AN INVESTIGATION OF THE VALIDITY OF THE X-RAY

CRYSTAL METHOD OF DETERMINING N AND e

Thesis by

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Abstract

To test the validity of the x-ray crystal method of determining N and e the crystal structure and densities of two polycrystalline metals, silver and aluminum, and one "perfect" crystal, powdered quartz, were determined.

The densities were determined by using a specific gravity bottle filled with distilled water and the following results were obtained.

Material	ρ at 25.0°C
Silver	10.4870 ± 0.0008 gm cm^{-3}
Aluminum	2.69839 ± 0.00019
Quartz (macroscopic)	2.64822 ± 0.00005
Quartz (fine powder)	2.64810 ± 0.00015

The lattice constants were measured in a Seeman-Bohlin focussing spectrograph and the following parameters were obtained.

Silver	$a = 4.08574 \pm 0.00004 \times 10^{-8}$ cm
Aluminum	$a = 4.04927 \pm 0.00002$
Quartz	$a = 4.91263 \pm 0.00009$
	$c = 5.40454 \pm 0.00011$

Using these results the following values on N and e were calculated.

	N	e
Silver	$6.0318 \pm 0.0006 \times 10^{23}$ mol gm mol^{-1}	$4.7957 \pm 0.0007 \times 10^{-10}$ esu
Aluminum	6.0258 ± 0.0007	4.8005 ± 0.0007
Quartz (1)	6.0239 ± 0.0005	4.8020 ± 0.0006
Quartz (2)	6.0280 ± 0.0005	4.7988 ± 0.0006

where the two different values for **quartz** are for two different values of the molecular weight of silicon.

The effect of distortion of the metals on the crystal structure and the density was investigated. The values obtained for powdered quartz are free from the objection that the density determination may not be representative of the thin layer at the surface of a crystal involved in the x-ray reflection.

Since the values of N and e obtained for silver and aluminum differ by many times the experimental error and the difference between a polycrystalline material and a "perfect" crystal is one of degree, and since after taking into consideration the unfortunate uncertainty in the molecular weight of silicon the values obtained using powdered quartz still seem to be in a slight disagreement with those obtained using large calcite crystals I believe that the best value of e obtainable by the x-ray method is $4.802 \pm 0.002 \times 10^{-10}$ esu.

INTRODUCTION

The problem of determining accurately Avogadro's number, N, and its associated constant, e, the charge of the electron is an important one. There are two direct and accurate procedures, the oil-drop method and the x-ray method. The former involves the value of the coefficient of viscosity of air about which there is no universal agreement as yet, and the latter contains certain fundamental objections as to the validity of the method. It is with a critical examination of the x-ray method that this thesis is concerned.

Information as to the submicroscopic absolute dimensions of the lattice of a crystal which we can obtain by means of x-ray diffraction permits the computation of Avogadro's number which is given by

$$N = \frac{M}{\rho\, f(a_1, a_2, a_3, \alpha_1, \alpha_2, \alpha_3)}$$

where M is the molecular weight of the crystal, ρ its density, and f the volume associated with one molecule. a_1, a_2, a_3 are the axial lengths and α_1, α_2, α_3 the inter-axial angles. Or if we assume $Ne = Q$, the Faraday, as known, we have $e = \frac{\rho f Q}{M}$.

For face-centered cubic crystals $f(a_1, a_2, a_3, \alpha_1, \alpha_2, \alpha_3)$ is $\frac{1}{4} a^3$. Thus to determine N for such systems it is necessary to know the molecular weight which is best found by chemical or mass-spectroscopic means, ρ which is best measured by immersion or a specific gravity bottle, and a, which is measured by means of x-rays through the Bragg equation

$$\lambda = \frac{2a}{\sqrt{\Sigma\, h^2}}\, \sin\,\Theta \left(1 - \frac{\delta}{\sin^2\,\Theta}\right)$$

where $\Sigma\, h^2$ is the sum of the squares of the Miller indices designating the particular plane used. Θ is the complement of the angle of incidence measured from the normal of the plane, $1-\delta$ is the index of refraction and δ is of the order of 10^{-6} and since in our work $\sin^2\,\Theta > 0.9$ this term may be neglected. For λ we use the ruled grating measurements of Bearden, Bäcklin and Södermann who independently found that the wavelength in absolute units is 1.00203 ± 0.000016 times the arbitrary Siegbahn wavelength.[14]

Quartz is a hexagonal crystal with three SiO_2 molecules in the conventional hexagonal unit cell. For such systems $\alpha_1 = \alpha_2 = 90^\circ$, $\alpha_3 = 120^\circ$, $a_1 = a_2 = a, a_3 = c$ and f becomes $a^2 c/2\sqrt{3}$. The Bragg equation takes the form $\lambda = 2\left\{\frac{4}{3a^2}(h_1^2 + h_2 h_2 + h_2^2) + \frac{h_3^2}{c^2}\right\}^{-1/2} \sin\,\Theta$ where $h_1, h_2, h_3 \geqslant 0$.

The difficulty with the x-ray method is twofold. In the first place the x-rays measure only a periodic spacing so that if either a more or less regular superstructure, random holes or imperfections in the lattice exist their presence will not affect the lattice constants as measured by the x-rays, but the measured density, which is the average density, will not be the true density of the periodic sections of the lattice. The existence of a superstructure (or mosaic structure) has been proposed by Zwicky[22] to account for certain mechanical

properties and habits of growth. He proposed that there are

periodic variations in the grating space in the crystal along a

direction normal to the planes. Their period would be of the order

of 10^{-6} cm and the superposition of such a long period on the inter-

planar spacing of 10^{-8} cm would not affect the relative positions

of the x-ray diffraction maxima and would have negligible effects on

their intensity. However, one would not expect the error introduced

in the density by the presence of the superstructure or imperfections

of the lattice to be the same for all crystals. Tu[1] measured the

density and lattice parameters of calcite, rocksalt, potassium chloride,

and diamond crystals and found that they gave a consistent value of N,

the largest deviation being *three* ~~one~~ parts in 10,000. Also, one would not

expect, if there is a regular superstructure, that the secondary com-

ponent would have exactly the same coefficient of thermal expansion

as the normal component. A. H. Jay[2] measured the thermal expansions

of silver, quartz and bismuth by the x-ray powder method, precision

measurements being employed. The macroscopic thermal expansion was

also measured by optical methods and the same values obtained indicat-

ing that the expansion of the atomic lattice does not differ from that

of the crystal as a whole. Thus the presence of a large secondary

component appears doubtful. However, it is one of the purposes of the

present investigation to work with lattices known to be distorted and

imperfect and to find how much these distortions affect the value of

the lattice constants of the periodic part of the lattice and the average density of the crystal. It will then be possible to correct for these distortions and to answer once and for all this criticism.

The second objection to the x-ray method is that because of the extinction of the x-rays in passing through the crystal the lattice constant of an extremely thin superficial layer (5×10^{-5} cm for calcite in the first order with Mo Kα) is measured, and this may not be representitive of the interior of the crystal. Allison and Armstrong[3] measured the wavelength of Mo Kα_1 in various orders of reflection from calcite and found

Order	Half-depth of penetration		λ	$\dfrac{\lambda_m - \lambda_1}{\lambda_1}$
	cm	no. of planes		
1	5×10^{-5}	1.6×10^3	0.707831 A$^\circ$	
3	4×10^{-4}	1.3×10^4	0.707902	0.01 %
4	6×10^{-4}	2×10^4	0.707850	0.003
5	1.2×10^{-3}	4×10^4	0.707840	0.001

and concluded that the lattice constant is uniform throughout the crystal. DuMond and Bollman[4] measured the density and lattice parameters of extremely fine powdered calcite, where the size of the individual crystals was of the order of the depth of half penetration of the x-rays. They found that within experimental error ~~that~~ the constants and density were identical with those of macroscopic calcite. While these experiments indicate the absence of any imperfections in the crystals used, the value of N would be on much surer ground if we

knew what imperfections are found and just what their effect is on the grating constant and the average density. The purpose of the present experiments was twofold. First, to answer the above question, and secondly to make a precision determination of the lattice constants and density of three new crystals by methods different from those employed by Tu[2] and Bearden[5]. Both measured their densities by immersion and their lattice parameters with a two crystal spectrometer. In the present research the densities were measured with a specific gravity bottle and the lattice parameters with a Seeman-Bohlin focusing spectrograph. Silver and aluminum were the imperfect crystals used and quartz was taken as a "perfect" crystal.

Powder samples of aluminum and silver were prepared by filing or sawing and these samples along with solid pieces which were as large as would enter through the neck of the specific gravity bottle were annealed together in a vacuum. The powder sample of quartz was prepared by breaking up optical clear quartz in a steel mortar by pounding with a heavy sledge hammer. The coarser grains were rejected by the fine screen through which the sample was sifted. The lattice parameters and density of these samples were measured. If we think of a sample of the material as made up of many small perfect crystals or crystallites, randomly situated relative to each other, then the resolving power of these units for x-rays will depend on their size, that is on the average number of perfectly periodically spaced planes that they

contain. Thus from the width of the diffraction pattern (Debye-Scherrer rings) it is possible to measure the average length of the periodic sections of the lattice or the size of the crystallites. In the case of the metals the powder and large pieces were then distorted by mechanical working and the new density, grating constant and size of crystallite were determined. Actually the shape and dimensions of the unit cell were found to be unaffected by working but the length of the regular periodicity was found to decrease. The density was found to change slightly, an increase for silver and a decrease for aluminum. On the basis of these measurements it is possible to estimate the density of "perfect" crystals of aluminum and silver.

THE DENSITY MEASUREMENTS

The weights used were calibrated against both a 50 gram and 1 gram standard obtained from Dr. Swift of the Chemistry Department. The method of double weighing with an analytical balance was employed throughout the experiments. The weighings could be depended upon to within 0.1 mg. In fact the specific gravity bottle was weighed many times over a period of several months and its weight (22 gm) corrected for air buoyancy never varied by more than 0.1 mg.

The specific gravity bottle was of conventional design and included a thermometer which could be read directly to fifths of a degree and estimated to twentieths. This thermometer as well as a second one used in the temperature bath were checked against a Bureau of Standards thermometer obtained from Mr. Weis of the Chemistry Department. The ground glass joint was reground with 600 carborundum for at first there was found to be considerable evaporation during the course of weighing. After it was reground the loss by evaporation was less than 5 mg in 24 hours. Let W be the apparent weight of the empty bottle. The bottle was then filled with freshly boiled redistilled water and placed in a temperature bath. The height of water in the capillary was roughly adjusted by removing some of it with a fine glass tube placed down the capillary. The final adjustment was accomplished by changing the temperature of the water bath. When the temperature was the same in the bath and the bottle and the top of the

liquid in the capillary was opposite the fiducial mark, then the bottle was removed, dried and weighed. Let the apparent weight be W_B. The volume of the specific gravity bottle is

$$V_t = \frac{W_B - W}{\rho_t} \left\{ 1 + \delta \left(\frac{1}{1.00} - \frac{1}{8.6} \right) \right\}$$

where ρ_t is the absolute density of water for the particular temperature,[6] δ is the density of air, and 8.6 the density of the brass weights. The laboratory distilled water was redistilled in an all glass still, freshly boiled, corked and cooled before using. This was found necessary for if this cooled water was exposed to the air for about five minutes and then corked again after twenty four hours the density increased by 0.005%. The result of 15 measurements when reduced by least squares gives as the volume of the bottle, at the temperature t

$$V_t = 24.92735 \pm 0.00008 + \left[t - 25.0 \right] (4.85 \pm 0.30)$$

The probable error in this and succeeding measurements was calculated by the method recommended by Birge .

Let W_S be the apparent weight of the sample whose density is to be measured; its mass is

$$M_S = W_S \left[1 + \delta \left(\frac{1}{\rho_S} - \frac{1}{8.6} \right) \right]$$

where ρ_S is the approximate density of the sample. The sample is

then placed in the specific gravity bottle and enough water added to cover it. The bottle is evacuated until the water boils. This makes sure that all occluded gases and bubbles are removed from the surface of the sample. The bottle is then filled with water, the temperature adjusted, and weighed giving the apparent weight W_V. The volume of water added is

$$V_S = (W_V - W_S - W)\left\{ 1 + \delta\left(\frac{1}{1.00} - \frac{1}{8.6}\right)\right\}$$

Thus the density of the sample is

$$\rho = \frac{M_S}{V_t - V_S}$$

The aluminum was annealed for 4 hours at a temperature of $350^{\circ}C$ in a vacuum furnace and allowed to cool in the furnace. The furnace was made of quartz, and the sample was placed in a porcelain dish. The following results were obtained

Density of Annealed Aluminum

T	W_S	ρ	ρ at $25.0^{\circ}C$
$23.20^{\circ}C$	10 gm	2.69867 gm cm^{-3}	2.69835 gm cm^{-3}
24.25	10	2.69877	2.69863
24.50	8	2.69880	2.69871
24.70	10	2.69829	2.69824
25.20	8	2.69812	2.69816
25.40	10	2.69816	2.69823
25.80	10	2.69845	2.69859
26.40	10	2.69801	2.69826
26.70	8	2.69803	2.69834

Av. 2.69839 ± 0.00005

The thermal coefficient of linear expansion of aluminum was taken as 2.2×10^{-5} per degree centigrade in reducing both the density and the lattice constant to $25.0^{\circ}C$.

Some annealed aluminum was placed in an arbor press and compressed without sudden impact so that the dimensions were changed by a factor of two. This should not change the lattice as much as hammering or severe working, but if there are any holes in the lattice they should be closed and the density increased. The following results were obtained.

Density of Pressed Aluminum

T	W_s	ρ	ρ at $25.0^{\circ}C$
$23.00^{\circ}C$	14 gm	2.69871 gm cm^{-3}	2.69835 gm cm^{-3}
24.05	14	2.69830	2.69813
25.20	14	2.69835	2.69839
			Av. 2.69829 ± 0.00004

One may conclude from the fact the density actually decreased a slight amount that there was no effect due to holes in the annealed crystals. The samples were severely worked by hammering and the density redetermined with the following results.

Density of Worked Aluminum

T	W_s	ρ	ρ at $25.0^{\circ}C$
$24.60^{\circ}C$	12 gm	2.69827 gm cm^{-3}	2.69820 gm cm^{-3}
25.15	12	2.69791	2.69794
25.70	12	2.69778	2.69790
			2.69801 ± 0.00006

The silver was annealed in the same furnace for 24 hours at 600°C, and allowed to cool in the furnace. The first five determinations in the following table were made. The sample was worked and reannealed, and the last three measurements are the resulting density determinations.

Density of Annealed Silver

T	W_s	ρ	ρ at 25.0°C
24.45°C	40 gm	10.4861 gm cm^{-3}	10.4859 gm cm^{-3}
25.20	40	10.4858	10.4859
25.20	40	10.4877	10.4878
26.10	40	10.4866	10.4872
26.20	40	10.4866	10.4873
23.60	40	10.4887	10.4879
24.45	40	10.4869	10.4867
25.90	40	10.4869	10.4874

Av. 10.4870 ± 0.0002

The thermal coefficient of linear expansion was taken as 1.9×10^{-5} per degree centigrade in reducing both the density and lattice constant to 25.0°C. The silver was then compressed without sudden impact in an arbor press and the density determined.

Density of Pressed Silver

T	W	ρ	ρ at 25.0°C
23.35°C	40 gm	10.4891 gm cm^{-3}	10.4881 gm cm^{-3}
24.20	40	10.4888	10.4883
25.40	40	10.4866	10.4868
22.95	29	10.4878	10.4866
24.25	29	10.4878	10.4874
25.10	29	10.4894	10.4895

Av. 10.4878 ± 0.0003

One concludes from the small increase in density that the annealed silver is not spongy nor does it contain large holes. The silver was then severely worked by hammering and its density measured.

Density of Worked Silver

T	W	ρ	ρ at 25.0°C
23.60°C	40 gm	10.4937 gm cm^{-3}	10.4929 gm cm^{-3}
24.15	40	10.4894	10.4889
25.20	40	10.4901	10.4902
26.00	40	10.4916	10.4922
			10.4911 ± 0.0006

I attempted to measure the density of fine silver powder prepared by chemical precipitation. It was obtained from Eimer and Amend. The density of the powder as it came from the maker was about 10.470 gm cm^{-3}, but after it was dried and remeasured it had fallen to 10.410 gm cm^{-3}. As the particles were almost colloidal in size an extremely thin surface impurity picked up while drying would be sufficient to explain the decrease in density. The powder had different "wetting" properties after it was dried and acted "greasy" and water refused to wet it. This surface coating was probably oxide for care was taken to prevent chemical contamination. The crystal structure of the fresh and dried samples was the same. In fact the density of silver prepared by chemical reactions seems to be quite variable. Kohlschutter and Eydmann[7] found values ranging from 9.945 to 10.499 for fine powder prepared by precipitation or decomposition of Ag_2O and Ag_2CO_3.

When the quartz powder was being prepared some pieces as large as would conveniently enter the neck of the specific gravity bottle were saved and their density determined.

Density of Macroscopic Quartz

T	W	ρ	ρ at 25.0°C
22.65°C	12 gm	2.64846 gm cm^{-3}	2.64824 gm cm^{-3}
22.80	12	2.64834	2.64814
23.50	12	2.64822	2.64808
24.50	12	2.64846	2.64841

Av. 2.64822 ± 0.00005

The thermal coefficient of volume expansivity was taken as 3.5×10^{-5} per degree centigrade in reducing the density to 25.0°C.

The density of the finely powdered quartz could not be determined as accurately as the density of the large pieces. The powder had a tendency to contain small air bubbles, but these were probably removed by boiling the water under vacuum. However, since some of the sample was almost colloidal in size it formed a suspension in the water and when the thermometer was inserted in the neck of the specific gravity bottle a small amount of water containing some quartz must be lost.

Density of Powdered Quartz

T	W	ρ	ρ at 25.0°C
23.05°C	14 gm	2.6483 gm cm^{-3}	2.6482 gm cm^{-3}
23.70	10	2.6484	2.6483
24.25	14	2.6480	2.6479
24.25	16	2.6471	2.6470
24.50	10	2.6489	2.6489
24.65	14	2.6480	2.6480
24.80	10	2.6484	2.6484

Av. 2.64810 ± 0.00015

The density of the powdered quartz seems to be identical with that of the macroscopic sample.

For comparison we include the results of density determinations made by other observers.

Density of Silver, Aluminum and Quartz at 25.0°C

Material	ρ	Observer
Silver (electrolytic)	10.4914 $gm\ cm^{-3}$	Timofeiev[22]
Silver (vacuum distilled)	10.4893	Kahlbaum[23]
Aluminum (cold rolled 99.97%)	2.698	Edwards[24]
Quartz	2.6483	Various I.C.T.[4-20]
Quartz	2.6479	Tu[1]

The quartz was an optically clear sample and apparently a perfect specimen. It was, I believe, found in California.

The aluminum was obtained through the courtesy of Wm. L. Fink of the Aluminum Company of America. He gave the following analysis

Aluminum	99.980%
Silicon	0.004
Copper	0.011
Iron	0.004
Titanium	0.001

The silver was obtained from Handy and Harmon, Bridgeport, Connecticut. The Applied Research Laboratories of Los Angeles gave the following analysis.

Silver	99.957%
Calcium	0.009
Silicon	0.014
Lead	0.004
Iron	0.006
Copper	0.010

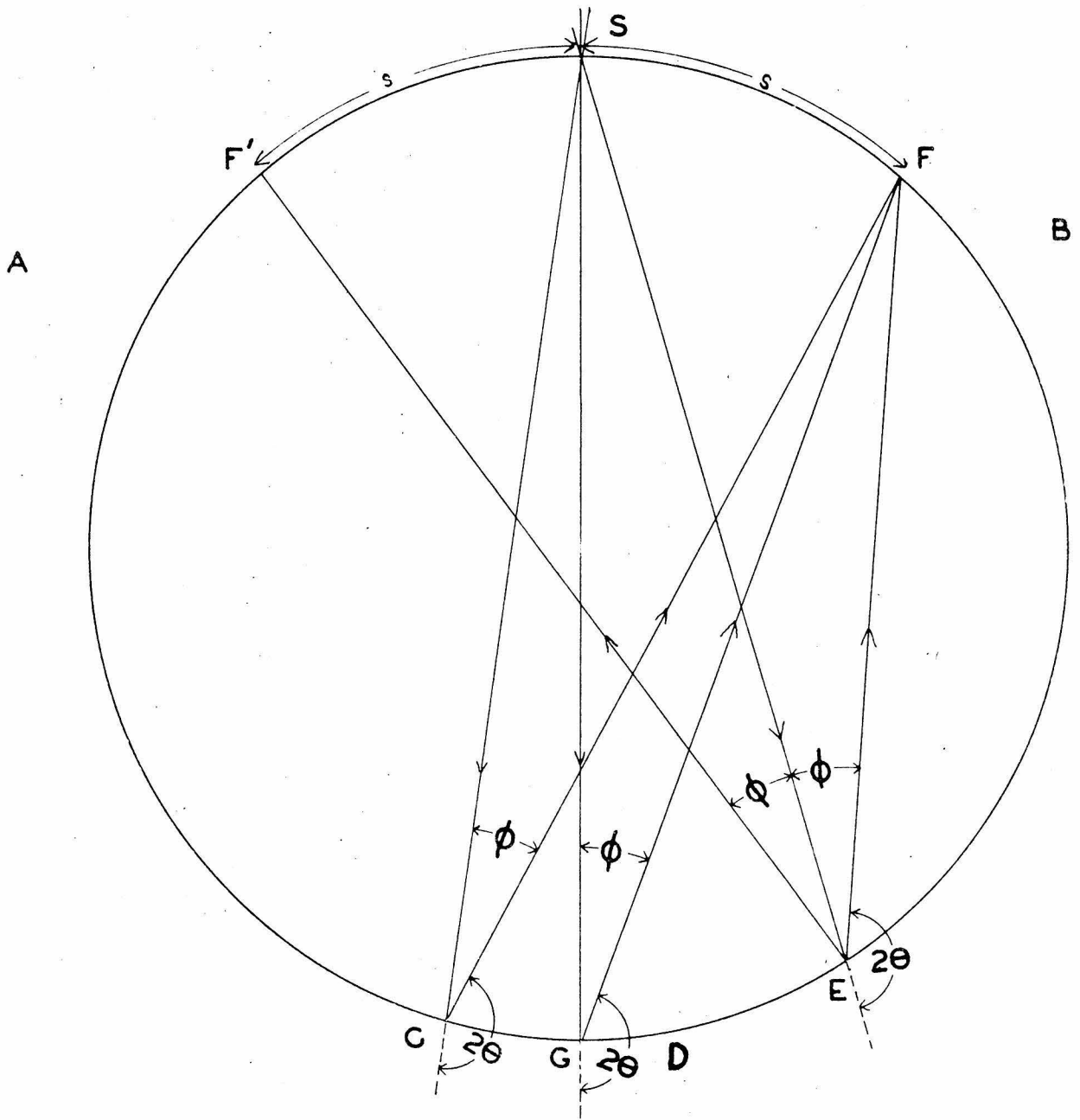Corrections will be made for the presence of these impurities.

FIG I THE SEEMAN BOHLIN FOCUSING SPECTROGRAPH

MEASUREMENT OF THE LATTICE CONSTANT

A Seeman-Bohlin focussing type of powder spectrograph was used because it gives strong lines with a relatively short exposure and if the wavelength of x-rays is chosen so that the Bragg angle for some plane or planes is nearly 90°it is capable of very great accuracy for sin Θ varies slowly with Θ in this region. The theory of this focussing type of camera is as follows. In Fig. 1 let the photographic film be placed on the arc ASB with a hole in its center so that divergent x-rays of wavelength λ can pass through the fine slit S. These x-rays will fall upon the powder samples placed along the arc CDE diametrically opposite the slit S. Since the powder sample contains a large number of tiny crystals randomly oriented there will be some crystals properly aligned, no matter where they lie on the arc CDE, to diffract the x-rays of wavelength λ from a given set of planes of grating space d to a particular point F according to the Bragg equation $\lambda = 2d \sin \Theta$, where Θ is the angle which the incident and diffracted rays each make with the atomic plane normal to the lattice distance d. That the camera is focussing is apparent when we consider that the arc SF subtends the same angle for every point along CGE. There will be crystals oriented in such a way as to diffract the x-rays of wavelength λ to the point F' such that the arcs F'S and FS are equal. The spectrograph gives a photograph which is symmetric with respect to the slit and by measuring F'SF we can find

2s without knowing the position of the slit. Now $2\theta = \pi - \phi$
or $\theta = \frac{\pi}{2} - \frac{\phi}{2}$ and if D is the camera diameter ϕ will be given by
s/D and Bragg's equation will become

$$d = \frac{\lambda}{2\sin\theta} = \frac{\lambda}{2\cos\frac{s}{2D}} \simeq \frac{\lambda}{2}\left(1 + \frac{s^2}{8D^2}\right)$$

and we see that when s is small ~~that~~ a large change in s makes a
small change in d . For example, in our camera where D = 17.5 cm

$$\frac{\Delta d}{d} \simeq \frac{s\Delta s}{4D^2} = \frac{s^2}{4D^2} \times \frac{\Delta s}{s} = \frac{s^2}{1220} \times \frac{\Delta s}{s}$$

and when s = 11 cm, which is as big as it is in any of the photographs
used, then a 1% change in s means a 0.10% change in d.

M. U. Cohen[8] has discussed the errors introduced by vertical
divergence of the beam, slit width, thickness of the powder sample,
shrinkage of the film and errors in the measurement of the camera
radius and he has shown that for cubic crystals $\frac{\Delta d}{d} \simeq k\, \phi \tan \phi/2$
and suggests plotting a against $\phi \tan \phi/2$ which when extrapolated to
$\phi = 0$ would give the correct value of the lattice constant. Two and
three parameter crystals can be treated similarly. However, in the
present work since only two values of ϕ were obtained from a photograph
of the metals it was felt that extrapolation using only two points
would be a dangerous procedure. Furthermore, such a procedure might
mask systematic errors of measurement. Therefore, the correction for
each error was made separately. In the case of the quartz ten lines
from six different planes were used, but the same method was used for by
examining the residuals in the least squares calculation we would have
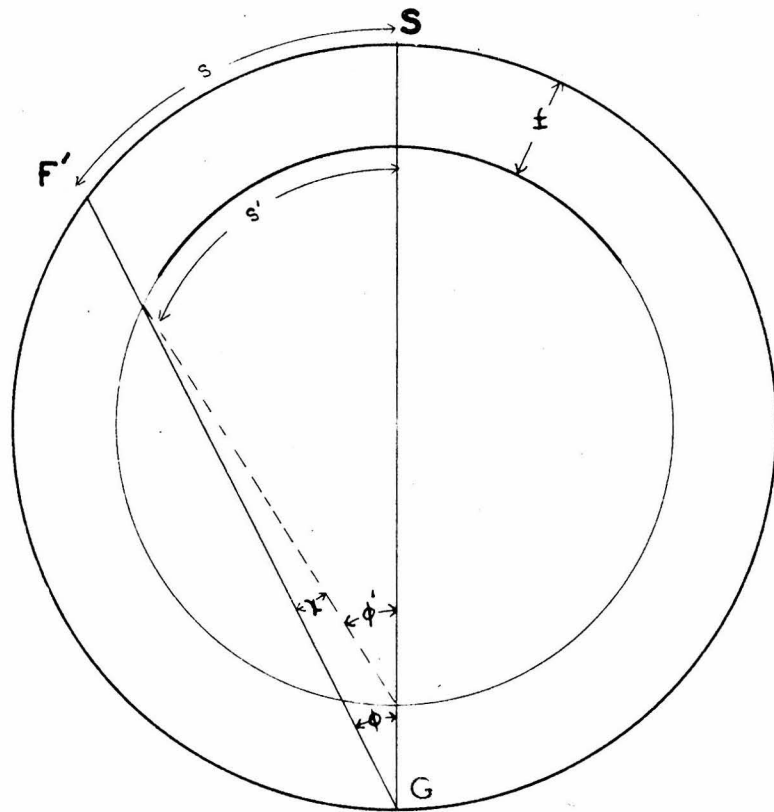an excellent check on the validity of our corrections.
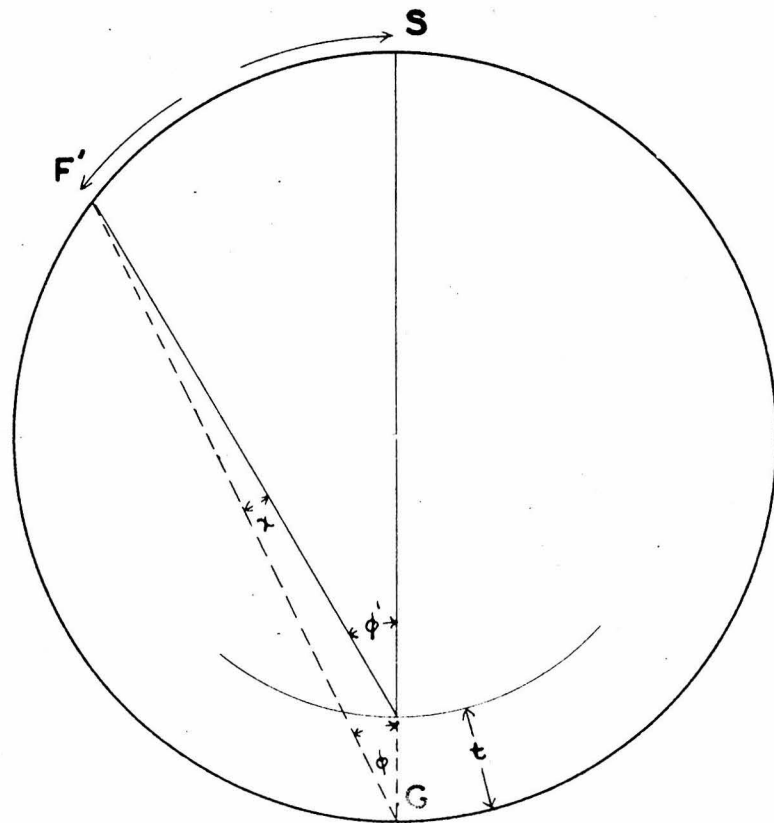
FIG 2 EFFECT OF FILM THICKNESS

FIG 3 EFFECT OF SAMPLE THICKNESS

ERRORS OF THE CAMERA

As the errors are all small they will be treated as independent.

<u>Thickness of the photographic film</u>. The effect is to broaden the lines and shift the maximum toward the slit. From Fig. 2, letting f be the thickness of the photographic film,

$$\emptyset = \frac{s}{D} \qquad \text{and} \qquad \emptyset' = \frac{s'}{D - 2f}$$

but $\qquad \emptyset' = X + \emptyset \qquad$ and $\qquad X = \frac{f}{D - 2f} \tan \emptyset$

so $\qquad s' = s(1 - \frac{2f}{D}) + f \tan \emptyset$

and since $\qquad \tan \emptyset = \frac{s}{D} + \frac{s^3}{3D^3} + \cdots$

therefore $\qquad s' = s(1 - \frac{f}{D} + \frac{s^2 f}{3D^3})$

The x-ray film has emulsion on both sides and if they are equally affected the maximum is shifted by $\frac{s - s'}{2}$. The correction to be added to the measured s is $\quad \triangle s_d = \frac{Sf}{2D}(1 + \frac{S^2}{3D^2})$. This error if uncorrected would introduce at most an error in d of 0.007%.

<u>Thickness of the sample</u>. The effect is to shift the maximum towards the slit S. Using Fig. 3 we see that $\emptyset$ is the measured angle but $\emptyset'$ is the angle that should be used in the calculation. As

$$\emptyset' = \emptyset + X \qquad\qquad \text{where} \quad X = \frac{t}{D - t} \tan \emptyset, \quad t \text{ being the}$$

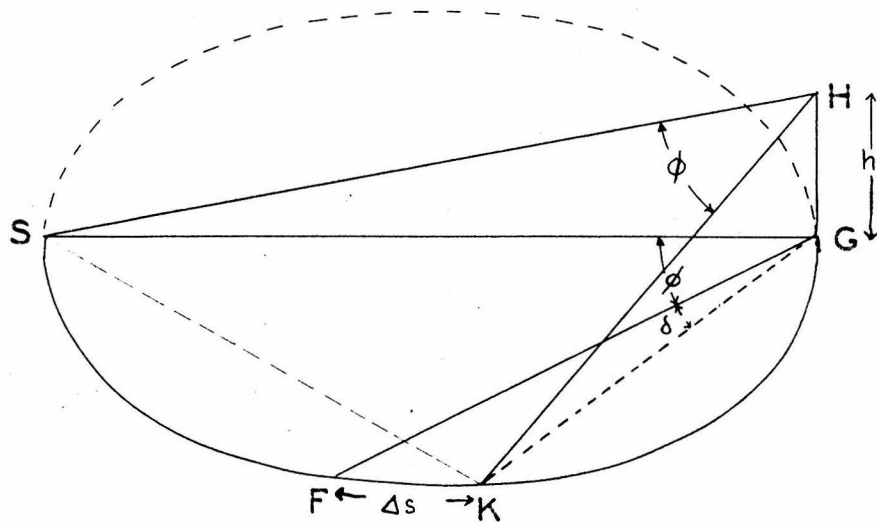film thickness, then $\qquad \emptyset' = \emptyset + \frac{t}{D - t} \tan \emptyset \quad$ or

FIG 4 EFFECT OF VERTICAL DIVERGENCE

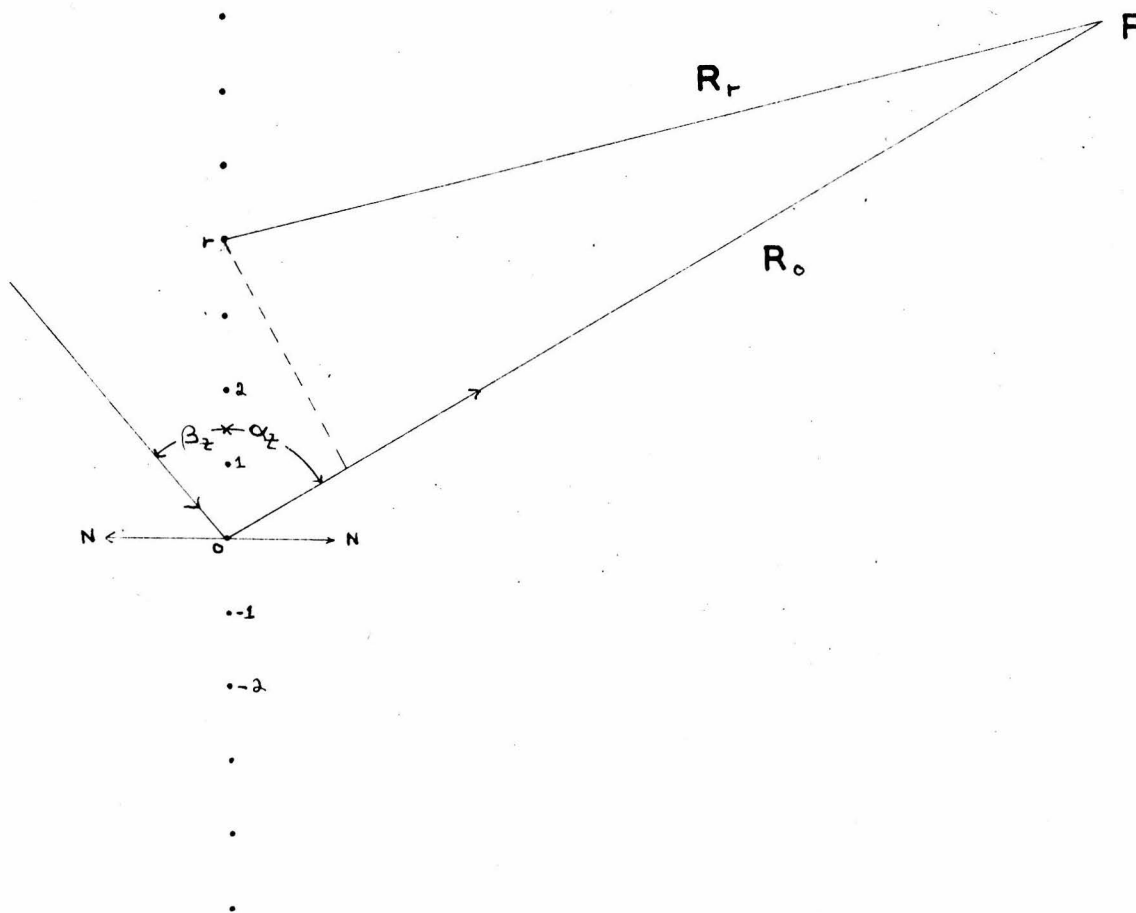
FIG 5 DIFFRACTION OF A LINE GRATING

$$\phi' = \frac{s}{D}\left\{1 + \frac{t}{D}(1 + \frac{s^2}{3D^2})\right\}$$

As the radiation is strongly absorbed in the sample it is only the surface layer that matters. The correction to be added is

$\Delta s_t = \frac{st}{D}(1 + \frac{s^2}{3D^2})$. This error if uncorrected would introduce at most an error in d of 0.040%.

Film shrinkage is corrected by making two marks on the film with a templet just after the exposure is completed and before developing. The distance between these marks is measured after developing and the shrinkage assumed to be uniform. The shrinkage was found to vary considerably from photograph to photograph and would on the average introduce in d an error if uncorrected of 0.033%.

Vertical Divergence of the Beam. The effect is to broaden the lines and shift the maximum away from the slit. Using Fig. 4, we see that since $\angle$ SKH $\simeq \pi/2$ ~~that~~

$$SK = (h^2 + D^2)^{1/2} \sin \phi \qquad \text{but}$$

$$\sin (\phi + \delta) = \frac{SK}{D} = (1 + \frac{h^2}{D^2})^{1/2} \sin \phi = (1 + \frac{h^2}{2D^2}) \sin \phi = \sin \phi + \delta \cos\phi$$

Therefore $\qquad\qquad \delta = \frac{h^2}{2D^2} \tan \phi$

And as the image of the focal spot is approximately a uniformly illuminated rectangle, the maximum is shifted by $\delta/2$. Then

$$\Delta s_v = \frac{h^2}{4D} \tan \phi = \frac{h^2 s}{4D^2}\left[1 + \frac{1}{3}(\frac{s}{D})^2\right]$$

is the correction to be subtracted. This error if neglected would introduce at most an error of 0.021% in d. The height of the illuminated sample is 2h.

Temperature of the sample. Because of the thermal expansion of the lattice a change of one degree centigrade introduces an error of about 0.002% in d. The temperature of the camera was checked several times during every exposure and it never varied more than half a degree. The camera dimensions were not affected by temperature by an appreciable amount.

Overlapping of the α doublets. If the lattices were less than 1000 A° on a side the diffraction patterns of the components of the K α doublet would begin to overlap due to the finite resolving power of the crystal grating and the apparent maximum would be shifted in position. A method of calculating the true maximum from the apparent maximum will be given. For a lattice 300 A° long, an error in d would be introduced of 0.020% if one used the position of the apparent maximum rather than of the true maximum.

When the crystal grating was longer than 2000 A° on a side the diffraction pattern consisted of distinct spots. As the length of grating decreased the spots became less distinct and began to overlap and when the length of grating was less than 1000 A° the lines on the photographic plate became quite uniform and began to broaden out considerably. From the amount of this broadening it is possible to calculate the length of the lattice or the size of the crystal.

FINITE RESOLVING POWER OF A CRYSTAL

We shall now derive an expression which connects the shape of the diffraction pattern with the length of the lattice. During the analysis we shall make the following assumptions.

1) The crystals are rectangular parallelopipeds with a simple orthorhombic lattice with axial lengths a_x, a_y, a_z and $2N_x + 1$, $2N_y + 1$, $2N_z + 1$ particles on a side respectively. The formula derived, however, will be more general than this, for the shape of the line depends only on the length of the lattice perpendicular to the Bragg plane.

2) The crystals are oriented at random.

3) The crystals are undistorted and act independently.

4) The radiation is monochromatic.

5) Absorption and extinction are negligible

Consider first normal incidence of a plane wave on a line grating (Fig. 5) composed of $2N_z + 1$ identical particles with the distance a_z between adjacent neighbors. Each point particle will send out a spherical wave of amplitude

$$F_n = Real \; \frac{C_z}{R_n} e^{2\pi i \left(\frac{R_n}{\lambda} - \frac{t}{T} \right)}$$

where T is the period and λ the wavelength of the incident radiation, C_z is a scattering constant, and t the time. Since $(2N_z + 1)a_z \lll R_0$ we have Fraunhofer diffraction and at P the vector amplitudes add algebraically. Also $(R_0 - R_r) = ra_z \cos \alpha_z$ so the amplitude at P is

$$F = F_0 + \sum_{-m}^{m} F_n =$$

$$Real \frac{C_z}{R_o} \left[e^{2\pi i \left(\frac{R_o}{T} - \frac{t}{T} \right)} + e^{\frac{2\pi i}{\lambda} \left(R_o - \frac{t\lambda}{T} + a_z \cos\alpha_z \right)} + e^{\frac{2\pi i}{\lambda} \left(R_o - \frac{t\lambda}{T} - a_z \cos\alpha_z \right)} \cdots \right.$$

$$\left. + e^{\frac{2\pi i}{\lambda} \left(R_o - \frac{t\lambda}{T} + a_z N_z \cos\alpha_z \right)} + e^{\frac{2\pi i}{\lambda} \left(R_o - \frac{t\lambda}{T} - a_z N_z \cos\alpha_z \right)} \right]$$

$$= Real \frac{C_z}{R_o} e^{2\pi i \left(\frac{R_o}{\lambda} - \frac{t}{T} \right)} \left[1 + e^{\frac{2\pi i}{\lambda} a_z \cos\alpha_z} \cdots + e^{-\frac{2\pi i}{\lambda} a_z N_z \cos\alpha_z} \right]$$

and if the incident plane radiation is not normal but makes an angle

β_z with the grating we have

$$F = Real \frac{C_z}{R_o} e^{2\pi i \left(\frac{R_o}{\lambda} - \frac{t}{T} \right)} \left[1 + e^{\frac{2\pi i}{\lambda} a_z (\cos\alpha_z + \cos\beta_z)} \cdots + e^{\frac{2\pi i}{\lambda} a_z N_z (\cos\alpha_z + \cos\beta_z)} \right]$$

Summing the geometric series we find

$$F = Real \frac{C_z}{R_o} e^{2\pi i \left(\frac{R_o}{\lambda} - \frac{t}{T} \right)} \left\{ \frac{\cos \frac{2\pi a_z N_z}{\lambda} (\cos\alpha_z + \cos\beta_z) - \cos \frac{2\pi a_z (N_z+1)}{\lambda} (\cos\alpha_z + \cos\beta_z)}{1 - \cos \frac{2\pi a_z}{\lambda} (\cos\alpha_z + \cos\beta_z)} \right\}$$

The average intensity over a period is independent of t and is proportional to the square of the amplitude.

$$I_z = C_z' \left\{ \frac{\cos \frac{2\pi}{\lambda} a_z N_z (\cos\alpha_z + \cos\beta_z) - \cos \frac{2\pi}{\lambda} a_z (N_z+1)(\cos\alpha_z + \cos\beta_z)}{1 - \cos \frac{2\pi}{\lambda} a_z (\cos\alpha_z + \cos\beta_z)} \right\}^2$$

Furthermore, since N_Z is large almost all the energy will be found in

the range $\frac{2\pi}{\lambda} a_z (\cos\alpha_z + \cos\beta_z) = 2 m_z \pi$ (the maximum), m_z

being an integer, to $\frac{2\pi}{\lambda} a_z N_z (\cos\alpha_z + \cos\beta_z) = (2m_z \pm 1) \pi$ (the first minima

on either side). Hence $\frac{2\pi}{\lambda} a_z (\cos\alpha_z + \cos\beta_z)$ may be considered as

differing from $m_z \pi$ by a small amount, and expanding we find

$$I_z = C_z'' \frac{\sin^2\left\{N_z \frac{2\pi}{\lambda} d_z (\cos\alpha_z + \cos\beta_z)\right\}}{\left[2m_z \pi - \frac{2\pi}{\lambda} d_z (\cos\alpha_z + \cos\beta_z)\right]^2}$$

For a three dimensional grating the total intensity will be

$$I = I_z I_y I_x = C_z'' C_y'' C_x'' \frac{\sin^2\left\{\frac{2\pi}{\lambda} N_z d_z (\cos\alpha_z + \cos\beta_z)\right\}}{\left[2m_z \pi - \frac{2\pi}{\lambda} d_z (\cos\alpha_z + \cos\beta_z)\right]^2} \times$$

$$\frac{\sin^2\left\{\frac{2\pi}{\lambda} N_y d_y (\cos\alpha_y + \cos\beta_y)\right\}}{\left[2m_y \pi - \frac{2\pi}{\lambda} d_y (\cos\alpha_y + \cos\beta_y)\right]^2} \times \frac{\sin^2\left\{\frac{2\pi}{\lambda} N_x d_x (\cos\alpha_x + \cos\beta_x)\right\}}{\left[2m_x \pi - \frac{2\pi}{\lambda} d_x (\cos\alpha_x + \cos\beta_x)\right]^2}$$

where α_x, α_y, α_z are not independent but satisfy $\cos^2\alpha_z + \cos^2\alpha_y + \cos^2\alpha_x = 1$

and also β_x, β_y, β_z must satisfy $\cos^2\beta_x + \cos^2\beta_y + \cos^2\beta_z = 1$
The maximum value of I occurs when the three denominators vanish
simultaneously. For a general wavelength the Bragg maximum will occur
when $\cos\alpha_z = \cos\beta_z = \frac{\lambda}{2d_z}$ $(m_z = 1)$, $\alpha_y = -\beta_y = \frac{\pi}{2} - \alpha_z$ $(m_y = 0)$
and $\alpha_x = \beta_x = \frac{\pi}{2}$ $(m_x = 0)$ (or any permutation of x, y, z).
(If there is a particular wavelength such that $\cos\alpha_x + \cos\beta_x = \frac{m_x \lambda}{d_x}$
$\cos\alpha_y + \cos\beta_y = \frac{m_y \lambda}{d_y}$ and $\cos\alpha_z + \cos\beta_z = \frac{m_z \lambda}{d_z}$
simultaneously where $m_x, m_y, m_z \neq 0$, we will have a Laue
maximum). We are interested in the diffraction pattern along the
arc SF in the plane SGF and the incident and diffracted wave normals
lie in this plane. Since nearly all the energy goes into a region
close to the central maximum, we will set $\alpha_x = \beta_x = \frac{\pi}{2} - \varepsilon$
where $\varepsilon \ll 1$ and let $\beta_z = \beta_0 + \delta$ where $\cos\beta_0 = \cos\alpha_0 = \left(\frac{4d_z}{2\lambda}\right)^{-1}$
and $\delta \ll 1$, and finally let $\alpha_z = \alpha_0 - \delta + \omega = \beta_0 - \delta + \omega$ where

$\omega \ll 1$. Then since ε and δ are small they can be varied independently. The cosine condition then requires that

$$\alpha_\eta = \frac{\pi}{2} - (\alpha_0 - \delta + \omega) \qquad \text{and} \qquad \beta_\eta = -\frac{\pi}{2} + (\beta_0 + \delta)$$

When we make these substitutions I becomes

$$I = C_z'' C_y'' C_x'' \frac{\sin^2 \frac{2\pi}{\lambda} N_z a_z \omega \sin\alpha_0}{\left(\frac{2\pi}{\lambda} a_z \omega \sin\alpha_0\right)^2} \times \frac{\sin^2 \frac{2\pi}{\lambda} N_\eta a_\eta (2\delta - \omega) \sin\alpha_0}{\left(\frac{2\pi}{\lambda} a_\eta (2\delta - \omega) \sin\alpha_0\right)^2} \times \frac{\sin \frac{4\pi}{\lambda} N_x a_x \varepsilon}{\left(\frac{4\pi}{\lambda} a_x \varepsilon\right)^2} d\delta d\varepsilon$$

This is the intensity in the direction ω from the central maximum F (Fig. 6) in the plane SGH when the crystal is oriented in the range $d\delta\, d\varepsilon$. Then by integrating over δ and ε we will take into consideration the random orientations of the crystals. Our substitutions have been so constructed that δ and ε can be integrated independently and during the integration the angle SGF" remains constant (Fig. 6). It is sufficient to integrate over the central maximum. Since

$$\int_{\text{central max}} \frac{\sin^2 \frac{4\pi}{\lambda} N_x a_x \varepsilon}{\left(\frac{4\pi}{\lambda} a_x \varepsilon\right)^2} d\varepsilon = \frac{N_x \lambda}{4\pi a_x} \int_{\text{central max}} \frac{\sin^2 \frac{4\pi}{\lambda} N_x a_x \varepsilon}{\left(\frac{4\pi}{\lambda} N_x a_x \varepsilon\right)} d\left(\frac{4\pi}{\lambda} N_x a_x \varepsilon\right)$$

$$= \frac{N_x \lambda}{4\pi a_x} \int_{-\pi}^{\pi} \frac{\sin^2 u}{u^2} du = K \frac{N_x \lambda}{4\pi a_x}$$

and $$\int_{\text{central max}} \frac{\sin^2 \frac{2\pi}{\lambda} N_\eta a_\eta (2\delta - \omega) \sin\alpha_0}{\left(\frac{2\pi}{\lambda} a_\eta (2\delta - \omega) \sin\alpha_0\right)^2} d\delta = \frac{N_\eta \lambda}{4\pi a_\eta \sin\alpha_0} \int_{-\pi}^{\pi} \frac{\sin^2 u}{u^2} du$$

$$= K \frac{N_\eta \lambda}{4\pi a_\eta \sin\alpha_0}$$
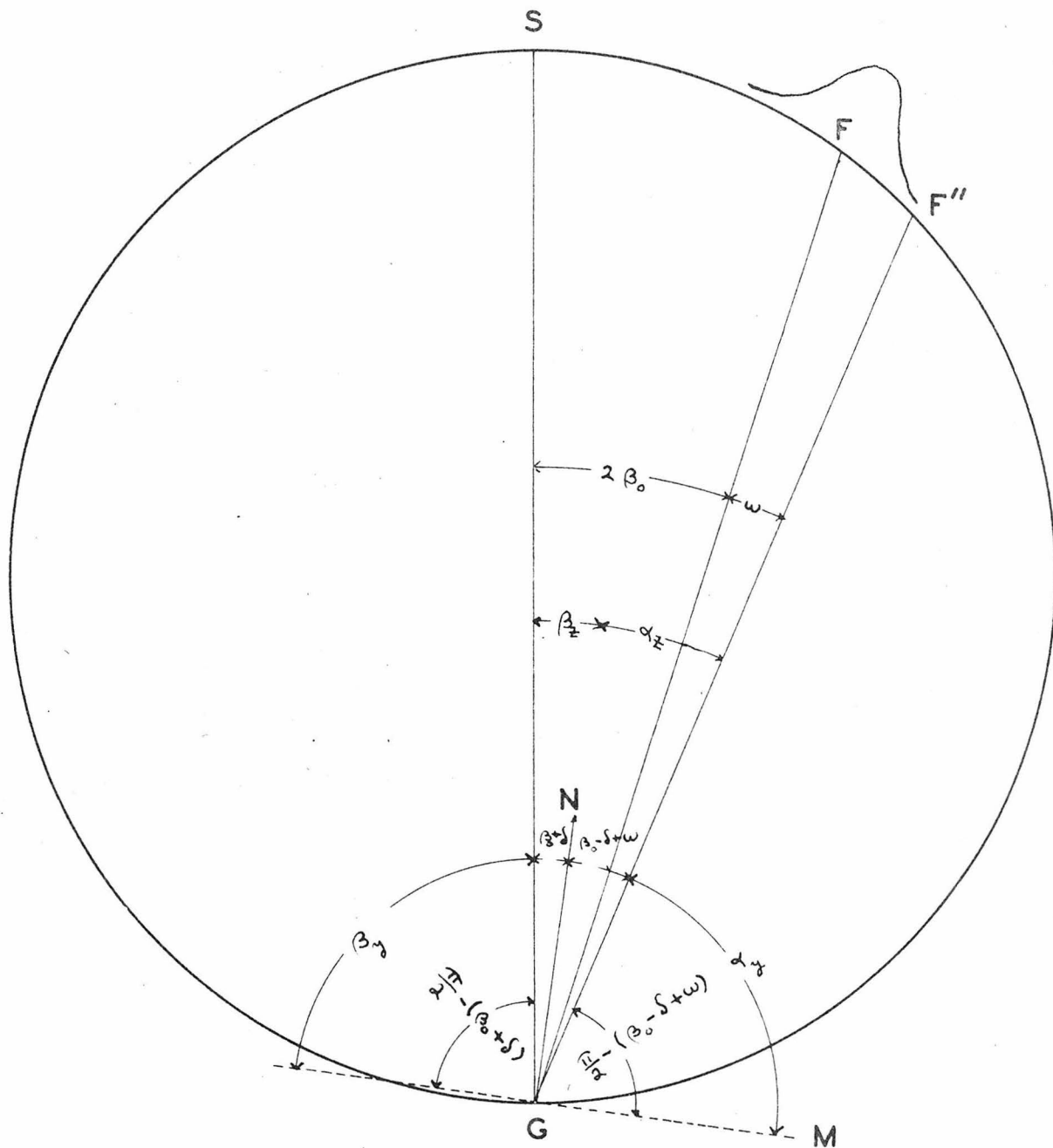
FIG 6 ORIENTATION OF THE CRYSTAL GRATING $(\alpha_x = \alpha_y = \pi/2)$

Then $I(\omega) = C'' \left(\dfrac{N_x}{a_x}\right)\left(\dfrac{N_y}{a_y \sin\alpha_0}\right) \dfrac{\sin^2 \frac{2\pi}{\lambda} N_z a_z \omega \sin\alpha_0}{\left(\frac{2\pi}{\lambda} a_z \omega \sin\alpha_0\right)^2}$

and we see that the shape of the line is independent of N_X, a_X, N_y and a_y and these factors affect only the total intensity. However, since x, y, z can be interchanged the diffraction pattern will consist of the sum of three patterns of different widths and intensities. For the moment then let us consider the crystals as cubic with a cubic unit cell.

Experimentally we determine the shape $I(\omega)$ and from it we wish to determine $2N_z a_z$ the depth of the lattice. It is most convenient to do this by measuring the average width which we define as the area under the curve divided by the maximum height. As $I_{max}(\omega) = I(\omega=0) = C N_z^2$

and $Area = \displaystyle\int_{central\ max} I(\omega)d\omega = \dfrac{C N_z \lambda}{2\pi a_z \sin\alpha_0} \int_{-\pi}^{\pi} \dfrac{\sin^2 u}{u^2} du = \dfrac{2.84\ C N_z \lambda}{2\pi a_z \sin\alpha_0}$

and since $\displaystyle\int_{-\pi}^{\pi} \dfrac{\sin^2 u}{u^2} du = 2.84$, then the average breadth of the

diffraction pattern is $B = \dfrac{Area}{I_{max}} = \dfrac{2.84\ \lambda}{2\pi a_z N_z \sin\alpha_0}$. Let $\Lambda = 2N_z a_z$

be the length of the crystal in the z direction; then $B = \dfrac{0.90\ \lambda}{\Lambda \sin\alpha_0}$

where B is expressed in radians. If we had used the breadth at the point of half maximum we would find $B' = \dfrac{0.89\lambda}{\Lambda \sin\alpha_0}$

Scherrer[9] gives $B' = \dfrac{0.94\ \lambda}{\Lambda \sin\alpha_0}$ in his derivation based on similar assumptions. Various investigators have calculated the value of the numerical coefficient for various shaped crystals and found that the line breadth is not particularly sensitive to variations in shape,

giving values ranging from .9 to 1.1.

When the cubic lattice does not have the same number of
particles on each side, our formula for B when applied to the observed
diffraction pattern gives for Λ the arithmetic mean value, $\frac{2}{3}(N_x + N_y + N_z)d$
Furthermore, let us consider the case where the cubic crystals have N
particles on each side but let the crystals be of different sizes.
Let the number of size N be $f(N)$. Then using our formula for B we
find

$$\frac{\Lambda}{d} = \frac{\int_0^\infty N^4 f(N)\, dN}{\int_0^\infty N^3 f(N)\, dN} = N_0 \frac{\int_0^\infty \left(\frac{N}{N_0}\right)^4 f\left(\frac{N}{N_0}\right) d\left(\frac{N}{N_0}\right)}{\int_0^\infty \left(\frac{N}{N_0}\right)^3 f\left(\frac{N}{N_0}\right) d\left(\frac{N}{N_0}\right)} = K' N_0$$

where N_0 is the maximum value of $f(N)$ and if we know $f\left(\frac{N}{N_0}\right)$ we can
calculate the value of the numerical constant K. For distributions
of particles we would experimentally expect this numerical constant
will not be greatly different from unity. On the average I think our
formula for B will give the most probable value of the length of the
lattice within 25%.

It is necessary to correct for slit width and vertical diver-
gence which give appreciable symmetric line broadening. In making these
corrections it will be necessary to expand $\int_0^a \frac{\sin^2 u}{u^2}\, du$
in a series and it will be very inconvenient to use more than two terms.

As $\int_0^a \frac{\sin^2 u}{u^2}\, du = a - \frac{a^3}{9} + \frac{2}{225} a^5 \cdots$

if we keep a $< 3/2$ two terms will represent the integral within 5%
error.

Each section of the slit of width $d\beta$ will give rise to a separate pattern with its maximum at a different position along SFF" (Fig. 6) but the resultant pattern which is the sum of all the separate patterns will be symmetric and the position of its maximum will be unchanged ($\omega = o$). Let the angular width subtended at the crystal sample by the rectangular slit be 2β. The area under the curve will be the sum of the areas due to each section of the slit of width $d\beta$.

$$A(\omega) = \frac{2.84 \, CN\lambda}{2\pi d \sin\alpha_0} \times 2\beta$$

The intensity distribution is given by

$$I(\omega) = C \int_{-\beta}^{\beta} \frac{\sin^2 \frac{2\pi}{\lambda} Nd(\omega+\beta)\sin\alpha_0}{(\frac{2\pi}{\lambda} d(\omega+\beta)\sin\alpha_0)^2} d\beta$$

and while this cannot be integrated directly its maximum value can be calculated. Before we do this let us include the correction due to the vertical divergence of the beam. We saw before that its effect is to spread out the intensity curves and shift the maximum to the point $\omega = \delta/2$. The area under the curve is

$$A(\omega) = \frac{2.84 \, CN\lambda}{2\pi d \sin\alpha_0} \times 2\beta \, 2\delta$$

and the intensity distribution is given by

$$I(\omega) = 2C \int_{0}^{\delta} \int_{-\beta+\delta}^{\beta+\delta} \frac{\sin^2 \frac{2\pi}{\lambda} Nd(\omega+\beta)\sin\alpha_0}{(\frac{2\pi}{\lambda} d(\omega+\beta)\sin\alpha_0)^2} d\beta \, d\delta$$

We can now calculate I_{max} (using the fact that it occurs at $\omega = \delta/2$) by expanding $\sin^2 u / u^2$ in a series and integrating term by term. Using only two terms the result is

$$I(\omega = \delta/2) = 2CN\beta\delta \left\{ 2N - \left(\frac{2\pi}{\lambda} \Lambda N \sin\alpha_0\right)^2 N \left(\frac{2}{9}\beta^2 + \frac{1}{2}\delta^2\right) \right\}$$

Thus

$$B = \frac{Area}{I_{max}} = \frac{2.84\lambda}{2\pi\Lambda N \sin\alpha_0 \left\{ 1 - \left(\frac{2\pi}{\lambda}\Lambda N \sin\alpha_0\right)^2 \left(\frac{\beta^2}{9} + \frac{\delta^2}{4}\right) \right\}}$$

For this formula to be a good approximation

$$\frac{\pi}{\lambda} \Lambda \left(\beta + \frac{\delta}{2}\right) \sin\alpha_0 \leq 3/2$$

The largest crystals we will try to measure have $\Lambda = 1000$ A°, the largest value of $\sin\alpha_0$ we will use is 0.25, the shortest wavelength 1.54 A°, and the largest value of $\delta/2$ used was 1.5×10^{-3}. This requires that $\beta \leq 2.3 \times 10^{-3}$ or in our camera the slit should be equal or less than 0.8 mm. A slit was built which had this width. When the expression for B is put into the practical form for the camera used, it becomes

$$\Lambda = \frac{5.53 \times 10^2 \lambda}{Bs \left\{ 1 - \frac{\Lambda^2 s^2}{\lambda^2}(4.6 \times 10^{-8} + 4.9 \times 10^{-10} s^2) \right\}}$$

At first the second term in the denominator is neglected and a preliminary value of Λ found. This is then inserted into the correction term and a final value of Λ calculated. B and s are both expressed in centimeters. The shape of the diffraction pattern was experimentally determined by taking a microphotometer trace of the photograph. As the lines on the photographs were curved, a set of circular defining slits having approximately the same radius of curvature as the lines on the photograph was built. Because of this curvature the height of

FIG 7 MICROPHOTOMETER TRACE OF AG SAMPLE
FOR CU K_α FROM THE $(5\bar{1}1)\,(333)$ PLANES

$\Lambda = 280\,°A$

K_{α_2}

K_{α_1}

$F(s)$

$\frac{1}{2}f(s+\delta)$

$f(s)$

$2.3 \times 10^{-3}\,°A$

s
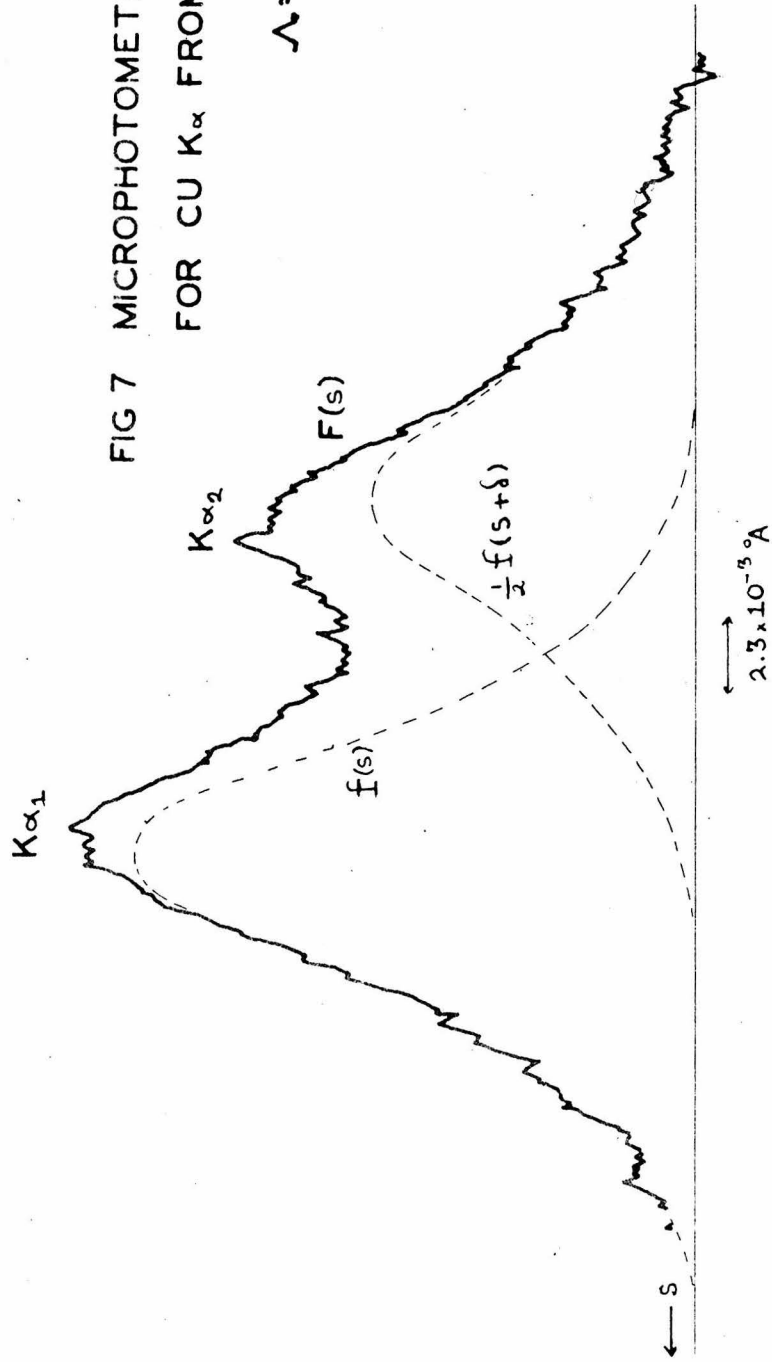
the illuminated portion of the photograph (perpendicular to the axis
of resolution) was kept as small as possible. The density of the film
was low so that the galvanometer deflection should be proportional to
the opacity of the film. A typical microphotometer trace is shown in
Fig. 7. The overlapping doublets were decomposed by using the doublet
separation taken from other photographs where the overlapping was very
slight and taking the intensity ratio of the K_{α_1} to K_{α_2} as 2. Let
$F(s)$ be the observed curve[10], then

$$F(s) = f(s) + \frac{1}{2} f(S + \delta) \qquad \text{and}$$

$$f(s) = F(s) - \frac{1}{2} F(s + \delta) + \frac{1}{4} F(s + 2\delta) \cdots$$

However, because of the geometry of the spectrograph δ is not a
constant but proporional to $1/s$, so care must be taken in applying the
above equation. Also because of this the curves will be slightly
unsymmetrical, being stretched out slightly on the long wavelength
side (smaller s). If it is only desired to fix the maximum of $f(s)$
this is done by plotting

$$f'(s) = F'(s) - \frac{1}{2} F'(s + \delta) + \frac{1}{4} F'(s + 2\delta) \cdots$$

for several points in the region of the suspected maximum, finding
some positive and some negative values. Then the point $f'(s) = 0$
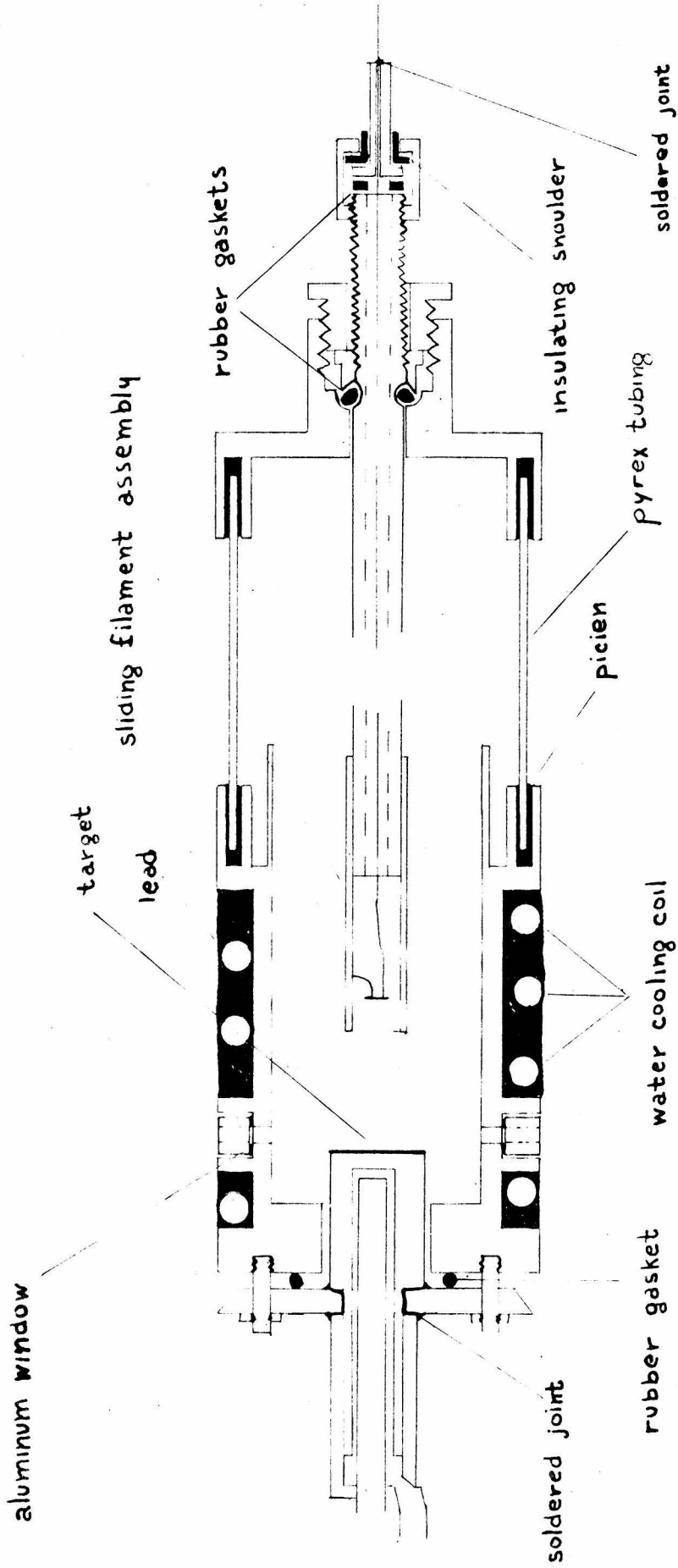will give the maximum of $f(s)$.

rubber gaskets

soldered joint

insulating shoulder

pyrex tubing

picien

sliding filament assembly

target

lead

water cooling coil

aluminum window

soldered joint

rubber gasket

FIG 8 SCHEMATIC DRAWING OF THE X-RAY TUBE

THE X-RAY TUBE

The source of radiation was an interchangeable target x-ray
tube designed and constructed by Dr.H.Kirkpatrick. I assembled the
tube for the first time and made minor revisions in the design. The
tube is shown schematically in Fig. 8. The heated filament assembly
was of commercial design and the current was supplied by an insulation
transformer and adjusted by a series resistance in the secondary. Its
distance from the target could be adjusted by sliding the whole assembly
in its holder, and 3/4 of an inch distance between the end of the fila-
ment assembly and the target gave a good focal spot. The target and
body of the tube were grounded and unrectified high voltage applied to
the cathode. The x-rays could emerge through three holes in the body
of the tube and close to the target so that a line focus was obtained.
These holes were made vacuum tight by covering with 0.001 inch aluminum
foil and sealing with picein. The foil was held firmly in place by
the slotted brass cleats shown in Fig. 8. The body of the tube as
well as the target were water cooled. The body was covered with lead
to prevent stray radiation. Two targets were built using ordinary
copper rod. One served as a source of copper radiation while the other
was chromium plated. These two materials were selected because the K
component of their characteristic radiation gave possible reflections
from silver and aluminum crystals with the Bragg angle equal to nearly
90°.

The tube was evacuated by a single stage brass oil pump built at Stanford University and used n-Butyl Phthlate. A Cenco Megavac was used as a forepump. The pressure was determined by means of a Knudsen Gauge, and once the tube was made "hard" the pressure could be kept about 5×10^{-6} mm. Hg, even while running. There was a low temperature trap between the pump and the tube and a mixture of acetone and solid carbon dioxide was employed as a refrigerant.

The actual operation of interchanging a target took about fifteen minutes but it required twelve hours pumping before it was hard enough to run again. One burned out filament was replaced. The heater wire is unsoldered at the extreme end of the cathode, and the filament assembly was removed through the target end. A new filament assembly was inserted. This seemed preferable to taking apart the cathode end of the tube which would involve replacing a rubber gasket which could not be conveniently painted if desired.

The camera is the same one used by Bollman and is fully described in his thesis[11]. A new rectangular slit of 0.80 mm width and 1.20 mm height was constructed by making a new slit plug of the same design but with a very small pin hole which was filed into a rectangular opening with a jeweler's file. The slit was replaced on the circumference within 0.001 inches. The camera was made vacuum tight by placing a piece of 0.0005 inch aluminum foil over the window, painting generously with glyptal, and clamping it firmly in place with the face plate. The camera was placed on a movable table drilled with three

holes into which the three legs of the camera fitted. The position
of the table was adjusted until the image of the focal spot was as
intense as possible and the rectangular image was symmetric across
the equatorial plane of the camera. The table was then waxed in place
so that the camera could be removed and then replaced in the identical
position. A film was placed diametrically opposite the slit and an
exposure of the image of the focal spot taken. The image was rectangu-
lar, being 3.2 by 0.8 cm with the greater dimension being the vertical
one. The diameter of the camera was checked and found to be identical
with that given by Bollman. (D = 6.905 inches). The camera slit was
as close to the target as possible, the distance between the center of
the target and the slit being about 4.5 cm. The camera was evacuated
to prevent scattering of the x-rays by the air.

The high voltage was controlled by means of an autotransformer
in the primary of the high voltage transformer. It was found that the
greatest contrast in the photographs was obtained when the copper
target was operated at 30,000 volts (r.m.s.) and the chromium target
at 20,000 volts (r.m.s.). A nickel filter was tried with the copper
radiation but the contrast was not increased. A normal exposure with
copper K_α radiation was one hour with 10 milliamperes current, and
with chromium K_α two hours with 10 milliamperes current. The powder
sample was placed on the camera circumference by making a paste of it
with a little Duco cement diluted about three to one with acetone.
This made an excellent binder with very little body. The foil, and

aluminum evaporated on mica were attached to the camera wall with a
small amount of stopcock grease.

The templet for making the fiducial marks on the film consisted
of two phonograph needles firmly imbedded in a brass bar. The film
was removed from the camera and placed between two plane and parallel
blocks of wood with the top block having two small holes through which
the needles could pass, and a light impression of the needle points
was made.

After the film was developed it was placed on a ground glass
viewer and a faint line ruled on each maximum of the diffraction pattern.
It was easy to see the point of maximum intensity with the eye but the
lines were so broad that they could not be distinguished under the
microscope of the comparator. The distances between the ruled lines
and between the needle points were measured on the comparator, the
ruled lines appearing quite sharp. Actually with such broad lines and
the crude way of marking the points of maximum intensity the accuracy
of measurement possible on the comparator is an unnecessary refinement.
But this method of measurement was used because after the lines have
been ruled on the photograph the comparator is an extremely impartial
instrument. I found that in making several measurements on the distance
between two points with a pair of dividers (as well as in recording
the swings of the pointer of the balance in the weighings) there was
a strong tendency to repeat the first observation. In the cases where
a microphotometer trace was taken the ruled lines appeared as very

narrow peaks and did not distort the general shape of the curve. Comparing the position of the ruled maximum with real maximum I estimate the error in using the ruled maximum to be for a single measurement 0.01 cm which represents at most an error of 0.009% in the lattice constant. Furthermore with the large number of photographs used, such errors, which I do not believe were systematic, should cancel out.

RESULTS OF THE X-RAY MEASUREMENTS

Both aluminum and silver are face-centered cubic crystals, and for such systems the interplanar distance for the (511) and (333) planes (and all permutations of the indices) is the same. If there is any change of shape of the unit cell the interplanar distances for the (333), $(\bar{3}33)$, $(3\bar{3}3)$ and $(33\bar{3})$ might all be different and these four planes would give rise to four separate diffraction patterns. If the distortion is small the patterns will overlap and give the appearance of a single but broader line. In the same way, with distortion, the permutations of the (511) indices will give rise to as many as twelve non equivalent interplanar distances.

For a general lattice with a_1, a_2, a_3 being the axial lengths and $\alpha_1, \alpha_2, \alpha_3$ the interaxial angles, the interplanar distance in terms of the reciprocal lattice (defined as $\underline{a}_i \cdot \underline{b}_j = \delta_j^i$)[25] is

$$\frac{1}{\underline{d}} = h_1 \underline{b}_1 + h_2 \underline{b}_2 + h_3 \underline{b}_3$$

and

$$\left(\frac{1}{d}\right)^2 = h_1^2 b_1^2 + h_2^2 b_2^2 + h_3^2 b_3^2 + 2h_1 h_2 \underline{b}_1 \cdot \underline{b}_2 + 2h_2 h_3 \underline{b}_2 \cdot \underline{b}_3 + 2h_3 h_1 \underline{b}_3 \cdot \underline{b}_1$$

and from our definition of b

$$b_1^2 = \frac{\sin^2 \alpha_1}{a_1^2 (1 - \cos^2 \alpha_1 - \cos^2 \alpha_2 - \cos^2 \alpha_3 + 2\cos\alpha_1 \cos\alpha_2 \cos\alpha_3)}$$

$$\underline{b}_1 \cdot \underline{b}_2 = \frac{\cos\alpha_1 \cos\alpha_2 - \cos\alpha_3}{a_1 a_2 (1 - \cos^2 \alpha_1 - \cos^2 \alpha_2 - \cos^2 \alpha_3 + 2\cos\alpha_1 \cos\alpha_2 \cos\alpha_3)}$$

Now we shall consider the case of cubic crystals which have undergone a small distortion where $a_1 = a + \Delta a_1$, $a_2 = a + \Delta a_2$, $a_3 = a + \Delta a_3$, $\alpha_1 = \frac{\pi}{2} - \epsilon_1$, $\alpha_2 = \frac{\pi}{2} - \epsilon_2$ and $\alpha_3 = \frac{\pi}{2} - \epsilon_3$. Then

$$\frac{1}{d^2} = \frac{h_1^2}{(a + \Delta a_1)^2} + \frac{h_2^2}{(a + \Delta a_2)^2} + \frac{h_3^2}{(a + \Delta a_3)^2} - \frac{2h_1 h_2 \epsilon_3}{a^2} - \frac{2h_2 h_3 \epsilon_1}{a^2} - \frac{2h_3 h_1 \epsilon_2}{a^2}$$

$$d \simeq \frac{a}{(h_1^2 + h_2^2 + h_3^2)^{1/2}} + \frac{h_1^2 \Delta a_1 + h_2^2 \Delta a_2 + h_3^2 \Delta a_3}{h_1^2 + h_2^2 + h_3^2} + \frac{h_1 h_2 \epsilon_3 + h_2 h_3 \epsilon_1 + h_3 h_1 \epsilon_2}{h_1^2 + h_2^2 + h_3^2} a$$

We see that for the (511) and the (333) planes the first term is the same. For any change in the length of the lattice, the second term always has the same sign for both positive and negative values of the h's. However, the third term is sometimes positive and sometimes negative and its average value is zero. Thus when we find that our diffraction patterns are broadened when the lattice is distorted by working it may be caused by either the finite resolving power of the shorter crystal grating or by the fact that we have formed several planes with nearly the same interplanar distance. However, if the position of the central maximum is unchanged we can say positively that there is no change in the axial lengths for $h_1^2 \Delta a_1 + h_2^2 \Delta a_2 + h_3^2 \Delta a_3$ cannot vanish for (333), (511), (151), and (115) simultaneously except $\Delta a_1 = \Delta a_2 = \Delta a_3 = 0$. This

assumes that all the crystallites are distorted in the same
manner. Furthermore, since a cubic face-centered lattice is
a close packed configuration it is difficult to see how the inter-
axial angles could be changed without altering the lengths of the
sides.

Since the volume of the unit cell is

$$V = a_1 a_2 a_3 \left[1 - \cos^2\alpha_1 - \cos^2\alpha_2 - \cos^2\alpha_3 + 2\cos\alpha_1\cos\alpha_2\cos\alpha_3 \right]^{1/2}$$

then when the unit cell is distorted as on the previous page the
volume becomes, considering only first order terms,

$$V = a^3 + a^2 \left(\Delta a_1 + \Delta a_2 + \Delta a_3 \right)$$

This second term is proportional to the average value of
$h_1^2 \Delta a_1 + h_2^2 \Delta a_2 + h_3^2 \Delta a_3$ when we consider all permutations of the
Miller indices. Therefore, if the latter term is zero (average
value of the interplanar distance unchanged), then the distortion
we have pictured changes the volume of the unit cell by second order
terms only. As the largest first order change in some interplanar
distance required to explain the observed width of line is 0.2%, any
second order effects are negligible.

The wavelengths used in the calculations were

	Siegbahn units	Absolute Angstroms
[12] Cu Kα_2	1.541232	1.544361
Cu Kα_1	1.537395	1.540516
[13] Cr Kα_2	2.28891	2.29356
Cr Kα_1	2.28503	2.28967

The results of the powder photographs of aluminum are as follows:

Lattice Constant of Annealed Aluminum Powder (99.98%) at 25.0° C

Radiation and Planes	a
Cu Kα (511) (333)	4.04919 A (absolute)
	4.04925
	4.04926
	4.04933
	4.04935
	4.04942
Cr Kα (222)	4.04914
	4.04919
	4.04924
	4.04937

Av. 4.04927 ± 0.00002

The estimated length of lattice was 2000 A°.

Lattice Constant of Annealed Aluminum Foil (99.80%) at 25.0 C

Radiation and Planes		a
Cu K	(511) (333)	4.04904 A° (absolute)
		4.04905
		4.04910
		4.04917
		4.04922
		4.04933
Cr K	(222)	4.04876
		4.04895
		4.04905
		4.04913
	Av.	4.04908

The estimated length of lattice was 1500 A°.

Lattice Constant of Worked Aluminum Powder (99.98%) at 25.0°C

Radiation and Planes		a	Lattice length	% change in a
Cu K_α	(511) (333)	4.04930 A° (absolute)	530 A°	0.001
Cr K_α	(222)	4.04872	740	−0.014

Lattice Constant of Worked Aluminum Foil (99.80%) at 25.0°C

Radiation and Planes		a	Lattice length	% change in a
Cu K_α	(511) (333)	4.04878 A° (absolute)	1200 A°	−0.007
		4.04917	490	0.002
Cr K_α	(222)	4.04878	740	−0.007

One may conclude that when the aluminum is worked by hammering smaller diffracting units having the same unit cell as the diffracting units in the carefully annealed sample are formed, and since a difference of 0.2% in some interplanar distances which were identical before the distortion would be required to explain the observed width and as in every case but one the maximum was shifted

by less than a 0.007% change in the average interplanar distance one concludes that the distortion occurs mainly in the layers separating the diffracting units. In all cases the microphotometer traces were symmetrical within the limitations mentioned on page 28.

Powder photographs were taken of aluminum evaporated on mica. The lines were extremely weak and difficult to measure for the sample was of the order of a wavelength of light thick. The results of the best photographs are

Lattice Constant of Evaporated Aluminum at 25.0°C

Radiation and Plane		a
Cu Kα	(511) (333)	4.0487 A° (absolute)
		4.0465
Cr Kα	(222)	4.0525

The last two measurements were from photographs where the lines were only visible on only one side of the slit, and may not be due to aluminum at all but to the mica onto which the aluminum was evaporated. It is also interesting to mention that in order to obtain the first photograph, which was the only really successful one, it was necessary to take the powder photograph immediately after the evaporation was finished or no lines were obtained. Furthermore, when a second exposure was tried one day later with the same sample used in the successful photograph the lines were no longer present. This I interpret as showing the aluminum crystals are no longer randomly orientated, but have taken up some preferred orientation on the

mica surface which was freshly cleaved just before the evaporation took place.

The results of the powder photographs of silver are as follows.

Lattice Constant of Annealed Silver (99.96%) at 25.0°C

Radiation and Planes	a	Type
Cr Kα (222)	4.08540 A° (absolute)	Powder
	4.08553	
	4.08569	
	4.08578	
	4.08578	
	4.08582	
Cu Kα (511) (333)	4.08586	
	4.08589	
	4.08596	
	4.08603	
	4.08621	
	4.08623	
Cr Kα (222)	4.08531	Foil
	4.08549	
	4.08553	
	4.08553	
	4.08574	
	4.08603	
	4.08604	
	4.08604	
Cu Kα (511) (333)	4.08543	
	4.08547	
	4.08549	
	4.08560	
	4.08566	
	4.08570	

Av. 4.08574 ± 0.00004

The estimated lattice length for both foil and powder is 2000 A°.

It will be noted that the results for silver are not as consistant as those for aluminum. This is mainly, I suspect, due to nonlinear film shrinkage, coupled with the fact that larger values

of s were used, With the large number of measurements used this
error should cancel out.

Lattice Constant of Worked Silver (99.96%) at 25.0°C

Radiation and Planes	a	Lattice Length	% change in a	Type
Cu K (511) (333)	4.08562 A°	280 A°	-0.004	Powder
	4.08530 (absolute)	230	-0.011	Foil
	4.08551	185	-0.006	Foil

Again the evidence is that the unit cell is not distorted
by working by hammering.

Six photographs using two different samples of quartz were
taken with Cu Kα radiation. The lines were indexed from similar
photographs taken by Bradley and Jay[26]. Six planes and ten different
lines were used. When lines from two different planes overlapped no
attempt to resolve them was made and they were omitted from the
calculation.

Interplanar Distances for Quartz at 26.0°C

Plane and wavelength	θ	Interplanar Distance
(216) Cu Kα$_2$	79.297°	.78429 A° (Siegbahn)
(216) Cu Kα$_1$	78.563	.78427
(234) Cu Kα$_2$	77.509	.78961
(234) Cu Kα$_1$	76.765	.78967
(421) Cu Kα$_2$	76.159	.79366
(315) Cu Kα$_1$	75.113	.79539
(420) Cu Kα$_2$	73.843	.80230
(420) Cu Kα$_1$	73.330	.80242
(331) Cu Kα$_2$	72.510	.80797
(502) Cu Kα$_1$	71.636	.80994

If we let a/c equal **k** these interplanar distances (see page 2) give rise to the following set of simultaneous equations which were solved by least squares

Residuals

21.8667	$+ \quad 2.6240 \; k^2$	$- \; a^2 =$	0	-20×10^{-4}
23.5005	$+ \quad 0.6528 \; k^2$	$- \; a^2 =$	0	31
24.0382	$+ \quad 0.0000 \; k^2$	$- \; a^2 =$	0	14
24.0310	$+ \quad 0.0000 \; k^2$	$- \; a^2 =$	0	-58
10.9659	$+ \quad 15.8162 \; k^2$	$- \; a^2 =$	0	-26
23.5163	$+ \quad 0.6299 \; k^2$	$- \; a^2 =$	0	$- 1$
15.7974	$+ \quad 9.9773 \; k^2$	$- \; a^2 =$	0	44
15.7949	$+ \quad 9.9757 \; k^2$	$- \; a^2 =$	0	6
5.7408	$+ \quad 22.1429 \; k^2$	$- \; a^2 =$	0	2
5.7410	$+ \quad 22.1440 \; k^2$	$- \; a^2 =$	0	9

giving $a^2 = 24.0368 \pm 0.0009$ and $a = 4.90275 \pm 0.00009$; also k^2 is 0.82626 ± 0.000025 and $c = 5.39362 \pm 0.00011$. When these measurements are changed into absolute Angstroms and corrected to 25.0°C using the following thermal coefficients of linear expansion, along the a axis $1.34 \; 10^{-5}$ per degree centigrade and along the c axis $0.7 \; 10^{-5}$ per degree centigrade, we find

Lattice Constants of Quartz at 25.0°C

$$a = 4.91263 \pm 0.00009 \; A° \; (absolute)$$
$$c = 5.40454 \pm 0.00011$$

There is no systematic trend to the residuals so our method of correcting for the errors of the camera is justified.

For comparison we include the results of other observers on the lattice constants of aluminum, silver and quartz.

Lattice Constants at 25.0° C

			Observer
Silver	a	4.0861 A° (absolute)	Neugebauer[27]
Aluminum	a	4.0496	"
Quartz	a	4.9132	Bradley and Jay[26]
	c	5.4044	

MOLECULAR WEIGHTS OF SAMPLES

For aluminum the molecular weight as determined by mass spectroscopic means was used. On the basis of $O_{16} = 16.0000$ its molecular weight is 26.9917[17]. (Aston's[17] value corrected to $C_{12} = 12.00388$). From the relative abundance of the isotopes of oxygen[18] the conversion factor of mass spectroscopic atomic weight to chemical atomic weight is 0.99973. When a small amount of impurity is present these foreign atoms will fit into the aluminum lattice without distorting it. Therefore the effective atomic weight is 26.989.

Al	$26.9917 \times 0.99973 \times 0.99980 =$	26.979
Si	$28.06 \times 0.00004 =$	0.001
Fe	$55.84 \times 0.00004 =$	0.002
Cu	$63.57 \times 0.00011 =$	0.007
Ti	$47.90 \times 0.00001 =$	0.000
		26.989 ± 0.001

In the case of silver the chemical molecular weight is used, and the effective molecular weight is found to be 107.858.

Ag	$107.880 \times 0.99957 =$	107.833
Pb	$207.21 \times 0.00004 =$	0.008
Fe	$55.84 \times 0.00006 =$	0.003
Si	$28.06 \times 0.00014 =$	0.004
Cu	$63.57 \times 0.00010 =$	0.006
Ca	$40.08 \times 0.00009 =$	0.004
		107.858 ± 0.002

The probable errors are estimated on the bases of the probable error of the chemical analyses.

Unfortunately there is no universal agreement about the atomic weight of silicon. The value accepted by the International Committee on Atomic Weights is based on the determination of Baxter[28], Weatherill, and Scripture who compared $SiCl_4$ and $SiBr_4$ with Ag and found the molecular weight of silicon to be 28.063 ± 0.003.

However, more recently Honigschmid[29] and Steinheil by comparing $SiCl_4$ with Ag found the molecular weight to be 28.105 ± 0.003 and Weatherill[30] and Brundage using the same method found 28.103 ± 0.003 as the molecular weight. Because of the large difference between these observers it is unsatisfactory to average their values so we shall carry through the calculation for quartz using two different values for its molecular weight, 60.063 ± 0.003 and 60.104 ± 0.003. The mass spectroscopic determination of the molecular weight of silicon gives 28.125 but this must be regarded as quite inaccurate for the calculation is based on some preliminary values of the relative abundances of the isotopes as measured by McKellar[31] using the band spectrum of SiN.

CALCULATION OF THE EXTINCTION COEFFICIENT

Equation (6.55) in Compton and Allison[19] giving the approximate extinction coefficient (along the actual path) is

$$\mu_e = \frac{4\pi \delta F}{Z \lambda \sin \theta_0}$$

where Z is the number of electrons in a unit cell, λ is the incident wavelength, θ_0 is the Bragg angle, and F is the crystal structure factor which is calculated by

$$F = \sum_j f_j \, e^{2\pi i (h\, x_j + h_2 y_j + h_3 z_j)}$$

where h_1, h_2, h_3 are the Miller indices of the plane for the Bragg angle θ_0, x_j, y_j, z_j are the positions of the jth atom in the unit cell, and f_j can be found from Pauling and Sherman[20] in terms of scattering from a free J. J. Thompson electron. The scattering from a single electron is from Compton and Allison (3.04)

$$\frac{e^4}{2r^2 m^2 c^4} (1 + \cos^2 \phi)$$

where ϕ is the angle between the primary and scattered rays and $\phi = 2\theta_0$.

δ which is *the unit decrement of* the index of refraction is found from (4.46) in Compton and Allison to be

$$\delta = \frac{n e^2 \lambda^2}{2\pi m c^2}$$

where n is the total number of electrons per cubic centimeter.

But $n = \frac{\rho}{M} \times \frac{N}{V} \times Z$ where ρ is the density in grams per cubic centimeter, M is the molecular weight, N is Avogadro's number, and V is the number of molecules per unit cell. Thus

$$\mu_e = \frac{Ne^6}{m^3 r^2 c^6} \quad \frac{\rho \lambda}{MV} \quad \frac{1 + \cos^2 2\theta}{\sin \theta} \quad \sum_j (F_j) e^{2\pi i(h_1 x_j + h_2 y_j + h_3 z_j)}$$

where F_j is the number taken from Table VII of Pauling and Sherman.

Now $\frac{Ne^6}{m^3 r^2 c^6} = \frac{6.06 \times 10^{23} \times (4.8)^6 \times 10^{-60}}{(9.03)^3 \times 10^{-84} \times (1.9)^2 \times 10^{-26} \times 3^6 \times 10^{60}} = 3.78 \times 10^{11}$

and if we express λ in Angstrom units

$$\mu_e = 3.78 \times 10^3 \frac{\rho \lambda}{MV} \quad \frac{1 + \cos^2 2\theta}{\sin \theta} \quad \sum_j (F_j) e^{2\pi i(h_1 x_j + h_2 y_j + h_3 z_j)}$$

Then for Cu Kα radiation reflected from the (333) (511) planes the depth of half penetration is for

Aluminum	1.4×10^{-4} cm	or	1.8×10^4 planes
Silver	5.8×10^{-5} cm	or	7.3×10^3

For Cr Kα radiation reflected from the (222) plane the depth of half penetration is for

Aluminum	6.1×10^{-5} cm	or	5.2×10^3 planes
Silver	1.6×10^{-5} cm	or	1.4×10^3

Thus in all cases the radiation penetrated throughout the diffracting units.

For quartz with Cu Kα radiation the depth of half penetration varies from plane to plane but is on the average about

1.3 x 10^{-4} cm or 1.6 x 10^{4} planes. The largest particles that could get through the screen were 5 x 10^{-3} cm but when a sample was viewed under a microscope the average size appeared to be about 5 x 10^{-4} cm. As the radiation could penetrate from either side this is equivalent to an effective thickness of 2.5 x 10^{-4} cm so that the x-ray information is fairly representative of all the sample used.

EFFECT OF DISTORTION ON THE METALS

We have seen that the unit cell is unchanged by working. Let us assume that samples of aluminum and silver are made up of blocks of undistorted unit cells separated by ammorphous or damaged layers of constant thickness. The measured density will be affected by these layers of constant thickness $2\Delta D$. Then the measured density will be

$$\rho = \frac{d^3 \rho_0 + 3d^2 \Delta D \rho'}{(d + \Delta D)^3}$$

or approximately $\quad \rho - \rho_0 = \frac{3\Delta D}{d}(\rho_0 - \rho')$

where ρ_0 is the true density, ρ' the density of the ammorphous or discontinuous layers, and d the length of one of the blocks. Thus for aluminum, since

$$\rho = 2.69839 \text{ gm cm}^{-3} \quad \text{for } d = 2000 \text{ A}^{\circ} \quad \text{at } 25.0^{\circ}C$$
$$\rho = 2.69801 \quad\quad\quad\quad \text{for } d = 500$$

we find $\rho_0 = 2.69853$ gm cm^{-3}. However, due to the sketchy nature of this calculation the value we will use in calculating N and e will

be the value found for the annealed sample with the probable error

equal to the difference between the annealed value $_\wedge$ plus the probable
$$\text{and } \rho_o$$

error of the annealed sample. We shall use as the density of alumin-

um at 25.0° C   2.69839 + 0.00019 gm cm^{-3}

    Following the same procedure for silver since

$$\rho = 10.4870 \text{ gm cm}^{-3} \quad \text{for d} = 2000 \text{ A}^{O} \text{ at } 25.0^{O}\text{C}$$
$$\rho = 10.4911 \quad\quad\quad\quad \text{for d} = 300$$
then$$\quad\quad \rho_o = 10.4864$$

and we will use 10.4870 ± 0.0008 gm cm^{-3} as the density of silver at

25.0^{O}C.

<center>CALCULATION OF N AND e</center>

    In making the calculations we shall give two probable errors,

the first will represent the errors in the lattice constant as com-

puted from the inner consistency of the experimental data, the error

in the density and the error in the molecular weight. The second

will include the probable error in the absolute measurement of the

wavelength of the x-rays and the error in Q. If our assumptions

are correct all the values of N and e should agree within the first

probable error, since the same value of Q and the wavelength was

used for all the substances. The value of Q^{15} used is

2.89270 ± 0.00021 x 10^{14} esu gm mol^{-1}

    For aluminum, using

$$\rho = 2.69839 \pm 0.00019 \text{ gm cm}^{-3} \text{ at } 25.0^{O}\text{C}$$
$$M = 26.989 \pm 0.001 \quad \text{gm gm mol}^{-2}$$
$$a = 4.04927 \pm 0.00002 \times 10^{-8} \text{ cm at } 25.0^{O}\text{C}$$

we find $N = 6.0258 \pm 0.0006 \times 10^{25}$ mol gm mol^{-1}
± 0.0007
$e = 4.8005 \pm 0.0004 \times 10^{-10}$ esu
± 0.0007

For silver, using

$\rho = 10.4870 \pm 0.0008$ gm cm^{-3} at 25.0°C
$M = 107.858 \pm 0.002$ gm gm mol^{-1}
$a = 4.08574 \pm 0.00004 \times 10^{-8}$ cm at 25.0°C

we find $N = 6.0318 + 0.0005 \times 10^{23}$ mol gm mol^{-2}
$+ 0.0006$
$e = 4.7957 + 0.0004 \times 10^{-10}$ esu
$+ 0.0007$

For quartz, using

$\rho = 2.64810 \pm 0.00015$ gm cm^{-3} at 25.0°C
$a = 4.91263 \pm 0.00009 \times 10^{-8}$ cm at 25.0°C
$c = 5.40454 \pm 0.00011$
$M = 60.063 \pm 0.003$ gm gm mol^{-1} (Baxter, Weatherill &
Scripture)

we find $N = 6.0239 \pm 0.0004 \quad 10^{23}$ mol gm mol
± 0.0005
$e = 4.8020 \pm 0.0003 \quad 10^{-10}$ esu
± 0.0006

but if $M = 60.104 \pm 0.003$ gm gm mol^{-1} (Honigschmid & Steinheil,
Weatherill & Brundage)

we find $N = 6.0280 \pm 0.0004 \quad 10^{23}$ mol gm mol^{-1}
± 0.0005
$e = 4.7988 \pm 0.0003 \quad 10^{-10}$ esu
± 0.0006

DISCUSSION OF THE RESULTS

If the molecular weight of quartz is in the range of 60.063 then the value of e obtained is in agreement with that given by Bearden[14], $4.8036 \pm 0.0005 \quad 10^{-10}$ esu. Bearden's value is based on the measurement of the lattice constant of large samples of calcite

with a two crystal spectrometer and the density of the large samples were determined by immersion. Both the density and lattice parameters have been measured by a great many observers and there is no doubt as to their value.

However if the molecular weight of quartz is in the range of 60.104 then the value of e will be in agreement with that obtained for aluminum. In such an event it is impossible to reconcile the values obtained using quartz and aluminum with those obtained using calcite without resorting to the concept of a more or less regular superstructure in the crystals.

Considering the results of silver and aluminum alone where there is no uncertainty in the molecular weights we see that the difference in the value of N obtained for the two materials is 0.10% while the largest experimental error is 0.001%. Thus some of our assumptions as to the nature of the polycrystalline metals must be invalid. In order to obtain agreement with the value of N obtained using calcite the value of the density must be increased. This suggests the presence of holes or gaps in the metals which would render the measured density less than the true density. However, the little metal crystals must part together in such a way that there is a reproducible percentage of very small spaces between the crystals for the density of different samples was the same and when an annealed sample was worked and reannealed the density returned to its original value. But the density of silver increases with working and that of aluminum

decreases. This I interpret as showing that working changes some of the crystalline structure into amorphous material which for silver and aluminum is less dense than the crystals (silver and aluminum expand on melting) and which can fill the holes and make the density greater, as in silver, or it can more than fill the holes and make the density less, as in aluminum.

These experiments show that there is certainly not a mosaic structure, even in the metals, which renders the value of N and e obtained by the x-ray method incorrect by more than 0.1%. Using the results of Tu[1] on the glancing angle and density of calcite, rocksalt, potassium chloride, and diamond and the latest value of their molecular weights we find the following values of N and e where the probable error neglects the uncertainty in the ruled grating measurements and the value of the Faraday.

For Calcite ρ = 2.71003 ± 0.00005 gm cm^{-3} at 18° C
d = 3.03557 ± 0.00001 x 10^{-8} cm at 18° C
$\phi(\beta)$ = 1.09602 ± 0.00001 at 18° C
M = 100.090 ± 0.005 gm gm-mol^{-1} [33]
N = 6.0235 ± 0.0003 x 10^{23} mol gm-mol^{-1}
e = 4.8024 ± 0.0003 x 10^{-10} esu

For KCl ρ = 1.98930 ± 0.00014 gm cm^{-3} at 18° C
d = 3.14541 ± 0.00004 x 10^{-8} cm at 18° C
M = 74.553 ± 0.003 gm gm-mol^{-1} [34]
N = 6.0214 ± 0.0005 x 10^{23} mol gm-mol^{-1}
e = 4.8040 ± 0.0004 x 10^{-10} esu

For Rocksalt d = 2.81962 ± 0.00003 x 10^{-8} cm at 18° C
(NaCl) ρ = 2.16418 ± 0.00014 gm cm^{-3} at 18° C
M = 58.456 ± 0.002 gm gm-mol^{-1} [34]
N = 6.0247 ± 0.0005 x 10^{23} mol gm-mol^{-1}
e = 4.8014 ± 0.0004 x 10^{-10} esu

For Diamond ρ = 3.5141 ± 0.0001 gm cm^{-3} at 18° C
(.89k) $\quad$ d = 3.56692 ± 0.00002 x 10^{-8} cm at 18° C
$\quad$ M = 12.0115 ± 0.0005 gm gm-mol^{-1} [33]
$\quad$ N = 6.0255 ± 0.0003 x 10^{23} mol gm-mol^{-1}
$\quad$ e = 4.8008 ± 0.0003 x 10^{-10} esu

(1.78) $\quad$ ρ = 3.5142 ± 0.0001 gm cm^{-3} at 18° C
$\quad$ d = 3.56683 ± 0.00002 x 10^{-8} cm at 18° C
$\quad$ N = 6.0258 ± 0.0003 x 10^{23} mol gm-mol^{-1}
$\quad$ e = 4.8006 ± 0.0003 x 10^{-10} esu

In the calculations we have taken 0.709268 x 10^{-8} cm as the absolute wavelength of MoK$_{\alpha 1}$ [32]. We see that the values of N and e obtained for these "perfect" crystals differ by many times the experimental error. We have no assurance that "perfect" crystals are not going to behave like the metals to some extent for the difference between a polycrystalline material and a "perfect" crystal is one of degree. I believe, therefore, that the assumption that calcite is a "perfect" crystal might invalidate the x-ray value of e by 0.04%. It is also significant that the value of e obtained for crystals other than calcite, with the single exception of KCl, is lower than the calcite value. Thus the best value of e obtainable by the x-ray method is 4.801 ± 0.002 x 10^{-10} esu. This value is a personal estimate. Actually the average value using my results and those of Tu[1] (weighing the metals as one-half and using the mean of the two values obtained for quartz) is 4.8013 ± 0.0004 x 10^{-10} esu. However, as the individual values differ by many times the experimental error the least squares probable error means nothing for the spread in values is not due to

statistical fluctuation but to something fundamental in the method.

The values of the lattice constants I determined were slightly lower than those given by other observers (page 40), the average being 0.009% lower. If this difference were real it would mean raising my value of e by 0.03%. Neither this nor the uncertainty in the molecular weight of quartz would change the conclusion reached.

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