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THE STRUCTURE OF VITREOUS SILICA

by

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ABSTRACT

Three independent determinations of the x-radiation scatter pattern from vitreous silica have been made. The methods used employed (1) copper K_{α} radiation and a Guinier camera, (2) molybdenum K_{α} radiation and a bent-cut NaCl crystal monochromator with a high angle diffractometer, and (3) zirconium filtered molybdenum K_{α} radiation with a high angle diffractometer, employing a mathematical procedure to determine the scattering corresponding to a monochromatic molybdenum K_{α} beam.

The resultant composite high precision pattern has been inverted to both the electronic and atomic (ionic) radial distribution sums. These sums indicate few or no stretched Si-O bonds and an Si-O-Si angle of 150° to 155° , corresponding to a local order similar to the high silica crystalline polymorphs, such as β -cristobalite.

Refinement of the local structure in terms of atomic (ionic) models indicates that at least a large fraction of vitreous silica has Si-O-Si angles close to 180° .

An investigation of the diffraction line broadening in thermally aged (1200 - 1300° C for twenty-four hours) specimens indicates that the nucleation rate is less than the crystallization rate, and the devitrification product is α -cristobalite.

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I. INTRODUCTION

The general problem of the structure and surface chemistry of inorganic gels and gelatinous precipitates is complicated by the fact that these hydrous oxides and hydroxides (and the corresponding anhydrous oxides) may exist in more than one crystalline form, and furthermore may consist of extremely small and imperfect crystals yielding extremely broad diffraction bands, or may be essentially "amorphous." In these laboratories, numerous studies [69] have been made concerning the crystalline or partially crystalline forms of such oxides as alumina, ferric oxide, titania, stannic oxide, silicon dioxide, etc., as well as numerous dual oxide systems [1, 41] (e.g. $\text{CuO-Fe}_2\text{O}_3$, $\text{BeO-In}_2\text{O}_3$, etc.). However, less attention has been given to the amorphous forms.

We have recently discussed [57] in a preliminary manner the effect of the "age" of the gels on the structure from the point of view that all or nearly all of these materials are essentially amorphous when freshly formed and rapidly "age" to form more crystalline particles.

It is the purpose of the present investigation to lay the intermediate groundwork for contemplated comprehensive studies on the hydrous oxide gels by considering the simplest of the anhydrous amorphous forms, "amorphous" silica (vitreous silica).

The plan of this investigation is to:

- (1) Critically review the theoretical and experimental work on the structure of vitreous silica,
- (2) Make three independent precise determinations of the monochromatic x-radiation scatter from vitreous silica covering the range

from $S = (4\pi/\lambda)\sin\theta = 0.1$ to 17.3, utilizing some new techniques,

(3) Improve and calculate the atomic and electronic distribution sums, and investigate the newer methods of normalizing the experimental data and the influence of using the ionic scatter factors,

(4) Propose consistent models of the local order from the atomic and electronic radial distribution sums and refine the model parameters by the method of nonlinear regression, and

(5) Attempt to follow the local structural rearrangement during the process of devitrification.

The five parts of this investigation will be presented in the order given above, followed by the results and a reconciliation of the results with the present knowledge of vitreous silica.

We would like to emphasize that it is our strong belief that the usual deletion of (4) from the sequence of all previous investigations (except perhaps one) is unwarranted and explains the lack of accurate knowledge of the local structure of vitreous silica.

II. HISTORICAL REVIEW OF THE INVESTIGATIONS CONCERNING THE STRUCTURE OF VITREOUS SILICA

A. Theories of the Structure of Vitreous Silica and X-ray Scatter Investigations

The structure of vitreous silica has been investigated by numerous workers, perhaps the first serious investigation being that of Randall and Rooksby [53]. From their analysis they proposed the crystallite theory of glass structure, that glasses are composed of small crystallites in a phase which is stable in the melting range of the material. This conclusion was based on the fact that the prominent diffuse halo from vitreous silica corresponds to the prominent line in an x-ray scatter pattern from a cristobalite powder; agreement, however, requires that the unit cell of the crystallites be 10 to 15% greater than cristobalite.

Warren argued that glasses are too homogeneous to be composed of small distinct crystallites, from his observation that the x-ray scatter pattern of vitreous silica is not a strong function of the thermal history of the sample and exhibits no low angle scatter [65]. Further, the mean dimension of the crystallites in vitreous silica would not be more than twice the diameter of the cristobalite unit cell from the breadth of the diffuse halo in the x-ray scatter pattern. Perhaps more significant is the fact that vitreous silica does not exhibit the density change of cristobalite at 200-300^o C.

Zacharisen developed the Random Network Theory of inorganic oxide glasses from the concept that the ligand fields in the amorphous and in

the crystalline phase of an oxide are approximately equal [73]. Thus the amorphous phase has a short range order equivalent to that in the crystalline phase, but the order at greater distances is random. As a consequence the amorphous phase is more energetic and should have a tendency to devitrify. From geometric and energetic considerations Zacharisen proposed the following four rules for the formation of an inorganic oxide. Glass with the approximate composition of A_mO_n :

- (1) The first A-coordination number for oxygen is no greater than two.
- (2) The first oxygen-coordination number for A is small.
- (3) The oxygen polyhedra may share corners, but not edges or faces.
- (4) If the network is to be three dimensional, at least three corners of each oxygen polyhedron are shared.

From experimental crystal data available in 1932 Zacharisen argued that the oxygen polyhedra of triangles and tetrahedra qualify under the restriction (2). Thus the Random Network Theory predicted that only the twelve oxides B_2O_3 , P_2O_3 , Sb_2O_3 , SiO_2 , GeO_2 , P_2O_5 , As_2O_5 , V_2O_5 , Sb_2O_5 , Cb_2O_5 and Ta_2O_5 would form glasses in the pure form, and that a binary glass A_mB_nO would exist if A was a network former, that is, one of the twelve cations mentioned above, or Al^{+3} (which is isomorphous with Si^{+4} in the SiO_4^{+4} tetrahedra) and $m > 0.5 > n$. The B atom is described as a network modifier, such as Ca^{++} or Na^+ .

Warren demonstrated that the Random Network Theory could account for the position, breadth, and magnitude of the prominent halo in the x-ray scatter pattern from vitreous silica if the idealized

structure* of β -cristobalite is assumed to about 5 Å and the remainder of the sample replaced with a continuum of SiO_2 molecules [66]. A few years later Warren [67] extended the Fourier integral calculation of the atomic radial distribution sum from the x-radiation scatter from monoatomic liquids, outlined by Zernike and Prins [77], to polyatomic materials and applied it to the scatter pattern from vitreous silica (and vitreous GeO_2) determined with monochromatic x-radiation in an evacuated camera over the $S = (4\pi/\lambda)\sin\theta$ range from 0.5 to 11.0. His atomic distribution sum indicated the existence of SiO_4^{4-} tetrahedra and that the Si-O-Si bond angle is approximately 180° .

The detailed assumptions of the Random Network Theory have been questioned by the production of glasses outside the composition range specified [59], such as the heavy lead glasses and glasses with higher O-coordination numbers like the .82 TeO_2 - .18 B_2O_3 glass investigated by Brady [5], which has a six-fold oxygen coordination. Also a few of the rare compounds in the twelve have never been isolated chemically pure in the amorphous state. Hagg [23] emphasized that glass formation is a rate process; even certain metallic alloys are amorphous if rapidly quenched [17]. Morey objected to the assumption that the latent heat of fusion was relatively small for glass forming oxides [43]. Nevertheless the Random Network Theory terminology is commonly used, its rules being a practical guide for commercial

* The β -cristobalite (high form) structure determination was first done by Wyckoff [71] in 1925 and indicated the space group was $\text{Fd}3\text{m}(0_h^7)$ with an Si-O-Si angle of 180° . We term this the ideal structure since investigations after 1932 indicate that even in β -cristobalite the Si-O-Si bond angle is about 150.0° on the average and the space group is $\text{P}2_13(\text{T}_4)$.

glasses; and the theory was easily extended to explain the sulfide glasses.

Porai-Koshitz and Valenkov [64] investigated the devitrification process of soda glass and samples of vitreous silica of different thermal histories with a small diameter x-ray camera with crystal monochromated radiation. The results of the devitrification investigation suggested to them that glass separates slowly into regions of a stoichiometric metasilicate and pure vitreous silica and then the regions crystallize independently. More convincingly, Porai-Koshitz and Valenkov showed that the devitrification products of a glass are the polymorphic forms stable at the temperature range of solidification, although the devitrifying temperature is hundreds of degrees lower. Thus silica recalls its form at solidification, perhaps, by existing as some perturbed form of this structure in the glassy phase.

These facts support the crystallite hypothesis and point to a few of the faults of the Random Network Theory. The Modern Crystallite Theory* was formulated by Porai-Koshitz from the suggested interpretations of his experiments given above and the postulate that the inter-crystallite matter be of the same density as the crystallites with distorted lattices.

It is difficult to interpret the abrupt changes in the thermal expansion or the viscosity in terms of the Modern Crystallite Theory, but this theory allows easy interpretation of some optical, infrared, and x-ray absorption edge measurements. Some of these properties can probably be explained in terms of the local order, which is a common

* This theory is identified as "Modern Crystallite Theory" to distinguish it from the crystallite theory of Randall and Rooksby.

ground of the two theories. For example, the band structure which produces the semiconductive properties is usually explained in terms of periodic structures, but the bands can also originate from aperiodic structures [22, 49]; several glasses such as As_2S_3 are semiconductors. To paraphrase Prod'Homme [52], it is a question of whether one would rather discuss a perfect imperfect crystal (Random Network Theory) or an imperfect perfect crystal (Modern Crystallite Theory).

Le Chatelier's [34] idea of two allotropic coexisting phases has been revived by Babcock [3] to explain the viscosity and thermal expansion in vitreous silica. Indeed most of the anomalous properties of glass can be explained in terms of two components [2]. Others [27, 42] hypothesize that these two components are:

(1) Loose structural units ("Structons" or "Micells") with mean dimensions of several hundred angstroms as reported from electron microscopy [51, 76], light scattering [12], low temperature work [10], and low angle x-ray scatter [26], and

(2) Interstitial material of approximately the same density filling the voids between the structural units.

Only Tilton [61] has proposed a definite structon called a "vitron." It is composed of clusters of pentagonal dodecahedra of SiO_4 ⁻⁴ tetrahedra. Because of the five-fold symmetry these units cannot form a periodic structure; thus some must distort to fill space. This model correctly predicts many of the physical properties such as noble gas diffusion, density, composition range of the binary silicate glasses, and the viscosity. Tilton claims that the vitron reconciles the crystallite and network theories, and he has given explanations of other physical properties in terms of the vitron [62].

The major criticism of the vitron or structon model is that glass formation is a dynamic process and a purely ionic model for silica is not entirely realistic. It is well known that the Si-O bond is about 50% covalent [6]. (Information on chemical bonding and its influence on glass formation is reviewed in an excellent article by Weyl [70].) Dietzel has explained the dynamic effects and the necessary bond configurations in terms of an interesting model [15]. Dietzel has also calculated the x-radiation scatter curves from four-, five-, six-, seven-, and eight-membered rings [47]. The results indicate that six-membered rings are most prevalent in vitreous silica. Unfortunately an artifact in Dietzel's x-ray scatter pattern at low angles from the continuum radiation may have led him to some incorrect conclusions [55].

The structure of vitreous silica has been reinvestigated as diffraction techniques and assumptions in the analysis have improved. The x-ray scatter investigations are:

(1) Hartlief [24] determined the absolute scattered intensity to $S = 7.0$ with an ionization chamber-electrometer arrangement similar to Bragg's, but the radiation was not monochromated. Unfortunately an artifact from the continuum radiation falsifies his data for $S = (4\pi/\lambda)\sin\theta$ less than 1.0 [55]. Thus his calculated atomic radial distribution sum should be considered with caution. Distances in the range from 1.0 to 5.0 Å are probably affected only slightly.

(2) Richter [54] determined the x-ray scatter pattern to $S = 17.3$, but the pattern was not exhibited nor the method discussed. The Warren function (atomic radial distribution sum) from the data exhibits much more detail, notably an additional O-O distance of 2.15 Å, but this additional detail may be due to an error at high S or to a

misnormalization of the data [21]. The Warren function calculated with an upper S limit of 10.3 was similar to Warren's original work.

(3) Norman [61] determined the interatomic distances probably by the Finbak function (the differential electronic radial distribution sum). Details of the experimental work and of the analysis are unknown to us.

(4) Zarzycki [74], from the data available to us, determined the scatter pattern from vitreous silica at 20°C and 1300°C for S less than 9.0 with monochromatic radiation by a focusing camera. He computed both the Warren and the Finbak functions and concluded that the Si-O-Si angle is in the range of 127° to 150° over the temperature range used. He shows that 140° to 145° might be expected from the local order in the polymorphic crystalline forms or as an average of all allowable bond angles. It is interesting to note that his Finbak function shows no indication of an oxygen-oxygen coordination in the 2.0-3.0 Å range.

(5) Mendel [39] uses monochromatic CuK_α radiation in his vitreous silica investigation; thus the range of S is less than 8.0. His Finbak function also shows no oxygen-oxygen coordination in the 2.0-3.0 Å range.

B. Neutron Scatter Investigations

Neutron scatter investigations on vitreous silica have the advantage that the cross section is independent of the scatter angle.

The three neutron researches are:

(1) Ruderman [56], working with the Columbia velocity selector, found peaks in the scatter pattern corresponding to $S = 2.38, 2.88, 3.26, 3.64, 5.77$ and 8.90 . To our knowledge the data were not converted to absolute intensities or further analyzed.

(2) Milligan, Levy, and Peterson [40], working with the Chemistry Division spectrometer at Oak Ridge, utilized monochromatic neutrons of wavelengths $1.31 \text{ \AA}$ and $0.764 \text{ \AA}$ to determine the scatter pattern to $S = 13.8$. The data were analyzed in a way analogous to the Warren calculation. This atomic radial distribution sum contains more character than Warren's, probably due in part to misnormalization or errors in the intensity at high S . An Si-O-Si angle of 142° was deduced.

(3) Weber and coworkers [13] worked from the total inelastic scattering to deduce the atomic radial distribution sum from 2% data calculated from the Einstein model and a semi-empirical model for inelastic scattering. The results are not pleasing in that the atomic radial distribution sum from the Einstein model does not resolve the first Si-Si coordination and the Si-Si distance from the semi-empirical model is more than twice the Si-O distance.

C. Electron Scatter Investigations

Electron scatter investigations on vitreous silica have an advantage over x-ray scatter because of the greater efficiency of the electron scatter process and because the electrons are easily monochromated. On the other hand, it is difficult to determine the diffracted intensity as accurately as may be done with x-radiation, and surface effects are difficult to remove. The investigations utilizing electrons are:

(1) Dixit [16] reflected electrons from the surface of several glasses. He observed a halo corresponding to the crystallographic $d = 1.50 - 1.55$. The intensity of this ring increased as the surfaces were polished, indicating that polishing a glass promotes crystallization.

(2) McClurg [38] used the atomic radial distribution sum as formulated by Pauling and Brockway [47] for electron diffraction over an unspecified S range. The $d_{Si-O} = 1.3 \text{ \AA}$ and $d_{O-O} = 2.2 \text{ \AA}$ are noticeably less than those determined by other methods. McClurg argues that this discrepancy is due to the fact that the electrons are primarily scattered from the surface, but the surface effect should increase, not decrease bond lengths.

D. Miscellaneous Investigations on the Structure of Vitreous Silica

Infrared and Raman spectra studies have not been quantitative except for a recent paper by Su, Borrelli, and Miller [60]. They have shown that the bands in vitreous silica are roughly predicted from a model comprised of a SiO_4^{+4} tetrahedron whose oxygens are bonded to infinitely heavy Si atoms, the Si-O-Si angle being assumed to be 180° . It is necessary that the bond lengths be statistically distributed to account for the diffuse nature of the bands, but the negligible temperature effects on the absorption frequencies indicate that the vibrations are harmonic. Zarzycki and Naudin interpreted their infrared absorption measurements in terms of the Stepanov and Prima theory to show that the tetrahedra in vitreous silica are distorted asymmetrically [15].

The ultrasonic attenuation and excess specific heat at low temperatures and a Raman band may be explained by a Schottky defect, a stretched Si-O-Si bond [8]. This defect is relieved by neutron irradiation. The elongated $d_{\text{Si-Si}} = 3.72$ to 3.88 and 10 to 20% of the Si-Si bonds must be elongated to explain the experimental data. Thus there should be a $d_{\text{Si-O}} = 2.2$ in the atomic radial distribution sum. This distance was observed only by Richter [54] and may be an error in the analysis [21]. In opposition to this concept, Schottky defects have not been found in the crystalline silicates [36].

The x-ray absorption spectra of silicon in vitreous silica has not been measured but the absorption spectra of germanium in amorphous germanium oxide, an isomorph of vitreous silica, has been determined [44]. The results indicate in a qualitative manner that the amorphous structure

is similar to the GeO_2 isomorph of quartz. It is perhaps significant that the amorphous GeO_2 used in this investigation was made by melting and quenching the hexagonal (quartz) form, and that the x-ray scatter experiments also indicate the Ge-O-Ge angle is less than the Si-O-Si angle, thus a more quartz-like structure [66, 75].

The results of these investigations, the results of the present investigation, and the proposed models are presented in Table I.

III. EXPERIMENTAL

A. Sample Preparation

The vitreous silica used in these investigations was prepared commercially by American Fused Quartz Company of Dover, New Jersey.

The specimens used in the Guinier reflection arrangement were cut and ground to the cylinder of the camera (a diameter of 57.3 mm) and were approximately 1.0 cm by 1.5 cm. The thickness of the specimen in the region of the incident x-radiation is 30.6 half-value layers for CuK_α radiation (2.80 mm). The specimens used in the Guinier transmission arrangement were cut and ground to flat plates approximately 1.0 by 1.5 cm. The thickness of these plates is 4.72 half-value layers (0.432 mm) and 8.50 half-value layers (0.588 mm) for samples A and B, respectively.

Specimens used in the diffractometers were 1.0 inch squares cut from the 0.125 inch thick (4.57 half-value layers for MoK_α radiation) plates as purchased.

Specimens used to study the devitrification process were prepared for the diffractometers. The specimens were thermally aged by inserting the specimen in a pre-heated Burrell furnace in a clean alumina furnace boat. After twenty-four hours at the specified temperature $\pm 5^\circ\text{C}$ the specimen was quenched to approximately 40°C in 15 seconds by moving the boat to the outermost region of the furnace tube. All heating and cooling was performed in a controlled dry nitrogen atmosphere.

B. Scattered Intensity Determinations

Three independent techniques were used to determine the scattered intensity as a function of the scattering angle, 2θ . One technique utilizes a Guinier camera. The other two use a basic diffractometer and differ only in the way monochromatic radiation is obtained; consequently they will be discussed together.

1. Diffractometer Techniques

The diffractometers and x-ray generators used in these investigations are commercially produced by North American Philips. MoK_α radiation was used in this approximate parafocusing geometry, and vertical divergence was controlled by a Soller slit system. The current of the x-ray generator was stabilized, as was the line voltage, and a 0.25 mfd. smoothing capacitor with a protective gravity activated vacuum switch was attached across the x-ray tube.

A special krypton proportional detector and a sodium iodide-thallium activated crystal scintillation detector were utilized, their output signal being fed to a suitable preamplifier and then to a type O.R.N.L. A1 or Atomic-Baird 204B linear amplifier. The amplified pulse was discriminated so that the center 80-90% of the input was counted on the attached scaler. A special control circuit caused:

- (1) A Clary printing timer to print the time required to accumulate a specified count, N , with an identifying number,
- (2) The diffractometer arm to be moved a specified angular increment ($\Delta 2\theta$), and,

(3) Initialization of the scaler and other equipment, thus beginning a new cycle.

Thus the basic apparatus determines the relative scatter pattern to a known relative error, $1/\sqrt{N}$ (where N is the number of counts accumulated at each value of 2θ), if the electronic equipment is stable for a sufficient length of time. The advantages and disadvantages of this technique are roughly the converse of those given for the Guinier camera (see page 19).

Assuming the long drift in the count rate to be linear for at least 48 hours, a region of data was redetermined in that period of time, the sets normalized, and data corrected according to the assumption. It was found that the total drift in the equipment was never greater than 1% a day, but there was often a definite trend for a week or more. This provides justification for the assumption.

The observed intensity has only two modifying functions. They are due to polarization,

$$(3-1) \quad M_{pol} = [(1 + \cos^2 2\theta') / (1 + \cos^2 2\theta' \cos^2 2\theta)]^*,$$

and sample absorption,

$$(3-2) \quad M_{abs} = [(1 - 1/x) - e^{-x'} (1 - (x' + 1)/x)]^{-1},$$

where $x = 2mW \csc(2\theta)$, $x' = \min(x, 2mT \csc\theta)$, W = beam width at sample, T = sample thickness, and m = linear absorption coefficient of the sample. As shown in Appendix A, this correction applies only where the solid angle defined by the counter slits is identical to the solid

* $2\theta' = 0$ if no crystal monochromator is used.

angle of the incident radiation. No correction should be made if the defining (scatter) slit is absent. Details of these calculations and their implementation on the Rice Computer are given in Appendix A.

a. Crystal monochromatization. The first monochromator utilized was a plastically bent and ground sodium chloride crystal monochromator. The x-ray tube housing was modified to incline 15.0° and the generator table was extended to accomodate the diffractometer in its new position with the monochromator attached to the tube housing. The beam was diffracted from the focusing monochromating crystal in the plane of the diffractometer, the optimum method for the physical arrangement of the diffractometer and x-ray tube according to experiments with other arrangements. It was possible to use an impressed voltage of 45 kv. and 20 ma. without difficulty with the higher or lower harmonics even when the less resolving but more efficient scintillation counter was used.

b. Pulse height and mathematical monochromatization. The second monochromator used with the diffractometer is an attempt to alleviate the following problems encountered with the first:

(1) Instrumental drift and maintenance, by requiring less time to determine the scatter pattern.

(2) The fabrication and alignment of the bent and ground crystal monochromators.

The approach is to determine the scatter pattern $s(k_\alpha \sin\theta)$ with polychromatic x-radiation, determine the energy distribution of the radiation $B(k)$, ($k = 4\pi/\lambda$, λ = wavelength), and solve the Fredholm integral equation of the first kind

$$(3-3) \quad s(k_{\alpha} \sin \theta) = \int_0^{\infty} B(k) I(\sin \theta, k) dk$$

for the scattered radiation from a monochromatic beam $I(\sin \theta, k)$. To an approximation explained in Appendix A, this problem has a practical solution if certain restrictions which are easily met in experiments of this type are placed on the nature of $B(k)$. They are:

$$(3-4a) \quad B(k) = d(k - k_{\alpha}) + g B'(k), \quad k_{\alpha} = 4\pi/\lambda_{K_{\alpha}}$$

$$(3-4b) \quad \int_0^{\infty} B'(k) dk = 1$$

where $d(x)$ is the Dirac delta function.

From the development in Appendix A the desired function $I(\sin \theta, k)$ is approximated by $I_1(k \sin \theta)$ carrying out the iteration

$$(3-5) \quad I_1(k_{\alpha} \sin \theta) = \sum_{j=0}^{\infty} (-g)^j s(k_{\alpha} \sin \theta)$$

$$I_1(k_{\alpha} \sin \theta) = s(k_{\alpha} \sin \theta) - g \int_0^{\infty} B'(k) I_{1-1}(k \sin \theta) dk$$

to the desired precision which is dependent on the accuracy and precision of the measurement of $B(k)$ and $s(k_{\alpha} \sin \theta)$.

The calculations associated with the diffractometer were done by routines running on the Rice Computer as described in Appendix A.

2. Guinier Camera Technique

A Guinier camera consists of a Johansson bent and ground crystal monochromator and a Seemann-Bohlin camera arranged so that the

diffracted beam is parafocused on the film emulsion for every angle of scatter within the camera limits. Soller slits were used to limit the vertical divergence. This camera, usually employed in precise determination of unit cell dimensions, has the following attractive attributes for liquid-like scatter research:

- (1) A relative intensity determination free from instrumental drift due to line voltage variations and electronic component aging, etc., an obvious property of all camera techniques,
- (2) A high ratio of scattered intensity to input power due to the parafocusing geometry and higher dispersion than other camera arrangements (twice the dispersion of a Debye-Scherrer camera of the same diameter),
- (3) Monochromatic radiation and a low background, both vitally important in liquid-like scatter determinations.

The difficulties with the Guinier camera are:

- (1) Intensity determinations require careful film processing, calibration, precise knowledge of the transmission ratios (film factors, etc.), and a sensitive but stable microphotometer. The precision of intensity measurements from film are rarely better than 10%, an undesirable property of all camera techniques.
- (2) The asymmetry of the geometry causes the relative intensity to be a function of several factors not ordinarily encountered.

The Guinier camera was calibrated with respect to 2θ by observing the diffraction pattern from copper foil; fiducial marks were then placed on all subsequent film at $2\theta = 0$ and $2\theta = \alpha$, the angle between the incident x-ray beam and the normal to the sample surface inside of the camera. Simultaneous determination of the diffraction pattern

from any standard crystalline material and the scatter pattern from vitreous silica is not practical due to the large difference in the efficiencies of the processes.

The films were microphotometered with a Kipp microphotometer; the intensity sensing element was a sensitive thermopile guarded from infrared radiation by a lithium fluoride window. Later, when the thermopile was found to be unstable, a cadmium sulfide-selenide detector circuit was utilized in its log linear range, which was determined by calibrations using various thicknesses of neutral density material.

The gamma curve of the photographic emulsion of the film (Kodak blue-sensitive one emulsion film) was determined, assuming the reciprocity law, in the usual manner of various time exposures of a stabilized x-ray beam. This information provides a calibration ratio R , the ratio between the actual incident radiation and that calculated from the microphotometer readings as a function of the calculated intensity, I_c .

The equation relating the relative intensity scattered through an angle 2θ to the observable quantities was found to be

$$(3-6) \quad I_s(2\theta) = M_{pol}(2\theta) M_{abs}(2\theta, \alpha) M_{air}(2\theta - \alpha) M_{foils}(2\theta - \alpha) \times \\ M_{div}(2\theta - \alpha) E_{film}(2\theta - \alpha) I_c(2\theta) R[I_c(2\theta)]$$

where

$M_{pol}(2\theta)$ = modification function due to polarization,
 $= (1 + \cos^2 2\theta') / (1 + \cos^2 2\theta' \cos^2 2\theta)$ and $2\theta'$ is the
scatter angle of the crystal monochromator,

$M_{\text{abs}}(2\theta, \alpha)$ = modification function due to the absorption of the specimen,

$= Z/[1 - \exp(-Z)]$ assuming that the x-ray beam is parallel and the specimen is a flat plate, $Z = m_s t [\sec(2\theta - \alpha) - \sec \alpha]$, m_s = linear absorption coefficient of the specimen, and t = the thickness of the specimen,

$M_{\text{air}}(2\theta - \alpha)$ = modification function due to the air scatter,
 $= \exp[m_{\text{air}} d \cos(2\theta - \alpha)]$, m_{air} = linear absorption coefficient of air, and d = the diameter of the camera,

$M_{\text{foils}}(2\theta - \alpha)$ = modification function due to the foils through which the radiation must pass to reach the emulsion,
 $= \exp[\sum_i m_i t_i \sec(2\theta - \alpha)]$, m_i = the linear absorption coefficient of the i^{th} foil, and t_i = the thickness of the i^{th} foil,

$E_{\text{film}}(2\theta - \alpha)$ = the efficiency of the emulsion
 $= 1/\{1 - \exp[-m_e t_e \sec(2\theta - \alpha)]\}$ assuming no secondary processes, m_e = linear absorption coefficient of the emulsion, t_e = thickness of the emulsion,

$M_{\text{div}}(2\theta - \alpha)$ = modification function due to the divergence of the scattered beam in the vertical plane of the camera,

$= 1/\ln\left\{[(1 + x^2)^{1/2} + x]/[(1 + x^2)^{1/2} - x]\right\}$ where
 $x = h/2 d \cos(2\theta - \alpha)$ and h is the height of the beam at the sample,

$I_c(2\theta)$ = the intensity calculated from the microphotometer results, and

$R[I_c(2\theta)]$ = the calibration ratio.

It is also possible to calculate the perturbations of the scatter pattern due to some experimental factors. The radiation scattered

through 2θ may be displaced by Δ in degrees 2θ due to

(1) Finite sample thickness. The displacement is

$$(3-7) \quad \Delta_t = (180/\pi d) t \sin 2\theta \sec \alpha \sec(2\theta - \alpha)$$

where t is the thickness of the sample in the same dimensions as d .

(2) Finite beam height. The displacement is

$$(3-8) \quad \Delta_h = (45/8\pi)(h/p)^2 \cot 2\theta \{1 + [p/d \sec(2\theta - \alpha)]^2\}$$

where p is the path length of the x-ray beam and h is the height of the beam.

(3) Misalignment of the sample. The error is

$$(3-9) \quad e_m = (180/\pi d) m \sin 2\theta \sec \alpha \sec(2\theta - \alpha)$$

where m is the estimated misalignment off the camera cylinder in the same dimensions as d .

If the x-ray beam is not focused but assumed parallel with a width w , the maximum spread is

$$(3-10) \quad \Delta_w = (180/\pi d) w \sec(2\theta - \alpha)$$

where w is the same dimensions as d .

No Lorentz factor enters since we are interested in intensity, not power, and no horizontal divergence correction is necessary since the diffracted beam is parafocused on the emulsion in that plane. Details

of these calculations and their implementation on the Rice Computer are given in Appendix B.

IV. ANALYSIS

Analyses of the local order in vitreous silica from scatter techniques have not been very quantitative. Most have calculated the atomic radial distribution sum (Warren function), determined the interatomic distances, estimated the coordination numbers and explained any inconsistencies by termination-of-series errors, or thermal or surface effects. The atomic radial distribution sum calculation is subject to errors originating from the assumptions in its formulation. All other investigations have used the electronic radial distribution sum (Finbak function) in which only the first Si-O and Si-Si neighbors were resolved. The lost first O-O peak has undoubtedly merged with the Si-Si, leading to a shortened Si-Si distance and an incorrect estimate of the Si-O-Si bond angle.

The present analysis, in an attempt to escape these difficulties, used the radial distribution sums only as a guide to the requirements of consistent structural models. These models, proposed with the expediciencies described below, were then refined in terms of the observed scatter by nonlinear regression.

The atomic and electronic radial distribution sums were calculated as described below. A third sum, the pair radial distribution sum, which provides a more accurate interpretation of the atomic radial distribution sum, is also described. No attempt, however, was made in this investigation to seek more information by a variation of the peak shape.

A. The Scattered Radiation from a Disordered Assembly of Semiclassical Scattering Centers

The total scatter from an assembly, Σ' , of scattering centers is

$$(4-1) \quad I^{\text{Total}} = I^{\text{Inc}} + I_e \sum_{i,j} f_i f_j e^{-S} g_{ij}^2 / 2 j_0(SR_{ij})$$

where $I^{\text{Inc}} = R \sum_i f_i^*$ is the total incoherent scattering from Σ' , f_i^* is the incoherent factor for the i^{th} center, R is the Klein-Nishina recoil factor, $I_e = (e^4/m^2c^4)(1 + \cos^2 2\theta)/2 r^2$ is the scatter from a Thomson electron if r is the distance from the scatter point to the observation point, f_i is the form factor of the i^{th} center, g_{ij}^2 is the variance from the mean distance R_{ij} between the i^{th} and the j^{th} center due to temperature and the static statistical distribution, and $j_0(x) = \sin x/x$ is the zeroth spherical Bessel function. The details of the derivation of (4-1) are given in Appendix C.

Over 50% of the radiation scattered at the higher angles is incoherently scattered; for this radiation the polarization function does not strictly apply, but it is impossible to eliminate it with the present counters and electronics. (Placing the monochromating crystal after the sample will only partially eliminate this problem and complicated alignment and construction difficulties.)

B. The Radial Distribution Sums

The radial distribution sums may be computed from (4-1) written in the form

$$(4-2) \quad S_i(S) = S \left\{ [(I^{\text{Total}} - I^{\text{Inc}})/I_e] - \sum_i f_i^2 \right\} = \sum_i \sum_{j \neq i} f_i f_j e^{-S^2 g_{ij}^2/2} \sin(SR_{ij})/R_{ij}$$

after their particular set of assumptions are made which allow the application of the Fourier integral theorem.

The Fourier sine and cosine transforms were performed on the Rice Computer utilizing the algorithm of Filon [18].

1. Atomic Radial Distribution Sum

The atomic radial distribution sum for polyatomic substances was first given by Warren [67]. Letting $\rho_i(r)$ be the number of atoms at a distance r from the i^{th} atom, each multiplied by its effective number of electrons, K_j , where

$$K_j = f_j/f_e, \quad f_e = \sum_j f_j / \sum_j Z_j, \quad \text{and} \quad g_{ij} = 0$$

for all i and j , Warren computes the atomic radial distribution sum

$$(4-3) \quad 4\pi r^2 \sum_i K_i \rho_i(r) = 4\pi r^2 \rho_0 \sum_i K_i + (2r/\pi) \int_0^\infty S_i(S) \sin Sr \, dS$$

where ρ_0 is the average electron density of the material, and low

angle scatter is neglected.

Unfortunately the modifying function of $\text{Si}(S)$, $1/f_e^2$, varies approximately as S^2 . Thus the Warren function is a sensitive function of $i(S)$ at high S values, exactly where the precision of $i(S)$ is low, and of termination-of-series errors. For this reason a convergence factor is commonly inserted into the modifying function, causing it to become $(1/f_e^2)e^{-A^2S^2/2}$.

2. Electronic Radial Distribution Sum

Finbak [19] and more recently Mendel [39] have proposed the electron radial distribution sum to alleviate the difficulties of the atomic radial distribution sum.

Letting k be an index over all electrons and $\rho_k(r)$ be the effective number of electrons at a distance r from the k^{th} electron but not counting those electrons in the same atom with the k^{th} , Finbak computes

$$(4-4) \quad 4\pi r^2 \sum_k^{\text{electrons}} \rho_k(r) = 4\pi r^2 \rho_0 \sum_i^{\text{atoms}} Z_i + (2r/\pi) \int_0^\infty i(S) \sin Sr \, dS,$$

neglecting the low angle scattering.

This function so closely approximates $4\pi r^2 \rho_0 \sum_i Z_i$ that it is necessary to use the differential electron radial distribution sum

$$4\pi r^2 \left[\sum_k^{\text{electrons}} \rho_k(r) - \rho_0 \sum_i^{\text{atoms}} Z_i \right].$$

This lack of resolution therefore prohibits any estimate of coordination numbers.

3. Pair Radial Distribution Sum

Waser and Schomaker [68] pointed out that diffraction is a pair interaction and that the fault of the atomic radial distribution sum was the attempt to consider pairs as the product of two independent quantities. Thus rather than n entities, where n is the number of types of scattering centers, it becomes necessary to consider $n(n + 1)/2$ entities, the number of kinds of pairs in the material.

The formulation of the pair radial distribution sum may be similar to that of Warren's except geometrical averages are more consistent than are the arithmetic.

$$\text{Thus let } f_a^2 = \sum_j \sum_{i \neq j} f_i f_j / \sum_j \sum_{i \neq j} K_i K_j$$

$$\text{such that } f_a^2 K_i K_j = f_i f_j.$$

(These conditions overdetermine the f_a^2 and K_i by $kn(n - 1)/2$ equations where k is the number of data points.)

Thus the Waser function may be calculated by

$$(4-5) \quad 4\pi r^2 \sum_i \sum_{j \neq i} K_i K_j \rho_{ij}(r) = 4\pi r^2 \sum_i K_i \rho_{i0} + (2r/\pi) \int_0^\infty M(S) S i(S) \sin Sr \, dS$$

where $M(S) = e^{-A^2 S^2 / 2} / f_a^2$ for this investigation. The assumption above on the consistency of the f_a^2 and K_i 's is of little consequence as the shape of $\rho_{ij}(r)$ can now be calculated.* It is

$$(4-6) \quad r \rho_{ij} = \int_{-\infty}^{\infty} u \rho_{ij}^{\text{true}}(u) T_{ij}(u - r) \, du$$

* The Warren function will agree with these results if

$$\rho_i = \sum_{j \neq i} K_j \rho_{ij}(r).$$

with the shaping function

$$T_{ij}(r) = (1/\pi) \int_0^\infty f_i f_j M(S) \cos Sr \, dS$$

For the particular $M(S)$ chosen in this investigation

$$r\rho_{ij}(r) = e^{-(r - R_{ij})^2/2 (A^2 + g_{ij}^2)}$$

if the assumptions are consistent. These Gaussian shaped peaks should have a width at half maximum of $4.694/\sqrt{A^2 + g_{ij}^2}$ so g_{ij} may be approximately determined.

C. Normalization of Observed Intensity

It is necessary to determine the proper scale constant, K , of the observed intensity, $I^{\text{Obs}}(S)$, such that $I^{\text{Total}} = K I^{\text{Obs}}$ in IV A, and B. It is possible to determine $I^{\text{Obs}}(S)$ absolutely but numerous experimental difficulties arise, so analytic methods have been developed.

The first method for determining K is a consequence of the fact that the scattered intensity due to interference effects becomes insignificant relative to the independent scatter

$$(4-7) \quad I^{\text{Ind}} = (I^{\text{Inc}}/I_e) + \sum f_i^2$$

as S becomes large. Thus K can be found from a simple normalization at a point at a high S value or by a criterion which is not so dependent on the accuracy of one measurement, such as

$$(4-8) \quad \min_{S_0} \int_{S_0}^{S_1} (K I^{\text{Obs}}/I_e - I^{\text{Ind}})^2 W(S) dS$$

where S_0 and S_1 are suitably large and $W(S)$ is a weighting function, usually monotonically increasing with S .

Often the experimental data does not extend to large enough values for (4-8) to be reliable, and it is necessary to correct for the interference effects due to the fluctuations in density of the scattering matter of the sample. Without any assumptions on the structure it is safe to assume that $4\pi r^2 \sum K_i \rho_i(r)$ should be zero for $r_0 < 1/2 \min(r_i + r_j)$ for all i and j where r_i is the atomic (ionic) radius of the i^{th} atom (ion) in the sample. Thus from (4-2) in terms

of the Warren theory [28]

$$(4-9) \quad K = \frac{\int_0^{S_{max}} S [I^{Ind} - (4\pi/3) \rho_0 r_0^3 \sum K_1 \Phi(Sr_0)] dS}{\int_0^{S_{max}} S (I^{Obs}/I_e) dS}$$

$$= \int_0^{S_{max}} S (I^{Ind}) dS / \int_0^{S_{max}} S (I^{Obs}/I_e) dS \text{ if } r_0 = 0$$

where $\Phi(x) = [3/x^2][(\sin x)/x - \cos x]$.

The weaker assumption that the radial distribution sums are not necessarily zero over any appreciable interval from $r = 0$ but simply approach zero as r approaches zero produces for the electron radial distribution sum [46]

$$(4-10) \quad K = \left(\int_0^{S_{max}} S^2 I^{Ind} dS - 2\pi^2 \rho_0 \sum_1 Z_1 \right) / S^2 \int_0^{S_{max}} I^{Obs} dS$$

and for the atomic radial distribution sum [33]

$$(4-11) \quad K = \left[\int_0^{S_{max}} (S^2 I^{Ind} / \sum f_1^2) dS - 2\pi^2 \rho_0 \sum_1 K_1 \right] / \int_0^{S_{max}} (S^2 I^{Obs} / \sum f_1^2) dS$$

These results follow from (4-4) and (4-3) respectively.

If the first few interatomic distances and coordination numbers may be safely assumed, then the overlap of the atomic (ionic) charge distributions may be taken into account in the calculation of K , as described by Mendel [39]. The result is the addition in the denominator of (4-10) of the term

$$4\pi \int_0^{S_{max}} S^2 \int_0^{\infty} \sum_k \rho_k(r) r^2 j_0(Sr) dr dS$$

where $\rho_k(r)$ is the density at r of electrons in the specimen but not

belonging to the atom containing the k^{th} electron. A similar term may be calculated for the atomic case. (4-9) may also be corrected for the first few interatomic distances by adding the term

$$4\pi \int_0^{S_{\max}} \sum_i \sum_{j \neq i} f_i f_j \cdot (S r_{ij}) r_{ij} dS$$

and letting $r_0 = (3 \sum_i \sum_{j \neq i} K_i K_j / 4\pi \rho \cdot \sum_i K_i)^{1/3}$.

D. Model Proposals and Their Refinement

Because of the absence of a finite repetitive unit cell in liquid-like structures the atomic arrangement must be specified over a large volume. Usually chemical reasoning and the radial distribution sums will not provide definite information for more than the first three or four nearest neighbors although the observed scattering may be most significantly affected by higher order neighbor pairs. In order to specify these larger distances in a way consistent with the stoichiometric ratio of types of scattering centers it is often convenient to consider Σ' as composed of subsystems Σ'' which obey the stoichiometric ratio of the material, are spherically symmetric, and scatter as a point. If this point is labeled p, then the scattering factor for the subsystem Σ'' is

$$f_{\Sigma'' p} = \sum_{i \in \Sigma''} f_i(s) j_0(sR_{ip}).$$

Often this assumption is poor but no other method for extending the structure has been devised which is less tedious, or which yields any additional information.

The scattered intensity is calculated for detailed center arrangement to the greatest possible limit where the stoichiometric ratio is valid. The structure is then extended with the subsystems Σ'' described above. At some greater distance, R_j , from the j^{th} scatter center it becomes reasonable to assume that the material is truly amorphous, composed of a continuum of the subsystems Σ'' . The diffracted intensity from the j^{th} center and the continuum is then

$$I_e e^{-S^2 g_j^2/2} f_j f_{\Sigma'''} \rho''' 4\pi \int_{R_j}^{sample} j_0(Sr) r^2 dr \\ \cong -(4\pi/3) I_e \rho''' R_j^3 f_j f_{\Sigma'''} e^{-S^2 g_j^2/2} \Phi(SR_j)$$

where $\Phi(x) = (3/x^2) (\sin x/x - \cos x)$, ρ''' is the density of Σ''' in the sample, and the low angle scatter has been neglected.

Thus the equation used for the calculation of the scattered radiation from a model assembly of scattering centers is

$$(4-12) \quad I^{Total} = I^{Inc} + I_e \left[\sum_i \sum_k n_{ik} f_i f_k e^{-S^2 g_{ik}^2/2} j_0(SR_{ik}) + \right. \\ \left. \sum_k \sum_l n'_{kl} f_k f_{\Sigma_l'} e^{-S^2 g_{kl'}^2/2} j_0(SR'_{kl}) - \right. \\ \left. (4\pi/3) \rho''' \sum_j f_j f_{\Sigma'''} e^{-S^2 g_j^2/2} \Phi(SR_j) R_j^3 \right]$$

Once a model structure is proposed the intensity scattered by it may be theoretically calculated as outlined above. If the agreement is not as expected, it is necessary to have a systematic method for refining the structural model. Several methods have been devised for this purpose for crystalline models. Only one of these methods, nonlinear regression, will be discussed for use with vitreous structures. The other methods are discussed for crystalline models by Buerger, who also provides an adequate bibliography on the subject [7]. Cohen has further shown that the least squares criterion is applicable even when the statistics are not Gaussian [10].

The set of values, $\{p_j^i\}$, for the parameter set, $\{p_j\}$, of I is sought which minimizes the sum of the squares of the error

$$(4-13) \quad [I^{\text{Obs}}(S_1) - P_0 I(P_j, S_1)]^2 / 2w_1$$

where $I^{\text{Obs}}(S_1)$, the observed intensity, has been observed on the set, $\{S_1\}$, and w_1 is the weighting factor of the measurement at S_1 .

If a trial structure is proposed whose parameter set $\{p_j''\}$ differs only slightly from $\{p_j'\}$, then it is reasonable to assume that

$$(4-14) \quad I_{\text{True}}(S_1) = P_0 I(P_k'', S_1) + A \cdot D$$

where $A_{ij} = \partial[P_0 I(P_k'', S_1)] / \partial P_j$ and $D_j = \Delta P_j$. Then (4-13) may be written

$$(4-15) \quad (1/2)(\Delta I - A \cdot D)^{\dagger} \cdot W \cdot (\Delta I - A \cdot D)$$

where $\Delta I_1 = I^{\text{Obs}}(S_1) - P_0 I(P_k'', S_1)$, $W_{ij} = \delta_{ij} w_1$, and δ_{ij} is the Kronecker delta. Provided that n , the dimension of the vector ΔI , is greater than m , the dimension of the vector D , a minimum may be found for some set of $\{\Delta P_j\}$ if they are linearly independent. Since the expression (4-15) is only quadratic in the ΔP_j 's, the set of normal equations becomes

$$(4-16) \quad B \cdot D = Z$$

where $B = A^{\dagger} \cdot W \cdot A$ and $Z = A^{\dagger} \cdot W \cdot \Delta I$. (4-16) has the symbolic solution

$$(4-17) \quad D = B^{-1} \cdot Z$$

A practical solution can be made by Jacobi elimination, or if the matrix B is diagonally dominant the Gauss-Seidel iteration technique may be used.

The assumption in (4-14) is not strictly valid so it is necessary to iterate this procedure. The method is equivalent to the search for roots of a function by Newton's method in m dimensions.

From the equations above it is also possible to determine the covariance of the parameters. Suppose that $(G^2)_{jk} = G^2(P_j, P_k) = G^2(\Delta P_j, \Delta P_k)$ and s_i is the standard deviation of the $I^{Obs}(S_i)$. Then from (4-17)

$$(4-18) \quad G^2 = [1/(n-m)][B^{-1} \cdot A^{\dagger} \cdot W \cdot s][B^{-1} \cdot A^{\dagger} \cdot W \cdot s]^{\dagger} = [s \cdot W \cdot s / (n-m)] B^{-1}$$

If w_i is the variance of the measurement at s_i , i.e. S_i^2 , then

$$G^2 = [n/(n-m)] B^{-1}$$

The calculations of the intensity from a proposed model and the refinement of the model were programmed for the Rice Computer in the algorithmic language of the Genie processor, becoming the first major computation compiled by the processor [29]. It was desirable to have these computations, which will be described elsewhere, in the higher level language in order to minimize the recoding when a new model was proposed.

E. Line Broadening Due to Crystallite Size

Most theoretical expressions for the mean crystallite dimension as a function of the observed diffraction line breadth B and the natural line breadth b are of the form

$$(4-19) \quad L = [K/(B-b)]\lambda/\cos\theta,$$

although Warren finds

$$(4-20) \quad L = [K/(B^2-b^2)^{1/2}]\lambda/\cos\theta$$

where K is a constant whose value is approximately 0.90. Due to the difficulty of obtaining an accurate determination of b it is only reasonable to use this expression when $b/B \ll 1$ so that the difference between (4-19) and (4-20) is not significant. Thus L may only be determined to 10% in the range of 10 to 1000 angstroms.

A derivation of (4-19) and (4-20) and their utility may be found in Klug and Alexander [32].

V. EXPERIMENTAL RESULTS

A. Scatter Patterns from Thermally Aged Vitreous Silica

The scatter patterns from specimens were determined with .016 mm. nickel foil filtered x-radiation from copper-targetted tube. 15 kilovolts were used in order further to improve the K_{α} to continuous radiation ratio. The scatter patterns differed from the pattern from an untreated specimen only in the superposition of crystalline diffraction lines corresponding to those of α -cristobalite. Visual inspection of the treated specimens shows that crystallization begins, as expected, at the surface. In the 1300°C sample less than 15% of the material remained amorphous.

The crystalline lines associated with the specimens and the mean crystallite dimension calculated from the line breadths are given in Table II. The K calculated by Bragg (0.890) and the form (4-20) were used since the crystallite shape is probably spherical and the diffraction lines were at the low 2θ [32].

B. Precise Intensity Determinations

1. Diffractometer Techniques

a. Crystal monochromator. Data were taken with crystal monochromated K_{α} radiation from a molybdenum targetted tube with an impressed voltage of 48 kv. and 18 ma. over the range of $S = 0.40$ to 17.0 . Observations were made at intervals $\Delta S \leq .04$ ($\Delta 2\theta = .25^\circ$) for $S = 0.40$ to 8.00 , $\Delta S \leq 0.6$ ($\Delta 2\theta = .50^\circ$) for $S = 8.00$ to 11.00 , $\Delta S \leq .12$ ($\Delta 2\theta = 1.00^\circ$) for $S = 11.00$ to 13.00 , and $\Delta S \leq .20$ ($\Delta 2\theta = 2.00^\circ$) for $S = 13.00$ to 17.00 . A constant count of 51200 was determined with a scintillation counter and the effect of machine drift was eliminated as described above. The data, converted into relative intensity, properly normalized, and corrected for polarization and sample absorption as described above, are shown in Figure 1. The statistics of this data indicate the precision is better than 1% everywhere. No attempt was made to eliminate the effect of the $K_{\alpha_1\alpha_2}$ doublet since the effect is negligible for a pattern as diffuse as that from vitreous silica [31].

As a check on the nature of the radiation from this apparatus the energy distribution of the incident beam was determined by replacing the sample with a rock salt analyzing crystal and observing the (200) reflection. The results are given in Figure 2.

b. Pulse height and mathematical monochromator. Data were taken with radiation from a molybdenum targetted x-ray tube with an impressed voltage of 35 kv. and 18 ma. filtered by 0.037 mm of zirconium. The data were recorded with a krypton proportional counter

and discriminator circuit. With a pulse height of 20 volts and a 13 volt acceptance width, the effective incident beam in 87% MoK_{α} radiation as determined by analyzing the beam with (200) reflection from a rock salt crystal shows that the remaining 13% of the beam is a low lying pedestal of continuous radiation. (Figure 2.)

The scattered intensity from the vitreous silica sample was determined according to the schedule of the crystal monochromated data except 102,400 counts were accumulated for each angular setting. The data were processed to correct for sample absorption, polarization, and machine drift, and also according to Equations (3-5) with $g = 0.148$ as determined from Figure 2 and Equations (3-4). The iteration (3-5) converged for $i = 3$ to .1% relative standard deviation. The relative difference between this data and the data taken by the crystal monochromator is less than 1% when the data are properly normalized. Since the short period fluctuations of the apparatus caused an error of .25 - .75%, the two determinations are equivalent.

2. Guinier Camera Technique

The Guinier camera was used with radiation from a copper targetted x-ray tube with an impressed voltage of 35 kv. and 20 ma. monochromated by $(10\bar{1}1)$ reflection from a bent and ground focusing quartz crystal monochromator. The vertical divergence of the beam was limited by a Soller slit system between the x-ray tube and the crystal. The camera was calibrated by the crystalline diffraction from copper, in both the reflection and transmission arrangements.

Data sets were taken for vitreous silica for α , the angle of

incidence of the beam to the surface of the sample, equal to 30° , 40° , and 45° with sample A, equal to 40° with sample B, and equal to 135° , 145° , and 150° with the reflection sample. Other typical parameters of the determinations, their method of measurement, and tolerances are given in Table III. These data were converted to intensity as described in III. B.2. and it was found that, except for the sample factor, all factors of Table III could be varied by 15% without a variation in the calculated intensity of more than 5% over the range of interest. The maximum error in any particular S due to misalignment of the sample was $\Delta S = .03$ and the maximum spread due to sample thickness and beam height was $\Delta S = .12$ over the range of interest for all determinations.

After correcting these data sets for background, a correction which was always less than 10% over the range of interest, the data sets for the same α agreed to 3% and for different α to 5%. The merger of the twelve transmission data sets and the four reflection data sets for untreated vitreous silica is presented in Figure 3. Over the range $S = (4\pi/\lambda)\sin\theta = 0.80$ to 7.00 the relative difference in the Guinier camera data and that from the diffractometer-crystal monochromator technique (Figure 1) is 8% and the qualitative features are similar. (The agreement of particular Guinier determinations was much better, in the order of 3 to 4%.)

C. The Radial Distribution Sums

1. Atomic Radial Distribution Sums

The independent scatter, I^{Ind} , from the sample was calculated assuming both the purely ionic and the purely atomic configurations. The sources of all necessary data for these calculations are given in Table IV. As seen from Table IV, it was necessary to terminate the calculations at $S = 4\pi(\sin\theta/\lambda) = 4\pi(1.10) = 13.82$. The K_i for the configurations were found to be $K_{\text{Si}} = 15.393$, $K_0 = 7.303$, $K_{\text{Si}}^{-4} = 14.749$, and $K_0^{-2} = 7.625$. The f_a for the two configurations when normalized together differ by less than 2%.

The data for untreated vitreous silica determined with the diffractometer-crystal monochromator technique (Figure 1) were normalized to these two I^{Ind} by the following six methods:

(1) Iteration of (4-8) with $W(S) = 1$, $S_0 = 10.0$, and $S_1 = 13.8$ until K was known to three significant figures.

(2) Iteration of (4-8) with $W(S) = S$, $S_0 = 10.0$, and $S_1 = 13.8$ until K was known to three significant figures.

(3) Calculation of K by Equation (4-9) with $S_{\text{max}} = 13.8$ and $r_0 = 1.00$.

(4) Calculation of K by Equation (4-9) with $S_{\text{max}} = 13.8$ and $r_0 = 0$.

(5) Calculation of K by Equation (4-11) with $S_{\text{max}} = 13.8$

(6) Calculation of K by Equation (4-11) with overlap correction assuming regular SiO_4^{-4} tetrahedra with $d_{\text{Si-O}} = 1.60$ and $S_{\text{max}} = 13.8$.

The K produced by these methods agreed to 5%. Due to the weak influence of the interferences above $S = 10.00$ or to pure chance,

(2) provided the most satisfactory normalization. A correction in the 4th significant figure of K was made by iteration on the radial distribution calculation until the desired shape of the sum was attained for r less than 1.00. Utilizing this normalization constant and assuming the density of the vitreous silica specimen to be 2.20, the atomic and ionic radial distribution sums were calculated. Differences between the ionic and atomic radial distribution sums were insignificant for r less than 4.0 due to the slight difference in the I^{Ind} . Since the radial distribution sums are very diffuse above $r = 4.0$, the differences in that region are not important.

The effect of the convergence factor $e^{-A^2 S^2 / 2}$ can be seen in the series of ionic radial distribution sums displayed in Figure 4 with $A = 0$, 0.054, and 0.080. The false peaks appearing in the ionic radial distribution sum with $A = 0$ were removed and the data reinverted to find the aliasing contribution to I^{Obs} . The result is displayed in Figure 5, with I^{Obs} given again for reference. The ionic radial distribution sum from this data is given in Figure 6.

The interatomic (interionic) distances and their standard deviation from the atomic (ionic) radial distribution sum listed in Table I were gotten from the Viervoll function [68] illustrated in Figure 7. The coordination numbers listed in Table I were determined from Figure 6 and were consistent for resolved coordinations with $A = 0.054$ and 0.080.

2. Electron Radial Distribution Sums

The independent scatter, I^{Ind} , for the purely ionic configuration was used for all electronic radial distribution sums since they are

somewhat less sensitive to differences in I^{Ind} .

The data for untreated vitreous silica determined with the diffractometer-crystal monochromator technique (Figure 1) were normalized by the following four methods:

(1) Iteration of (4-8) with $W(S) = 1$, $S_0 = 10.0$, and $S_1 = 13.8$ until K was known to three significant figures.

(2) Iteration of (4-8) with $W(S) = S$, $S_0 = 10.0$, and $S_1 = 13.8$ until K was known to three significant figures.

(3) Calculation of K by Equation (4-10) with $S_{\text{max}} = 13.8$.

(4) Calculation of K by Equation (4-10) with overlap correction assuming regular SiO_4^{-4} tetrahedra with $d_{\text{Si-O}} = 1.60$ and $S_{\text{max}} = 13.8$.

The K 's produced by these methods are in close agreement but method (4) produces a slightly better K . A correction in the third and fourth significant figures of K was made by iteration on the differential electron distribution sums until the desired shape of the sum was attained for r less than 1.00.

The differential electron radial distribution sum was computed with $S_{\text{max}} = 8.0$ and $S_{\text{max}} = 13.8$, and the results are displayed in Figure 8. With the lower S limit the sum is similar to Zarzycki's [74] and Mendel's [39]. The higher S limit produces higher resolution, separating the O-O and Si-Si correlations, but also produces some disturbing spurious peaks.

D. Models and Their Refinement

Two distinct forms of the general problem of formulating and refining a model of the atomic structure of a vitreous material were utilized in this investigation. The first method was simply to propose from chemical and crystallographic data a model which does not require periodicity and is consistent with the radial distribution sums. From this model the set* $\{q_i\} = \{n_{ik}, g_{ik}, R_{ik}, n'_{kl}, g'_{kl}, R'_{kl}, g_j, R_j\}$ was calculated, and this set was considered to be the linearly independent set of parameters in the refinement program.** This method has two serious faults--computational difficulties due to the large parameter set, and the fact that the result may be inconsistent since no geometrical limitations between parameters have been made. Due to these faults this method is called the inconsistent refinement.

The second method required that the model be defined in terms of a smaller set of parameters $\{p_j\}$ such that $q_i = q_i(p_j)$; thus the geometrical and other restrictions may be imposed. This method, the consistent refinement, replaces the faults of the inconsistent refinement with the inconvenience of deriving the functions $q_i(\{p_j\})$ and the necessity of reprogramming $q_i(\{p_j\})$ and $\partial q_i / \partial p_j$ every time a new model is considered. These two factors and the limited storage capacity of

* The parameters of I^{Total} in Equation (4-12).

** It was possible to fix the values of $\{g_j\}$, $\{R_j\}$ and $\{n_{ik}, n'_{kl}\}$ during the refinement. In fact, it was convenient to fix $\{R_j\}$ and $\{n_{ik}, n'_{kl}\}$ since $R_j = R_j(n_{ik}, n'_{kl}, \rho''')$ from density considerations, and the coordination numbers, n_{ik} and n'_{kl} , are specified from stoichiometry.

the Rice computer severely limited the models refined with this technique.

1. Results from the Inconsistent Refinement

The inconsistent refinement was applied to three models for vitreous silica. The first two of these were unsuccessful in that the parameters did not sufficiently approximate the correct values or were not sufficiently independent. Since these models are significant, they will be briefly reviewed and details of the successful model will follow.

The first model is essentially that proposed by Milligan et. al. [40] and considered by Zarzycki [74]. The SiO_4^{-4} tetrahedra are oriented such that a plane defined by the centroid (silicon) and two vertices (oxygen), V_1 and V_2 , of a tetrahedron, T_1 , will bisect and be perpendicular to the face nearest V_1 of the tetrahedron sharing V_2 with T_1 . Given the silicon-first oxygen distance (about 1.60 Å), this model, the edge to face model, defines all distances (silicon-first oxygen, oxygen-first oxygen, silicon-second oxygen, and oxygen-second oxygen) which have values less than 4.5 Å for a given silicon-oxygen-silicon angle, α . If the face to edge assignment is random, the set silicon-second silicon and oxygen-third oxygen distances can be calculated. Further distances could be calculated if the existence of rings of tetrahedra were proposed, as Dietzel has done [47]. Assuming $\alpha = 142^\circ$, the silicon-first oxygen distance = 1.60 Å, and random assignment, the coordination numbers and distances less than 5.0 Å

according to Milligan et. al. [40] are given below.*

(5-1a) Face to Edge Model

Coordination sphere radius (Angstroms)	One silicon atom [†] surrounded by	Two oxygen atoms each surrounded by
0.0	1 silicon atom	1 oxygen atom
1.60	4 oxygen atoms	2 silicon atoms
2.62	---	6 oxygen atoms
3.03	4 silicon atoms	---
3.40	4 oxygen atoms	2 silicon atoms
3.98	8 oxygen atoms	4 silicon atoms
3.79	---	6 oxygen atoms
4.54	---	6 oxygen atoms
4.96	---	6 oxygen atoms
4.93	12 silicon atoms	---

[†] Although the discussion in this section will be in terms of atom-atom correlations, ionic form factors were used. A few refinements were checked with atomic form factors, such as the last consistent refinement, and the parameters were only altered in the third significant figure.

* These results are slightly erroneous in that there should be five oxygen-second oxygen coordinations of 4, 4, 4, 4, and 2 pairs. Thus it is impossible to get a 6, 6, and 6 partition as indicated above. Similarly there are twelve distinct (but only nine probable) silicon-second silicon coordinations and numerous distinct (perhaps all thirty-six) silicon-third oxygen coordinations. No attempt to improve this model along these lines was made for reasons given for the failure of the refinement.

The model was made stoichiometric by modifying the coordination scheme as below.

(5-1b) Stoichiometric Face to Edge Model

Coordination sphere radius (Angstroms)	One silicon atom surrounded by	Two oxygen atoms each surrounded by
0.0	1 silicon atom	1 oxygen atom
1.60	4 oxygen atoms	2 silicon atoms
2.62	---	6 oxygen atoms
3.03	4 silicon atoms	---
3.40	2 oxygen atoms	2 silicon atoms
3.98	4 oxygen atoms	4 silicon atoms
3.79	---	3 oxygen atoms
4.54	---	3 oxygen atoms
4.96	---	3 oxygen atoms
4.97	12 SiO ₂ molecules	---
	continuum at 5.68 Å	continuum at 4.42 Å

The SiO₂ molecule has a scattering factor of

$$f_{Si}(S) + 2f_o(S)j_o(S R_{Si-O})$$

as explained in IV. D., and the atom-continuum distance was calculated from the consistency with the density of 2.20. The continuum is also assumed to be composed of SiO₂ molecules. The root-mean-square deviations g_{ij} of these distances were estimated to be 0.20 Å, 0.50 Å, and 1.50 Å for atom-atom, atom-molecule, and atom-continuum correlations,

respectively.

The failure of the inconsistent refinement of this model to converge is due to the large number of parameters (twenty) and the similar dependence of I^{Total} on the 3.79 Å and 3.98 Å coordination spheres. Removing the g_{ij} parameters from the refinement did not eliminate the divergence of the refinement.

The second model is derived from the local order in the vitron as developed by Tilton [61]. When the model is made stoichiometric and consistent with a density of 2.20, the coordination scheme is given by (5-2).

(5-2) Stoichiometric Pentagonal Dodecahedron Model

Coordination sphere number (Angstroms)	One silicon atom surrounded by	Two oxygen atoms each surrounded by
0.0	1 silicon atom	1 oxygen atom
1.60	4 oxygen atoms	2 silicon atoms
2.60	---	6 oxygen atoms
3.20	4 silicon atoms	---
4.00	12 oxygen atoms	6 silicon atoms
4.19	---	6 oxygen atoms
4.92	6 oxygen atoms	3 silicon atoms
4.99	---	12 oxygen atoms
5.18	12 silicon atoms	---
5.93	---	12 oxygen atoms
6.14	12 oxygen atoms	6 silicon atoms
6.79	---	9 oxygen atoms
7.15	---	6 SiO ₂ molecules
7.33	24 SiO ₂ molecules	---
	continuum at 7.62 Å	continuum at 6.28 Å

The root-mean-square deviations g_{ij} of R_{ij} were assigned 0.20, 0.80, and 2.50 Å for the atom-atom, atom-molecule, and atom-continuum distances, respectively. The calculated I^{Total} from these parameters shows seven strong peaks at $S = 1.00, 1.85, 2.80, 3.65, 4.45, 5.30,$ and 6.40 . Refinement failed probably due to the similarity of dependence of I^{Total} on the coordination spheres with radii 4.00 and 4.19, 4.92 and 4.99, or 5.93 and 6.14. The large number of parameters (twenty-eight) may have also caused some difficulty. Larger g_{ij} (about 1.50 Å) were used for coordination spheres with radii above 5.50 Å in an attempt to cause the first two peaks to coalesce to give the observed peak at $S = 1.50$. This was also unsuccessful.

The third and successfully refined model was derived from the first model, but the troublesome coordination spheres were eliminated by using the molecular approximation for small interatomic distances. The refinement was over the sampling set $\{I^{\text{Obs}}(S_i)\}$ where $S_i = .6(.1)12.00$, and a density of 2.20 was assumed. The g_{ij} 's were added one at a time until the refinement ceased to converge. The best parameters are presented as the first of the present results in Table I and are invariant in the first two significant figures under refinement to minimum absolute or minimum relative error. The residual used in the structure analysis of crystals [7]

$$(5-3) \quad R = \sum_i |I^{\text{Total}} - I^{\text{Obs}}| / \sum_i I^{\text{Obs}}$$

has the value of 0.070 for these parameters. The I^{Total} and I^{Obs} are illustrated in Figure 9.

2. Results from the Consistent Refinement

As explained before, the consistent refinement places restrictions on the parameters $\{q_i\}$ in (4-12). The geometrical restrictions were derived in the coordinate system illustrated in Figure 10. In that figure a reference SiO_4^{-4} tetrahedron is chosen and a plane, P, passed through two vertices (oxygen atoms), O and O', and the centroid (the silicon atom). The threefold axes of the tetrahedron through O and O' are taken as the axes Z and Z' of the sphere coordinate systems with origins at the center of O and O', respectively. P is taken as the x-z plane of these systems and the O system is left-handed and O' is right-handed. Thus the centroid (silicon atom) of the neighboring tetrahedra which share O and O' can be described in these systems and it is possible to calculate the oxygen-first oxygen, silicon-first silicon, silicon-second oxygen, silicon-second silicon distances relative to the silicon-first oxygen distance.*

If all oxygen atoms are assumed to have approximately equivalent ligand fields, then $\theta' \cong \theta$ and $\phi' = \pm \phi, \pm \phi \pm 60^\circ$. Thus a model was set up with the parameters $\{p_i\}$ where

- p_1 = the silicon-first oxygen distance,
- p_2 = the silicon-oxygen-silicon bond angle = $180^\circ - \theta$
- p_3 = the angle of orientation of the neighboring silicon, ϕ ,
- p_4 = the root-mean-square deviation of atom-atom and atom-molecule correlations, and

* In order to determine the oxygen-second oxygen and oxygen-third oxygen an angle specifying the orientation of the oxygen triangles of the neighboring tetrahedra would have to be given, and the calculation is not trivial.

p_5 = the root-mean-square deviation of atom-continuum correlations.
 If only one neighboring silicon may approach a given face, the inter-atomic distances are given in (5-4).

(5-4) Consistent Bent Bond Model

Coordination sphere radius	One silicon atom surrounded by	Two oxygen atoms each surrounded by
0.0	1 silicon atom	1 oxygen atom
p_1	4 oxygen atoms	2 silicon atoms
$\sqrt{8/3} p_1$	---	3 oxygen atoms
$2p \sin(p_2/2)$	4 silicon atoms	---
$d_1(p_3)^{\dagger}$	1 oxygen atom	1 SiO_2 molecule
$d_1(-p_3)$	1 oxygen atom	1 SiO_2 molecule
$d_1(60^\circ + p_3)$	1 oxygen atom	1 SiO_2 molecule
$d_1(60^\circ - p_3)$	1 oxygen atom	1 SiO_2 molecule
$d_1(-60^\circ + p_3)$	1 oxygen atom	1 SiO_2 molecule
$d_1(-60^\circ - p_3)$	1 oxygen atom	1 SiO_2 molecule
$d_2(60^\circ + p_3)^{\ddagger}$	3 SiO_2 molecules	---
$d_2(60^\circ - p_3)$	3 SiO_2 molecules	---
$d_2(-60^\circ + p_3)$	3 SiO_2 molecules	---
$d_2(-60^\circ - p_3)$	3 SiO_2 molecules	---
	continuum of SiO_2 molecules at 5.68 Å	continuum of SiO_2 molecules at 4.43 Å

$$^{\dagger} d_1(\theta) = p_1 [11/3 + (8/3)(\cos \theta - \sin \theta \cos \theta' / \sqrt{2})]^{1/2}$$

$$^{\ddagger} d_2(\theta') = p_1 4\sqrt{2/3} \sin \frac{\theta}{2} \left\{ 1 - \cos^2 \frac{\theta}{2} \left[\cos^2 \frac{\theta}{2} \left[1 - \cos^2 \left(\frac{\theta + \theta'}{2} \right) - \sin^2 \left(\frac{\theta - \theta'}{2} \right) \right] \right. \right. \\ \left. \left. - \sqrt{2} \sin \frac{\theta}{2} \cos \left(\frac{\theta + \theta'}{2} \right) \cos \left(\frac{\theta - \theta'}{2} \right) \right] \right\}^{1/2}$$

Refinements beginning with $p_1 = 1.60 \text{ \AA}$, $p_2 = 150^\circ$, 160° , and 165° and $p_3 = 10^\circ$, 20° , and 30° * all led to p_2 approaching 180° , or even oscillating about it. As p_2 approaches 180° , I^{Total} becomes independent of p_3 and the set of linear equations becomes ill-conditioned. Thus two models were set up assuming the silicon-oxygen-silicon bond angle to be 180° . The interatomic distances which can be calculated are given in (5-5) in terms of the silicon-first oxygen distance, the first parameter of these models.

(5-5) The Unbent Bond Model

Coordination sphere radius	One silicon atom surrounded by	Two oxygen atoms surrounded by
0.0	1 silicon atom	1 oxygen atom
p_1	4 oxygen atoms	2 silicon atoms
$2\sqrt{2/3} p_1$	---	6 oxygen atoms
$2p_1$	4 silicon atoms	---
$3\sqrt{19/27} p_1$	12 oxygen atoms	6 silicon atoms
$(8/3)p_1$ } $4\sqrt{2/3} p_1$ }	---	9 oxygen atoms
$4\sqrt{2/3} p_1$	12 SiO_2 molecules	---
	continuum of SiO_2 molecules at $5.68 \text{ \AA}$	continuum of SiO_2 molecules at $4.423 \text{ \AA}$

The first unbent bond model was made even more approximate so as to compare with the successful inconsistent refinement. This was

* I^{Total} is cyclic in p_3 every 60° because of the threefold axis. Thus it is sufficient to consider $0 \leq p_3 \leq 30^\circ$.

done by replacing the oxygen-second silicon coordination with oxygen-SiO₂ coordination, and by removing the widely dispersed oxygen-second oxygen coordination and half of the oxygen-oxygen pairs so that the model is again stoichiometric. The parameters of this model were,

p_1 = the silicon-first oxygen distance,

p_2 = a constant of proportionality between the atom-atom and atom-molecule coordination distances R_{ij} , and their root-mean-square deviations, g_{ik} (i.e., $g_{ik} = p_2 R_{ik}$), and

p_3 = a constant of proportionality between the atom-continuum distance and its root-mean-square deviation (i.e., $g_j = p_3 R_j$).

The consistent refinement converged quickly to $p_1 = 1.61$ Å, $p_2 = .12$, and $p_3 = .25$ from minimizing either the relative or absolute error over the sampling set $\{I^{Obs}(S_1)\}$ where $S_1 = 1.0(.10)13.6$. The residual for this data was .07 and the relative standard deviation was 9%. The refined model is given as the second of the present results in Table I and the corresponding I^{Total} is illustrated in Figure 11 as $I^{.07}$.

For later discussion I^{Obs} and the I^{Total} for $p_1 = 1.60$ Å, $p_2 = .04$, $p_3 = .30$ but the Si-O-Si bond angle set to 165° and $\omega = 10^\circ$ is also displayed in Figure 11 as $I^{.18}$. The residual is .18 and the relative standard deviation is 33%.

The final unbent bond model utilized the coordinations as listed in (5-5) and the following parameters:

p_1 = the silicon-first oxygen distance,

p_2 = the root-mean-square deviation of the atom-atom correlations,*

* This dependence of the deviations is suggested from the radial distribution sums where the first few peaks have the same half-widths.

p_3 = the root-mean-square deviation of the atom-molecule correlations, and

p_4 = the root-mean-square deviation of the atom-continuum correlations.

The refinement converged to $p_1 = 1.590 \text{ \AA}$, $p_2 = 0.170 \text{ \AA}$, $p_3 = 0.380 \text{ \AA}$, $p_4 = 1.593 \text{ \AA}$ with a residual of 0.06 and a relative error of 8.0%. The refined model is given as the third of the present results in Table I and the corresponding I^{Total} is illustrated in Figure 12. The root-mean-square deviation of the diffuse oxygen-second oxygen correlation could be fixed proportional to the deviations of the other atom-atom correlations. For the results given above it was six times (i.e., $1.02 \text{ \AA}$) the other atom-atom correlations. A maximum of $.80 \text{ \AA}$ is suggested from (5-5) and p_2 .

V. CONCLUSIONS

The crystal-monochromated scattered radiation from vitreous silica was determined to a relative error of less than 1% over the range of $S = (4\pi/\lambda)\sin\theta = 0.20$ to 17.3. Results from the Guinier camera agree to 8% or better, which is a reasonable agreement for a film technique. Results from the mathematical monochromator are in better agreement than expected (1%).

The atomic (ionic) radial distribution sum calculated from this data with $S_{\max} = 13.8$ is more resolved than previous results but without the large spurious peaks appearing in the sum computed by Richter [54]. The Si-O-Si angle computed from this sum is 150° . Because of the small area of the peak at 2.15 Å and the conclusions of Liebau [36], the Schottky defect explanation of the excess low temperature specific heat and of the ultrasonic sound attenuation appears unlikely. This small peak would probably be explained if the peak shape for the silicon-first oxygen and oxygen-first oxygen correlations were computed as outlined in IV. B. 3., judging from previous calculations of this kind.

The electronic radial distribution sum computed with $S_{\max} = 8.0$ agrees with those of Mendel [39] and Zarzycki [74], but when computed with $S_{\max} = 13.8$ the silicon-first silicon and oxygen-first oxygen correlations are separated. Thus the Si-O-Si angle can be computed with better precision. It was found to be $150^\circ \pm 12^\circ$, somewhat higher than Zarzycki's result of $142^\circ \pm 17^\circ$.

The scattered intensity calculations from proposed models refined with the inconsistent method contain only one fact not seen directly in

the radial distribution sums. The major peak in the scatter pattern from the model is too broad if temperature factors are used which produce the correct height for this peak. The Si-O-Si angle is about 155° , very similar to that derived from the radial distribution sums.

The consistent refinement indicated that it is necessary that the Si-O-Si angle be near 180° to produce good agreement between the observed and the calculated intensities. Again the major peak is too broad.

The third of the present results is, however, in better agreement about the major peak, and the root-mean-square deviation for atom-atom correlations agrees well with the half-widths in the atomic (ionic) radial distribution sums. Only the already dispersed oxygen-second oxygen correlation seems to require an unreasonably large deviation.

Although the major peak shape is perhaps a little too strongly dependent on the $\{R_j\}^*$, the large breadth of this peak in the calculated intensity is primarily due to correlations at $r \cong 5.00 \text{ \AA}$. Thus the experimental and computational results suggest that there is a fraction of vitreous silica with an Si-O-Si angle close to 180° and a fraction which is much more distorted, having no very definite correlation above 3.0 or 4.0 $\text{\AA}$. This would not contradict Tilton's proposed structure and suggests the nature of the two structural components of vitreous silica. On the other hand, a consistent refinement of Tilton's model or the true face to edge model eliminating the molecular approximation for correlations less than 6.0 $\text{\AA}$ may diminish the breadth of the major peak.

* Warren in his early model calculations of the scattered intensity to $S \cong 3.0$ varied the oxygen-continuum distance independent of the density and the silicon-continuum distance to improve the agreement with the observed data [65].

If the Si-O-Si angle is an indication of the local structure, then the local structure is similar to that of α -cristobalite.

The results of the diffraction line broadening due to thermally aging vitreous silica indicate that the crystallization rate is much greater than the nucleation rate and that the devitrification product is cristobalite. These facts are in agreement with those of Porai-Koshitz [64] and have been interpreted by Weyl [70].

VII. APPENDICES

A. Reduction of Diffractometer Data to Relative Intensity

Data from the diffractometer has been reduced to relative unpolarized scattered radiation as a function of $S = (4\pi/\lambda)\sin\theta$ by consideration of the following factors:

- (a) The geometry of the diffractometer,
- (b) The polarizing effect of the sample and the monochromator,
- (c) The effect of limiting the horizontal angle subtended by the counter and the absorption coefficient of the sample,
- (d) The effect of the energy distribution of the beam incident on the sample, and
- (e) A non-zero background.

These factors will be discussed in this order for the crystal monochromator and filtered radiation arrangements. Finally, the data reduction routine written for the Rice Computer will be described.

1. The Scattered Intensity Calculation

a. The geometry of the diffractometer. The horizontal plane of the diffractometer with a bent and ground crystal monochromator is illustrated in Figure A1. S is the target of the x-ray tube, M the crystal monochromator, P the parallel plate specimen, D the parafocal point, and C the window of the counter tube. The dashed circle is the cross section of the focal cylinder of the diffractometer at a lower 2θ setting, a consequence of the constant arm length $FP = PD = PD'$ of the diffractometer. Because of the constant arm length there is no

air absorption factor and the solid angle subtended by the counter tube is not a function of 2θ .

The vertical divergence is limited by Soller slit systems at P and F. The parafoveal point D is not exact, due primarily to the horizontal divergence of the beam and the flatness of the sample, as illustrated in Figure A1.*

When filtered radiation was used the x-ray source is at F in Figure A1.

b. Polarization factor for scattered radiation. From Figure A1 it is seen that the scatter from the crystal monochromator and sample are both measured in the horizontal plane of the diffractometer. Thus the modification function, $M_{pol}(2\theta)$, is easily calculated to be

$$(A-1) \quad M_{pol}^{-1}(2\theta) = (1 + \cos^2 2\theta' \cos^2 2\theta) / (1 + \cos^2 2\theta')$$

where $2\theta'$ and $2\theta = 180^\circ - \varphi$ are the scattering angles from the crystal monochromator and the sample respectively.

In the case of filtered radiation $M_{pol}^{-1}(2\theta)$ reduces to

$$M_{pol}^{-1}(2\theta) = (1 + \cos^2 2\theta) / 2$$

c. The effect of a limited horizontal angular divergence and a low linear absorption coefficient of the sample. In order to improve the parafoveating property of the diffractometer it is necessary to

* The line shape is further distorted by the divergence of the $K_{\alpha_1\alpha_2}$ doublet. This could be improved by causing the scatter from the monochromator and the sample to be in opposite senses, so as to merge the $K_{\alpha_1\alpha_2}$ doublet after the diffraction from the sample.

limit the horizontal divergence of the x-ray beam by slits near F and D such that the horizontal divergence is the same for the counter and the x-ray tube target. This will cause the scattered intensity to be modified as a function of 2θ depending on the linear absorption coefficient of the sample. Making the assumption that the beam is parallel at the sample, one may calculate this effect from Figure A2. If the parallel beam of width W is incident on the parallel plate specimen of thickness T with a glancing angle θ , then the scattering volume at a depth t is proportional to

$$dv(t) = 2[(W/2)\csc\theta - t]\cot\theta dt$$

and the path length of the radiation in the sample scattered through 2θ at depth t is

$$p(t) = 2t \csc\theta$$

With these quantities the function modifying the intensity $M_{abs}(2\theta)$ may be calculated from

$$M_{abs}^{-1}(2\theta) = 4m/W \int_0^{T'} e^{-mp(t)} dv(t)$$

where $T' = \min[T, (W/2)\sec\theta]$ and m is the linear absorption coefficient of the specimen. A convenient form of $M_{abs}^{-1}(2\theta)$ is

$$(A-2) \quad M_{abs}^{-1}(2\theta) = [1 - 1/x] e^{-x'} [1 - (1 + x')/x]$$

where $x = 2mWcsc2\theta$ and $x' = \min(x, 2mTcsc\theta)$. As m becomes large, x and x' increase and $M_{abs}(2\theta) \rightarrow 1$ and the correction becomes insignificant.

A limiting form of this correction ($x' = x$) has been derived and experimentally verified by Levy [35].

d. The effect of the energy distribution of the beam incident on the sample. Suppose that the beam incident on the specimen is not sufficiently monoenergetic but has an energy spectrum $B(k)$ where $k = 4\pi/\lambda$, and λ is the wavelength. Letting $I(\sin\theta, k)$ be the scattering from the specimen of monochromatic x-radiation with a wave number k , then the scatter of the beam $B(k)$ is

$$(A-3) \quad s(k_{\alpha} \sin\theta) = \int_0^{\infty} B(k) I(\sin\theta, k) dk$$

where $k_{\alpha} = 4\pi/\lambda_{K_{\alpha}}$ is a convenient constant. In order to find I , the desired quantity, it is necessary to solve this Fredholm integral equation of the first kind, provided a unique solution can be shown to exist.

It is sufficient to let

$$(A-4) \quad I(\sin\theta, k) = I(k \sin\theta)$$

since only the Klein-Nishina factor has the more general form

$R = R(\sin\theta, k)$ in (4-1) and R varies slowly from 1.0 to 1.105 for $S = 0$ to 8.6 for CuK_{α} , and 1.0 to 1.185 for $S = 0$ to 17.5 for MoK_{α} radiation. Making this assumption and change of variable

$\ln k = x$, $\ln k_{\alpha} = x_{\alpha}$, and $\ln(\sin\theta) = y$, (A-3) becomes

$$(A-5) \quad s_0(y) = \int_0^{\infty} B_0(y-x) I_0(x) dx$$

where $s_0(y) = s(e^x \alpha e^y)$, $B_0(Z) = e^{-Z} B(e^{-Z})$, and $I_0(x) = I(e^x)$.

(A-5) is a convolution integral and may be solved by utilizing Fourier transforms. Let

$$F(G) = \sqrt{\frac{1}{2\pi}} \int_{-\infty}^{\infty} G(x) e^{ihx} dx$$

be the Fourier transform of G if $G(x)$ is L^2 integrable. Similarly, let

$$F^{-1}(H) = \sqrt{\frac{1}{2\pi}} \int_{-\infty}^{\infty} H(h) e^{-ihx} dh$$

be the inverse Fourier transform of H if $H(h)$ is L^2 integrable, and

$$F^{-1}[F(G)] = G$$

almost everywhere. Then

$$\begin{aligned} F(s_0) &= \sqrt{\frac{1}{2\pi}} \int_{-\infty}^{\infty} I_0(x) \int_{-\infty}^{\infty} B_0(y-x) e^{+iyh} dx dy \\ &= \sqrt{\frac{1}{2\pi}} \int_{-\infty}^{\infty} I_0(x) e^{+ixh} dx \int_{-\infty}^{\infty} B_0(x') e^{ix'h} dx' \end{aligned}$$

by changing variables of integration $y-x = x'$ and the order of integration. Thus

$$F(s_0) = \sqrt{2\pi} F(I_0) F(B_0)$$

which provides the solution

$$(A-6) \quad I_0 = F^{-1}F(I_0) = \frac{1}{\sqrt{2\pi}} F^{-1}[F(s_0)/F(B_0)]$$

if s_0 and B_0 are L^2 integrable. In order to fulfill this condition $s_0(y)$ must have its definition range extended over positive y . A suitable extension is

$$\begin{aligned} s_0(y) &= s_0(-y), \text{ for } y < 0, \\ &= \lim_{y \rightarrow 0} s_0(y), \text{ for } y = 0. \end{aligned}$$

Thus the solution to (A-3) under the assumption (A-4) exists and is unique, but the Fourier solution above is impractical and does not make use of the fact that

$$(A-7) \quad I(k_\alpha \sin \theta) \doteq s(k_\alpha \sin \theta).$$

Phillips [50] has presented a numerical technique for the solution of problems of this type with auxiliary conditions, and Twomey [63] has applied conditions similar to (A-7). It was found that (A-7) was such a good approximation that a simple successive substitution method provides an adequate solution, and the computational requirements were easier to meet with the facilities available.

Fracturing the effect of the K_α radiation from those of the continuum and other characteristic radiations,* $B(k)$ is

* Earlier results have shown that the elimination of $K_{\alpha 2}$ radiation from the doublet $K_{\gamma 1 \gamma 2} = K_\alpha$ is not necessary for x-radiation scatter patterns as diffuse as that from silica [31].

$$B(k) = d(k - k_\alpha) + g B'(k)$$

where $d(x)$ is the Dirac delta function and

$$\int_0^\infty B'(k) dk = 1,$$

Then (A-3) becomes

$$\begin{aligned} s(k_\alpha \sin \theta) &= \int_0^\infty B(k) I(k \sin \theta) dk \\ &= I(k_\alpha \sin \theta) + g \int_0^\infty B'(k) I(k \sin \theta) dk. \end{aligned}$$

If $S = k_\alpha \sin \theta$, then

$$I(S) = s(S) - g \int_0^{k_{\text{Einstein}}} B'(k) I(k S/k_\alpha) dk$$

where k_{Einstein} is the k value above which $B(k) = 0$. This Fredholm integral equation of the second kind may be solved by successive substitution where

$$I_0(S) = \sum_j (-g)^j s(S)$$

and

$$(A-8) \quad I_1(S) = s(S) - g \int_0^{k_{\text{EINSTEIN}}} B'(k) I_{1-1}(kS/k_\alpha) dk.$$

If $s(S)$ and $B(k)$ are real, continuous, and bounded, then the sequence $I_i(S)$

is absolutely and uniformly convergent to a unique solution $I(S)$ provided $I_{i-1}(S)$ can be extended as described below and

$$(A-9) \quad g \left\{ \max[B'(k)] \right\} k_{\text{Einstein}} < 1,$$

a sufficient but not necessary condition. In equations (A-8) it is apparent that $I_1(S)$ can be calculated for $0 < S < k_{\alpha}$ but the next step of the iteration requires that $I_1(S)$ be known for $0 < S < k_{\text{Einstein}} > 2k_{\alpha}$. If $s(S)$ is determined to a sufficiently high $S = k_{\alpha} \sin \theta$, then it may be extended such that

$$(A-10) \quad s(k S/k_{\alpha}) = s(S) \quad \text{for } k < k_{\alpha}$$

$$= s(k_{\alpha}) \quad \text{for } k_{\alpha} > k > k_{\text{Einstein}}$$

The incident beam spectra was determined for filtered radiation with an analyzing crystal. The $I(\sin \theta, k)$ for a crystal may be written as

$$I(\sin \theta, k) = \sum_{i,j} C_{ij} d(2\lambda n_i/d_j - k \sin \theta)$$

from Bragg's equation, where d is the Dirac delta function [Appendix C, Equation (C-4)]. Then the observed scatter calculated from (A-3) is

$$(A-11) \quad s(S) = \sum_{i,j} C_{ij} B(2\lambda n_i/d_j \sin \theta)$$

Thus from knowledge of the Einstein limit k_{Einstein} and proper selection of the analyzing crystal, $B(k)$ may be determined.

e. The non-zero background. It is impossible to determine the real background in any scattering experiment of this kind because it would require replacing the sample with a material with exactly the same absorption properties but without any structure. The approximation made in the diffractometer arrangement was to repeat the experiment with no sample. The relative standard deviation of the resulting scatter pattern is

$$(A-12) \quad G_r = \sqrt{G^2 + G_B^2} / (I - I_B) \\ = \sqrt{1 + (I_B/I)^2} N/N_B / N (1 - I_B/I)$$

where I , N , and G (I_B , N_B , and G_B) are the observed intensity, the number of counts taken, and the standard deviation of the (background) scatter pattern, respectively.

2. Data Reduction

Data from the diffractometer were converted to scattered intensity as a function of $S = (4\pi/\lambda) \sin\theta$ by a program running on the Rice Computer. The correction for instrumental drift described above and the modifying functions (A-1) and (A-2) were applied and statistics of the measurement compiled. The background was determined as suggested above, processed as the scattered intensity and subtracted from the data.

Data requiring mathematical monochromation were further processed by another program written for the Rice Computer which carries out the iteration of (A-8) utilizing 2-point Gaussian integration. The accuracy of the final $I_1(S)$ is checked by simply reducing the increment

of integration by a factor of 10.

Details of these routines are given elsewhere.

B. Reduction of Guinier Film Data to Relative Intensity

Data from the exposed film in the Guinier camera have been reduced to relative unpolarized scattered radiation as a function

$S = (4\pi/\lambda)\sin\theta$ by consideration of the following eight factors:

- (a) The geometry of the Guinier camera,
- (b) The dependence of the measurable quantity, the light transmission of the film, on the exposure of the film,
- (c) The polarizing effect of the sample and the monochromator,
- (d) The finite thickness and absorption coefficient of the sample,
- (e) The x-radiation absorption by air,
- (f) The x-radiation absorption of the shields necessary to protect the film from other radiation,
- (g) The efficiency of the film emulsion in recording the scattered radiation, and
- (h) The non-zero background.

These factors are described in this order below for both the asymmetrical reflection and transmission Guinier arrangements. The calculations in (d), (e), (f) and (g) will assume that the x-radiation is a parallel beam of width w and height h incident on a parallel plate specimen of thickness t as illustrated in Figure B5. The angle $\omega = 2\theta$ for the transmission arrangement and $(180^\circ - 2\theta)$ for the reflection arrangement since the incident x-radiation is in the PF and the FP directions, respectively.

It is also possible to calculate perturbations in the scatter pattern since the geometry is only approximate in the experiment. Some

of these perturbations will be calculated.

Finally, the data reduction routine written for the Rice Computer will be described.

1. The Scattered Intensity Calculation

a. Geometry of the Guinier camera. The geometry of the Guinier camera is shown in Figure B1 for the reflection arrangement and in Figure B2 for the transmission arrangement. In both figures, S is the line source of x-radiation and M is the bent and ground crystal monochromator which focuses the radiation at point F. The specimen at P scatters the radiation to a point D. Due to this geometry, the radiation scattered through the angle 2θ will be focused at point D, as can be easily seen from the figures. Thus the scattering angle α may be determined if the angle of incidence α , the point O, and the diameter or some equivalent information-bearing set of measurements is known.

In the arrangement used in this investigation it was found convenient and satisfactory to mark O and a spot $10''$ from O with the focused x-radiation. An exposure of less than one second with x-radiation from a copper targetted tube running at 20 kilovolts and 5 milliamperes was sufficient for this purpose.

If μ is the distance between these two marks, the 2θ in degrees corresponding to the point D is given by

$$(B-1) \quad 2\theta = \left| \alpha + 57.3 \overline{OD} / \mu \right|$$

for the transmission method as computed from Figure B1, and by

$$(B-2) \quad 2\theta = 180^\circ - |180^\circ + 5 \overline{OD}/\mu - \alpha|$$

for the reflection method as computed from Figure B2. $\overline{OD}$ is measured on the film with the positive direction away from the focal point F. Since only the ratio of the two film measurements appears in these expressions, film shrinkage is automatically compensated.

There is no modification of the observed intensity due to the divergence of the scattered radiation in the horizontal plane of the Guinier camera since $\partial(\alpha)/\partial(\overline{OD})$ is constant from (B-1) and (B-2). Due to the finite beam height, h , at the sample, the vertical divergence of the scattered radiation does modify the observed radiation. The modifying function $M_{div}(2\theta-\alpha)$ is found from

$$M_{div}^{-1}(2\theta-\alpha) = \int (1/r) dt$$

where r = the distance from the infinitesimal element of sample dt upon which the beam is incident, to the center point where the intensity is measured. If the measurement is taken at the intersection of the plane bisecting the incident beam and the camera cylinder of diameter d , then

$$r^2 = [d \cos(2\theta-\alpha)]^2 + t^2$$

and

$$\begin{aligned} (B-3) \quad M_{div}^{-1}(2\theta-\alpha) &= \int_{-h/2}^{h/2} dt / \{ [d \cos(2\theta-\alpha)]^2 + t^2 \}^{1/2} \\ &= \ln \{ [(1+x^2)^{1/2} + x] / [(1+x^2) - x] \} \end{aligned}$$

where $x = h/2d \cos(2\theta - \alpha)$.

Two poor characteristics of the Guinier camera are apparent from the figures. The first is that the sample must be ground to the cylinder of the camera and should be infinitely thin so as to scatter only at the surface of the cylinder. The second and more serious fault is that a small misalignment of the film or the sample off of the surface of the camera cylinder will cause poor focusing and indeterminacy in high 2θ for the transmission arrangement and low 2θ for the reflection arrangement. For this reason it is necessary to use single emulsion film such as Kodak blue-sensitive x-ray film.

b. The determination of the intensity incident on the film emulsion. The extraction of intensity information from photographic film is complicated by the fact that the observable quantity, the light transmission, is not directly proportional to the intensity incident on the emulsion multiplied by the exposure time. The method used in this experiment will be discussed and the relative intensity incident on the emulsion, I_C , determined as a function of the light transmission.

The microphotometer used in this investigation is illustrated in Figure B3. The incandescent filament, W, was focused on the emulsion side of the film at point I by a suitable lens system, L_1 . The lens system, L_2 , focused the image of the filament on the thermopile slit, T. L_1 was adjusted slightly out of focus to eliminate fluctuations due to the grain size of the emulsion. The best adjustment of L_1 appeared to be closely approximated by adjusting L_1 for maximum transmission. In this condition the filament image was approximately .5 x 10 mm and centered about the .30 x 5.0 mm thermopile slit.

A suitable mechanism pulls the film encased in two glass slides such that the emulsion always coincides with I. Speeds of 0.641, 1.282, and 2.562 mm/minute are possible with this mechanism.

The voltage generated in the thermopile is proportional to the power of the radiation incident upon it. Because of the fixed slit this voltage is proportional to the light transmitted by the film. The thermopile is connected to a critically damped Moll galvanometer, G.

The image filament lamp, C, was focused by the lens system, L_3 , on the mirror on the shaft of G. This reflected beam was tracked by two photocells, P, connected in an amplifier and null-seeking circuit which controls a reversible tracking motor. Proper adjustment of the impressed voltage on C and the rheostats in the amplifier will stop the system from hunting. Adjustment of W will provide proper sensitivity. The pen, Q, connected to the photocells records on the chart, was usually driven at 0.50 inches/minute in these investigations. Thus the chart reading from a base line, CB, corresponding to zero transmission through the optical system, will be proportional to the transmission of the system.

The light transmitted through an optical system is

$$T = I 10^{-D} = I 10^{-\sum D_i}$$

where I = the incident intensity and D_i the optical densities of the media through which the light passes. For the system illustrated in Figure B3, let D_N , D_{NS} , and D_I be the optical densities of the unexposed film, the exposed film, and the remainder of the optical system, respectively. Then

$$\begin{aligned} T_N &= I \cdot 10^{D_N} \cdot 10^{-D_I} \\ &= I K' \cdot 10^{-D_N} \end{aligned}$$

is the apparent transmission of the unexposed film, and

$$\begin{aligned} T_{NS} &= I \cdot 10^{-D_{NS}} \cdot 10^{-D_I} \\ &= I K'' \cdot 10^{-D_{NS}} \end{aligned}$$

is the apparent transmission of exposed film. If C_{NS} and C_N are the chart readings for exposed and unexposed film, respectively, it follows that

$$\frac{C_N - C_B}{C_{NS} - C_B} = 10^{D_{NS} - D_N}$$

or
$$D_{NS} - D_N = \log \frac{C_N - C_B}{C_{NS} - C_B} .$$

For x-radiation the optical density versus relative exposure, E_R , curve for most x-ray films is found to be linear for densities of 0.6 to 3.0. (For the optical region this is, of course, incorrect.) This has been verified for the film used in this investigation and only film densities well within the linear region were used. Since the law of reciprocity is true for x-radiation,

$$I_C = K'' E_R/t = K'''(D_{NS} - D_N)$$

where I_C is the intensity incident on the emulsion, t is the exposure time, and K'' and K''' are constants. Holding the time of exposure constant, the relative scattered intensity, I_C , reaching the film may be determined by the relation

$$(B-4) \quad I_C = K \ln \frac{C_N - C_B}{C_{NS} - C_B}.$$

In the case where the optical density is not linear with respect to the exposure, it is convenient to compensate for it with $R(I_C)$, the ratio of the true exposure to the calculated exposure, as a function of the calculated I_C . A typical calibration curve $R(I_C)$ is given in Figure B3 for the one emulsion blue-sensitive Kodak x-ray film used in this investigation.

When the thermopile was found to be unstable, it was replaced by a circuit whose light sensitive element is a cadmium-sulfide, cadmium-selenide photoconductor purchased from Clairex Corporation (Type CL-505L). This circuit is illustrated in Figure B4, and the response to light was found by neutral density film strips to be

$$R(P) \propto P^{0.748}$$

where P is the light power. The response is illustrated in Figure B4.

c. Polarization factor for the scattered radiation. From Figures B1 and B2 it is seen that the scatter from the crystal monochromator and sample is measured in the same plane. Thus the modification function due to polarization, $M_{pol}(2\theta)$, is easily calculated to be

$$(B-5) \quad M_{pol}^{-1}(2\theta) = \frac{1 + \cos^2 2\theta' \cos^2 2\theta}{1 + \cos^2 2\theta'}$$

where $2\theta'$ and 2θ are the scattering angles for the crystal monochromator and the sample respectively.

Unfortunately the polarization factor applies rigorously only to the coherent scattered radiation. The incoherent scattered radiation constitutes up to 50% of the total scattered radiation at high scattering angles, but there appears to be no practical method for improving the calculation or the experimental arrangement.

d. The effect of finite thickness and absorption coefficient of the sample. The absorption of x-radiation by the specimen causes the intensity to be modified since the path length is a function of 2θ and α . If in the reflection arrangement the scattering process occurs when the photon is t' deep in the specimen, then the path length is

$$\begin{aligned} P_R(2\theta, \alpha) &= t' \sec(\pi - \alpha) + t' \sec(2\theta - \alpha), \\ &= t' [\sec(2\theta - \alpha) - \sec \alpha]. \end{aligned}$$

In the transmission arrangement the path length is

$$\begin{aligned} P_T(2\theta, \alpha) &= (t - t') \sec \alpha + t' \sec(2\theta - \alpha) \\ &= P_R(2\theta - \alpha) + t \sec \alpha. \end{aligned}$$

The modifying function $M_{abs}(2\theta, \alpha)$ may be calculated by

$$M_{\text{abs}}^{-1}(2\theta, \alpha) = (1/t) \int_0^t e^{-m_s P_R(2\theta, \alpha)} dt$$

and the $M_{\text{abs}}(2\theta, \alpha)$ for the transmission arrangement is multiplied by the unimportant constant $e^{m_s t \sec \alpha}$. Disregarding this constant, the modifying function becomes

$$(B-6) \quad M_{\text{abs}}^{-1}(2\theta, \alpha) = (1 - e^{-Z})/Z$$

where $Z = m_s t [\sec(2\theta - \alpha) - \sec \alpha]$ for both arrangements. Thus $M_{\text{abs}}(2\theta, \alpha) \rightarrow 1$ as $\theta \rightarrow \alpha$ or $\theta \rightarrow 0$.

e. The x-ray absorption by air. The diffracted beam passes through $d \cos(2\theta - \alpha)$ of air as illustrated in Figure B5. Thus the intensity is modified by $M_{\text{air}}(2\theta - \alpha)$ due to the linear absorption coefficient m_{air} where

$$(B-7) \quad M_{\text{air}}^{-1}(2\theta - \alpha) = e^{-m_{\text{air}} d \cos(2\theta - \alpha)}.$$

f. The effect of the x-ray absorption of foils protecting the film from other radiation. Because x-ray film is exposed by all electromagnetic radiation, it is necessary to shield the film with a material opaque except in the x-ray region. Since any shield will have a finite linear absorption coefficient, its effect on the scattered radiation must be considered. From Figure B5 it is obvious that the modification function from foils before the film is

$$(B-8) \quad M_{\text{foils}}^{-1}(2\theta - \alpha) = e^{-\sum_i m_i t_i \sec(2\theta - \alpha)}.$$

The index i runs over all the film shields of thickness t_i with absorption coefficients m_i , and the foils are assumed to be planar and parallel to the film.

g. The efficiency of the film emulsion to record the scattered radiation. The density of the film emulsion is approximately linearly dependent on the exposure over each interval of the path length of the radiation in the emulsion. Since the path length is

$$p(2\theta-\alpha) = t_e \sec(2\theta-\alpha)$$

the efficiency of the film emulsion will also be a function of $(2\theta-\alpha)$. If second order processes are neglected, then the efficiency is proportional to the amount of radiation absorbed, which is

$$\begin{aligned} \text{(B-9)} \quad E_{\text{film}}^{-1}(2\theta-\alpha) &= 1 - e^{-m_e p(2\theta-\alpha)} \\ &= 1 - e^{-m_e t_e \sec(2\theta-\alpha)} \end{aligned}$$

where m_e is the linear absorption coefficient for the film emulsion.

h. The non-zero background. It is impossible to determine the real background in any scattering experiment of this kind because it would require replacing the sample with a material with exactly the same absorption properties but without any structure. The approximation made in the reflection arrangement was to repeat the experiment with no sample. In the transmission arrangement the unscattered x-ray energy per unit area is $T e^{-m_s t \sec \alpha}$, where T is the exposure time. The background pattern was then taken with no sample and the power

settings the same as before, but the exposure time was T' . For both arrangements this no sample scatter pattern was analyzed in the same manner as the scatter pattern from the sample and the intensity multiplied by $K' = (T/T')e^{-m_s t \sec \alpha}$ ($K' = T/T'$), and subtracted from the pattern from the sample in the transmission* (reflection) arrangement.

2. Perturbations of the Scatter Pattern due to Non-ideal Geometry

Due to a finite sample thickness and a finite beam height and width, the geometry of the Guinier camera is not perfect. In this section quantities which indicate the distortions of the scatter pattern due to these factors will be computed. Some of these were calculated by deWolff for the transmission arrangement [14]. His results will be reviewed. Other results were not found in the literature but were calculated during this work, assuming a planar specimen of thickness t and a parallel beam of width w and height h incident on the specimen. These calculations will utilize Figure B5, in which the angle $\varphi = 2\theta$ for the transmission case and $180^\circ - 2\theta$ for the reflection arrangement since the incident x-radiation is in the PF and FP directions, respectively.

a. Beam energy distribution effects. The crystal monochromator will not completely eliminate the K_{α_2} radiation. Thus it is convenient not to eliminate the doublet but to merge it effectively with the K_{α_1} radiation over a region about $2\theta_0$ by arranging the camera such

* Note that the factor $e^{-m_s t \sec \alpha}$ was neglected in the calculation in the sample absorption modifying function in the sample scatter pattern. Thus if the background data is not modified by M_{abs} , then $K' = (T/T')$.

that scattering from the sample and the monochromator are in opposite senses and

$$(B-10) \quad (\overline{MF}) \tan \theta' / d = \cos(2\theta_0 - \alpha)(\tan \theta_0 - \tan \theta').$$

This result follows from the fact that the divergence of the K_{α_1} and K_{α_2} radiation upon diffraction is

$$\Delta\theta = \tan \theta (\lambda_{K_{\alpha_1}} - \lambda_{K_{\alpha_2}}) / \lambda.$$

For the experimental arrangement used in this investigation

$$\tan \theta_0 = (\overline{MF}/d) \tan \theta' / \cos \alpha \approx 2 \tan \theta' / \cos \alpha$$

in the transmission case* and

$$\tan \theta_0 = (2\overline{MF}/d) \tan \theta' / \cos(\alpha - \pi) \approx 4 \tan \theta' / \cos \alpha$$

in the reflection case.

b. Sample thickness effects. Consider Δ_t , the spread in degrees 2θ of radiation scattered through 2θ due to the finite thickness t of the sample. From Figure A5 it is seen that the path length of the radiation through the sample is $t \sec(\psi - \alpha - 2\theta)$. This causes the diffracted beam width to be $t \sec(\psi - \alpha - 2\theta) \sin \psi$ and the projection on the film to be $t \sec(\psi - \alpha - 2\theta) \sin \psi \sec(2\theta - \alpha)$. Thus

* The result given by deWolff[14] is apparently in error by a factor of 2.

$$(B-11) \quad \Delta_t = \frac{180}{\pi d} t \sec(\varphi\alpha - 2\theta) \sin\theta \sec(2\theta - \alpha) \\ = \left| \frac{180}{\pi d} t \sec\alpha \sin 2\theta \sec(2\theta - \alpha) \right|$$

with t and d in the same dimensions.

c. Beam height effects. Because each region scatters radiation through 2θ in a cone, the diffraction pattern will be spread when a line source of height h at the sample is used. The divergence is

$$(B-12) \quad \Delta_h = \frac{45}{8\pi} \left(\frac{h}{p}\right)^2 \cot 2\theta (1 + p/d)^2 \sec^2(2\theta - \alpha)$$

where p = the path length of the x-radiation from the source to the focal point.

d. Beam width effects. The finite width w of the beam does not spread the diffracted beam to a first approximation because of the parafoocusing geometry. A very pessimistic indication of the spread due to the width w may be calculated by assuming the beam to be parallel. The projection of the beam on the camera cylinder is $w \sec(\varphi\alpha - 2\theta)$ and will be the same at the point D. Thus

$$(B-13) \quad \Delta_w = \frac{180}{\pi d} w \sec(\varphi\alpha - 2\theta) \\ = \left| \frac{180}{\pi d} w \sec\alpha \right|,$$

a constant for any experiment.

e. Misalignment effect. If the effective scattering center of the sample is off the camera cylinder by a distance m , the error in 2θ

of the scatter pattern is

$$(B-14) \quad e_m = \frac{180}{\pi d} m \sec \alpha \sin 2\theta \sec(2\theta - \alpha)$$

where m and d are in the same units. This result is calculated as the thickness effect.

3. Data Reduction

The data in the form of the microphotometer traces were tabulated with a suitable angular increment and input with all the experimental parameters to a data reduction routine on the Rice Computer. This routine calculates the relative scattered intensity from

$$(B-15) \quad I = M_{\text{pol}}(2\theta) M_{\text{abs}}(2\theta, \alpha) M_{\text{air}}(2\theta - \alpha) M_{\text{foils}}(2\theta - \alpha) \times \\ M_{\text{div}}(2\theta - \alpha) E_{\text{film}}(2\theta - \alpha) R[I_c(2\theta)] I_c(2\theta)$$

as a function $S = (4\pi/\lambda)\sin\theta$, the possible error in 2θ , e_m , and the broadening $\Delta_t + \Delta_h$. Details of the routine are given elsewhere.

C. DETAILED ANALYSIS

1. Theoretical Scatter from an Assembly of Semi-classical Scatterers

In 1915 Debye demonstrated that the x-radiation scatter from a system of randomly oriented structural units exhibits interference effects which depend upon the distances between the scattering centers within the structural unit [11]. Although the particular application illustrated by Debye has been superseded by advances in physics, the concept and the calculation, interpreted on the molecular level, remain valid. This calculation was extended and organized for glasses by Warren and was utilized in his early investigations of silica [67]. We shall review and extend this calculation in the following paragraphs.

a. Classical diffraction. Consider the scattering from a classical system of electrons, Σ . If the incident radiation is monochromatic and unpolarized, the radiation scattered through an angle 2θ by a single electron was shown by Thomson to be

$$(C-1) \quad I_e = A_e^2 = I(r_0/R)^2 (1 + \cos^2 2\theta)/2$$

where I is the incident intensity, and R , the distance from the electron to the point of observation, is assumed to be much larger than the classical electron radius, $r_0 = e^2/mc^2 = 2.82 \times 10^{-13}$ cm, where e is the electronic charge, m the electronic mass, and c the velocity of light.

The field strength of the radiation scattered by Σ is

$$A = A_e \sum_j e^{2\pi i d_j}$$

where $d_j = d_j(2\theta)$ expresses the phase of the field strength scattered by the j^{th} electron and that scattered by an arbitrary electron which will be called the origin. If the incident radiation is parallel to the unit vector u_i , the scattered radiation along the unit vector u_s , r_j a vector from the origin to the j^{th} electron, and S a vector equal to $(2\pi/\lambda)(u_s - u_i)$, then the field strength of the scattered radiation becomes

$$A = A_e \sum_j e^{iS \cdot r_j}$$

Often it is convenient or necessary to consider Σ as composed of subsystems each of which scatters approximately as a point charge. In particular, in subsystems such as atoms and molecules the scattering of x-radiation is a cooperative effect and nonclassical processes are possible. Let the subsystems of Σ be called scattering centers, be fixed in space, and located by the vector r_i' from the origin. If $\rho_i(r')$ is the density of electrons about the origin of the scattering center, then the scattered radiation field strength may be written as

$$(C-2) \quad A = A_e \sum_{\Sigma'} e^{iS \cdot r_i} \int \rho_i(r') e^{iS \cdot r'} dv_i$$

where $r_j = r_i + r'$, Σ' is the system of fixed scattering centers, and the integration is over the volume of the i^{th} scatter center.

b. Semi-classical diffraction. Because of the nonclassical processes mentioned above, the integral in (C-2) should be

calculated in terms of relativistic quantum mechanics. The results of such a calculation indicate that the scattered radiation from a scattering center is of two types, coherent and incoherent. The coherent scattered radiation will have the same phase as the scattered radiation from the classical electron, but the incoherent radiation will have a random phase and $k = 4\pi/\lambda$ is slightly decreased due to the Compton effect. Thus (C-2) may be written as

$$A = A_e \sum_j (f_j + K^{1/2} f_j^* e^{id_j^*}) e^{iS \cdot r_j}$$

where $f_j = f_j(S)$ is called the form factor for the j^{th} center, $f_j^* = f_j^*(S)$ is the amplitude of the incoherent scattered radiation from the j^{th} center, d_j^* is a random phase angle, and $K = K(S, k)$ is the Klein-Nishina factor. Note that the functional form given f_j and f_j^* implies that the subsystems are assumed to have spherical symmetry. It is not necessary to assume this symmetry but it is sufficient for the purpose of this investigation.

Because of d_j^* the incoherent scattering may not participate in the diffraction phenomena, and we can write the total intensity of the scattered radiation as

$$(C-3) \quad I^{\text{Total}} = I_e \sum_j K f_j^{*2} + I_e \left| \sum_j f_j e^{iS \cdot r_j} \right|^2$$

the first term being the incoherent part, $I^{\text{Inc}} = I^{\text{Inc}}(S, k)$, and the second, the coherent part, $I^{\text{Coh}} = [A^{\text{Coh}}(S)]^2$.

Considering the field strength of the coherent scattered radiation from

$$A^{\text{Coh}} = A_e \sum_j f_j(S) e^{iS \cdot r_j}$$

it is apparent that f_j may be regarded as the number of effective electrons scattering for S from the j^{th} center.

Often it is convenient or necessary to decompose the problem further, that is, to consider Σ' as a collection of subsystems. For example, Σ' may be composed of a system Σ'' repeated by a linear translation in three linearly independent directions, in which case Σ' is a single crystal. The Σ'' with least non-zero volume is called the unit cell. If u_1, u_2, u_3 is a set of three vectors, each of which has the direction and magnitude of an edge of the unit cell, and $m = (n_1, n_2, n_3)$ is a vector of three indices by which the unit cells in Σ' can be ordered, then the amplitude of the coherent scattered radiation can be written as

$$A^{\text{Coh}} = A_e \sum_m e^{iS \cdot R_m} \left(\sum_k f_k e^{iS \cdot r_k} \right), R_m = m \cdot (u_1, u_2, u_3)$$

where the vectors R_m and r_k sum to r_j' . If the system Σ' has the same symmetry as the unit cell, this equation can be written

$$(C-4) \quad A = A_e N_1 N_2 N_3 \prod_j \left\{ \frac{\sin[(1/2)N_j S \cdot u_j]}{N_j \sin[(1/2) S \cdot u_j]} \right\} e^{i(N_j+1)S \cdot u_j/2} \sum_k f_k e^{iS \cdot r_k}$$

The factor in braces approaches one if $S \cdot u_j = 2N\pi$ for integer N but otherwise approaches zero with increasing N_j , the maximum of N_j .

When Σ' is noncrystalline, then (C-3) can be written with

$$R_{ik} = r_i - r_k \text{ as}$$

$$I^{\text{Total}} = I^{\text{Inc}} + I_e \sum_{i,k} f_i f_k e^{iS \cdot R_{ik}}$$

In such cases the set of linking vectors, $\{R_{ik}\}$, each kind of neighbor pairs can be assumed to be both numerous and random, thus isotropic. Thus the total scattered intensity is equal to

$$\begin{aligned} \text{(C-5)} \quad I^{\text{Total}} &= I^{\text{Inc}} + I_e \sum_{i,j} f_i f_k (1/4\pi) \int_0^\pi \int_0^{2\pi} e^{iSR_{ik} \cos\theta} \sin\theta \, d\theta \, d\psi \\ &= I^{\text{Inc}} + I_e \sum_{i,k} f_i f_k j_0(SR_{ik}) \end{aligned}$$

where $j_0(x) = (\sin x)/x$ is the zeroth spherical Bessel function, and R_{ik} is now the length of the vector R_{ik} .

Interestingly, the diffraction peaks from a crystalline material correspond to distances of $n\lambda/2 \sin\theta$ according to Bragg, while the scatter peaks correspond to distances of $(n + 1/4)\lambda/2 \sin\theta$ for n a positive integer.

c. Thermal and statistical effects. As mentioned in the development of (C-5), Σ' is a system of fixed semi-classical scattering centers. In reality, any observed system will be at a finite temperature and the thermal agitation of the scattering centers will affect the intensity of the scattered radiation. It is also convenient to consider the R_{ij} in classes such as the nearest neighbor distance, the second nearest neighbor distance, and so on. The distances in any particular class may have some static distribution as well as thermal fluctuations. If g_{ij} is the root-mean-square deviation of the R_{ij} then the total scattered intensity is approximately

$$(C-6) \quad I_T^{\text{Total}} = I^{\text{Inc}} + I_e \sum_{i,j} f_i f_j e^{-S^2 g_{ij}^2 / 2} j_0(SR_{ij})$$

as shown by James [30]. This result is rigorous only if $g_{ij} < R_{ij}$. The thermal effect on the incoherent scattering appears not to be important to this investigation.

2. Radial Distribution Sums

A generalized radial distribution may be calculated by considering (C-6) as written as

$$S i'(S) = 4\pi \int_0^\infty \sum_i e_i \sum_j e_j r \rho_{ij}(r) \sin Sr \, dr$$

where $i'(S) = (I^{\text{Total}}/I_e - I^{\text{Ind}})$, $I^{\text{Ind}} = I^{\text{Inc}}/I_e + \sum f_i^2$, and $\rho_{ij}(r)$

the effective number of scatter electrons at S for the entities for which we want the effective density of the j^{th} entity at a distance r from the i^{th} but identically zero if the i^{th} and j^{th} entities belong to the same scattering center. Thus in the case of the electron radial distribution sum $e_i = 1$ and of the atomic radial distribution sum with the atoms being also the scattering centers $e_i = f_i$.

Since the structure is random $\rho_{ij}(r) \rightarrow \rho_{ij}^0$ as r increases. If $N(r)$ is a function which accounts for the limits of the sample, then $N(0) = 1$ and $N(r)$ decreases monotonically to zero as r increases. Thus

$$(C-7) \quad Si(S) = 4\pi \int_0^{\infty} \sum_i e_i \sum_j r [\rho_{ij}(r) - \rho_{ij}^0] N(r) \sin Sr \, dr$$

where $Si(S) = Si(S) - I^{la}(S)$, and

$$I^{la}(S) = 4\pi \int_0^{\infty} \sum_i e_i \sum_j r \rho_{ij}^0 N(r) \sin Sr \, dr,$$

the scattering at low angles due to the size of the specimen or other more macroscopic distances within the specimen. Since $\rho_{ij}(r)$ approaches ρ_{ij}^0 rapidly compared with the trend of $N(r)$ away from 1, $N(r)$ may be replaced by 1 in the right hand side of (C-7).

In general $e_i = e_i(S)$ and in order to apply the Fourier integral theorem it is necessary to approximate e_i with $H_i e_o(S)$ where H_i is independent of S . Thus applying the transform to (C-7) the radial distribution sum is found to be

$$(C-8) \quad 4\pi r^2 \sum H_i \sum H_j \rho_{ij} = \\ 4\pi r^2 \sum H_i \sum H_j \rho_{ij}^0 + (2r/\pi) \int_0^{\infty} [Si(S)/e_o^2(S)] \sin Sr \, dS$$

3. Normalization of the Observed Intensity

The methods for determining K such that $I^{Obs} = I^{Total}$ outlined in the text follow directly from (C-7) depending on the short range order that can be assumed safely, or from (C-8) assuming $\rho_{ij}(r)$ approaches zero with r . The overlap corrections follow from application of the Fourier sine transform to (C-7) but not the orthogonality condition to the term containing $\rho_{ij}(r)$. The result may be written as

$$(C-9) \quad 0 = 2\pi^2 \sum H_i \sum H_j \rho_{ij} + (1/r) \int_0^\infty S \{ [i(S)/e_o^2(S)] - I^{ov}(S) \} \sin Sr \, dS$$

where

$$I^{ov}(S) = 4\pi \int_0^\infty \sum H_i \sum H_j \rho_{ij} j_0(Sa) a^2 \, da$$

As r approaches zero (C-9) becomes

$$(C-10) \quad 0 = 2\pi^2 \sum H_i \sum H_j \rho_{ij} + \int_0^\infty S^2 \{ [i(S)/e_o^2(S)] - I^{ov}(S) \} \, dS$$

which is the result given in the text. Neglecting $I^{ov}(S)$ produces (4-10) and (4-11).

AMORPHOUS														
MODELS					RADIAL DISTRIBUTION ANALYSIS									
X-RAY SCATTER					ELECTRONIC									
ATOMIC (IONIC)					ELECTRONIC									
PRESENT RESULTS					ELECTRONIC									
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LOCAL STRUCTURAL PARAMETERS			RADIAL DISTRIBUTION ANALYSIS		OTHER		CRYSTAL STRUCTURE ANALYSIS																			
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• THE BEGINNING OF THE CONTINUUM (THE STANDARD DEVIATION OF THE BEGINNING)

... THE NEIGHBORS IN BRACKETS HAVE BEEN REPLACED WITH AN SiO_2 MOLECULE AT THIS DISTANCE.

TABLE II. MEAN CRYSTALLITE DIMENSION
IN THERMALLY AGED VITREOUS SILICA

Thermal History	Diffraction Line Position (2θ) In Order of Observed Intensity	(hkl) α -cristobalite $P4_12_1(?)$	Mean Crystallite Dimensions from Diffraction Line Broadening
1240° $\pm$ 5°C 24 hours	22.0°	(101)	200Å
1260° $\pm$ 5°C 24 hours	22.0° 36.3° 31.4°	(101) (200), (112) (102)	250Å
1280° $\pm$ 5°C 24 hours	22.0° 31.4° 36.3° 28.5° 47.2°	(101) (102) (200), (112) (111) (113)	350Å
1300° $\pm$ 5°C 24 hours	22.0° 36.3° 28.6° 31.5° 47.1° 48.7° 57.3° etc.	(101) (200), (112) (111) (102) (113) (212) (301)	500Å

TABLE III. EXPERIMENTAL PARAMETERS AND METHODS OF DETERMINATION FOR
GUINIER CAMERA TECHNIQUE

Method of Determination	Calculated $m = (u/\rho)\rho$ Measured t	Measured Factor by Visual Estimate	Measured Factor by Micropho- tometer	Litera- ture*	Value Used
Factor for CuK_{α}					
2θ (deg.)		13.40		13.40	13.40
(mt) _{sample} $t = 0.432\text{mm}$	3.28				3.28
(m _{air} d.) $d = 57.3$				.06677	.06677
(mt) _{paper} $t = .103 \pm .003\text{mm}$		.1050 $\pm .020$	.1285 $\pm .002$	.0720	.1285 $\pm .002$
(mt) _{aluminum foil} $t = 0.0508\text{ mm}$	.6685			.5679	.6635
(mt) _{film base} $t = 0.2100$	.2274**				.2274
(mt) _{film emulsion} $t = .008\text{ mm}$	0.291***				0.291 $\pm .020$
(mt) _{entire film} $t = .2210\text{ mm}$		.522 ± 0.40	.535 $\pm .020$		.536 $\pm .020$

* Guinier, A.: X-ray Crystallographic Technology (Hilger and Watts, London, 1962).

** Assumed to be cellulose acetate with density = 1.50

*** Calculated from (mt)_{film base} and (mt)_{entire film}

TABLE IV. SOURCES OF FACTORS APPEARING IN THE INDEPENDENT SCATTER
FOR ATOMS AND IONS OF SILICON AND OXYGEN

Information and Source	Maximum ($\sin\theta/\lambda$)
Atomic Form Factors	
Oxygen	
Coherent	1.30
Berguis, J. et al.: "New Calculations of Atomic Scattering Factors," Acta Cryst. <u>8</u> , 478 (1955).	
Incoherent	1.50
Milberg, M. E. and Brailsford, A. D.: "The Atomic Incoherent Scattering Intensities of Boron, Oxygen and Carbon," Acta Cryst. <u>11</u> , 672 (1958).	
Silicon	
Coherent	1.10
James, R. W. and Brindley, G. W.: "Some Numerical Calculations of Atomic Scattering Factors," Phil. Mag. <u>12</u> , 81-112 (1931).	
Incoherent	1.10
Freeman, A. J.: "X-Ray Incoherent Scattering Functions for Non-Spherical Charge Distributions: Si, Si ⁺⁴ etc.," Acta Cryst. <u>12</u> , 929 (1959).	
Ionic Form Factors	
Oxygen	
Coherent	1.30
+ 1 Well factor from Suzuki, T.: "Atomic Scattering Factor for O ⁻² ," Acta Cryst. <u>13</u> , 279 (1960).	
Incoherent	1.10
Bewilogua, L.: "Über die inkohärente Streuung der Röntgenstrahlen," Phys. Zeits. <u>32</u> , 740-744 (1931).	

TABLE IV. continued

Silicon			
Coherent			1.30
Berguis, J. et al.: "New Calculations of Atomic Scattering Factors," Acta Cryst. <u>8</u> , 478 (1955).			
Incoherent			1.10
Freeman, A. J.: "X-ray Incoherent Scattering Functions for Non-Spherical Charge Distributions: Si, Si ⁺⁴ , etc.," Acta Cryst. <u>12</u> , 929 (1959).			
Dispersion Factors, f' , f'' ($f = f_0 + f' + i f''$) From <u>International Tables of X-ray Crystallography</u> (Kynoch Press, Birmingham, 1959), Vol. III, 293.			
Oxygen			
CuK _α	$f' = 0.0,$	$f'' = 0.1$	0.60
MoK _α	$f' = 0.0,$	$f'' = 0.0$	1.30
Silicon			
CuK _α	$f' = 0.2,$	$f'' = 0.4$	0.60
MoK _α	$f' = 0.1,$	$f'' = 0.1$	1.30
Anisotropic Effects			
McWeeny, R.: "X-ray Scattering by Aggregates of Bonded Atoms," Acta Cryst. <u>4</u> , 513 (1951).			
Klien-Nishina Factor			
Compton, A. H. and Allison, S. K.: <u>X-rays in Theory and Experiment</u> (D. Van Nostrand Company, New York, 1949), p. 236.			

Figure 1.

The independent scattered intensity, I^{Ind} , and the normalized observed scattered intensity of crystal-monochromated molybdenum K $_{\alpha}$ x-radiation from vitreous silica. I^{Obs} has been corrected for polarization, sample absorption, and instrumental drift.

Figure 2.

The energy distribution of the effective molybdenum K_{α} incident beam from NaCl (200) crystal monochromator (open circles) and from (.037 mm) zirconium filter and pulse height discriminator monochromator (closed circles). Both distributions were determined with a NaCl analyzing crystal and a krypton proportional counter for power settings of 35 kv. and 18 ma. on the x-ray tube which was equipped with a 0.25 mfd. smoothing capacitor.

Figure 3.

The scattered radiation from vitreous silica
determined with crystal monochromated CuK_{α} radiation
by the Guinier camera technique.

Figure 4.

The effect of the convergent factor $e^{-A^2 S^2/2}$ on the atomic (ionic) radial distribution sum calculated from the results in Figure 1.

Figure 5.

The inversion of the atomic (ionic) radial distribution sum with $A = 0$ and with spurious peaks at S less than $1.0 \text{ \AA}$ removed, $I_{\text{mod}}^{\text{Obs}}$, and the observed data, I^{Obs} .

Figure 6.

The corrected atomic (ionic) radial distribution sum.

Figure 7.

The Viervoll function for vitreous silica. The correlation peaks are symmetrical in this function.

Figure 8.

The differential electron radial distribution sums
with the upper S integration limits of 8.0 and 13.8.

Figure 9.

The I^{Total} from the inconsistent refinement, $I^{\text{Model}1}$, corresponding to the first of the present results in Table 1, and the observed data, I^{Obs} .

Figure 10.

The coordination system of the bent bond model used
with the consistent refinement.

Figure 11.

The I^{Total} corresponding to an intermediate result, $I^{.18}$, leading to the second of the present results, $I^{.07}$, and the observed data, I^{Obs} .

Figure 12.

The I^{Total} corresponding to the third of the present results, I^{Model_3} , and the observed data, I^{Obs} .

Figure A1.

The geometry of the diffractometer with $2\theta = 180^\circ - \phi$ and parafoal point, D, and at lower 2θ with parafoal point D'. The x-ray source is at S, the bent-cut NaCl crystal monochromator is at M, the specimen is at P, and the counter window is at C.

Figure A2.

The specimen absorption correction. A parallel x-ray beam of width W is incident on a specimen of thickness T at a glancing angle of θ . The counter tube window subtends the same angle in the horizontal plane as does the x-ray source.

Figure B1.

The geometry of the Guinier camera in the asymmetrical reflection arrangement. The beam from the source at S is diffracted through an angle $2\theta'$ by the bent-cut crystal monochromator at M. The beam passes the parafocal point F and strikes the specimen, P, at an angle α . The beam scattered through 2θ is parafocused at D, a point on the film cylinder.

Figure B2.

The geometry of the Guinier camera in the asymmetrical transmission arrangement. The beam from the source at S is diffracted through an angle $2\theta'$ by the bent-cut crystal monochromator at M. The beam passes to the parafocal point F after striking the specimen, P, at an angle α . The beam scattered through 2θ is parafocused at D, a point of the film cylinder.

Figure B3.

The photo-conductor network and its response to light.

Figure B4.

The microphotometer schematic and the response of Kodak one emulsion blue sensitive film in the density range used in this work.

THE RESPONSE OF KODAK ONE EMULSION BLUE SENSITIVE FILM

Figure B5.

The calculation of factors affecting the film density relative to the actual radiation scattered through 2θ by the specimen P of thickness t from the beam parafocused at f . The scattered radiation strikes the film cylinder of diameter d at D. The angle of incidence of the beam is α and has a width w at the specimen. $\varphi = 2\theta$ for the transmission arrangement and $180^\circ - 2\theta$ for the reflection arrangement.

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