THE RICE INSTITUTE

RADIAL DISTRIBUTION STUDIES ON VITREOUS SILICA

by

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A THESIS

SUBMITTED TO THE FACULTY

IN PARTIAL FULFILLMENT OF THE

REQUIREMENTS FOR THE DEGREE OF

MASTER OF ARTS

Houston, Texas
May, 1960

Approved
W. O. Milligan
May 24, 1960

CONTENTS

CHAPTER I: AN AUTOMATED AND DIGITALIZED X-RAY SCATTERING APPARATUS

A completely automatic x-ray scattering apparatus has been constructed that records in digital form on paper tape (a) the scattering angle (2θ), and (b) the time required to produce a prescribed number of counts. The apparatus is especially designed to record scattering data from poorly scattering materials such as the "amorphous" solids. The full-wave rectified power supply utilizes a 0.25 mfd. smoothing capacitor. Proportional or scintillation counter tubes with pulse height selection, and x-radiation rendered monochromatic by beta filters or by cut and bent crystals are provided.

. 1

CHAPTER II: ELIMINATION OF THE $K_{\alpha_1 \alpha_2}$ DOUBLET IN SCATTER PATTERNS OF X-RADIATION

An analytical method is proposed for transforming scatter patterns from doublet x-radiation into the pattern of monochromatic x-radiation.

. 15

CHAPTER III: RADIAL DISTRIBUTION ANALYSIS OF VITREOUS SiO_2

Because of recent developments in the methods and means of Fourier analysis of x-radiation scatter patterns, a new analysis of vitreous silica has been made. The results are in agreement with the excellent pioneering work on vitreous SiO_2 by B. E. Warren, if the diffraction data is corrected by a factor with the same functional form as the Debye-Waller temperature factor. The effective Debye θ_D equals 360°K which agrees with the θ_D calculated from velocity of sound measurements.

. 24

CHAPTER I

AN AUTOMATED AND DIGITALIZED X-RAY SCATTERING APPARATUS

I. INTRODUCTION

Experimental x-ray scattering data from poorly crystalline materials, "amorphous" solids, or liquids have usually been obtained by photographic methods,[1-4] the results being subject to the limitations of the emulsion and the microphotometric step. More recently, geiger, proportional, and scintillation counter tubes have been employed,[5-8] despite the fact that some investigators have expressed doubts concerning their use in the detection of weak scattering from the "amorphous" solids.

In this laboratory we have been using proportional counters for the study of "amorphous" solids for almost a decade. During the past three years we have developed an apparatus that is completely automated and digitalized, in which the statistical accuracy may be selected and held constant during the course of an experiment. It is the purpose of this paper to describe the present form of this device.

II. EXPERIMENTAL

An ideal x-ray scatter measuring apparatus for the study

of "amorphous" solids and other poorly scattering materials would provide intense and strictly monochromatic x-radiation. In practice these two requirements are contradictory. We believe the apparatus described in this paper provides an optimum compromise between these and other requirements of a more practical nature. The apparatus utilizes certain improvements to stabilize and intensify the x-radiation, pulse height selection, a beta filter or a cut and bent crystal to monochromatize the radiation, and complete automation to permit continuous recording of data.

For practical reasons it is desirable to have an apparatus which is reliable, easy to maintain, and flexible. Some of these features are present in several of the commercially available x-ray diffraction units. The particular unit used in recent work in this laboratory is a water-cooled Norelco diffraction unit equipped with a standard goniometer, voltage regulator, and milliampere stabilizer.

When counting techniques are used, it is important that the characteristics of the counting apparatus and the intensity of incident radiation be held constant, or that they be monitored in some way. The x-radiation could only be accurately monitored by another counting apparatus whose characteristics would also have to be monitored or held constant. These characteristics are not easily monitored, so we attempt to hold them and the incident intensity constant. The line voltages of all electronic equipment in the apparatus, which is shown in block form in Fig. 1, are stabilized by type CVH

Sola transformers, which also serve as filters for some power-line transients.

The intensity of the characteristic radiation is readily enhanced by using higher voltages. Such higher peak voltages, likewise, tend to increase the continuous radiation, to shorten the lifetime of sealed x-ray tubes, and to cause overloading of the counting system in the maximum voltage regions of the cycle. However, a useful increase by a factor of 2 in the intensity without the disadvantages corresponding to anincrease in the peak voltage can be achieved by increasing the duty cycle without raising the peak operating voltage. This was accomplished by placing a 0.25 mfd. 60 KV. capacitor (protected by a 50,000 ohm resistor) in parallel with the x-ray tube. As a safety device a solenoid-gravity operated vacuum switch shorts the capacitor through a 3 megohm protective resistor when the x-ray tube is cut off.

In photographic techniques the x-radiation has usually been monochromated by using a suitable beta filter, a flat[9] or a bent and cut[10, 11] sodium chloride crystal, or some modification of these methods.[12] In counter tube techniques the usual procedure has been to use a suitable K_β filter in conjunction with a pulse height selecter. We have used this procedure and also a procedure utilizing a special goniometer arm which employs a bent and cut sodium chloride crystal with a suitable slit system to monochromatize the scattered radiation before it enters the counter tube. The counting rate is somewhat less than that obtained under identical conditions

using only a beta filter.

For continuous automatic operation a control box was built which completely automates the apparatus in such a way that the statistical accuracy is constant at all angles. Any scanning procedure will produce a scatter pattern with a variable accuracy, and because of the uncertainty of ratemeters it appears to be necessary to take a constant count at a finite number of specified angles. For radial distribution analysis it is even more important, for it is necessary to get diffraction data with higher accuracy at large θ values where the scattered intensity is very weak. Thus the control box is programmed to (a) increment the spectrometer angle, 2θ, by a specified constant, $\Delta 2\theta$, (b) pulse the printing timer to print the time required for a constant count together with a code number for the angle 2θ, upon receipt of a signal from the scaler indicating that the count is equal to a fixed constant. At the end of its one minute cycle, the box then resets the timer and the scaler and restarts the count. The control box consists, as one would guess, of a synchronous motor driving a system of three cams. The cams activate microswitches which govern the relays which perform the steps listed above. The value of $\Delta 2\theta$ may be varied from $1/32^{\circ}$ to 2° and the constant count may be varied from 160 to 4,096,000.

III. RESULTS AND CONCLUSIONS

The overall stability of the apparatus was checked by (a) setting the apparatus to observe a scatter pattern at a

constant angle, 2θ, for a period of days, then (b) cutting off the x-ray generator and observing Mn K x-rays from a Fe^{55} source for a similar period of days. We found in repeated experiments that the overall stability under both sets of conditions over a forty-eight hour period fell in the range of ± 1.0 to $\pm 1.5\%$. The statistical standard deviation for the constant count used (25,600) was $\pm 0.6\%$; thus the x-ray generator is more stable than the associated electronic circuits.

Figure 2A is a comparison of the degree of monochromatization achieved in the two methods we have used. The bent-cut system described in the caption of that figure eliminates all radiation except that of the K_α line which is, of course, the $K_{\alpha_1 \alpha_2}$ doublet. The beta filter passes the K_α line with a low pedestal of continuous radiation, which composes less than 15% of the total radiation. The K_β line has been reduced to an integrated intensity less than 0.05% of that of the K_{α_1} line.

In Figure 2B the scatter patterns of vitreous silica determined by the two methods are compared and agree within 2% if the error is measured as the closest approach of one graph to a specified point on the other. This is the error which is important in radial distribution studies, not the error in the intensities at a particular angle. 2% is twice the experimental accuracy, and this result is in agreement with Brady's results on other vitreous substances.[13] In most radial distribution studies, the atomic form factors involved

have not been experimentally verified to better than 5%, if they have been verified at all. It seems, therefore, that filtered radiation is sufficient for most radial distribution studies, in which only 2% data is needed. For precision work a double bent crystal monochromator should be used, the K doublet eliminated, and other corrections made to the scatter pattern.[14, 15, 16]

In Figure 3, A and B are the scatter patterns from powdered silicon metal and a sodium chloride single-crystal, respectively. The powdered silicon metal pattern is drawn so as to show the difference in the line profiles. A close inspection of the vitreous silica and the sodium chloride patterns will verify that this same difference is also present in them. Since the optical arrangements were identical, we believe that the difference in the distortions is due more to differences in the instrumental error functions than to the continuous radiation not eliminated by the beta filter.[15] The continuous radiation should contribute to widening the half width and the instrumental error functions to producing assymmetry of the line although the effects are not exclusive. The patterns are more symmetrical for the crystal monochromatized case because the crystal and slit system diffracts the beam in the opposite direction to that in which the sample diffracts it. This distorts the line profile in the opposite direction, thus causing it to appear more symmetrical.

IV. ACKNOWLEDGMENTS

We are grateful to Dr. H. A. Levy, Oak Ridge National Laboratory, for very helpful discussions over the past several years, and to Dr. G. W. Brady, Bell Telephone Laboratories, for recent discussions. We would like to thank Mr. E. H. Hemmen for excellent machine work.

We appreciate the generosity of Oak Ridge National Laboratory and Humble Oil and Refining Company in loaning to us several items of equipment.

This research was supported in part by a grant from The Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund.

Figure 1. Block diagram of automated and digitalized x-ray scattering apparatus.

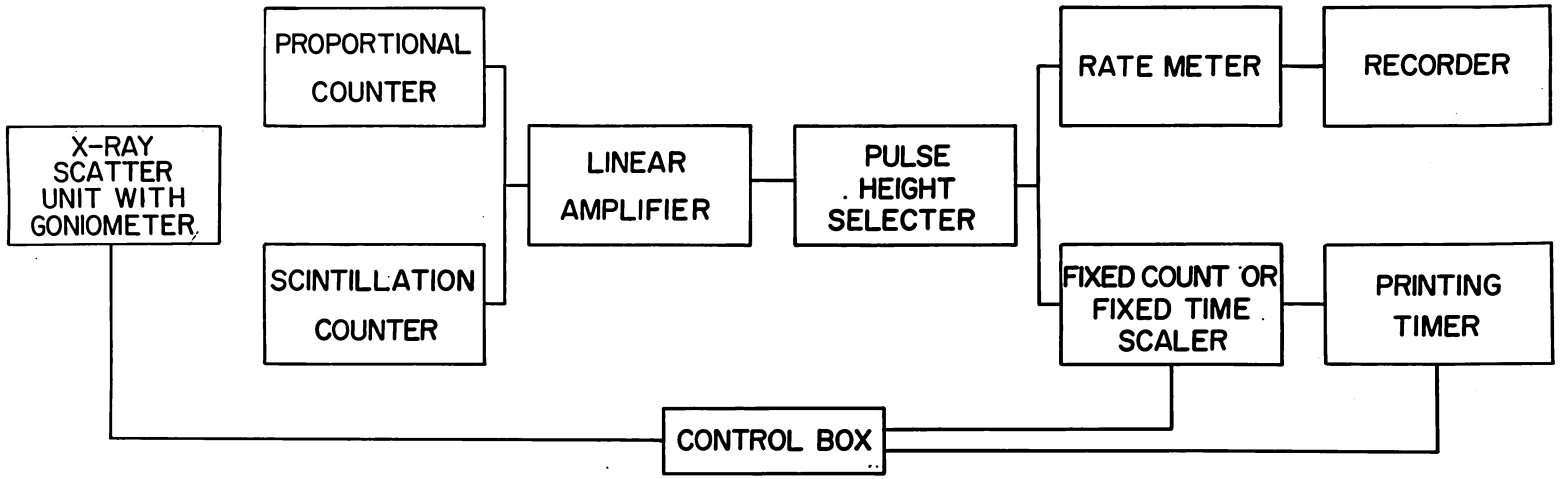
PROPORTIONAL COUNTER
X-RAY SCATTER UNIT WITH GONIOMETER
SCINTILLATION COUNTER
LINEAR AMPLIFIER
PULSE HEIGHT SELECTER
RATE METER
RECORDER
FIXED COUNT OR FIXED TIME SCALER
PRINTING TIMER
CONTROL BOX

FIGURE 1

Figure 2. (A) Energy distribution in x-radiation from an Mo anode as viewed by a proportional counter tube with tracking pulse height selection and with (1) a Zr beta filter (closed circles) and (2) a bent-cut sodium chloride crystal monochromatizing system (open circles). (Half filled circles imply that the data points of both data sets coincide.) In both cases the defining and the receiving slits were $1/30^{\circ}$ slits and the intensities were corrected by the appropriate polarization factor. (B) The most intense scatter peak from vitreous silica as viewed by a proportional counter tube with (1) a Zr beta filter (closed circles) and (2) a bent-cut sodium chloride crystal monochromatizing system (open circles). In both cases the defining and the receiving slits were 1° and the intensities were corrected by the appropriate polarization factor.

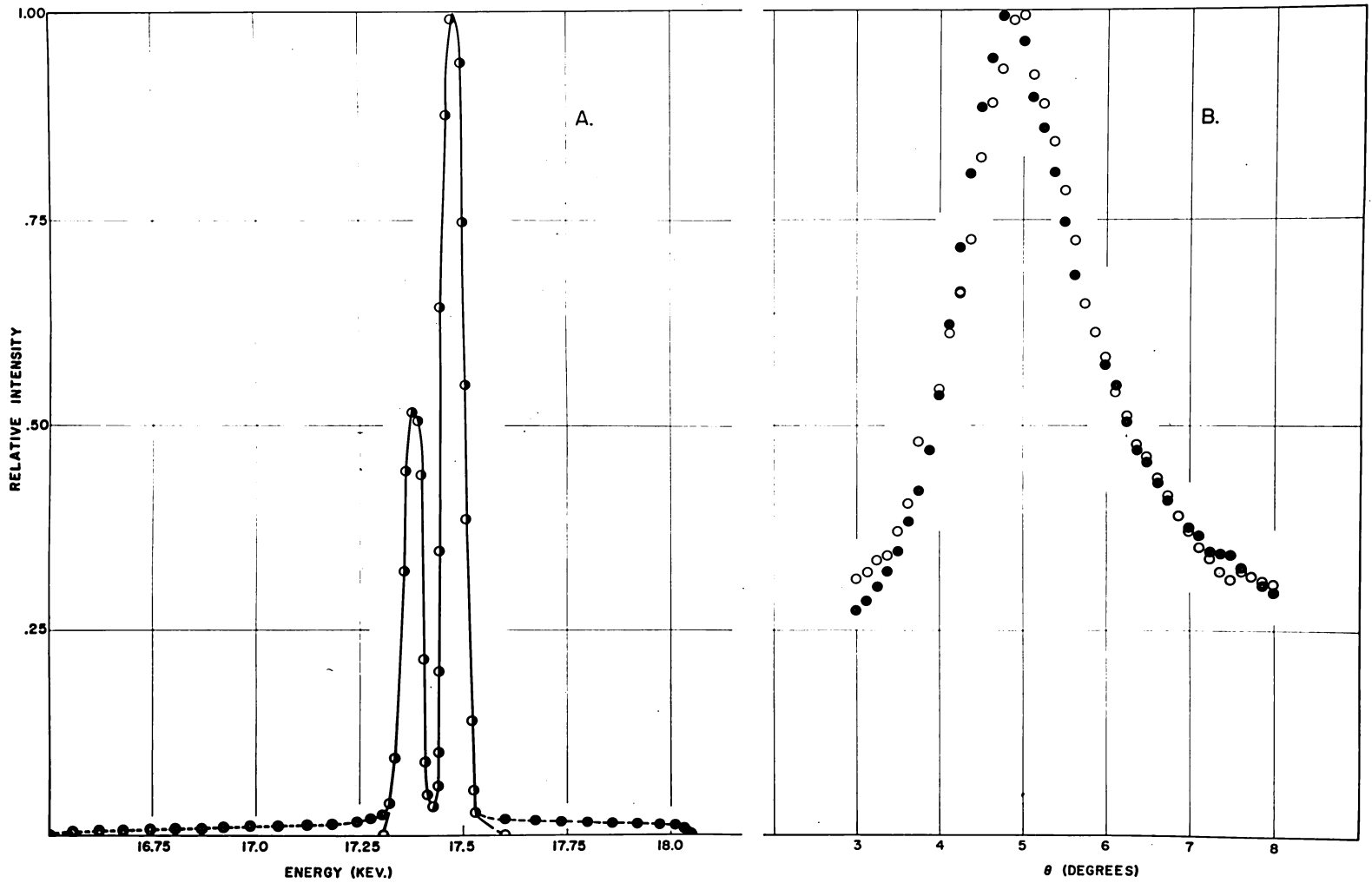
1.00
.75
.50
.25
RELATIVE INTENSITY
A.
16.75
17.0
17.25
17.5
17.75
18.0
ENERGY (KEV.)
B.
3
4
5
6
7
8
θ (DEGREES)

FIGURE 2

Figure 3. (A) The (111) reflection from silicon metal and (B) the (400) reflection from a flat sodium chloride single crystal, as viewed by a proportional counter tube with (1) a Zr beta filter (closed circles) and (2) a bent-cut sodium chloride crystal monochromatizing system (open circles). (Half filled circles imply that the data points of both data sets coincide.) In (A) and (B) the defining and receiving slits were $1/2^{\circ}$ for both cases and the intensities were corrected by the appropriate polarization factor.

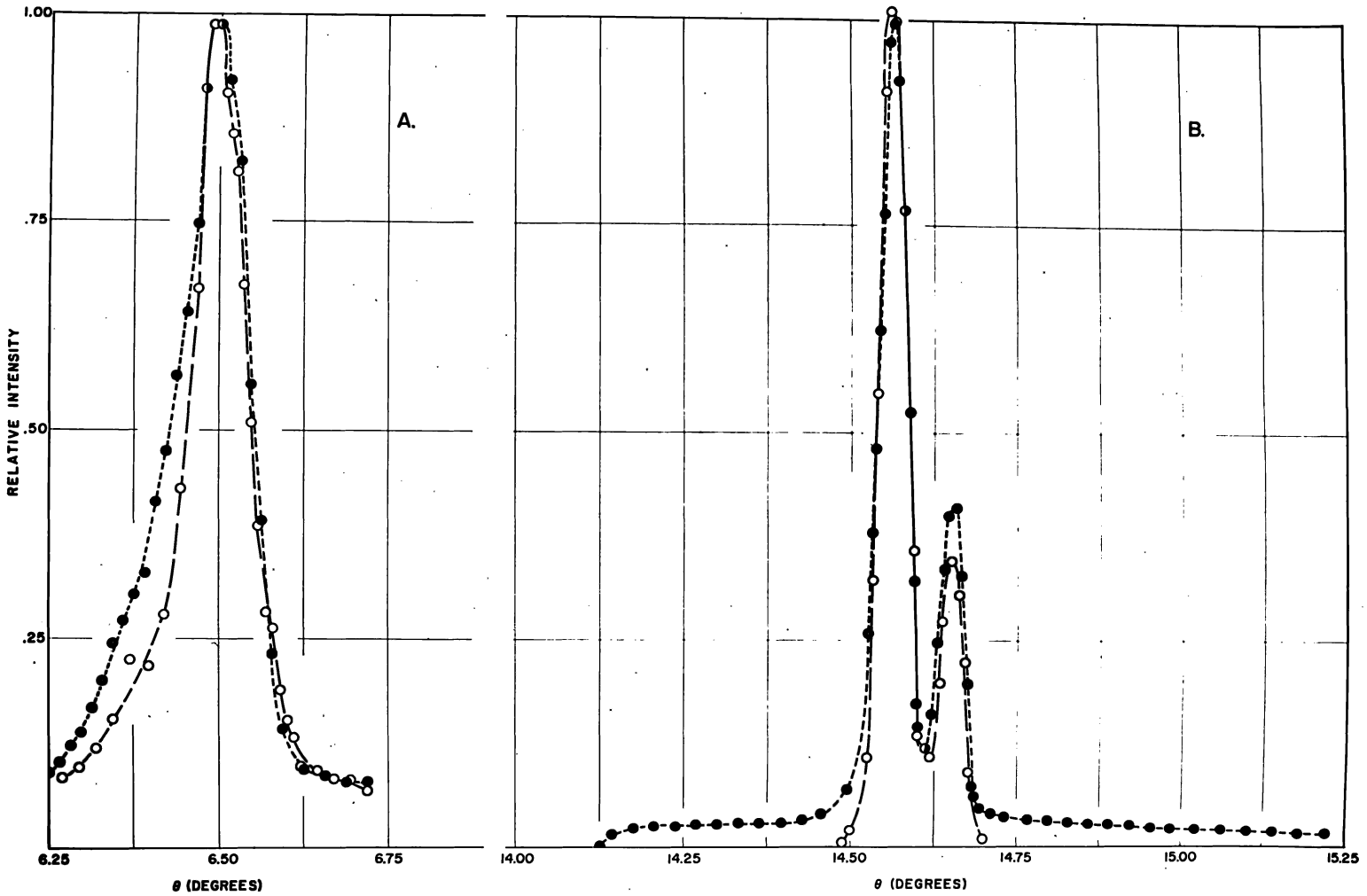
1.00
.75
.50
.25
RELATIVE INTENSITY
A.
6.25
6.50
6.75
θ (DEGREES)
B.
14.00
14.25
14.50
14.75
15.00
15.25
θ (DEGREES)

FIGURE 3

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CHAPTER II

ELIMINATION OF THE $K_{\alpha_1 \alpha_2}$ DOUBLET IN SCATTER PATTERNS OF X-RADIATION

In x-ray studies it is often desirable to have a highly monochromatic source. However, the use of double crystal monochromators to eliminate the K_{α_2} line from x-radiation produced by modern x-ray equipment presents difficulties since the large decrease in the intensity requires unreasonably long pattern determination times. A compromise can be made which allows the use of a system of slits and a single bent and cut crystal to eliminate all radiation other than the K_{α_1} and K_{α_2} lines, which causes only a reasonable decrease in intensity, and analytical elimination of the K_{α_2} line from the scatter pattern.

Let $I(k_\alpha x)$ be the relative scatter intensity of the substance in question, which is obtained with x-radiation partially monochromatized with the single crystal system, and $x = \sin\theta$, being the bragg angle, and $k_\alpha =$ the wave number of the unresolved K_α line. Let $B(k)$ be the relative intensity of the incident beam as a function of the wave number $k = 2\pi/\lambda$. $B(k)$ should be determined by replacing the sample with an analyzing crystal, but with no other changes. If $M(kx_i)$ is the relative intensity which would be observed with a monochromatic source at θ_i, then

$$I(k_\alpha x_i) = \int_0^\infty B(k)\, M(kx_i)\, dk. \qquad (1)$$

Now if the single crystal monochromator is correctly aligned, only the K_{α_1} and K_{α_2} lines in the natural ratio of their integrated intensities, 2:1, are directed to the counter tube. Thus we may express the function B(k) approximately as

$$B(k) = 2/3\ \delta(k-k_{\alpha 1}) + 1/3\ \delta(k-k_{\alpha 2}) \qquad (2)$$

where $\delta(k)$ is the Dirac delta function. In this way the line profiles of the K_{α_1} and K_{α_2} lines are assumed to be identical and to be instrumental in nature. Thus equation (1) becomes

$$I(k_\alpha x_i) = 2/3\ M(k_{\alpha 1} x_i) + 1/3\ M(k_{\alpha 2} x_i) \qquad (3)$$

Suppose we chose an increment x_i such that

$$k_{\alpha 1} x_i = k_{\alpha 2} x_{i+1} \qquad (4)$$

Then from (3)

$$M(k_{\alpha 2}x_i) = 3\, I(k_\alpha x_i) - 2M(k_{\alpha 2}x_{i+1})$$
$$= 3/2 \sum_{j=0}^{\infty} (-1/2)^j\, I(k_\alpha x_{i-j-1}) \qquad (5)$$

where

$$x_{i-j-1} = [k_{\alpha 2}/k_{\alpha 1}]^j\, x_{i-1}$$

The second form of equation (5) is used to determine a "foothold," so to speak, and then the first form may be used to find the subsequent points in a backward order. Table 1 illustrates the dependence of the increment in the scatter angle, $\Delta 2\theta$, on the scatter angle, 2θ, required by condition (4).

It is important to notice that accuracy is lost in this procedure. In regions where I(kx) is approximately constant the error is increased by a factor of 3. In regions with a positive slope the loss in accuracy is even greater. An alternative form of equation (5) which does not have such a large accuracy loss is

$$M(k_{\alpha 1}x_i) = 3/2\, I(k_\alpha x_i) - 1/2\, M(k_{\alpha 1}x_{i-1})$$
$$= 3/2 \sum_{j=0}^{\infty} [-1/2]^j\, I(k_\alpha x_{i-j}) \qquad (6)$$

The second form is used to determine a "foothold" and the first form is used to find subsequent points in a forward

order. The loss in accuracy occurs in this case when the slope is negative. Figure 1 illustrates the use of equation (6) on the (111) reflection from powdered silicon metal. The loss in accuracy causes the artificial wiggles to the right of the derived peak (dashed lines).

If the $I(k_{\alpha}x)$ is renormalized to $M(kx)$, it can be seen that the curves do not differ by more than .002 = $\Delta(kx)$ in the horizontal direction in the case of molybdenum K_{α} radiation. For the usual amorphous substances the pattern never has a slope sufficiently great for this correction to exceed 1.0%, which would require experimental data better than .4% accurate. The correction in the radial distribution function is much less. If higher accuracy is desired, it is necessary to use smaller increments and either utilize the experimentally obtained $B(k)$ and an iteration procedure with equation (1), or use the above method and correct for the line profile.[1]

Recently it was brought to our attention that D. T. Keating has developed this method but without the recursive form, which is very convenient for hand calculations, and without concern for the increase in error.[2]

TABLE 1

$\Delta 2\theta$ at various angles 2θ for Mo K_α radiation as required by condition (4).

2θ	$\Delta 2\theta$
30°	.183°
60°	.417°
90°	.683°
120°	1.200°
150°	2.683°

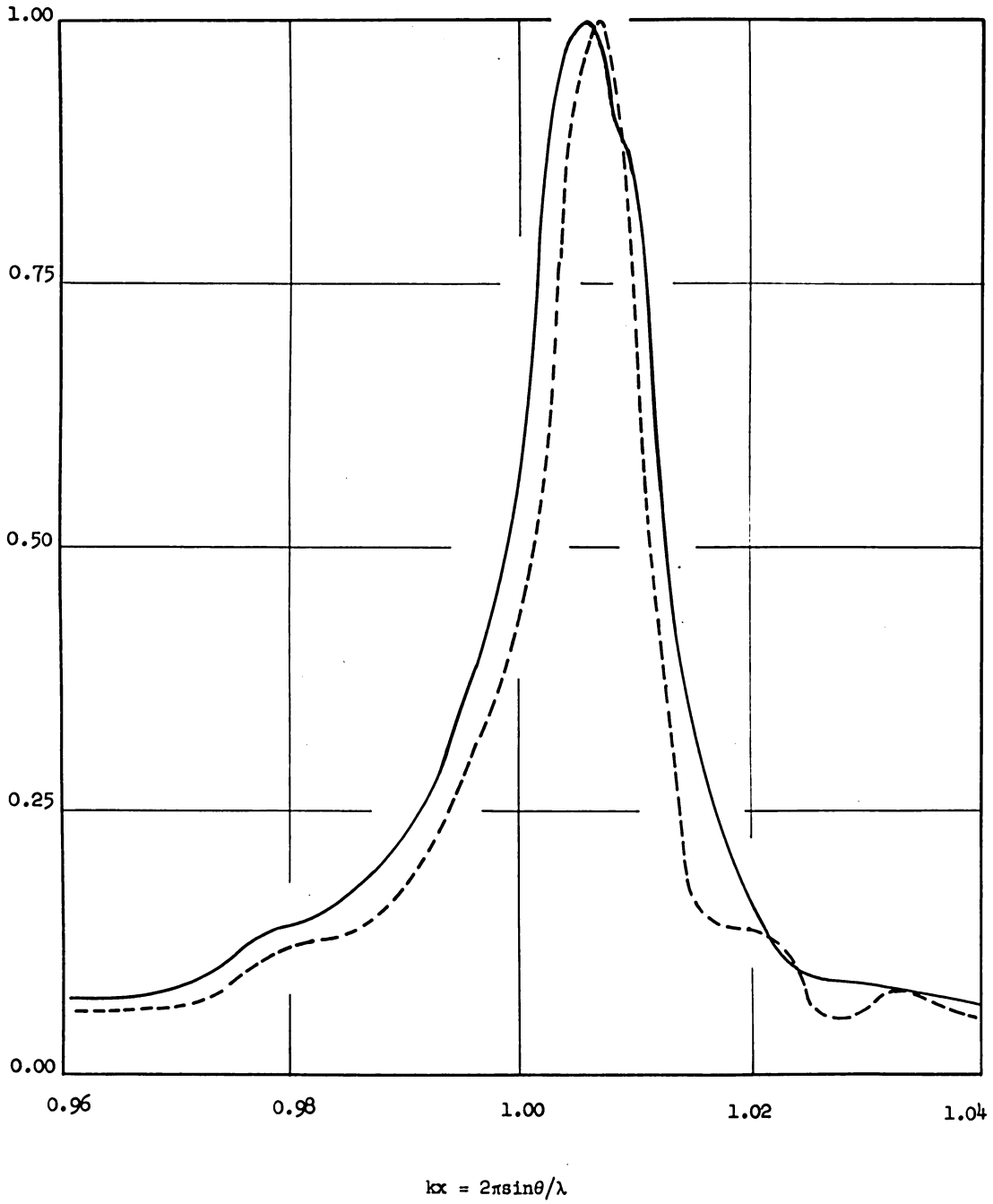
ACKNOWLEDGMENTS

The author wishes to express his gratitude to Dr. W. O. Milligan who suggested the problem.

This research was supported in part by a grant from The Petroleum Research Fund administered by The American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund.

Figure 1. The (111) reflection from silicon metal observed with molybdenum K $\alpha_{1,2}$ radiation (solid line) and the analytically deduced (111) reflection for molybdenum K α_1 radiation under identical conditions (dashed line).

The molybdenum radiation was partially monochromatized to K $\alpha_{1,2}$ radiation by using a bent-cut sodium chloride crystal and a suitable slit system. The defining and receiving slits were $1/2^\circ$. The analytical result was renormalized for better comparison.


1.00
0.75
0.50
0.25
0.00
0.96
0.98
1.00
1.02
1.04
kx = 2πsinθ/λ

NOTES

1. L. Alexander, J. Appl. Phys., 25, 155 (1954).

2. D. T. Keating, Rev. Sci. Inst., 30, 725 (1959).

CHAPTER III

RADIAL DISTRIBUTION ANALYSIS OF VITREOUS SiO_2

I. INTRODUCTION

B. E. Warren investigated vitreous SiO_2 and B_2O_3 by Fourier analysis in 1936.[1] This pioneering research produced surprisingly good results considering the stage of development of x-ray scatter equipment and of calculating equipment, and the uncertainty of other factors theoretical and experimental in nature. His results for vitreous SiO_2 supported Zachariasen's concept of the structure, this work now being the textbook example of the Fourier analysis method.[2] The B_2O_3 results have, however, recently been questioned in the literature.[3,4]

As one would expect, time has improved several factors since Warren's investigation. These factors are:

1. The experimental data can now be determined to 1% by the use of counter tubes. The use of photographic techniques involves absorption and film corrections and a microphotometer scan which introduces a 10% error even with the modern refined methods. Warren and co-workers were only able to observe the scattering from μ = .6 to μ = 11.0. Today we can

easily determine the scattering from $\mu =$ .3 to $\mu =$ 17.0, or to higher values if necessary.

2. Recently many new calculations of the atomic scattering factors have been done and more complete expressions for the incoherent scattering have been derived.[5,6,7,8,9]

3. Ways of performing the calculations with greater accuracy have been devised. Warren used a graphical harmonic analyzer whereas today it is possible to use digital computer methods and eliminate human error.

4. A new formulation of the theory has been recently derived by Finbak.[10]

5. Recent investigations of the calculational errors and studies of the nature of the Fourier analysis have indicated some common causes of errors and how to avoid them. The resulting radial distribution function of Warren's investigation of vitreous SiO_2 has the characteristics (notably the peak at $r = .8$ Å) which indicated errors in the calculations to Grjotheim and co-workers.[3] Recent studies of SiO_2 have also had bad calculation errors.[11,3]

Thus we were prompted to investigate the radial distribution of vitreous SiO_2.

II. A BRIEF HISTORICAL SKETCH OF THE THEORY

In the 1920's x-ray workers became interested in the

scatter patterns from liquids, amorphous substances, and gases. Workers of that period first described the structure as very small crystalline particles packed in a random way. This, when worked out in detail, implies the low angle scattering should be large, while experimentally it was found to be small.

In 1925 Debye wrote a paper on the scattering of x-radiation from gases, in which he introduced the idea of the radial distribution function.[12] This function is the probability of an interelectronic distance occurring within the sample. Two years later, Zernike and Prins published a paper discussing a one-dimensional example, employing Fourier's integral theorem to show how the distribution function could be determined by the observed scatter pattern.[13] Debye and Menke then produced the first quantitative calculation of the atomic distribution function for the case of liquid mercury and put the theory into the three-dimensional form.[14] A few years later, B. E. Warren modified the theory to apply to the case of amorphous substances with more than one kind of atom.[1]

In 1946 Finbak, under the influence of Sir W. L. Bragg, made a critical analysis of this subject and developed the theory from a different point of view.[10] By considering the electronic distribution function at the onset, Finbak has assumed that the diffraction is due to pairs of electrons, while Debye's theory and its later variations implied that the diffraction is due to pairs of atomic electron clouds.[15]

It is Finbak's theory which will be discussed briefly here in order to facilitate later discussions of the calculations. The formulation, however, will be along the lines of Warren's because Finbak's notation is vague and hides many of the assumptions of the theory.

III. A BRIEF SKETCH OF FINBAK'S FORMULATION

The total observed intensity of scattering of x-radiation of wavelength λ by a system of electrons, at a distance R from the center of the system, and at a scattering angle 2θ, is:

$$I_{EXP} = (e^4 I_o / m^2 c^4 R^2)\, P(\mu)\, A(\mu)\, D(\mu)\, I(\mu) + I_{back}(\mu) \qquad (1)$$

$I_{back}(\mu)$ is the background intensity; $A(\mu)$, the absorption factor; $D(\mu)$ the temperature factor; $P(\mu) = (1 + \cos^2 2\theta)/2$, the polarization factor; $\mu = 4\pi \sin\theta/\lambda$; e and m are the charge and mass of the electron; c the velocity of light; and I_o the intensity of the radiation incident on the specimen.

The corrected intensity of the radiation by a system of Thomson electrons, as developed by Debye, is:

$$I(\mu) = \sum_m \sum_n (\sin \mu r_{mn})/\mu r_{mn} \qquad (2)$$

if r_{mn} is the distance from the mth electron to the nth electron.[16] The summations are over all electrons in the system.

Supposing that the electron system is composed of atoms,

(2) may be written as

$$I(\mu) = \sum_{p} \sum_{n} \sum_{m}^{P} \sum^{P} (\sin\mu r_{mn})/\mu r_{mn} + \sum_{n}{}' \sum_{m}{}' (\sin\mu r_{mn})/\mu r_{mn} \qquad (3)$$

where the sums superscribed with a P are over all the electrons of the pth atom in the specimen. The second term is the sum over all cases where the nth electron is not associated with the same atom as the mth electron. Now by definition,

$$I^{p}_{\text{Atomic}}(\mu) = \sum_{n}^{P} \sum_{m}^{P} (\sin\mu r_{mn})/\mu r_{mn} \qquad (4)$$

where I^{p}_{Atomic} is the atomic scattering of the atom p. It has been shown quantum mechanically that

$$I^{p}_{\text{Atomic}}(\mu) = \left| \sum_{m} f_{p;mm} \right|^{2} + R(\mu)\left(Z_{p} - \sum_{m} \sum_{n} |f_{p;mm}|^{2}\right)$$
$$= I^{p}_{\text{COH}} + I^{p}_{\text{INC}}. \qquad (5)$$

with the first term corresponding to the coherent scattering and Z_p being the number of electrons in atom p. The second term corresponds to the incoherent scattering, and

$$R(\mu) = 1/[1 + h\,(1 - \cos 2\theta)/mc\lambda]^{3} \qquad (6)$$

is the Breit-Dirac recoil factor, if h is Planck's constant.[5]

$$f_{p;mn} = \int \psi^*_{p;m} \psi_{p;n} \exp(i\, S\cdot r\, 2\pi/\lambda)\, dv \qquad (7)$$

where $\psi_{p;m}$ is the wave function of the mth electron in atom p. $S = s - s_0$ where s, s_0 are unit vectors along the reflected and the incident directions.

Now let $4\pi r^2 \rho_m(r)\, dr$ be the probability density of electrons not in the atom, with electron m being in a spherical shell centered about electron m of radius r and of thickness dr. Then

$$I(\mu) = \sum_p I^p_{Atomic}(\mu) + \sum_m \int \rho_m(r)\, 4\pi r^2 \frac{\sin\mu r}{\mu r}\, dr \qquad (8)$$

$$= \sum_p I^p_{Atomic}(\mu) + \int [\sum_m \rho_m(r)]\, 4\pi r^2 \frac{\sin\mu r}{\mu r}\, dr$$

which is strictly valid only if the environments of all the electrons were only functions of r. This assumption, though often made without comment in many papers on this subject, is sufficient to destroy the accuracy of the results of a radial distribution study. This assumption must be kept in mind when interpreting the results of this calculation.

Letting $\rho(r) = \sum_m \rho_m(r)$, the electron distribution sum, and ρ_0 equal the average density of electrons, (8) becomes

$$E(\mu) = I(\mu) - \sum I^{P}_{Atomic}(\mu) \tag{9}$$
$$= \int_0^\infty 4\pi r^2[\rho(r) - \rho_o] \frac{\sin\mu r}{\mu r}\, dv + 4\pi\rho_o \int_0^\infty r^2 \frac{\sin\mu r}{\mu r}\, dr$$

The second integral is zero except as $\mu \to o$. By applying the Fourier integral theorem to (9) we have:

$$4\pi r^2[\rho(r) - \rho_o] = \frac{2r}{\pi} \int_o^\infty \mu E(\mu) \sin\mu r\, d\mu \tag{10}$$

All quantities in $E(\mu)$ may be determined experimentally or by knowing the stochiometric ratio of the substances in the specimen. There are, however, some problems of a practical nature which must be solved. First the absolute intensity of $I(\mu)$ must be determined. Equation (9) implies that $I(\mu)$ approaches the atomic scattering as μ increases. Thus normalizing the $I(\mu)$ curve to the atomic scattering curve at large μ puts it on an absolute basis. Because $I(\mu)$ is experimentally determined only between two finite limits, it is necessary to extrapolate to zero and to infinity. The errors in this extrapolation and other systematic errors have also been discussed by Finbak, Grjotheim, and Klug and Alexander.[3,10,17]

In the theory as given by Warren, the $E(\mu)$ function is replaced by

$$i(\mu) = [I(\mu) - \sum_{p} I^{p}_{Atomic}(\mu)] \sum_{p} Z_{p}^{2} / \sum_{p} I^{p}_{COH}(\mu)$$

Because $I^{p}_{COH}(\mu)$ decreases with increasing μ, errors in the scatter pattern at high angles and the extrapolation of the pattern to infinity become critical. In order to eliminate this trouble, an artificial temperature factor $\exp(-a\mu^2)$ has been used by many workers.[18] The calculation outlined in (9) is much more pleasing for it puts a more even emphasis upon the complete experimental scatter pattern.

On the other hand, if one argues that the mechanism of the observed scatter is due to the atomic electron clouds, then $\rho(r)$ will be the probability density of effective electrons and the coordination numbers will be small. The interatomic distances, however, should not be so strongly affected.

IV. CALCULATION OF THE ELECTRON DISTRIBUTION SUM, $\rho(r)$

To eliminate the manual work, and human error, an electronic computer was utilized for processing the experimental data to find the electron distribution sum. In order to facilitate computer scheduling and to check the computation at certain points the calculation was divided into logical steps. They are:

1. Calculation of $I(\mu)$ from $I_{exp}(2\theta)$ and $I_{back}(2\theta)$. $I_{exp}(2\theta)$ and $I_{back}(2\theta)$ are entered in the form of

the time required for a certain constant count at the angle 2θ. The output data is the intensity $I(\mu)$ as defined in (1).

2. Calculation of the scale factor necessary to put $I(\mu)$ on an absolute intensity basis. The program performs a least square fit of $I(\mu)$ to $I^{P}_{Atomic}(\mu)$ over a specified region of μ. The square of the error at μ is weighted by μ^2.
3. $I(\mu)$ is extrapolated to zero and to infinity and the output data has a specified constant increment of μ. The cubic interpolation formula was used to insure smoothness of the derived curve.
4. $E(\mu)$ is determined according to (9) and the data is prepared in form for step 5.
5. The calculations indicated in (10) are carried out. The artificial temperature factor $\exp(-a\mu^2)$ is also included in this calculation. The integration is performed in the way described by Filon.[19] This method is a modification of Simpson's rule for the particular case of the Fourier sine transform. More elaborate methods were not used for the sake of simplicity and computing time.[20]

The programs for these five steps are written for any computer which utilizes the Wolontis Interpretive system.[21] The calculation at each step may easily be illustrated graphically by the use of existing programs for the I.B.M.

650, Burroughs 205, or the Univac Solid State 80.[22,23,24] The first four programs require less than thirty minutes each and the fifth requires five hours for the usual calculation, if an I.B.M. 650 is used.

V. PROCEDURE AND DISCUSSION

The sample used in this investigation was from a commercially prepared sheet of purified transparent vitreous silica.

The x-ray scatter pattern was obtained at room temperature from the x-ray diffraction apparatus described in Chapter 1. A K_β filter in conjunction with a Kr proportional counter and pulse height selecter system was used to monochromatize the scattered beam. The curve at low μ values was determined with copper K_α radiation and at higher values with molybdenum K_α. The background count in each case was taken by replacing the receiving slit with a slab of lead two millimeters thick. After the background intensity was subtracted and the polarization, temperature, and the absorption factors had been applied, the molybdenum pattern was normalized to the independent scatter curve for molybdenum radiation on vitreous SiO_2 and the copper pattern normalized to the molybdenum pattern. The curves agreed quite well when the difference in the Breit-Dirac factor was taken into account. The experimental intensity was accurate to 1% over the complete range of μ = .3 to 17.3.

The absorption correction we applied was recently derived by H. A. Levy.[25] It has the form

$$A(\mu) = \frac{w\alpha}{2\eta}\left[1 - (1-e^{-x})/x\right]$$

$$x = 2\alpha\eta/\sin 2\theta$$

where α = width of the primary beam in the plane of incidence, w = the width of the beam normal to the plane of incidence, and η is the linear absorption coefficient of the sample. Due to the small defining and receiving slits used, this correction did not have a large effect on the data.

Workers with amorphous materials have, to our knowledge, never applied the usual Debye-Waller temperature correction factor, but use the artificial temperature correction factor $\exp(-A\mu^2)$, on the $E(\mu)$ function.[26] This is merely to suppress termination-of-series errors and the loss of accuracy which occurs at large μ values. In Finbak's formulation it is not usually necessary to apply this correction for reasons previously discussed.

We have assumed that although the Debye-Waller theory does not apply to amorphous solids, the temperature correction will have the same functional form, $\exp(-B\mu^2)$. Upon choosing a value of B which makes the diffraction pattern approach the independent scatter curve in the proper way, we may calculate an effective Debye θ_D. The Debye θ_D thus calculated is 370°K. The Debye θ_D calculated by measurements on the velocity of sound is 357°K if SiO_2 is assumed to have ionic

structure. The reduced specific heat, as one would expect, does not resemble the Debye function. Rough estimates from the value of the specific heat and its slope at room temperature indicate an effective Debye θ_D of 800° to 1000°. Figure 1 illustrates the effect of this correction factor on the intensity data.

VI. RESULTS AND CONCLUSIONS

Comparing Figure 1 with the similar diagram in Warren's original paper, we see that the atomic scattering factors were used. It is felt that the ionic model is more realistic, so we have used the ionic structure factors. It is also noticeable that Warren's first peak is more intense by approximately 25% and does not have the superimposed peak at $\mu = 2.2$. We feel this was due to a microphotometric error, for when film darkening is dense the greatest error is introduced in that technique. Otherwise the scatter patterns are in good agreement.

Figure 2 is a comparison of the radial distribution functions calculated by Warren's formulation and by Finbak's formulation. The artificial peaks remain in the Warren graph despite the use of an artificial temperature correction $\exp(-.008\mu^2)$. They appear to originate from the termination of the integral rather than from an error in the diffraction pattern. This was demonstrated empirically by using several $E(\mu)$ functions corresponding to different normalizations of

$I(\mu)$ to $I^{P}_{Atomic}(\mu)$ and by arbitrarily modifying $I(\mu)$ at critical μ values where maxima could cause the observed peaks in the radial distribution function. These changes were always within the experimental accuracy, 1.0%. These modifications did not affect the radial distribution function for values of μ greater than 1.5, and below 1.5 the locations of the peaks were slightly shifted.

The calculation from Finbak's formulation had even less detail than was expected. This illustrates why Finbak's formulation has not been used to estimate the coordination numbers.

The interatomic distances determined by these two methods coincide with Warren's earlier results to 2% in either case. The distances are generally smaller than those in Warren's original paper. This is primarily due to the difference in the methods of determining the interatomic distances. We have used the $\sum_m K_m 4\pi r \rho_m$ curve, the method suggested by Viervoll, while Warren used the $\sum_m K_m 4\pi r^2 \rho_m$ curve.[27] The coordination numbers are somewhat smaller than those originally given by Warren but not enough to show a change in the structure of amorphous silica. The area under the O-O peak is slightly larger than Warren's, but this is due to an artificial peak from the termination error which is at 2.16Å. These results are shown in Figure 1.

A possible structure which would produce such a diffraction pattern is on the average a regular tetrahedron of four oxygen atoms with a side 2.63Å centered about each

silicon atom. Each oxygen is a member of two such tetrahedrons and the average Si-O-Si bond is bent with an angle of 160^{o}. One crystalline form of SiO_2 can be formed from such tetrahedra if the Si-O-Si bond is straight, so this structure appears to be a likely one also.

A more complete description of the structure and the effect of aging (simulated by heat treating) will be given in a later paper.

VII. ACKNOWLEDGMENTS

We are indebted to Shell Development Company for the use of their I.B.M. 650 and other facilities.

We appreciate the generosity of Oak Ridge National Laboratory and Humble Oil and Refining Company in loaning to us several items of equipment.

This research was supported in part by a grant from The Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund.

The author wishes to express his gratitude to Professor W. O. Willigan for his patience, helpful advice, and assistance throughout all phases of this research.

Figure 1. $I(\mu)$, the x-radiation scatter pattern of vitreous SiO_2 in electron scatter units normalized to the independent scatter pattern (dashed line), (1) after corrections for background, polarization, and absorption (circles), and (2) also after the additional correction for temperature assuming $\theta_D = 400^{\circ}K$ (solid line).

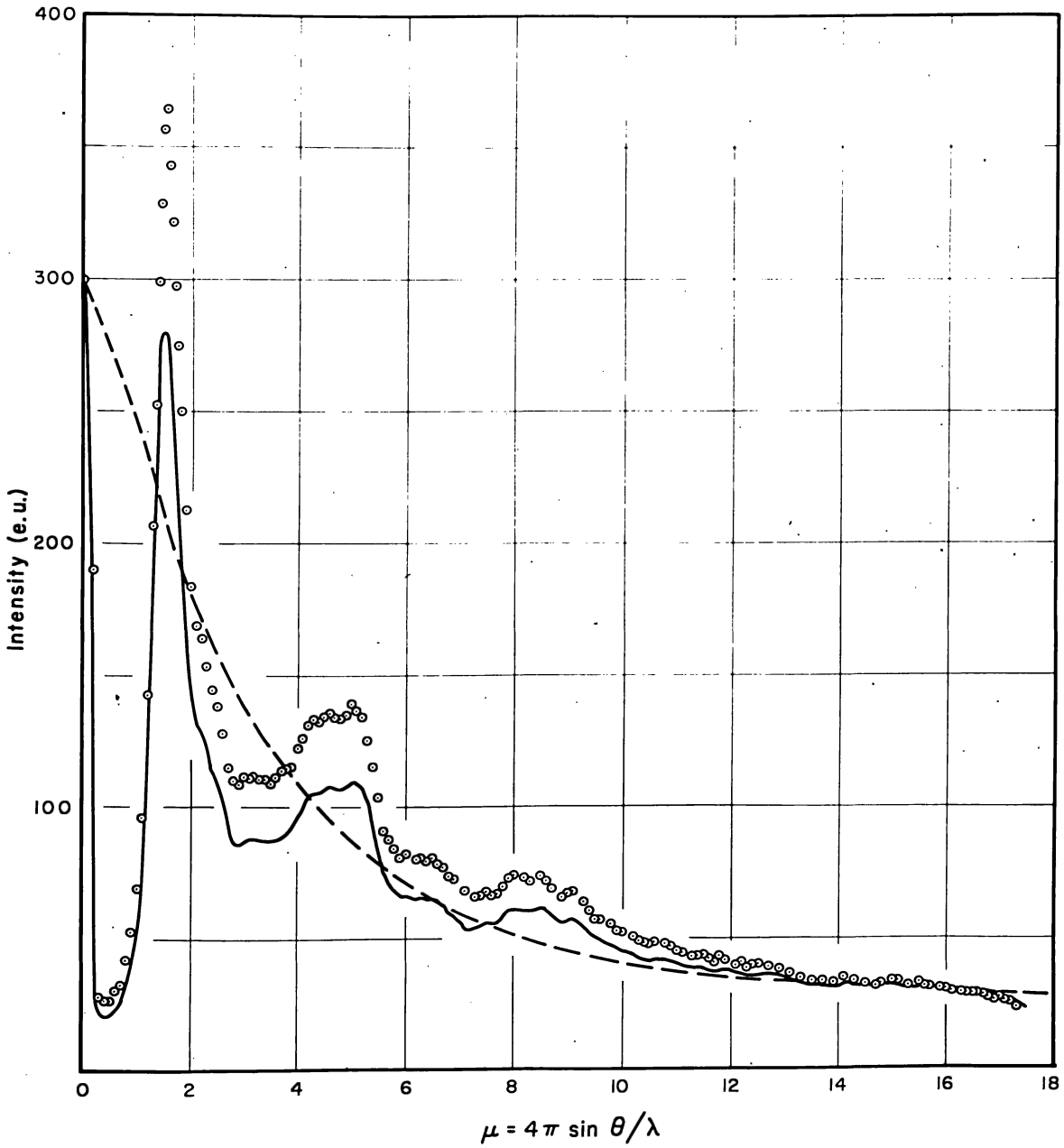

400
300
200
100
Intensity (e.u.)
0
2
4
6
8
10
12
14
16
18
μ = 4π sin θ/λ

Figure 2. The electron distribution sum from (1) Warren's formulation (solid line), and (2) Finbak's formulation (dashed line).

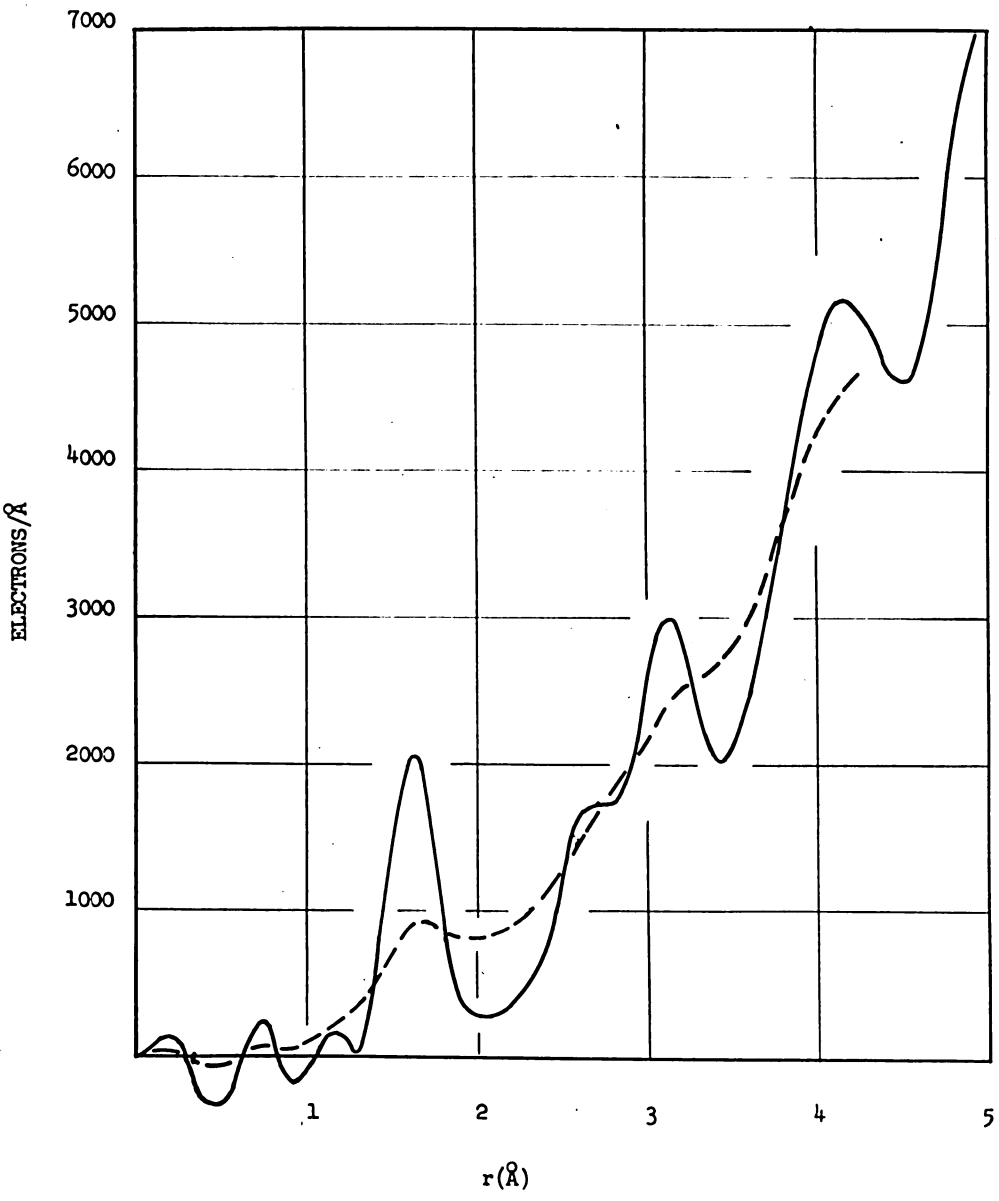

7000
6000
5000
4000
3000
2000
1000
ELECTRONS/Å
1
2
3
4
5
r(Å)

TABLE I

	Warren's Calculation	Our Calculation		Results From Crystalline Forms Of SiO_2
		Warren's Formulation	Finbak's Formulation	
Nearest Neighbor: Si-O				
Distance:	1.62 Å	1.61 Å	1.63 Å	1.60 Å
Coordination Number:	4.3	3.8	3.6	4.0
Second Nearest Neighbor: O-O				
Distance:	2.65 Å	2.63 Å		2.61 Å
Coordination Number:	5.9	6.2	(not resolved)	6.0
Third Nearest Neighbor: Si-Si				
Distance:	3.2 Å	3.1 Å		3.2 Å
Coordination Number:	4.8	4.5	(not resolved)	4.0

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