.0282 (0.0032)	2.83				
$\mathbb{B}_2$	0.1012 (0.0007)	0.1383 (0.0008)	0.1740 (0.0041)	3•73				

189 STUL 0 9 91 SUAL DUAL 0 1 0	720005000000000000000000000000000000000	20255255255900125552509920022555559555952220525402742227 71719253255555555555250922023555555552502124228 71119253255555555555555555555555555555555			9420894209942942942099730694242089420894208942099420994209111111111110094208111111110000000000000000000000000000	SCSMASSSSSSSSTSCONTERSSCONTS POLOTETLASSLS MODUMON STADUGLESSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSS	0920559095504255009925290T0T0955228265582082529725 5582202092655299959595520995264554099222555585955 5682202092655255555555555555555555555555555		うろろうゆうり 0000222222222222222222200000000000000	42089428942089420894248094248099420894208
HON CHEER ON NEW CHEER CHEER	TELL 400	1085 1085	0	9	91 97	66.02 90/3	STOR	0	9 47	0 0
0 0 0	769	0	U	2	y 1.	9944 L 0	0	C	77	C
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13016	14	(continu	ind)				
12 K	1	Fo	Po	h	15	1	Po
2 14 14 14 14 14 14 14 14 14 14 14 14 14 1	000000000000000000000000000000000000000	$\begin{array}{c} 1089\\ 1775\\ 7650\\ 1598\\ 109550\\ 15985\\ 109550\\ 109550\\ 1094768\\ 29476879\\ 10957692\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 1095022\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 109502\\ 1095$	1074 1074 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072 1072	680246824680246813579135791246802468 121624682468246813579135791246802468 121682	22222222222222222222222222222222222222		$\begin{array}{c} 5444135242403839662307541123347474743615349063396623075411233477593490633966230754111111117775934906339663396623075541112334774744361534906633966336153490663366636663666366663666636666666666$
4 22	0	135	24	22	22	2	426

re

# Table 4 (continued)

h	is.	1	Fo	Fo
105701057010246802468013570105702468024681357 111120246802468013570105792468024681357	135791357920246802468013579135792468024681257	333333333333334444444444444455555555555	10203168917645403606233995278738213674144900030707 1032699724539988262888285278738213674144900030707 1032699729988262888285278738213674144900030707	1236748212071891115817555081015448859996144289967 1017592431071891224891755508101544884859996144289967 12877777777777777559081015944884859996144289967

h	k	1.	P'o	<sup>ju</sup> o
91 13 15 7 0 2 4 6 8	1135702468	7777888888	722 1173 774 787 956 4955 1026 586 1281 839	697 1059 764 802 860 5094 1056 600 1304 871
10 12 14 1 3579	10 12 14 1 579	888999999	1460 470 239 519 274 790 1569	1441 534 690 1038 471 314 770 1513
11 13 24 6 8 10 1	11 13 24 6 8 10 1	99 10 10 10 10 10	1377 950 1110 635 546 1553 1129 470	1304 922 1127 793 1586 966 386
3	3	11	456	606

#### Chapter VI

Discussion of Negults

### Accuracy

The appreciant between the observed and calculated structure factors listed in Table 4 is cenerally cuite roof. The average value of | Fo - Mal is three times the estimated stundard deviation of Po based on counting statistics alone. but this is to be expected in view of certain experimental errors, and the difficulty in obtaining accurate permetions for extinction and background effects. One of the everysentel errors is due to the  $\lambda/2$  convenent of the neutron beam. This component is known to be less than 9.4% of the component, but if a stron; reflection due to the  $\lambda/2$  component is superisposed on a real reflection due to the Acomponent, a large error will result. The deficiency in the method used to correct for extinction has been discussed earlier. In the once of the breisground, the difficulty in obtaining recurste corrections crises because it is not known bor the inelastic scattering make up under the Frage reflection due to its coherent ac monent.

The final atomic coordinates obtained using X-rays and neutrons are conversed in Table 3. Only three of the positional parameters differ by more than twice the larger of the two outlineted standard deviations. These differences

may be significant but they do not alter the details of the orystal structure as discussed by Joier (1960).

All of the temperature factors obtained using neutrons are much lower than the corresponding values obtained using  $\lambda$ -rays. Since fils techniques were used with N-rays, and counter techniques were used with neutrons, a systematic difference in the values of  $\Xi_{\mathbf{r}}$  obtained might be expected. The ratio of the T.'s determined from the two sets of temperature factors for an intermediate value of 6 is constant enough to confirm the fact that the difference is mainly systematic.

The average temperature factor is also lover than the average values quoted for similar structures determined using neutron diffraction and counting techniques. This difference can likely be attributed to the difficulty in obtaining necurate corrections for background and extinction effects as discussed earlier.

## Liscussion of the Structure

The neutron diffraction results confirm the details of the eluminosilicate framework as given by Heler. The average interatoxic distances of 1.62 Å for the 51 - 6 bond and 1.75 Å for the Al - 6 bond remain unchanged.

From a consideration of both the interatomic distance between the water molecule and the surrounding oxygen atoms in the framework, and the electrostatic charge distribution, deler suggested that the water molecule is linked to  $C_1$  and  $O_V$ 

by hydrogen bonds. The location of the hydrogen stond indicated in Pigure 5:6 shows that this suggestion was correct. Table 5 lists the bond lengths and angles associated with the water molecule, and Figure 6:1 illustrates the configuration of the molecule. The oxygens are linked by bent hydrogen bonds, with the hydrogens lying almost in the 0-0-0 plane.

		Dond 1	en_the	
0 vi -	0,	2.84 ± 0.03 5 2.86 ± 0.04 5 2.84	Cvi - Cv	$3.01 \pm 0.03 \overset{\text{a}}{\text{b}}$ 2.99 $\pm 0.04 \overset{\text{b}}{\text{b}}$ 2.96
0 vi -	- 11-	0.98 ± 0.02	0v1 - 12	0.94 ± 0.03
h.	- G <sub>1</sub>	1.87 ± 0.02	H2 - 0.	2.13 = 0.03
		H <sub>1</sub> - H <sub>2</sub> -	1.56 = 0.03	
		Bond /	ingles	
		$O_1 = O_{VI} = O_V$	1.24.2 0 B	
		$\mathbf{H}_1 = \mathbf{O}_{\mathbf{V}1} = \mathbf{H}_2$	107.9 0	
		0, - H <sub>1</sub> - Ovi	168.90	
		Dy -lla - Dy	1.54.20	

Table 5. Dond Longths and Logles for the Later Molecule in

e - 1 showled of al (1961)

Several neutron diffraction studies of hydrated compounds have emphasized the constancy of shape of the unter molecule. The hydrogen bonds are bent in order to delatain a tetrahedral angle of about  $109^{\circ}$  for the H -  $\circ$  - H angle.



Figure 6:1. Hydrogen bonds in natrolite.

Table 6 summarizes the available information about bond angles in hydrates by comparing the H = 0 = H angle in the water molecule with the environmental angle 0 = 0 = 0 which the neighbouring oxygen atoms subtend at the centre of the water molecule.  $GuSO_4.5H_2O$  is the only drystal studied which has 0 = 0 = 0 angles which are significantly greater than the tetrahedral angle. The results of Eacon and Curry for this crystal show that the water molecule resists attempts to open out the H = 0 = H angle as effectively as it resists closing-up. In natrolite, the 0 = 0 = 0 angle is even greater than the similar angles in copper sulphate, so that the almost tetrahedral angle obtained for the water molecule is a more pronounced example of the way in which the molecule maintains its favoured shape in spite of an environment which attempts to open out the H = 0 = H angle.

## Sacle 6. Lond Angles in Hydrates

ناد.	DE	5:13	200

Angle

12 - 13 - 14	0-0-0
109.1° 109.9°	109.50
107 °	114°
103° 107°	01, ° 102 °
106°	á. e
108°	97°(r-01)
1.56	108°
111° 105° 109°	121° 122° 130°
108	134°
	<u>H - 0 - H</u> <u>199.1°</u> 109.9° 107° 107° 106° 108° 108° 101° 105° 109° 108°

A comparison of the available 0 - H and 0 - H = -0 bond lengths indicates that there is a close relationship between them. As the 0 - H = -0 distance decreases, the 0 - H distance increases. For large 0 - H = -0 distances, the hydrogen atom remains intimately connected with the water molecule, but as this distance is decreased, the hydrogen atom is shared by the two oxygens. Atoji and Hundle, (1958) have compared the two coud lengths for several orystals.

The hydrogen bounds in natrolite are of the long kind. Therefore, we expect the O = E distances to be short, and this is indeed the case. The lengths of 0.94 Å and 0.98 Å are not significantly different from the value found for free water molecules in steam.

## COMMENT.Y.

- The details of the clusinosiliente fraction in natrolite as detorsined from the neutron diffraction data agree with those previously determined from X-ray unit.
- 2. The hydrogen bonds link the enter solecule to  $\mathcal{O}_{\mathbf{r}}$  and  $\mathcal{O}_{\mathbf{v}}$  .
- The vector indicate restate attenpts of the large environmental angle 0 - 0 - 0 to open the 2 - 0 - 1 engle.
- 4. The C-H distances in the water molecule are short in keeping with the long C H --- C distances.

Amendix A - Hodifications to Dectrogoniometer

The diffractometer is a standard General Electric Dru X-ray spectrogenionseter modified so that it can sean in steps as well as continuously. The direct drive of the standard instrument was replaced by a slip clutch, and the motion of the driven side of the clutch is controlled by a solenoid activated locking pin. The driven side of the clutch can be locked in position at the end of every revolution (one revolution corresponde to a counter movement of 1 minute of are) so that the vidth of each step in a scan can be controlled by varying the length of time that the solenoid is operating. This operating time is controlled by the esthode coupled monostable multivibrator shown in Figure A:1, which allows the instrument to scan in steps of 1 to 6 minutes of are when a 100 r.p.m. drive motor is used. Anneally F - Description of Grystal Crienter

The crystal orienter is a copy of the one designed by Levy and peterson at the Cak Aidge National Laboratory (see darrett, 1954). It is made up of seventeen stacked rings forming a drum. A drive motor located at the base of the orienter, operates through a slip slutch and turns the drum about its gris. Then one of the lug: connected to each ring makes contact with a steel finger, the drum is held in place. The finger can be lined up with each ring in turn by notivating a solenoid connected to the finger. In this way, the drum



# STEP SCAN CONTROL CIRCUIT



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and the crystal mounted on it can be oriented submatically in seventeen predetormined positions. The drum can also be oriented manually using a worm gear located at the base of the arum.

Algendin C - Bra Counter Type Br29

The  $BT_3$  counter, supplied by the commercial products division of Atomic Energy of Canada Ltd., is a cylinder 13 inchee in length by 1 inch in diameter filled to 60 cm. of  $T_3$ . pressure with  $BF_3$  enriched to over 90, in  $B^{10}$  (see Fouler and funnichiffe, 1950). The active length of the cylinder is 6 inches, and this gives a consitivity of approximately 50, for axially directed neutrons. Figure 3:6 shows the pulse distribution curve for  $BF_3$  counter 71. Stray neutrons are prevented from entering the side of the counter by a 2 inch thick shield of boron carbide in paraffin.

The esthede follower shown in Figure C:) is attached directly to the back of the  $F_3$  counter and souples the counter to the applifying circuits.

Anomain ) - Flusion Counter Type 200 - 2/00 110

The fitcion counter, also say lied by the conserval products division of Atomia Energy of Canada Etd., is a planeparallel-plate type (see Scienzie, 1959). Each plate of the counter is control with a 1.5" diameter circle of uranium enricheu in  $0^{235}$  to give an officiency of 0.13. For the detection of thermal neutrons. The pulse distribution surve for this counter





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is shown in Figure 3:7.

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