AN ELECTRON DIFFRACTION STUDY OF KAOLINITE

by

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Fig. 2. Nickel Oxide

INTRODUCTION

The decomposition of kaolinite has previously been studied utilizing X-ray diffraction means (2, 4, 8). In the latest X-ray study the structure of the unground kaolinite was satisfied by a triclinic cell consisting of one layer per unit cell with cell dimensions as follows:

a = 5.14 A.	α = 91.8°
b = 8.93 A.	β = 104.5°
c = 7.37 A.	γ = 90.0°

The first studies of kaolinite made by Gruner (4) showed it to be monoclinic with two structural layers per unit cell, and each layer being constructed of a sheet of SiO_4 tetrahedra on which rests a sheet of $Al(OH)_6$ octahedra. The chemical formula of kaolinite is $Al_2Si_2 \cdot O_5(OH)_4$ or in terms of its oxides $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. The slight change in the proposed structure between the monoclinic and triclinic model was necessary to account for the new lines observed using higher resolving cameras (2).

Upon placing this kaolinite in a ball mill and grinding it for a period of twenty-five weeks, the kaolin was seen to undergo a change in structure (13). This could best be explained by postulating that the kaolinite destroyed its structure completely and that the resulting amorphous silica, the alumina groups, and the free bases recombined into some material presumably similar to a permutite, which is relatively stable. This assumption was checked by various authors (2, 4,

9) by treating with 0.5N NaOH. Other samples were treated with 0.5N NaOH and were washed with 0.1N HCl. This treatment in effect would dissolve any free silica or alumina that might have been released by grinding. "Permutite" means an apparently amorphous sodium-alumina-silicate with a high base exchange capacity, without reference to any definite silica-alumina ratio (9).

Kaolinite that was ground for four and ten weeks was each found to change the X-ray patterns from triclinic to a pseudo-monoclinic type of structure (8). This was caused by the dry grinding which fractured the kaolinite plates across their faces and thereby gave various degrees of disorders. One disorder was that the SiO_4 tetrahedra sheet could rest on the $Al(OH)_6$ octahedra sheet in three different ways. The result of this disorder added vectorially to give a zero resultant and a pseudo-monoclinic symmetry. The lines appearing on a powder pattern of this type of sample could be assigned indices based on a monoclinic cell. In addition to these random features within the kaolin layers, the layers themselves may be displaced with respect to each other by integral multiples of b/3 (2, 6, 8). This, in effect, would cause all lines with k indices different than 3 to be reduced in intensity or to vanish completely (1).

The first electron diffraction study of kaolinite was carried on by Hendricks (6) in which he obtained results similar to Gruner (4). These results considered kaolinite to have

monoclinic symmetry, and were later shown to be in error because of the lack of resolution in the X-ray and electron diffraction cameras.

Pinsker, Lapidus, and Tatarinova (14) of U.S.S.R. have made a similar study of kaolinite utilizing the fact that the thin crystals of kaolinite, when placed in an aqueous solution, settled onto a flat surface with their a and b axis parallel to this surface. This would allow both transmission and oblique textured pictures to be taken. Their results were completely alien to all previous studies. Neither the previously proposed monoclinic nor triclinic models of kaolinite satisfied their empirical results.

It is the purpose of this study to attempt to duplicate the work of these men by means of electron diffraction equipment. They have made no mention of grinding kaolinite or of using a specific sample technique.

CONSTRUCTION OF THE ELECTRON DIFFRACTION UNIT

The basic construction of the electron diffraction unit was carried out by R. E. Joynson and E. J. Marak (7, 10). There have been many modifications and additions to the unit to facilitate refinement of the electron beam, to promote efficiency and ease of operation, and to improve the appearance of the apparatus.

Two front panels were added on which all of the controls

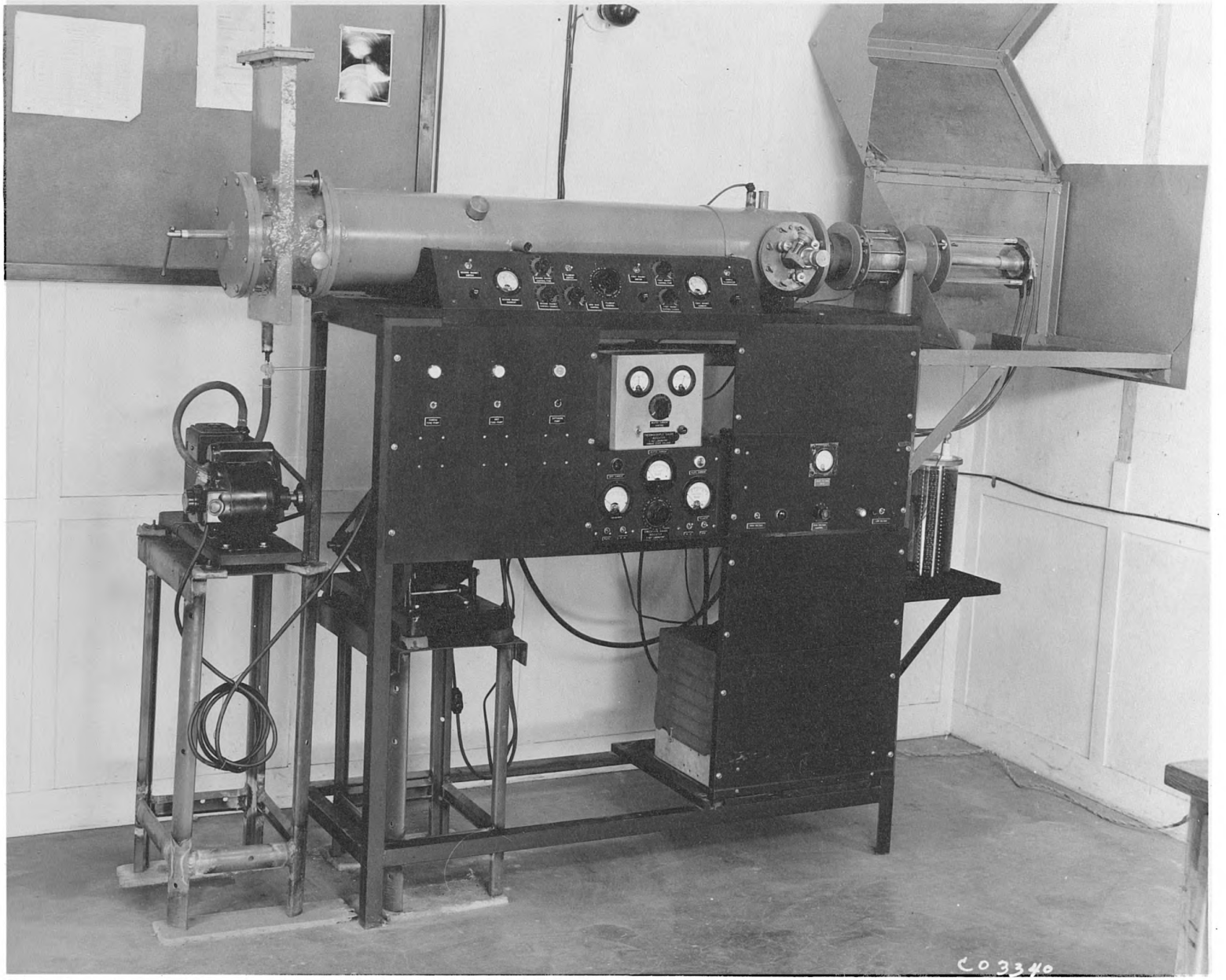
were placed. The one panel, containing the controls for the filament, the grid-bias, and the two magnets with their various switches, was so designed that one operator could view the screen while making adjustments necessary for optimum operation. The other panel contained the switches for the vacuum pumps.

The camera vacuum pump and the plate chamber valve were added to facilitate changing of the film. To change the film, the plate valve was turned into its valve seat; this isolated the plate chamber from the rest of the electron diffraction unit. The old film was removed and the new film inserted. The vacuum pump was turned on for a period of fifteen minutes so as to remove most of the air. It was then sealed off and the plate chamber valve opened. This reduced the vacuum to approximately 10^{-3} mm of Hg, and in one hour the entire system recovered its original vacuum of 4×10^{-5} mm of Hg. It was noted that the new film contained much water vapor, thereby increasing the time for obtaining the desired vacuum.

EXPLANATION OF PLATE I

The electron diffraction unit

PLATE I



The High Voltage Power Supply Unit

A radio-frequency type of power supply was used because of the voltage range desired, the greater ease in filtering, and because of the lighter and smaller components required than would be otherwise necessary at conventional power frequencies. The output of the power supply was variable from a negative 20 to 45kv with a voltage regulation of approximately .05 per cent. The high voltage was controlled by varying the screen grid potential on the oscillator tubes. The power supply was divided into three sections as shown in Plate II.

The R. F. Chassis. The r.f. chassis was composed of a 1/4 inch thick, polystyrene base plate placed on an inverted 13x17x3 inch, cadmium plated, steel chassis. Two or three 6L6 tubes were used in parallel as oscillators, depending upon the voltage and power requirements. The coil used was a Spellman 10-15 kv coil, capable of supplying a current of two milliamperes. The power oscillator was of the standard type with a grid-tickler winding supplying feedback to sustain oscillation. The output of this r.f. oscillator was fed into a quadrupler circuit in which the radio frequencies were rectified, filtered, and quadrupled by the tube and condenser arrangements.

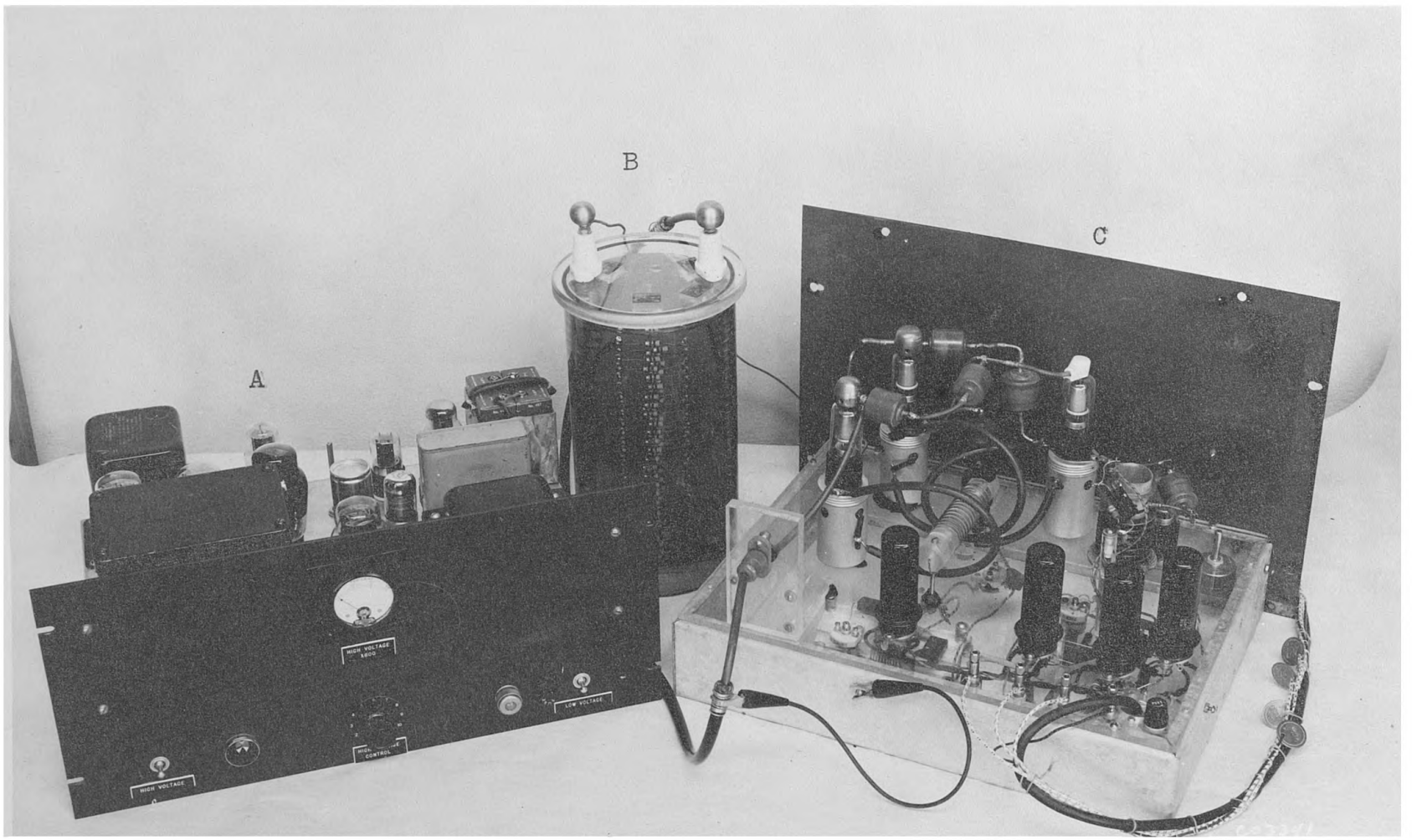
The four rectifier tubes used were type 1B3. Because of the variation desired in the high voltage, the filaments were supplied from a relatively stable source. The circuit diagram

EXPLANATION OF PLATE II

The high voltage power supply unit

A - The regulator chassis
B - The bleeder resistors
C - The r.f. chassis

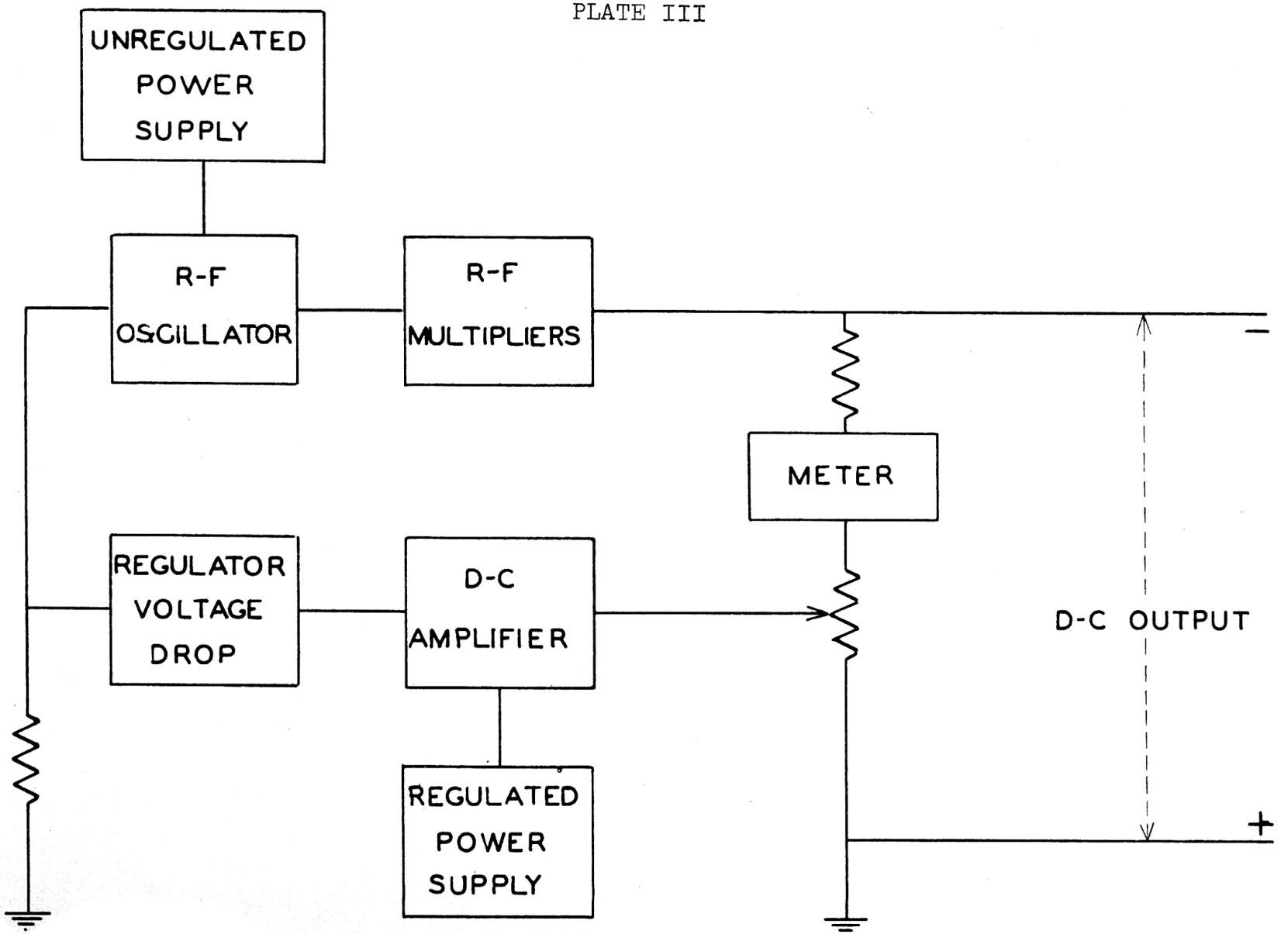
PLATE II



EXPLANATION OF PLATE III

The high voltage power supply block diagram

PLATE III


UNREGULATED POWER SUPPLY
R-F OSCILLATOR
R-F MULTIPLIERS
METER
REGULATOR VOLTAGE DROP
D-C AMPLIFIER
REGULATED POWER SUPPLY
D-C OUTPUT
−
+

is shown in Plate IV. Since the first rectifier filament was at ground potential, it was supplied directly from the 6.3v filament transformer with a current limiting resistor in series The other three rectifier filaments at 10, 20, and 30 kv, respectively, were supplied by a separate Hartley oscillator circuit. The output of this Hartley oscillator was electron-coupled to the primary of another tuned coil above the chassis, with all coils being placed as far apart as possible and at right angles to each other. Each filament secondary consisted of a single turn of co-axial cable which had its outer metallic shielding removed. This single turn was tuned to resonance with a 1370 micro-micro-farad condenser.

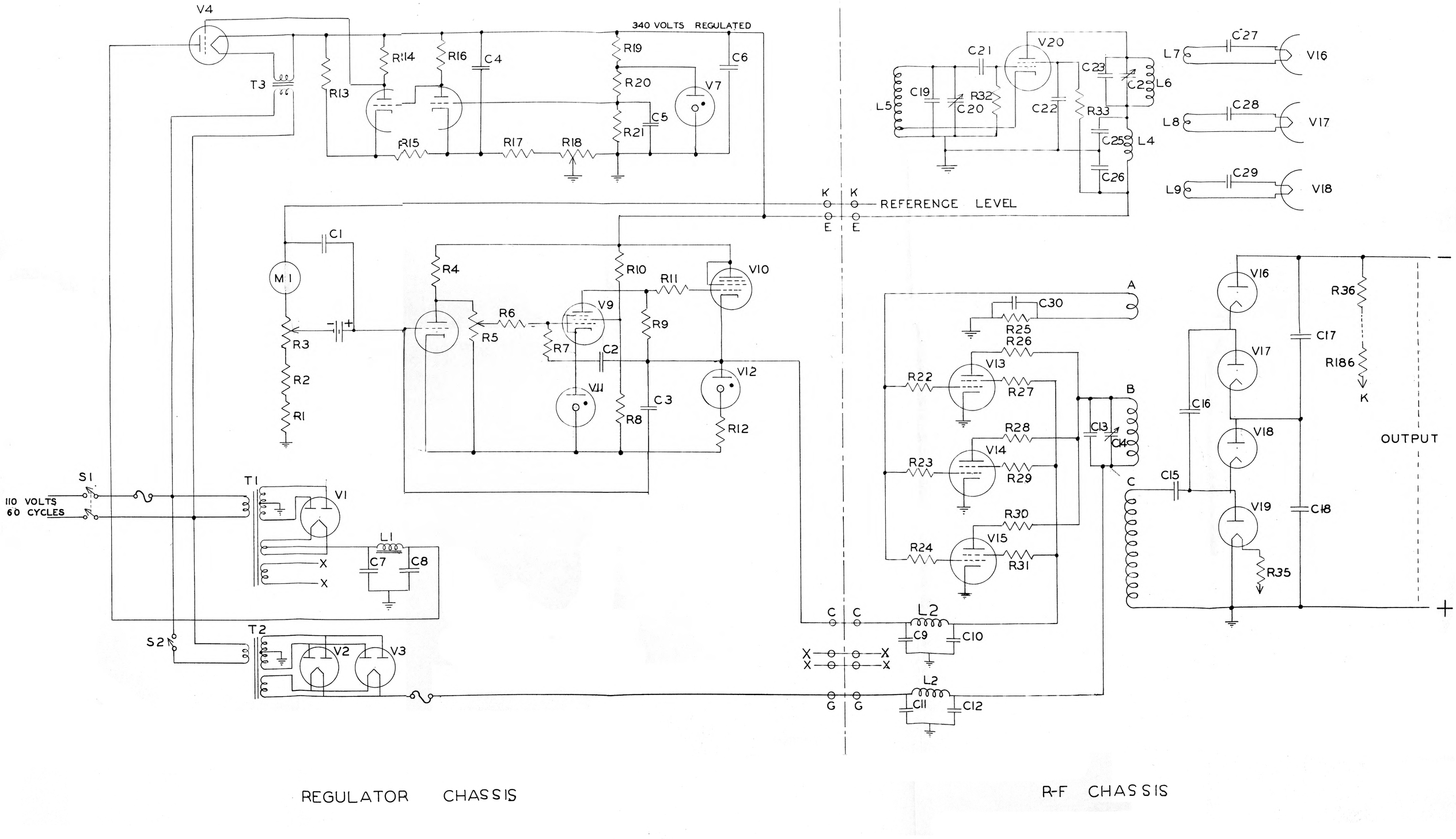
Because of the high voltages present, all components had to be spaced at a potential differential of 10 kv per inch or greater. The socket connection and the plate caps of the high voltage rectifier tubes were protected with corona shields. The socket shields were aluminum cups with rolled edges, a diameter of two inches, and a depth of three inches. The corona guards on the tube caps were made from a one inch brass rod, one end of which was rounded with a 1/2 inch radius and the other end drilled to fit the tube cap. All connections were made either with 1/8 inch brass rods or tightly wound springs wherever flexibility was needed.

The high voltage output was applied directly across a bank of bleeder resistors.

EXPLANATION OF PLATE IV

The high voltage power supply unit

A - Grid tickler winding
B - Primary winding
C - Secondary winding
L1 - 10 henry choke
L2, L3, L4 - 2 mh choke
L5 - Hartley oscillator coil for filaments
L6 - Electron-coupled load coil
L7, L8, L9 - Filament pickup loops
C1 - .02 mf condenser
C2, C3 - .01 mf condenser
C4, C6 - 4 mf condenser
C5 - 0.5 mg condenser
C7, C8 - 8 mf condenser
C9, C10, C11, C12 - .01 mf condenser
C22, C25, C26, C30 - .01 mf condenser
C13 - 5280 mmf condenser
C14, C20 - 100-200 mmf condenser
C15, C16, C17, C18 - 300 mmf, 30,000 volt condenser
C19, C21 - 250 mmf condenser
C23 - 275 mmf condenser
C24 - 50 mmf condenser
C27, C28, C29 - 5370 mmf condenser
R1 - 5 megohm resistor
R2 - 2 megohm variable resistor
R3 - 5 megohm potentiometer
R4, R9, R14, R16 - 0.33 megohm resistor
R5 - 2 megohm potentiometer
R6 - 1,000 ohm resistor
R7 - 200,000 ohm resistor
R8, R13 - 30,000 ohm resistor
R10 - 24,000 ohm resistor
R11, R19, R33 - 10,000 ohm resistor
R12 - 7,500 ohm resistor
R15 - 6,200 ohm resistor
R17 - 150 ohm resistor
R18 - 1,000 ohm variable resistor
R20 - 300,000 ohm resistor
R21 - 51,000 ohm resistor
R22, R23, R24 - 500 ohm resistor
R25 - 25,000 ohm resistor
R26, R28, R30 - 10 ohm resistor
R27, R29, R31 - 39,000 ohm resistor
R32 - 3,900 ohm resistor
R35 - 50 ohm variable resistor
R36 to R186 - 3 megohm resistor
T1 - Power transformer for regulated supply
T2 - Power transformer for unregulated supply
T3 - Filament transformer
V1, V2, V3 - 5U4G
V4 - 6B4G
V5, V6, V8 - 6SL7
V7 - VR105
V11, V12 - V75
V9 - 7G7
V10 - 6AG7
V13, V14, V15, V20 - 6L6
V16, V17, V18, V19 - 1B3G


340 VOLTS REGULATED
REFERENCE LEVEL
K K
E E
110 VOLTS
60 CYCLES
OUTPUT
REGULATOR CHASSIS
R-F CHASSIS

amperes whereas if both screen and plate voltage were controlled, the current would have been 120 milliamperes or greater.

The d.c. amplifier consisted of a 6SL7, 7G7, a 6AG7 series tube triode connected, and a VR75. The voltage variation necessary for the control of high voltage was 150 to 340 volts. The B-supply for the amplifier was a regulated supply of 340 volts output. The B-supply for the plates of the r.f. oscillator was not regulated because of the high current demands. Any fluctuation in this voltage was compensated by the d.c. amplifier controlling the screen potential. The unit was checked for line variations and its output remained constant for line voltages between 95 to 130 volts.

The Second Magnet and Collimators

A second magnet was added to facilitate focusing of the electron beam and also to make the unit adaptable as a shadow microscope (18). The magnification of the unit was then dependent upon the relative strengths of the currents in the magnets and the object distance from the focal point of the electron beam. Images of 200 mesh per inch screen were obtained.

For diffraction purposes, the collimators, referred to as a pinhole assembly, were placed inside the magnet closest to the electron gun. The grid and anode holes were purposely

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For diffraction purposes, the collimators, referred to as a pinhole assembly, were placed inside the magnet closest to the electron gun. The grid and anode holes were purposely

made large so that a rather high beam current was obtained. The grid hole found most acceptable was 0.125 inch in diameter; the grid hole was large enough so that the high voltage would reach into the filament and accelerate electrons toward the anode. The negative bias potential of the grid effectively reduced, by electro-static means, the size of the grid hole. The anode aperture was 0.250 inch in diameter. Both grid and anode were nickel plated to eliminate trouble-some zinc ions that normally would be emitted from the brass base metal upon electron bombardment.

After the electrons passed through the anode they were in an electrostatic, field-free space. The electrons were then focused by the electro-magnetic focusing coils and by the pinhole assembly. The second collimating hole of the pinhole assembly was large enough so that the electrons just skimmed by and yet small enough so that rays scattered or diffracted at a small angle by the leading edges of the first pinhole were stopped (15). The pinhole assembly was constructed of a copper tube 6.3 cm long, with the first pinhole .07 cm in diameter and the second pinhole .22 cm in diameter.

The Beam Current

The total current supplied to the electron gun was 500 microamperes with average filament potentials. The current lost was 100 microamperes; it was due to corona and leakage

through the filament transformer insulation. Thus, the actual total anode current was 400 microamperes. To determine the beam current, a beam stop was mounted on the sample holder in series with an 0-100 microameter. This apparatus was placed inside the diffraction unit and viewed through a port. It was found that the beam current was less than one microampere.

The anode current was great enough to generate considerable X-rays when they struck the nickel anode. A lead hood was made and placed over the gun assembly to stop this radiation.

EXPERIMENTAL TECHNIQUES

The samples to be studied must satisfy several conditions if they are to give satisfactory electron diffraction patterns. First of all they must be thin enough to transmit a large fraction of the incident electrons. Secondly, the samples must remain the same in vacuum and under electron bombardment. Finally, they must be mounted on a suitable support.

The support used for transmission patterns consisted of a disk of fine mesh metal screen with 200 meshes per inch as produced by RCA. For some samples such as magnesium oxide and other smoke particles, this metallic base was sufficient (16, 18). The smoke particles were caught on the wire mesh screen by passing it over a flame. More frequently, the samples required additional support other than the screen. This was provided by a two per cent solution of collodion in

amyl acetate. This provided a strong thin film which was amorphous and did not add crystalline lines to the diffraction pattern.

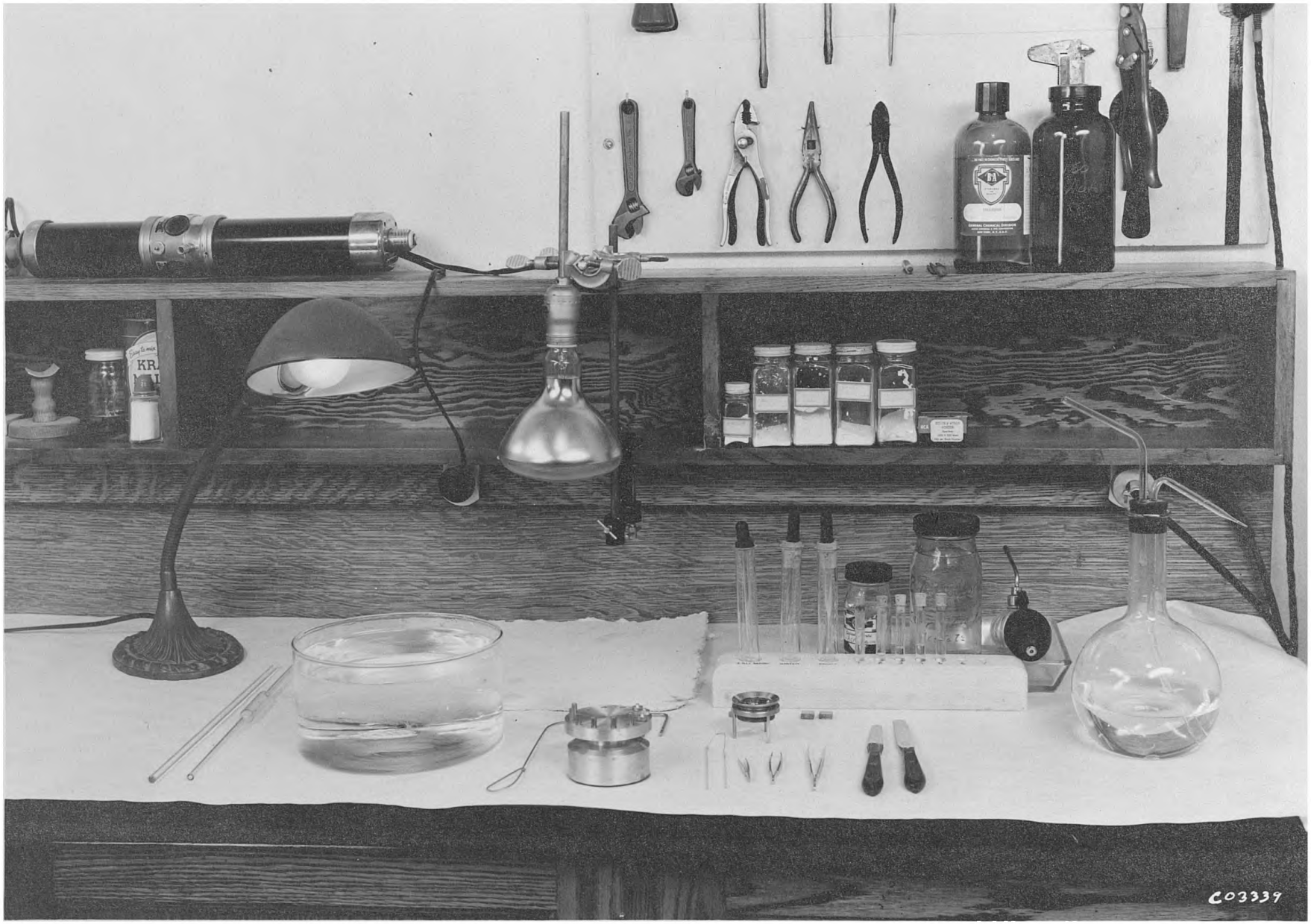
The apparatus for preparing this film is shown in Plate V. A single drop of the two per cent solution of collodion in amyl acetate was placed on the clean surface of distilled water. When the water surface was touched, the drop spread over a large area and the amyl acetate evaporated leaving the thin film of collodion. The screen disks were then placed on the film and both the film and screen were removed with a wire loop to be placed on one of the brass cylinders of the sample preparation holder. After the excess water had evaporated or had been drawn off with a micropipette, the sample was added.

The sample was usually prepared by placing it in an aqueous solution, shaking well, and depositing a drop of this solution upon the collodion film and screen. Studies made of thin films of aluminum by Jukherjee and Row (11) indicate that optimum conditions for obtaining good diffraction patterns from aluminum are with sample thickness of 580A. Thinner or thicker samples gave fewer and wider diffraction lines. The samples of kaolinite which gave the best results were, in general, prepared by placing 11 milligrams of kaolin into 8 cubic centimeters of water and shaking well. Because of small beam current and the low atomic number of the elements in kaolinite, the scattering was relatively weak; therefore long exposures of four minutes had to be taken.

EXPLANATION OF PLATE V

The sample preparation table

PLATE V



The patterns of magnesium oxide and nickel oxide, as shown in Plate VIII, were taken with one and thirty-second exposures, respectively. The sample specimens for reflection patterns were rectangular blocks of nickel measuring 1x1x0.5 cm. One of these square faces was used as the surface to be investigated. This face was highly polished by using a lapidary wheel, rouge, and water. The specimen was then slightly oxidized in a clean flame and immediately placed into the diffraction unit. The aim was to obtain a clean and slightly matt surface of the material (3). Materials which had been touched with the fingers or exposed for an appreciable time to the atmosphere were almost certain to be covered with a thin film of grease or other contamination. This contamination may have been sufficient to prevent the formation of a pattern characteristic of the material itself (16).

It was found that there were many parameters present in the alignment and adjustment of the apparatus. The optical and electrical paths were slightly displaced from each other for maximum beam intensity. The filament found most satisfactory utilized a five-mil, tungsten wire which was bent into a one-eighth inch long, sharp point. The above arrangement allowed any setting of the filament voltage. With other shapes and sizes of filaments, the beam would be deflected with increase or decrease of filament voltage producing a misalignment. Since the filament was heated with alternating current, a symmetrical arrangement of the current supply

was used to keep the filament at a constant potential. Also, the grid-bias adjustment and filament voltage were interdependent.

EXPERIMENTAL RESULTS

The results, by means of electron diffraction, were analogous to X-ray diffraction studies. Aside from sample thickness and sample preparation, the same lines should be present in X-ray and electron diffraction. Sproull (15) mentions that the intensities of scattered cathode rays are proportional to E^2, where E plays a role in electron diffraction equivalent to that of the atomic structure factor f in X-ray diffraction. The intensities of the scattered X-rays are proportional to f^2, where E and f are related by the equation

$$E = \frac{1}{16\pi^2} \cdot \frac{Z-f}{\left(\frac{\sin\theta}{\lambda}\right)^2}$$

where Z = atomic number
θ = Bragg angle or half the scattering angle
λ = wave length of the phase waves

In comparing E with f a factor of the order of 10^4 exists between the two, and a factor of some 10^7 exists between the scattered intensities. This accounts for the relatively short exposures needed in electron diffraction studies.

In samples of nickel oxide, iron oxide, and magnesium oxide there was 100 per cent correlation among all lines in

X-ray and electron diffraction patterns, showing that the above equation was valid.

The average exposure encountered in the electron diffraction work was three minutes, while for X-ray diffraction it was from 12 to 48 hours.

It was found that the electron diffraction patterns of ground kaolinite had lines with k indices other than 0 or 3. This indicates that the electron diffraction samples showed no disorders as were experienced by the X-ray diffraction samples. The only explanation for these differences was that the electron diffraction samples were too thin to show disorders.

In this study it was also necessary to consider the diffraction pattern as the surface of the reciprocal lattice perpendicular to the electron beam. Since the kaolinite samples were prepared by settling the kaolin crystals in an aqueous solution onto a flat surface, the a and b axis were parallel to this surface (9). Therefore, the electron diffraction pattern represented the surface a^* b^* of the reciprocal lattice (14). The reciprocal lattice in this case was formed by circles since the a and b axis of kaolinite were found to be irregularly oriented. This orientation gave the value of l equal to zero, and gave the h and k all possible values as noted in Tables 1 and 2.

The values obtained from transmission patterns as recorded in Tables 1 and 2 agree very well with those of Pinsker and associates (14). The data shown are the result of some 150

exposures. Of these, the best 5 to 10 exposures of each type of kaolin sample were used to average the data shown in Table 2. However, the accuracies in this study were to three significant figures. In comparing the calculated d spacings for the triclinic and monoclinic cells in Table 1, it was noted that in general they agree to three significant figures. Therefore, utilizing the data from the transmission patterns, it was not feasible to ascertain which type of unit cell satisfied the kaolinite data at this time.

Table 1. Comparison of the calculated spacings of kaolinite on the basis of triclinic and monoclinic unit cells, and the comparison of observed spacings found in this study and in the one by Pinsker and associates.

d_{hkl} in A	Calculated spacings		By Pinsker and associates	Observed spacings
	Triclinic	Monoclinic		
020	4.463	4.455	4.435	4.395
$1\bar{3}0$	2.56	2.55	2.56	2.56 -
040	2.231	2.225	2.23	2.32 -
150	1.675	1.675	1.68	1.672
060	1.487	1.484	1.49	1.486
260	1.272	1.275	1.29	1.289
170	1.232	1.232	1.235	1.242
080	1.117	1.112	1.11	1.14

Table 2. Observed 'd' spacings found in this study of unground, four week ground, ten week ground, and twenty-five week ground kaolinite.

d_{hkl} in A	Unground kaolinite	Four week ground kaolinite	Ten week ground kaolinite	Twenty-five week ground kaolinite
020	4.29	4.34	4.41	4.40
$1\bar{3}0$	2.58	2.44	2.43	2.03
040	2.33			
150	1.69	1.68	1.64	1.75
060	1.48	1.48	1.48	1.49
260	1.29	1.27	1.23	1.25
170	1.245	1.23		

EXPLANATION OF PLATE VI

Patterns made with the electron diffraction unit

Fig. 1. Unground kaolinite

Fig. 2. Kaolinite ground four weeks

PLATE VI

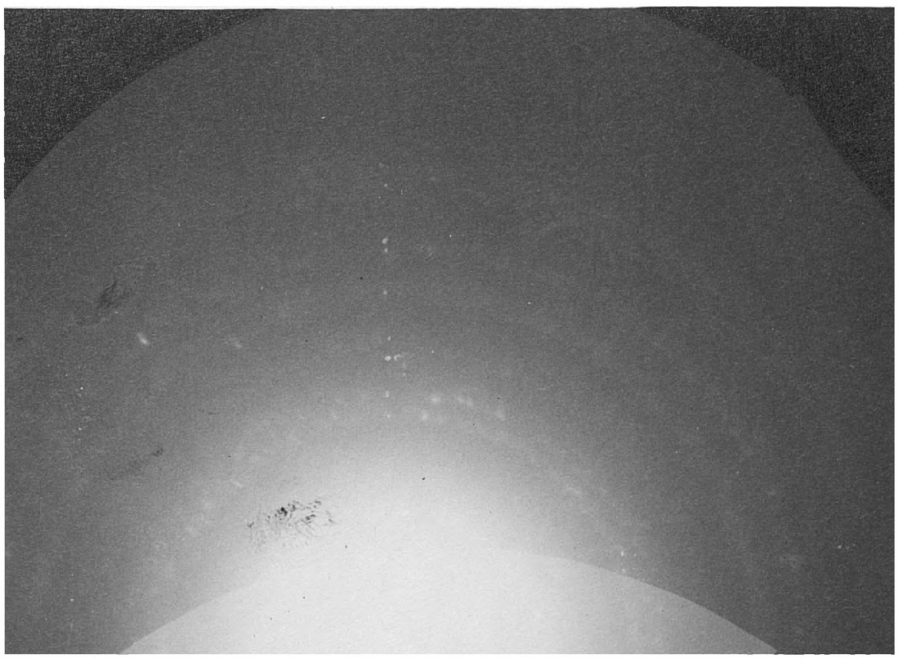


Fig. 1.

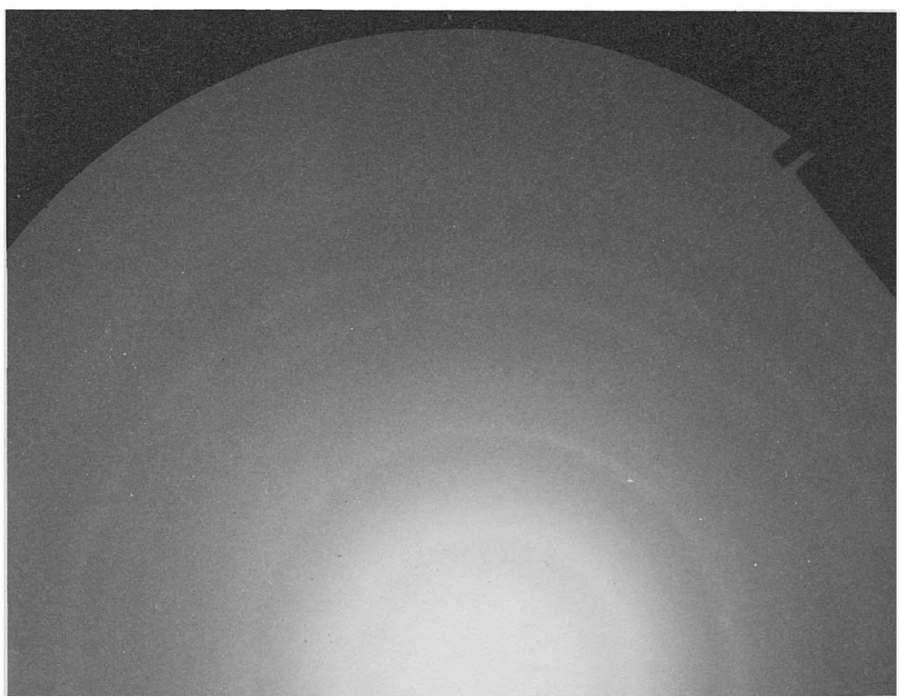


Fig. 2.

EXPLANATION OF PLATE VII

Patterns made with the electron diffraction unit

Fig. 1. Kaolinite ground ten weeks

Fig. 2. Kaolinite ground twenty-five weeks

PLATE VII

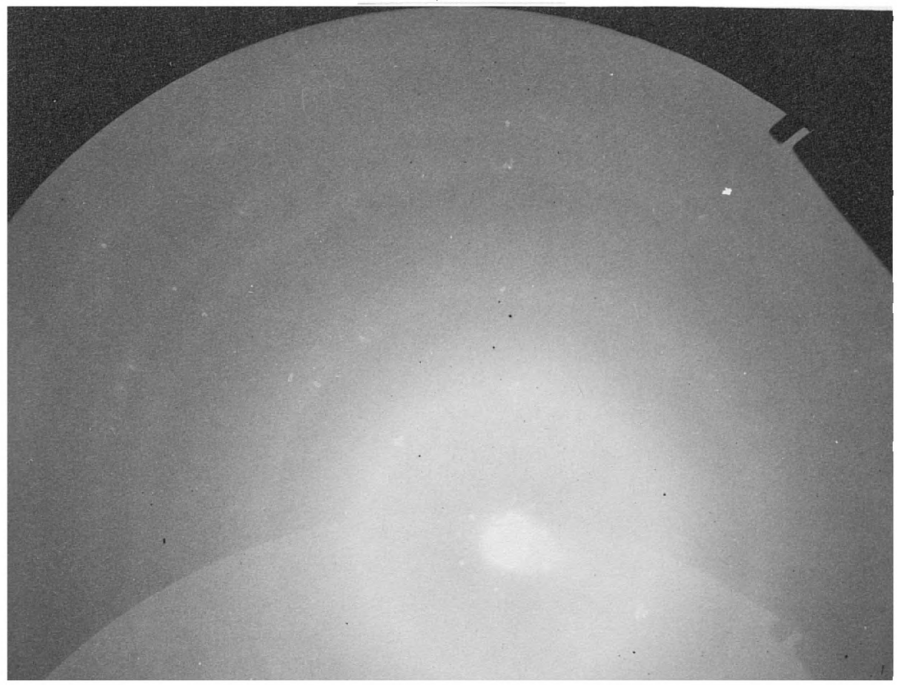


Fig. 1.

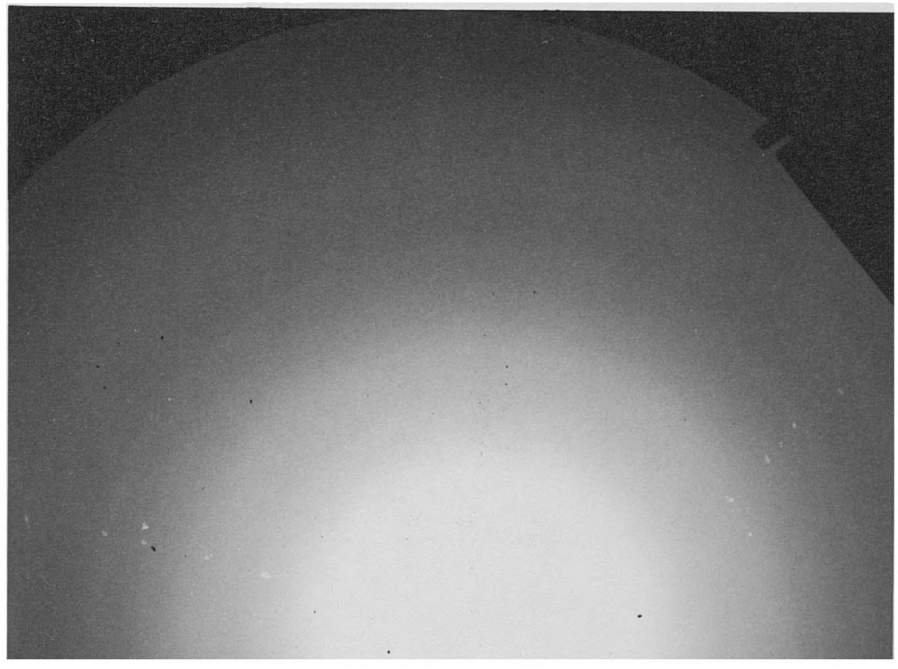


Fig. 2.

EXPLANATION OF PLATE VIII

Patterns made with the electron diffraction unit

Fig. 1. Magnesium oxide

Fig. 2. Nickel oxide

PLATE VIII

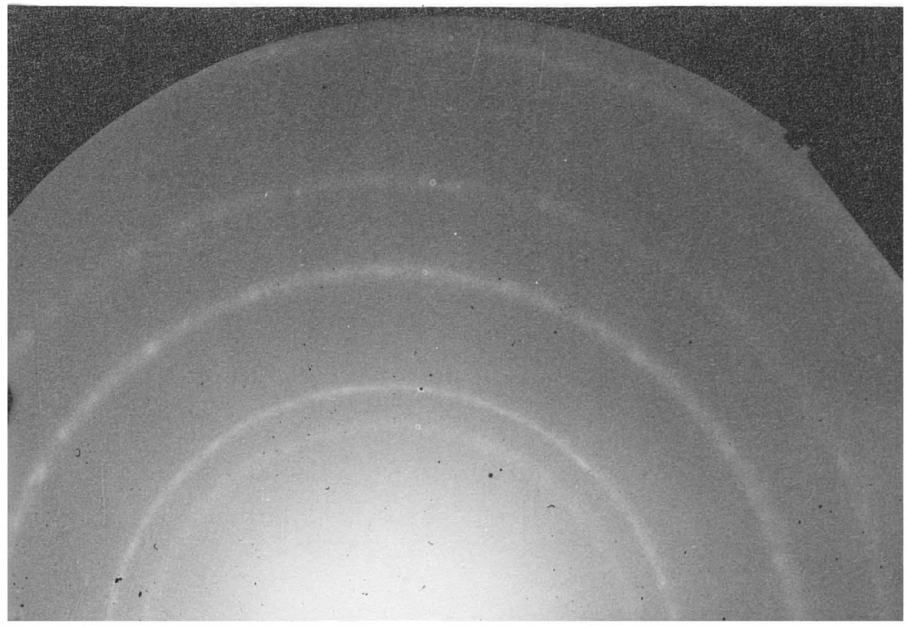


Fig. 1.

Fig. 2.

Because of the preferred orientation previously mentioned, Pinsker and associates turned to oblique textured patterns (reflection) to clarify the problem. This type of pattern was not obtained in this study. Various methods of sample preparation were attempted to obtain reflection patterns One process was to deposit kaolinite directly upon the collodion film without any other support. This proved unsuccessful because the collodion lacked mechanical strength. Another method was to use a screen as a support, but no reflection patterns were obtained. Kaolin was deposited on a flat nickel surface and a pattern was obtained. However, this showed no preferred orientation since the sample was either too thick or else not enough water had been used so that the crystals could settle properly with the a and b axis parallel to the nickel surface. X-ray techniques were used in the attempt to determine any preferred orientation; the results were identical with electron diffraction patterns.

Possibly, the reason for lack of patterns was that Pinsker et al. (14) used an electron beam current of some 60 microamperes with exposures of three minutes. In this study the beam current was below one microampere which would require an appropriate longer exposure of 30 to 40 hours which was not attempted.

SUMMARY AND CONCLUSIONS

At this point it was impossible, by electron diffraction means, to substantiate the findings of Pinsker and associates (14). As shown in Table 1, the difference in calculated d spacings for the monoclinic and triclinic unit cell is in the third decimal place. With this in mind, it was impossible to determine, to the needed accuracy, the actual d spacing of the unit cell. The results of using a Hayes X-ray camera found kaolinite triclinic as did also the results of Kissinger (8) and Brindley and Robinson (2).

In the process of this study much work had been done towards improving and refining the electron diffraction unit. A regulated forty-kilovolt power supply was constructed as a device to accelerate the electrons. A second electro-magnet and additional apertures were inserted into the unit to refine the beam so as to obtain sharp diffraction lines. The alignment of the electron gun, the electro-magnets, apertures, sample and sample-holder was found to be critical. The optical and electron beam axis were found to be displaced slightly from each other.

The techniques involved in sample preparation were found to be very exacting. Sample thickness and cleanliness determined whether or not a diffraction pattern could be obtained. It was concluded that the limiting factor in this study was the low electron beam current.

ACKNOWLEDGMENT

Special acknowledgment is extended to Dr. R. D. Dragsdorf for his cooperation and assistance during this research. Appreciation is also extended to Dr. L. D. Ellsworth and other members of the Department of Physics for their cooperation and interest in this study.

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AN ELECTRON DIFFRACTION STUDY OF KAOLINITE

by

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A considerable amount of research has been conducted on the crystal structure of kaolinite and the changes that occur when this mineral is ground in a ball mill. Papers have been published that ascertain the structure of kaolinite utilizing X-ray techniques. However, Pinsker, Lapidus, and Tatarinova, using electron diffraction means, state that the present proposed structure of kaolinite does not satisfy their empirical findings. It was the purpose of the present thesis to duplicate their work by using electron diffraction techniques.

For this study the construction of the electron diffraction unit had to be completed, a high voltage power supply constructed, and various other refinements mandatory for efficient operation of the unit incorporated.

The major problem encountered in this construction was that of the high voltage power supply. It had to be well regulated for changes in load and in line voltages. For regulation a simple feedback system was used which sampled a portion of the high voltage and corrected, by proper amplifying circuits, any changes in the output voltage. Caution had to be exercised in preventing corona and other losses due to the high voltage. The final results were a regulated supply of varying voltages from 25 to 45 kilovolts.

One of the additions and changes in the electron diffraction unit was the insertion of a second focusing magnet and collimators; this allowed the system to be used as a shadow microscope. Pictures of low magnification were obtained of

200 mesh per inch screen placed in the path of the electron beam. Other changes in the beam forming components were those of the existing diameters of collimating holes. This was done to achieve as large a beam intensity as possible through only a relatively small solid angle. A refinement to the electron diffraction unit was the addition of a plate chamber valve such that the camera holding the film could be removed without disturbing the vacuum in the rest of the system. Front panels were also added to facilitate adjustment procedures, appearances, and dependability of operation.

The actual study of kaolinite was accomplished by depositing small amounts of the mineral on a collodion film supported by a fine-mesh metal screen. These samples were then placed in the path of the electron beam in such a fashion that diffraction patterns occurred. Diffraction patterns were also obtained of nickel and iron oxides.

The empirical results of Pinsker, Lapidus, and Tatarinova were not substantiated in their entirety due to the relatively low electron beam current of our diffraction unit.