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Fast-Neutron-Induced Changes in Quartz and Vitreous Silica*

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The course of the changes produced by exposure in nuclear reactors and the subsequent alteration of the radiation-induced property changes caused by heating were followed by measuring the dilatation, refractive index, rotatory power, and birefringence. The fast-neutron dosages determined by a comparison of radiation damage in several substances are used to give a consistent scale for presenting the effects seen from the initial changes to nearly the saturation state, despite the many irradiation facilities used for the work. The property changes resulting from heating specimens irradiated to various extents are given. The damaging phenomena are explained in terms of the interaction of the scattered atoms with the silica structure, and the annealing phenomena in terms of the behavior of the anticipated structural changes. On the basis of the effect of displaced atoms and thermal spikes on solid structures there are delineated a number of classes of radiation damage among insulators. For one of these, silica is taken to be the prototype. Thermal spikes cause the displaced atoms to be accommodated by a local deformation, which is depicted as analogous to the rapid inversions in which a minor reorientation of the Si-O tetrahedra occurs without extensive disruption of the structure. The resulting gradually accumulating disorder is considered the basic formulation of a metamictization for which the damaging of quartz thus becomes the simplest example. The same basic processes are considered to take place in vitreous silica; but since the substance is already disordered, the changes which take place are minor, the slight compacting of the structure evidently representing mainly the partial freezing-in of a high-temperature state produced by the thermal spike.

INTRODUCTION

THE fast-neutron-induced changes in vitreous silica and quartz have been the subjects of a number of papers to which the reader wishing to learn the historical development of the subject is referred.[1–14] In these papers it has been clearly established that when quartz is irradiated with fast neutrons, it gradually becomes disordered into an amorphous form which is indistinguishable from the end product of the irradiation of vitreous silica and which is somewhat different from ordinary vitreous silica. The several investigators of these neutron-induced changes have studied different properties over restricted dosage ranges and have performed the irradiations in different reactor facilities. Because of the difficulties in determining the effective flux and the general confusion which has existed in this subject[15] over a period of years, it has not been possible to correlate adequately the neutron dosage required to obtain the effects they reported. In addition, there have been gaps in our knowledge of the behavior over the whole dosage range.

Results published by this author and his co-workers[9,11] covered the initial effects, one irradiation at about 5×10^{19} n/cm^2, and one irradiation performed at a somewhat higher temperature, but extending to saturation or near-saturation. All of the annealing data they have published (except an abstract of an oral paper[14]) refer to specimens from one irradiation at about 5×10^{19} n/cm^2. A peculiarity ("anti-annealing") in the annealing of the density changes appeared in the temperature range below 600°C, but optical properties were not measured precisely enough to note such detail; and it was expected from the general course of the property changes induced by the radiation that this peculiarity would be dependent on the amount of radiation-induced property change present before annealing. The work of Wittels *et al.* has covered mostly x-ray and some density determinations, and over a range of dosages starting considerably beyond the range of the low dosages investigated by this author and his co-workers, and extending to about 10^{20} n/cm^2, leaving another gap between his most extended irradiation and saturation, a region for which, because of the extensive disorder, x-ray investigation is not the most suitable one. There are only a few annealing observations published by Wittels *et al.*, and some of these are controversial. The dosages for Berman's specimens are not known, and even their relative values are uncertain, having been based on thermal neutron fluxes and reactor operating data in several different reactor facilities, data which are notoriously unreliable[15] for estimating the neutron flux responsible for radiation damage in substances like quartz.

The individual observations of the neutron-induced changes in quartz and vitreous silica which have been published leave too many gaps to give a picture of the range of the phenomena. The subject has become of

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* Based on work performed under the U. S. Atomic Energy Commission.

[1] Berman, Klemens, Simon, and Fry, Nature **166**, 864 (1950).

[2] R. Berman, Proc. Roy. Soc. (London) **A208**, 90 (1951).

[3] P. G. Klemens, Proc. Roy. Soc. (London) **A208**, 108 (1951).

[4] W. Primak, "A Summary and Bibliography of Some Research on Radiation Damage in Ceramic Materials Performed at the Argonne National Laboratory," Argonne National Laboratory, Lemont, 1953 (unpublished).

[5] M. Wittels, Phys. Rev. **89**, 656 (1953).

[6] Primak, Fuchs, and Day, Phys. Rev. **92**, 1064 (1953).

[7] Primak, Fuchs, and Day, Bull. Am. Ceram. Soc. **33**, 25 (1954).

[8] M. Wittels and F. A. Sherrill, Phys. Rev. **93**, 1117 (1954).

[9] Primak, Fuchs, and Day, J. Am. Ceram. Soc. **38**, 135 (1955).

[10] J. S. Lukesh, Phys. Rev. **97**, 345 (1955).

[11] W. Primak and H. Szymanski, Phys. Rev. **101**, 1268 (1956).

[12] J. H. Crawford and M. C. Wittels, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1955* (United Nations, New York, 1956), Vol. 7, paper A/Conf. 8/P/753.

[13] There are a number of papers relating to color changes which are not referred to since the relation of the color changes to the disorder is usually not treated.

[14] W. Primak, Bull. Am. Phys. Soc. Ser. II, **1**, 136 (1956).

[15] W. Primak, Nuclear Sci. and Eng. **2**, 320 (1957).

TABLE I. Irradiation data.

Irradiation reference No.	Reactor	Exposure	Dosage[a] 10^{18} n/cm^2	Specimens reference No.
...	...	none	none	868, 430, 836, 837, 835, 867
50	Hanford	289 Mwd/aT	49[b]	764, 765, 766, 767
51	Hanford	296 Mwd/aT	50[b]	760, 761, 762, 763
52	Hanford	638 Mwd/aT	108[b]	410, 752, 753, 754, 755
53	Hanford	1060 Mwd/aT	180[b]	430, 756, 757, 758, 759
106	MTR (*L*-43)	2×10^{20} $n_{\text{th}}/\text{cm}^2$	$\sim$300	371, 768, 378, 770
107	LITR (*C*-29)	785 006 kwh	7.9	671, 666, 665
108	LITR (*C*-28)	353 551 kwh	11	670, 669
111	*CP*-5	13 649 kwh	0.57	683, 684
111+117	*CP*-5	29 420 kwh	1.17	683′, 684′

[a] The time integral of the damaging flux as described in the text.
[b] These were used to construct the figures. A dosage 6% greater might be a better value.[15]

special interest since controversies concerning the explanation of the effects have arisen.[16] In the present paper, results are reported for specimens which were irradiated for dosages covering the whole range of the effects, and a particular attempt was made to secure dosages at which our knowledge was deficient. The effects observed when specimens irradiated at these various dosages were annealed are also reported. Because of the large number of measurements which were required, the properties selected for systematic measurement were several which could be measured precisely and quickly. These were dilatation, refractive index, rotatory power, and birefringence.

EXPERIMENTAL

Specimens

Quartz.—These were cut or broken from natural quartz of optical quality, presumably Brazilian. Group (A): The specimens 836, 764, 760, 752, and 756 were strips about 3 cm×6 mm×1 mm, the long axis parallel to the *c* axis within 1°, with a line ruled near either end of one broad face. The broad faces were polished and originally were flat to several fringes per cm, parallel to 5–20 fringes per cm. After irradiation, specimens 764, 760, 752, and 756 were ground and polished on one face to improve the flatness and the parallelism was made poorer. Group (B): The specimens 837, 765, 761, 753, and 757 were strips about 3 cm×6 mm×$1\frac{1}{2}$ mm, the long axis perpendicular to the *c* axis within 1.5°, with a line ruled near either end of one broad face. The broad faces were polished and originally were flat to 1 fringe per cm and parallel to about 20 fringes per mm. After irradiation, specimens 765, 761, 753, and 757 were ground and polished on one face to improve flatness. Group (C): The specimens 430, 666, 670, and 371 were disks 7-mm diameter by 3 mm thick, faces polished, flatness $1\frac{1}{2}$ fringes per cm, parallelism 10 fringes per cm. Group (D): The specimens 868, 683, 410, 430, 671, and 768 were small fragments ($\frac{1}{2}$–3 mm across) of irregular shape.

Vitreous Silica.—Group (E): The specimens 835, 665, 669, 867, and 378 were cut from commercial plates of optical quality (not of homogeneous refractive index) presumably made by fusing natural quartz. They were about 2 mm thick and $\frac{1}{2}$–2 cm on edge. The polished faces were flat to several fringes per cm. Group (F): The specimen 770 was a fragment broken from a disk of unknown source. Group (G): The specimens 766, 767, 762, 763, 754, 755, 758, and 759 were specially prepared plates 3 cm×6 mm×$1\frac{1}{2}$ mm with a line ruled near either end of one broad face; the broad faces were polished and were mostly flat to 5–10 fringes per cm, and their parallelism varied considerably but most were 5–20 fringes per cm. After irradiation, specimens 767, 763, 755, and 759 were ground and polished on one face to improve flatness.

Irradiations

The irradiation data are given in Table I. The irradiation reference numbers are consistent with those reported in other papers of this author. The dosage is that described elsewhere[15]; it is the time integral of the neutron flux which, distributed over a two-decade range of energies as k/E (k a constant and E the energy of the neutron) at energies at the upper end of the abundant part of the pile neutron spectrum, approximates the neutrons responsible for the damage; it was obtained by comparison of damage found in other samples (usually diamond or graphite) present in the irradiation, or interpolated from other studies in the same irradiation facilities. The following notes give additional description of significance in describing the irradiations.

Hanford Irradiations.—These were performed in the test holes of the Hanford reactors. The samples were wrapped in aluminum foil, several of the flat samples being wrapped together. They were inserted into $\frac{1}{2}$-in. aluminum tubes (the single casings as described by Primak, Fuchs, and Day[17]). These single casings lay in a larger aluminum tube, the test hole, which was water jacketed.[17] The temperatures of the samples are estimated to have been below 60°C. The first post-irradia-

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[16] P. G. Klemens, Phil. Mag. **1**, 938 (1956).

[17] Primak, Fuchs, and Day, Phys. Rev. **103**, 1184 (1956).

tion measurements reported here were inaugurated more than two years after the conclusion of the irradiations. The exposure is the number of megawatt days of energy expended by fission per ton by the fuel rods adjacent to the sample.

LITR Irradiations.—These were performed in lattice positions of the Oak Ridge National Laboratory LITR reactor. Hole *C*-28 was an empty lattice position; hole *C*-29 was within a fuel element. The samples were placed in a perforated can and hence were in contact with process water (the reactor coolant). This water is estimated to have been at about 50°C; but since it was not subjected to forced circulation it may have been at slightly higher temperatures locally. The exposure is given in terms of the fission energy expended by the whole reactor during the irradiation.

MTR Irradiations.—These were performed in empty lattice positions and near the center-line of the Materials Testing Reactor. Samples were placed in perforated aluminum cans and were in contact with process water which was circulated through the reactor. Sample temperatures are estimated as having been below 40°C. The exposure is given in terms of the thermal neutrons estimated to have traversed the samples during the irradiation.

Measurements

Density.—The densities were all determined by floating the sample in a liquid mixture whose density was approximately that of the sample (methylene bromide—propyl alcohol for densities near that of vitreous silica, bromoform—hexanol—pentanol for densities near that of quartz). The temperature of the mixture was adjusted until the density of the sample was nearly matched, and the density of the liquid was then determined by one of the following methods: (i) flotation of a standard sample in the liquid and use of the temperature coefficient of volume expansion of the liquid as determined with a dilatometer (0.000864 cm^3/deg for the bromoform-hexanol-pentanol mixture, 0.001112 cm^3/deg for the methylene bromide-propanol mixture); these density determinations were reliable to only about 1/3000 because the composition of the liquid altered between determinations; (ii) weighing a 6.8-ml bob suspended in the liquid from an analytical balance; bob volume calibrated by weighing the bob in water; surface tension correction for suspension wire applied; flotation temperatures adjusted to several hundredths degree; densities reliable to 1/20 000; or (iii) use of a 5-ml Ostwald pycnometer in the usual manner; pycnometer calibrated by weighing water; densities reliable to 1/5000.

Linear Expansion.—(iv) The distance between the ruled lines of the samples in Groups (A), (B), and (E) were determined with a Gaertner model M1205C comparator fitted with the photoelectric setting device described by Tomkins and Fred.[18] The steel comparator screw was calibrated at the National Bureau of Standards, at 20°C. Since most measurements were made at 25±1°C, a correction of +1/20 000 was applied to the readings. The readings of length of the samples on a particular part of the screw were usually reproducible to better than 1/30 000 for the length of these samples. However, successive readings of lengths were not quite so reproducible and are considered reliable to about 1/10 000.

Refractive Index.—Two methods were used. (v) Some of the refractive indices were determined with an Abbé refractometer. These are probably not reliable beyond the third decimal place. (vi) Most of the refractive indices were determined with a spectrometer arranged as a Pulfrich refractometer.[19] This method can give indices of refraction to better than the fourth decimal. (vii) However, in many cases the surfaces of plates were not sufficiently plane to obtain this accuracy and hence can be considered as only somewhat more reliable than the third decimal.

Rotatory Power.—This was measured in one of three ways: (viii) using a conventional petrographic microscope; readings reliable to 1°; (ix) using a petrographic microscope fitted with a Laurent half-shade device and an eyepiece analyzer reading to 0.05°; determinations reliable to 0.2°; (x) using a conventional polarimeter; determinations reliable to 0.1°.

Birefringence.—(xi) Relative retardations less than 250 mμ were determined by a method (attributed to Wiedemann by Pockels[20]) using the petrographic microscope arranged as described by Primak, Delbecq, and Yuster.[21] These readings are reliable to about 3 mμ in regions of uniform retardation and about 5 mμ elsewhere. (xii) Retardations up to 2500 mμ were determined with a graduated quartz wedge (American Optical Company) used with a petrographic microscope. These readings are reliable to 10 mμ. (xiii) Retardations above 2500 mμ were determined by method (xii) except that suitable additional retardation plates (whose retardation was measured by method (xii) were inserted in the optical train. These determinations are reliable to about 25 mμ.

Annealings

All of the annealings reported in this paper were step annealings. The sample was heated at the desired temperature for a period of time of order of magnitude 10^3 sec. It was then cooled, measured, and the heating repeated at a higher temperature. Different heating arrangements were employed in different temperature ranges.

(xiv) Some annealings below 260° were performed by placing samples in a basket which was inserted into a petroleum oil or silicone oil (Dow Corning 550) bath

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[18] F. S. Tomkins and M. Fred, J. Opt. Soc. Am. **41**, 641 (1951).

[19] W. Primak, Anal. Chem. **29**, 1237 (1957).

[20] F. Pockels, *Lehrbuch der Kristalloptik* (B. G. Teubner, Leipzig, 1906), p. 227.

[21] Primak, Delbecq, and Yuster, Phys. Rev. **98**, 1708 (1955).

TABLE II. Physical properties of various specimens.

Specimen No.[a]	Length Original (microns)	Length Irrad. (microns)	Expansion (%)	Density (g/cm³)[b,c]	Refractive index Ordinary (ω_D)	Refractive index Extraordinary (ϵ_D)	Thickness (mm)	Relative retardation (mμ)	Birefringence (mμ/mm)
836					1.5443	1.5533	1.003	9115	9088
764	27 952	28 046	0.336	2.5362(26.1)			1.029	5585	5429
760	27 959	28 053	0.338	[2.6473(27.5)]	1.5262	1.5321	0.999	5305[d]	5310[d]
752	27 877	28 356	1.718	[2.2134(23.0)]	1.4904	1.4913	1.060	1075[e]	1014[e]
756	27 963	28 832	3.106	[2.2054(26.1)]	1.4701		0.99	90[d]	91[d]
								Rotation (deg)	Rotatory power (deg/mm)
837							1.51	32.8	21.8
765	27 962	28 500	1.925	2.5380(25.4)			1.52	24.5	16.1
761	27 957	28 497	1.932	[2.6471(27.5)]	1.5198	1.5258	1.52	24.7	16.3
753	27 929	29 304	4.923	[2.2049(26.4)]		1.4966	1.52	3.80	2.5
757	27 912	29 689	6.366	[2.2128(23.3)]	1.4697		1.57	<0.02	0.013
666				2.6378[f]			3.05	65.55	21.49
670				2.6333[f]			3.05	65.4	21.45
835					1.4585				
766	27 828	27 575	−0.906	2.2638(24.9)					
767	27 959	27 707	−0.903	2.2642(24.8)					
762	27 907	27 656	−0.900	2.2637(25.1)	1.4698				
763	27 955	27 703	−0.903	[2.2034(27.4)]	1.4698				
754	27 848	27 707	−0.865	2.2617(26.1)	1.4692				
755	27 872	27 632	−0.861	[2.2031(27.5)]	1.4692				
758	27 879	27 658	−0.793	2.2578(27.8)					
759	27 931	27 703	−0.816	[2.2032(27.6)]	1.4686				

[a] Specimens 836, 837, 835 unirradiated. See Table I.
[b] Temperature (°C) of density determination in parentheses.
[c] In brackets—after heating to 1100°C.
[d] After annealing at 168°C.
[e] At a particular point on the specimen.
[f] By method (i); others by method (ii).

whose temperature was controlled to several hundredths of a degree. The annealing time is given as the time the samples dipped into the bath. The temperature was read with a mercury-in-glass thermometer and is probably reliable to 1°C.

(xv) Some annealings were conducted by placing a sample in a density tube which was placed in contact with a nickel block lying in an electrically heated tubular furnace whose temperature was controlled by a Brown Electronik strip chart automatic potentiometer recorder controller. Temperatures were controlled to ±5°C. Temperature was read with a platinum −10% rhodium couple (the same one used in previous work[11]); but since the thermocouple was not especially calibrated, readings can be considered reliable to only about 5°C in the upper temperature ranges. All cold junctions were placed in an oil bath thermostated to within 0.3°C at about 37.5°C, as read on a 0.1 degree mercury-in-glass thermometer. The time given for these annealings was the time of contact of the sample with the nickel block and probably represents the true annealing time to within 5%.

(xvi) Some annealings were performed using method (xv) except that temperature regulation was refined by the use of Gouy modulation of the regulating thermocouple.[22] Temperatures were controlled to better than 1°C.

(xvii) The specimens were placed into a 10-mm vitreous silica tube into which was then inserted a platinum −10% rhodium thermocouple connected to a second automatic recording potentiometer. The tube was heated as described in method (xvi). The time of annealing given is that for which this auxiliary thermocouple was within 5°C of the control temperature. At temperatures above 600°C enough current was induced in the thermocouples to cause the control temperature to skip noticeably when the automatic potentiometer calibrated itself; by 973°C this amounted to at least 3 deg.

(xviii) For annealing temperatures in excess of 1000°C a platinum-wound furnace without a nickel block was used, and it was regulated by hand by using a variable transformer.

Results

The properties of unirradiated and irradiated specimens are given in Tables II and III. The quartz specimens in Groups (A) and (B) and the vitreous silica specimens in Group (G) were originally prepared for length measurements and presented special problems in measuring the optical properties. Some of the specimens were not flat enough for index of refraction measurements [see (vii) above]. After irradiation some of these specimens were ground and polished and may have been heated to about 150°C for several minutes when they were set in wax for the purpose. Specimens 761 and 763 were studied extensively, and it was concluded that

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[22] W. Primak, Rev. Sci. Instr. 27, 877 (1956).

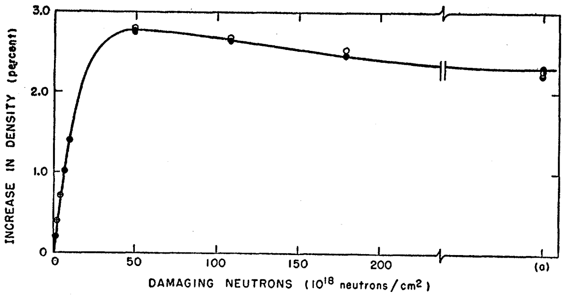

FIG. 1. Change in density of vitreous silica on irradiation in nuclear reactors: open circles—calculated from the expansion; solid circles—from density determinations; crossed circles—from the expansion measurements given in reference 9; half-open circles give correct relative densities of what was originally a quartz sample (vertically divided circle) and a vitreous silica sample (horizontally divided), the solid circle at this dosage is from an accurate density determination made about two years later. The dosage at (*a*) is estimated at 250 to 400 on the scale.

their indices of refraction were not uniform. Confirmation of this was found in measurements of birefringence of simultaneously irradiated specimens 764, 760, and 762. The birefringence [methods (xii), (xiii)] varied from one part of these specimens to another by several hundred mμ/mm. In the case of specimen 762 it varied from 800 to 1300 mμ/mm, about 50% of the total birefringence. For these specimens the data given in the tables and graphs are for a particular marked point on the specimen. The birefringence measured here may not correspond to that obtained from the refractive index measurements [method (vi)]. Further evidence of nonuniformity was found in measurements of rotatory power. Under crossed Nicols specimens 765 and 761 showed evidence of biaxiality. When examined by method (xi) (birefringence), specimen 761 was seen to be greatly strained symmetrically. The edge showed a retardation of 35 mμ/mm and the center (slow axis at right angles to the slow axis for the edge) a retardation of 20 mμ/mm, with a neutral zone between. The sign of the birefringence was such as would have been produced had the central region been in tension: that is, if the edge had undergone a greater dilatation than the center. The photoelastic effect in quartz was determined to be of such a magnitude that the tension of the central region must have been about 800–900 psi.

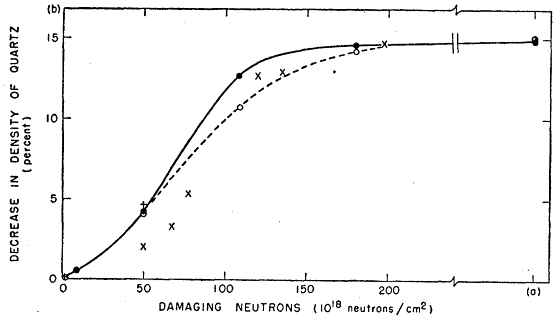

FIG. 2. Change in density of quartz on irradiation in nuclear reactors: solid circles—from density determinations; open circles—calculated from the expansion; half-open circle—point corresponding to similar half-open circle of Fig. 1; crossed circles—from the expansion measurements in reference 9; cross—from the density given in reference 9; **×**'s—from Wittels and Sherrill.[8] The dosage at (*a*) is estimated at 250 to 400 on the scale; the density change at (*b*) corresponds to unirradiated vitreous silica.

Figures 1–6, in which are plotted the property changes as a function of dosage, are mostly self-explanatory. Because of the large property change, the use of the differential expressions

$$-\frac{\Delta\rho}{\rho_0}=\frac{\Delta V}{V_0}=2\frac{\Delta a}{a_0}+\frac{\Delta c}{c_0},$$

(where ρ is the density, V is the volume, c and a are the respective lengths parallel and perpendicular to the c axis, the subscript 0 refers to the unirradiated state, and the Δ refers to the difference of the irradiated state from the unirradiated one) gives a large error; hence the relations

$$\delta=\frac{\Delta V}{V_0}=2\frac{\Delta a}{a_0}+\frac{\Delta c}{c_0}+\frac{\Delta a^2}{a_0^2}+2\frac{\Delta a\Delta c}{a_0c_0}+\frac{\Delta a^2\Delta c}{a_0^2c_0},$$

$$\frac{\Delta\rho}{\rho_0}=V_0\Delta\left(\frac{1}{V}\right)=\frac{-\delta}{1+\delta},$$

were used to construct Fig. 2. For convenience in describing the remaining results and discussing them, the disordering will be divided into 3 stages with rather indefinite boundaries at the dosages 50×10^{18} and 110×10^{18} neutrons/cm^2. These stages will be referred to by the Roman numerals I, II, and III, and the initial and later portions of each stage will be referred to by the

TABLE III. Density and refractive index of several specimens.

Specimen No.[b]	Density[a] Temperature (°C)	Density (g/cm³)	Refractive index
867	27.7	2.2033	
496	27.1	2.6481	
868	27.0	2.6483	
410′	27.1	2.3100	
410″	26.5	2.3114	
410‴	25.4	2.3138	
430′	27.7	2.2615	
430″	27.5	2.2623	
430‴	27.5	2.2624	
371	24.8	2.2552	1.4678
378	25.1	2.2546	1.4671
683		2.6473	
683′		2.6465	
665		2.2273	1.4643
669		2.2341	1.4647
684		2.2055	
684′		2.2077	

[a] Specimens 683, 683′, 665, 669, 684, 684′, density determined by method (i); remaining ones, by method (ii).

[b] The marks on 410 and 430 refer to particular fragments taken from vials marked 410 and 430, respectively. Specimen 683 after irradiation 117. Specimen 683′ after irradiation 117+124. Specimens 867 and 430 were not irradiated.

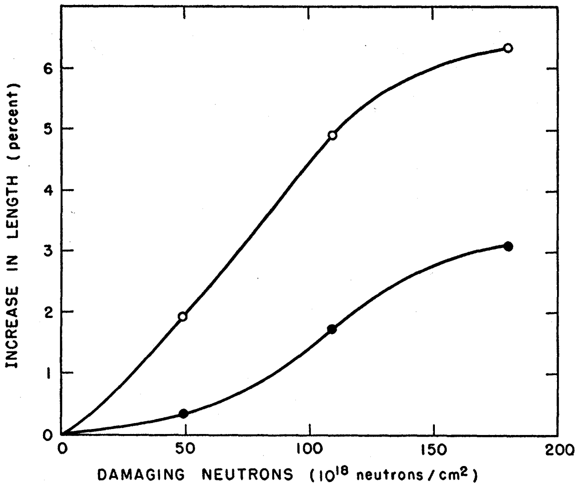

FIG. 3. Nuclear-reactor radiation-induced linear expansion of quartz cut parallel (solid circles) and perpendicular (open circles) to the optic axis. For the initial changes see Primak, Fuchs, and Day,[9] but note that their expansions are mislabelled.

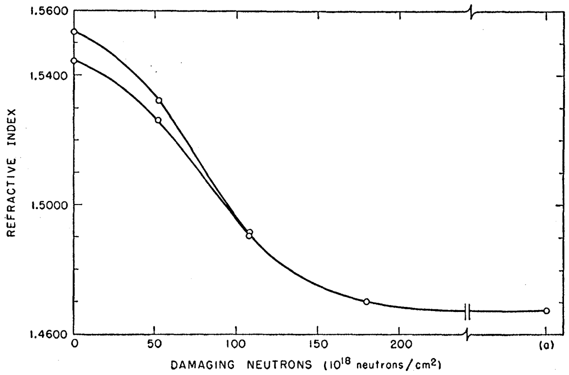

FIG. 5. The behavior of the refractive index of quartz on irradiation in nuclear reactors. The dosage at (*a*) is estimated at 250 to 400 on the scale.

capital letters A and B (e.g., for "IIB" read "in the later portion of the intermediate stage"). This is done not with the intention of implying any discrete phenomena, but to avoid having to pick out a particular point in what will be depicted as a continuum of states, in which different phenomena become apparent in rather indefinite overlapping regions. The changes in properties which occurred on heating the irradiated specimens are described below.

The density changes resulting from heating [by method (xv)] a specimen of irradiated quartz from IA, a specimen of irradiated quartz from IIIB, and a specimen of vitreous silica irradiated simultaneously with the latter are shown in Figs. 7(a) and (b). The specimens were heated separately for $\frac{1}{2}$-hr intervals in rotation and hence may not have been annealed at exactly the same temperatures. Density determinations were made by method (i).

The changes in expansion, refractive index, rotatory power, and birefringence of suitable specimens of irradiated quartz from Groups (A) and (B) and irradiated vitreous silica from Group (G) resulting from heating were determined for specimens of three different irradiation dosages: IB,† IIIA, IIIB. Specimens were inserted in the heating bath or furnace for approximately half-hour periods. An attempt was made to employ successive temperatures which had a fixed ratio on the absolute scale. The nine specimens were heated simultaneously at each of the successive temperatures (°C) 125, 165, 208, and 258 for 30 min by method (xiv). They were heated in groups of three specimens at the next series of temperatures by method (xvii). At the temperatures (°C) 312, 368, 432 they were within 5° of the stated temperature for 26 min; at 501, for 27 min; at 579, six for 28 min and three others for 32 min; at 662, for 27 min; at 756, for 27 min; at 859, six for 28 min and three for 30 min; at 972, for 28 min. Three of the specimens reached a temperature of 974°C during part of the annealing at 972°C. At 1100°C (nominal) method (xvii) was used: the first group was at 1095±3°C for 21$\frac{1}{2}$

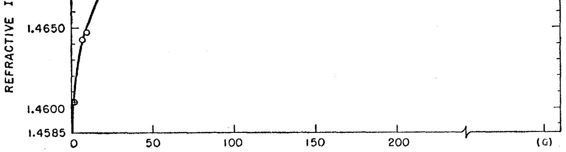

FIG. 4. The behavior of the refractive index of vitreous silica on irradiation in nuclear reactors: open circles—vitreous silica; crossed circle—datum from reference 9; solid circles—data for quartz. The dosage at (*a*) is estimated at 250 to 400 on the scale.

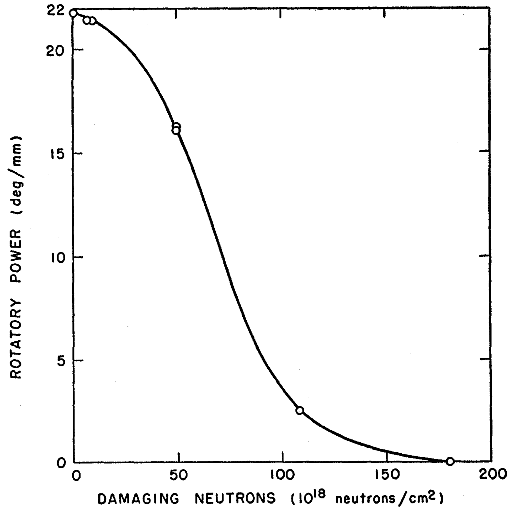

FIG. 6. The behavior of the rotatory power of quartz on irradiation in nuclear reactors.

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† *Note added in proof.*—In the figure captions this is referred to as IIA.

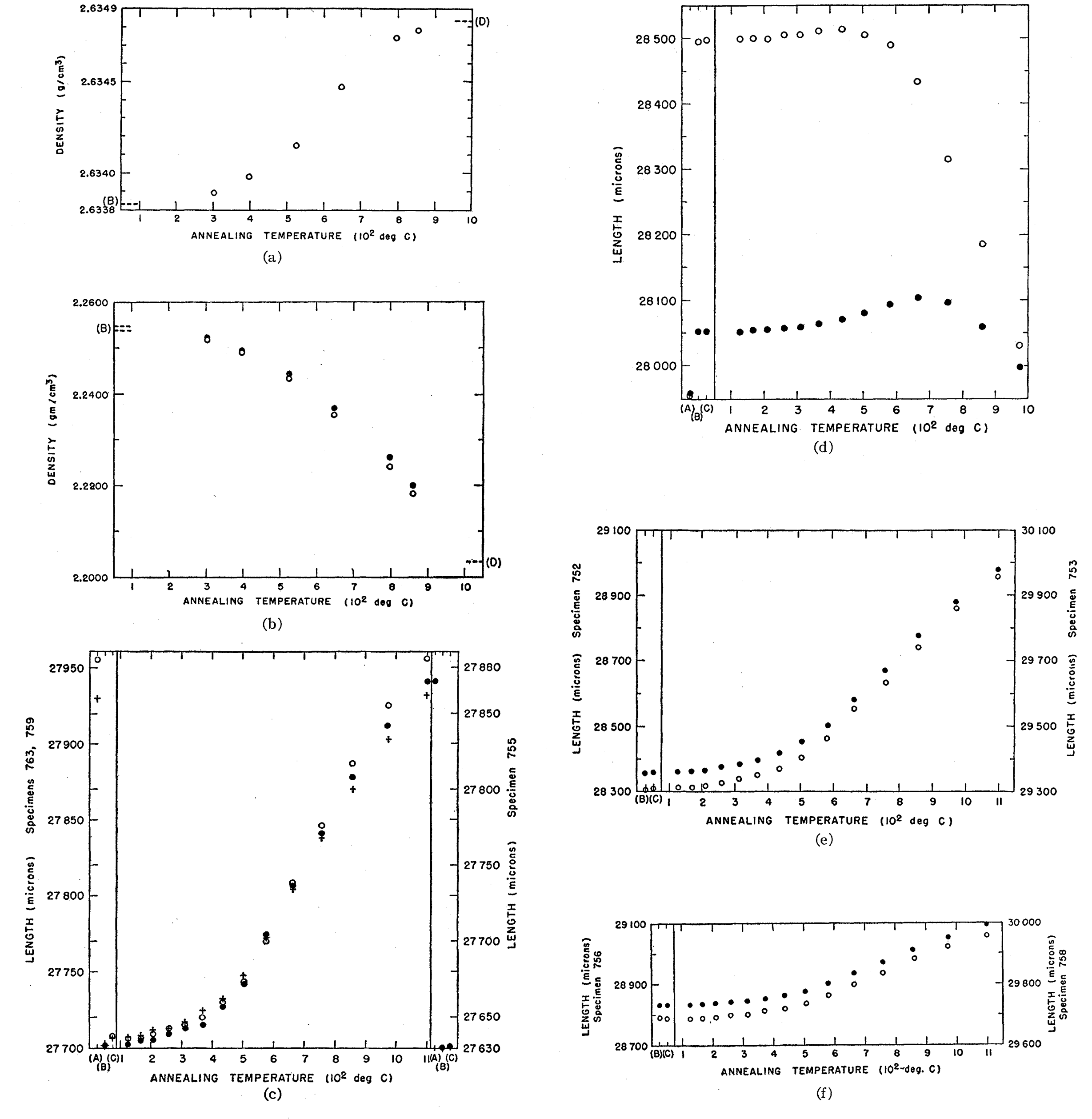
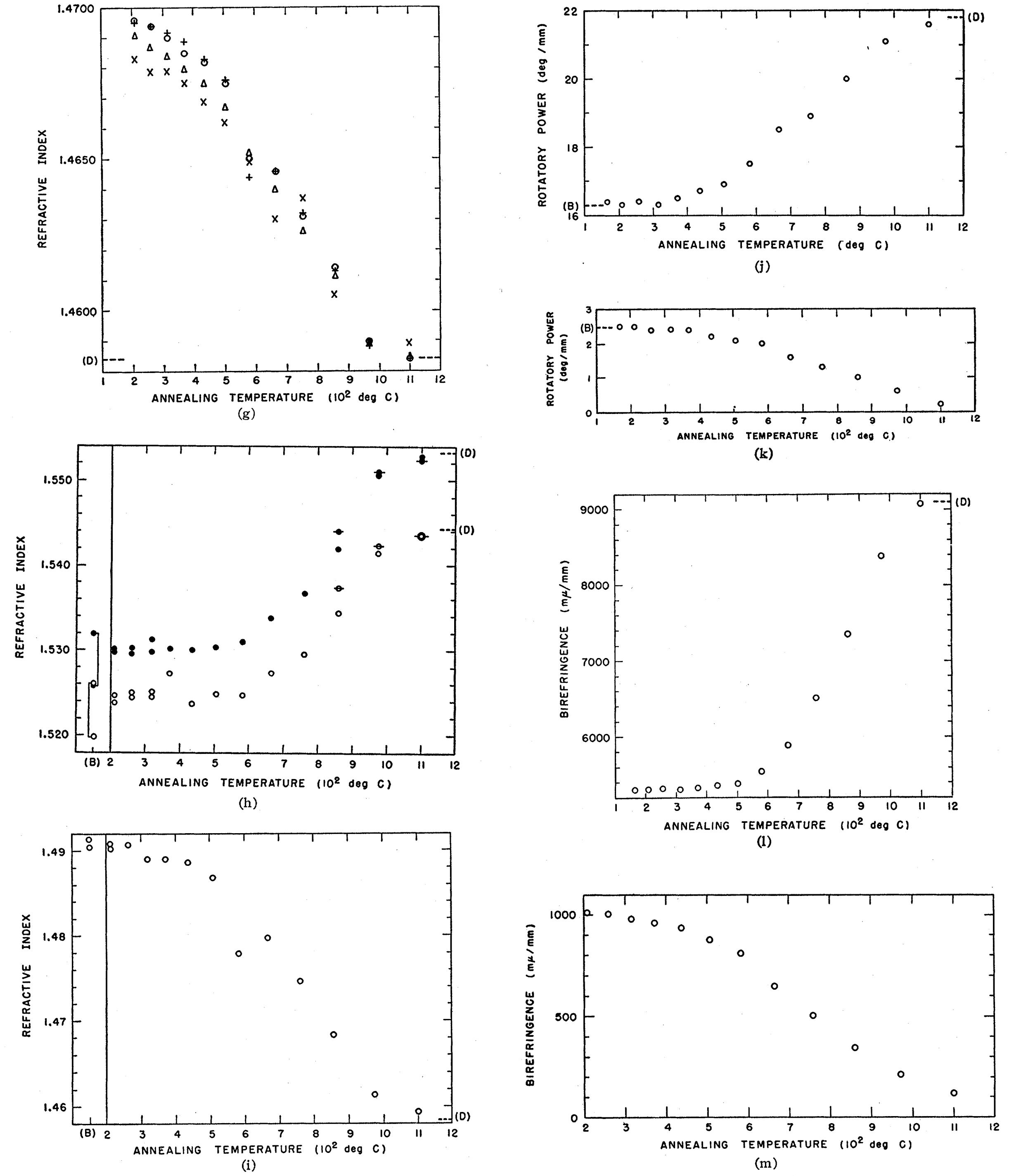


FIG. 7. The properties of irradiated vitreous silica and quartz after heating to successively higher temperatures for approximately half-hour periods. In each case the point or value at (*A*) is the property before irradiation; at (*B*) the property after irradiation but before annealing; at (*C*) the property after polishing one face (if this was done; some heating resulted when the sample was set in wax); at (*D*) the accepted value of the property of unirradiated material. (a) Density of irradiated (early stage) quartz specimen 671. (b) Density of irradiated (very late final stage) quartz specimen 768 (solid circles) and of simultaneously irradiated vitreous silica specimen 770 (open circles). (c) Lengths of vitreous silica specimens 763 (open circles), 755 (solid circles), and 759 (crosses). (d) Lengths of irradiated (late in early stage) quartz specimens 760 (parallel to *c* axis) (solid circles) and 761 (perpendicular to *c* axis) (open circles). (e) Lengths of irradiated (early final stage) quartz specimens 752 (parallel to *c* axis) (solid circles) and 753 (perpendicular to *c* axis) (open circles). (f) Lengths of irradiated (late final stage) quartz specimens 756 (parallel to *c*-axis) (solid circles) and 757 (perpendicular to *c* axis) (open circles). (g) Refractive index of irradiated vitreous silica specimens 763 (crosses), 755 (triangles), and 759 (×'s), and irradiated (late final stage) quartz specimen 757 (circles). (h) Ordinary refractive index (open circles) and extraordinary refractive index (solid circles) of irradiated (early intermediate stage) quartz specimen 761 and simultaneously irradiated quartz specimen 760 (ruled circles). When two of the same points are given for the same annealing, they represent the refractive indices corresponding to the extremes of the indefinite zone of total reflection in the Pulfrich method of determining the refractive indices. (i) Refractive index of irradiated (early in final stage) quartz specimen 753. For the significance of the two points at the same annealing temperature, see (h). (j) Rotatory power of irradiated (early intermediate stage) quartz specimen 761. (k) Rotatory power of irradiated (early final stage) quartz specimen 753. (l) Birefringence of irradiated (early intermediate stage) quartz specimen 760. (m) Birefringence of irradiated (early final stage) quartz specimen 752.



min, the second group at 1099±3°C for 25 min, and the third group was at 1098±6°C for 22 min. Graphs of the properties which were measured after these heatings are presented in Figs. 7(c) through 7(m). Some of the observations are not easily represented in graphical form. Specimen 761 (strained, comments above) developed a crack during the heating at 662°C. The crack originated at one end in a small chip which was originally introduced by a pair of forceps used to handle the specimen. The crack terminated in a star formed at about $\frac{1}{3}$ the length of the specimen. The strain was redistributed about the crack; but there was no evidence of any annealing of the strain after this heating, after any of the previous heatings, nor after the next one. However, after the heating at 859°C the strain, as indicated by the birefringence, had nearly vanished. After the first few heatings the specimens were cleaned in hot sulfuric acid—chromic acid cleaning solution to remove organic material which could char on the specimens during the heating and interfere with the optical measurements. In this operation performed before the 1100°C heating, the specimens were chilled too suddenly, and specimens 760 and 761 each broke into several pieces. These were heated and the properties which could be measured on the pieces were determined. Computation of the birefringences and rotatory powers from the retardations and the rotations required the specimen thickness. This was measured after the 1100°C heating, and the thickness after the other heatings was computed from the fractional length changes of the specimens of orientation perpendicular to these and which were irradiated simultaneously. Accordingly, these thicknesses (and hence also the birefringence and rotatory power) possess a consistency which exceeds their accuracy. The densities were determined after the 1100°C heating and are entered in Table II in brackets. These specimens had been ground and polished flat on one side before the heatings. As the heatings progressed they became warped to an extent which made precise determination of the refractive indices of some of them difficult.

The following x-ray diffraction observations were made. No sign of powder lines were detected in a Weissenberg picture of a fragment of specimen 761 subsequent to the 1100°C heating. A powder pattern of another portion of specimen 761 subsequent to the 1100°C heating was sharp and indistinguishable from that of a sample of unirradiated quartz. Specimen 645 was material which had been subjected to the differential thermal analyses (DTA) described elsewhere.[9] Its powder pattern (subsequent to the DTA) possessed diffuse lines. A small portion of specimen 645 was heated to 1100°C for $\frac{3}{4}$ hour, and the powder pattern of the heated material possessed sharp lines and was indistinguishable from that of unirradiated quartz. Forward reflection cassette pictures were taken of the specimens 752 and 756, both subsequent to the 1100°C heating; and they were compared with a similar picture of an unirradiated specimen of vitreous silica of the same shape. The pictures were all of amorphous substances, but showed some slight differences. That of specimen 756 showed a slightly heavier halo than that of the comparison sample, and that of specimen 752 showed evidence of some "pseudo-crystalline" aspect as manifested by some slight low-angle streaking due to the white x-ray radiation.

DISCUSSION

The several hypotheses which have been suggested in the past[4,5,6,16,23] to account for the behavior of particular properties, or the property changes in a portion of the range of the disordering phenomena, do not account for the observations presented in this paper. This discussion will be directed mainly to the presentation of a theory of the structural changes accompanying the atomic events of the damaging and the annealing, consonant with the present observations and with other published data.

Effects in Vitreous Silica

The changes observed in vitreous silica are examined first because they seem to follow a simpler course both on irradiation and on annealing, and because similar phenomena must occur in quartz when it has become considerably disordered. The rapidity with which the property changes take place in vitreous silica (Figs. 1–6) is their most prominent feature. If the effects were to be attributed to atomic events initiated by the scattering of neutrons, then from a comparison of the property changes observed in vitreous silica and graphite with variously moderated neutrons it was concluded[15] that most of the observed damage was to be related to energetic silicon and oxygen atoms dissipating about 10^4 ev in elastic collisions in a small region.[24] If these events may be considered to produce changes which are largely nonannealing at the irradiation temperatures, then the saturation period $(1-e^{-1})$ occurs at about 1.2×10^{19} damaging neutrons cm^{-2} (from Fig. 1), and from previous calculations this indicates[24] that about 4×10^4 atoms are involved in the "severely damaged regions." These regions are therefore at temperatures in excess of 2500°C at such times, and their lifetime is $\sim10^{-12}$ sec. At these temperatures the requirements of bonding distances and angles arising from coordination and charge distribution must be less severe than at lower temperatures. Only the slightest deformation of the Si-O tetrahedra are possible, but greater deformation of these configurations with respect to each other can occur. This seems to occur in such a way as to make the structure more compact with respect to the Si-O tetrahedra, to compensate for the thermally increased Si-O distances. This compacted structure must then be frozen in as the thermal spike chills.

There are several data which support the above hypothesis directly. Lukesh[10] investigated the change in the x-ray diffraction pattern resulting from irradiation of vitreous silica. If his results are compared with the analysis of the pattern made by Warren *et al.*,[25] it is evident that the major changes found by Lukesh correspond to increasing the range of the distribution of first Si-Si distances and decreasing their mean value, and to

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[23] W. Primak, Phys. Rev. **98**, 1854 (1955).

[24] W. Primak, Phys. Rev. **103**, 1681 (1956).

[25] For example as quoted by B. E. Warren, J. Appl. Phys. **8**, 645 (1937).

decreasing second Si-Si distances to an even greater extent. This is shown by the shift of the first peak which corresponds to first Si-Si distances. This peak is shifted to a value corresponding to an Si-Si distance smaller than that observed in cristobalite, as indeed might have been expected, since the irradiated glass is of about the density of cristobalite while being a disordered material. At $\sin\theta/\lambda=0.35$ there is a peak in vitreous silica corresponding to second Si-Si distances which is partially resolved from an O-O peak at $\sin\theta/\lambda=0.40$. On irradiation, the Si-Si peak is shifted into the O-O peak, and the two peaks appear more nearly like one peak in the irradiated material. The peaks corresponding to O-O distances which are seen are those for neighbors, and they seem relatively unaffected, as the hypothesis requires, for the deformation is mainly in the nature of adjoining tetrahedra being bent or twisted with respect to each other. Further support for the hypothesis is found in the course of the annealing reported here and in previous papers.[9,11] The properties change on annealing and gradually revert to those of ordinary vitreous silica. Some earlier work[11] seemed to indicate a frequency factor of 10^8 per second. Some newer work, results of experiments intended to determine the frequency factor directly,[26] has indicated it to be somewhat larger, perhaps 10^{10} per second, and has indicated that the processes are first order. These results seem to accord better with the relaxation of locally strained bonds than with diffusion phenomena.

The major contribution to the refractive index of silica is made by the oxygen ions, for their refractivity $[R=(n^2-1)/\rho(n^2+2)$, where n is the refractive index and ρ is the density$]$ is 2 orders of magnitude greater than that for the silicon ions.[27] The refractivity as a function of dosage (Fig. 8) decreases slightly, from 0.124 to 0.1232, in the period where the density increases by some 2%. Since the nearest oxygen distances do not seem to alter, the effect is to be attributed to a small change in the polarizability of the oxygen ions by the silicon ions. An effect of this kind is well known.[28] The change in the refractive properties of vitreous silica for variously caused dilatations ($\Delta V/V_0$ where V is the volume) can be compared. For a thermal dilatation $V_0\Delta R/\Delta V$ is 2.0; for an elastic dilatation[29] it is about 0.034; for the total change in the early stages of the irradiation it is 0.02; and for the total change found very late in the irradiation it is about 0.02. The same effect can be seen in considering $-V_0\Delta n/\Delta V$: for a thermal dilatation[30] it is 8; for an elastic dilatation[29] it is about 0.34; for the total change in the early stages of irradiation it is about 0.45, in the intermediate stages 0.40, and in the late stages 0.37. The final alteration thus seems to be approaching a compacting of the structure rather than an ordering or disordering.

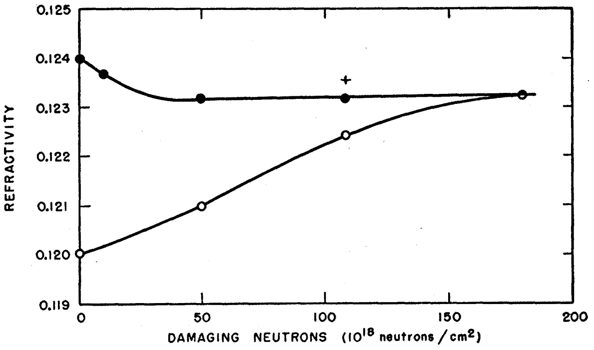

FIG. 8. The behavior of the refractivity of quartz (open circles) and vitreous silica (solid circles) on irradiation in nuclear reactors. The cross is the value obtained when using an erroneous density as described in the text.

The appearance of an early maximum change in the properties of vitreous silica, followed by a small decrease, might be explained either by the inhomogeneity of the compacting being gradually removed, or by a slight local ordering in the original compacting being disordered as atoms are displaced and accommodated. The time scale of the events favors the latter explanation.[31]

Effects in Quartz

That the phenomena involved in the disordering of the quartz are very much more complex than those involved in vitreous silica can be seen immediately from the behavior of the expansions. From the facts that the final product has the same density as vitreous silica, is optically isotropic with the same optical properties, anneals in the same manner, and gives on annealing a product with the same properties, it must be concluded that this final product of the disordering of quartz on irradiation is isotropic and vitreous, and it therefore has an axial ratio unity. The gradual transition of an anisotropic body to an isotropic body will here be termed an "isotropization" to distinguish such a course from the actual change to an amorphous body, which among natural substances disordered by their own radioactive content has been termed a metamictization. If the isotropization were to proceed as a homogeneous deformation (i.e., a scalar-tensor effect, e.g., like the thermal dilatation) then it could be described by two constants, the radiation expansion along the c axis and the radiation expansion perpendicular to it. The total expansions $1+(\Delta c/c_0)$ and $1+(\Delta a/a_0)$ for such an isotropization, involving the observed volume change of 17.4% and the known original axial ratio 1.1, are easily

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[26] H. Szymanski and W. Primak (unpublished).

[27] H. Mueller, J. Am. Ceram. Soc. **21**, 27 (1938).

[28] S. Glasstone, *Textbook of Physical Chemistry* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1940), p. 530.

[29] W. Primak and D. Post (to be published).

[30] R. B. Sosman, *The Properties of Silica* (Chemical Catalogue Company Inc., New York, 1927).

[31] It would seem from the results presented here that the statements of Wittels and Sherrill[8] on the crystallization of vitreous silica are incorrect. They may have observed either (a) a devitrification, probably accelerated by surface impurity, or (b) the crystallization of partially disordered irradiated quartz.

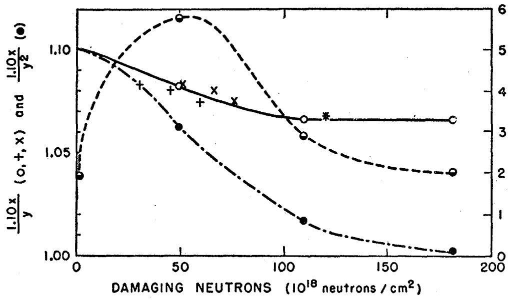

FIG. 9. Behavior of ratios of the radiation-induced expansions perpendicular and parallel to the optic axis of quartz. Full line: open circles—axial ratio computed from the expansion parallel and perpendicular to the original optic axis, i.e., 1.10 x/y; **×**'s—Wittels' data[12] for the axial ratio; crosses—Wittels' data[8] for the axial ratio plotted at dosages which in the work reported here correspond to the density changes reported by him. *Note added in proof.*—M. C. Wittels [Phil. Mag. **2**, 1445 (1957)] received while this article was in press, shows that in II there is a large difference between the density measured directly and that obtained from the x-ray diffraction peaks assuming the symmetry of quartz. Accordingly, Wittels' axial ratios obtained from the latter kind of data are probably inappropriate for this graph. Dot-dash line: solid circles 1.10 x/y^2. Dotted line: half-open circles—ratio of the expansions perpendicular and parallel to the original optic axis, i.e., $(y-1)/(x-1)$. The quantities are defined as follows: $x=1+(\Delta c/c_0)$, $y=1+(\Delta a/a_0)$, where $\Delta a/a_0$ and $\Delta c/c_0$ are the fractional expansions perpendicular and parallel to the original optic axis, respectively.

computed as follows:

$$[1+(\Delta a/a_0)]^2[1+(\Delta c/c_0)]=1.174,$$
$$1+(\Delta a/a_0)=1.1[1+(\Delta c/c_0)],$$

and the solutions $[1+(\Delta a/a_0)]=1.088$ and $[1+(\Delta c/c_0)]=0.990$ are obtained. Thus, such a homogeneous deformation requires an 8.9% expansion perpendicular to the c axis and a 1.0% contraction along the c axis. Indeed, if no expansion or contraction along the c axis were to occur, isotropization by a homogeneous deformation would require a 21% volume increase, 1% more than is required to give the density of unirradiated vitreous silica. Since in fact the final expansion observed along the c axis is about half that observed perpendicular to the c axis, it is obvious that an homogeneous deformation is not involved.

The radiation expansion of quartz was investigated earlier[9] parallel to the c axis and perpendicular to it, in the initial stages of irradiation, for the period involving about 0.025% to 0.12% change in density. The ratio of the fractional expansions $P=(\Delta a/a_0)/(\Delta c/c_0)$ was initially about 2 and was increasing appreciably so that at the end of this period it was about 2.3. This may be compared with the similar properties, the ratio of the linear compressibilities and the ratio of the thermal expansions, whose respective values[30] are 1.43 and 2.0. It would thus seem that initially the radiation damage of quartz behaves as if random disorder is being introduced into the crystal. Then the expansion perpendicular to the c axis continues to increase at a somewhat increasing rate, while the rate of expansion along the c axis declines somewhat. Thus P increases in value, eventually reaching a value between 5 and 6 at a dosage between 40×10^{18} and 60×10^{18} neutrons/cm^2, as shown in Fig. 9.

The work of Wittels *et al.*[8,12] shows that during all of I the material preserves its crystal symmetry in some degree, and it may be imagined that the large rise in P is an indication of some conformity to the axial requirements of a homogeneous deformation. However Klemens'[3] analysis of Berman's[2] thermal conductivity data shows that the disorders involved are a mixture both of small disordered regions and much larger ones.[32] The accumulation of the latter (which would seriously affect the crystal symmetry) suggests a mechanism for explaining the later anomalies of the axial expansions.

The thermal spikes which seem to play so dominating a role in the irradiation of vitreous silica should be equally present here according to the ordinary considerations of the flow of heat, contrary to some suggestions made earlier.[33] At the temperatures which were shown to be significant in the discussion of the role of thermal spikes in vitreous silica, the thermal conductivity of quartz and vitreous silica must be nearly the same.[34] If vitrification could proceed in such thermal spikes, then, as soon as they became effective, disordering would be virtually completed by a dosage of 30×10^{18} neutrons/cm^2. No such phenomenon is observed in the disordering of quartz, and hence it is concluded that the region of the thermal spike does not become vitrified, even though its temperature is far above the melting point for a time several orders of magnitude longer than the atomic vibration period. This is not entirely surprising. The viscosity of liquid SiO_2 is very great even at ordinary pressures, and it is difficult to obtain homogeneous vitrification even in the melting pot. A failure to obtain a vitrification (which would be of the nature of the sluggish transformations) in the thermal spike under conditions of pressure which, from Le Chatelier's principle, would favor the crystalline form is not, therefore, surprising. On the other hand, one might expect that the behavior hypothesized for vitreous silica may occur here too: a phenomenon which is analogous to the rapid inversions in quartz. This is the relaxation of the firmness of the binding permitting the Si-O tetrahedra to slightly alter their relations with respect to neighboring tetrahedra. The effect in the disordered quartz would be to alter the local configuration about an individual atom. How the order at a particular point would be affected would depend on the phasal relations of the local configurations to each other, and these might be improved or worsened in particular cases, but statistically would, of course, lead to vitri-

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[32] This distribution is related to the product of the distribution of scattered atoms and the pile neutron distribution, not to the distribution along the range of the scattered atom as depicted by Klemens.[16] The range of the scattered atom is so short that it effectively forms only one cluster in general.

[33] W. Primak, Phys. Rev. **98**, 1854 (1955).

[34] See C. Zwikker, *The Physical Properties of Solid Materials* (Pergamon Press, London, 1954), Figs. 9–28.

fication. Here the displaced atoms (in the sense used by Seitz) play a role which they cannot play in vitreous silica. The latter is a random network with no phasal relations between the local configurations, and hence the displaced atoms are accommodated with little alteration to the statistical order. However, when the local configurations of the partially disordered quartz accommodate displaced atoms, the phasal relations between the local configurations are altered; the x-ray diffraction pattern due to the high-index planes vanishes eventually; and all that remain are the diffuse maxima, a lattice with disorder "frozen in" (analogous to the maxima of the temperature diffuse scattering). The material is now in II. This view of the gradual, almost uniform, disordering of quartz, to which one is led by comparing the behavior of several of the properties and by comparing the time scale of the changes in quartz and vitreous silica, avoids all the difficulties of enormous macroscopic strains which Klemens[16] has hypothesized.

The material in IA anneals simply over a broad range of temperatures suggesting a broad activation-energy spectrum for annealing of the disorder. In IB complex behavior appears. Some properties of the material (notably the refractive index) remain stationary until a fairly elevated temperature is reached [about 500°C for the case given here, Fig. 7(h)]. Other properties like the birefringence, the rotatory power, and the x-ray diffraction patterns[6] begin to return to those of quartz at a lower temperature (about 350°C for the cases given here). The density and axial expansions [Figs. 7(a)(b)(d)(e)(f)] show an effect which has been termed "anti-annealing" by some[35]: an alteration toward the properties of disordered material at lower temperatures; then at higher temperatures the properties alter to those of quartz. This inversion from "anti-annealing" to "annealing" occurs at different temperatures for the respective axial expansions. The anti-annealing at the lower temperatures seems to be nearly the same for both axial expansions, and if it is assumed to be an isotropic expansion and independent of the negative aeolotropic axial expansion observed at higher annealing temperatures, then the inversion temperature will be lower for the greater negative axial expansion as was found. On the basis of this reasoning it was suggested[14] that these observations were to be explained by a phase separation, one phase being deformed crystal quartz, and the other phase being amorphous silica within the crystal. The fraction of each can be calculated if it is assumed that the amorphous material is that observed in the irradiation of vitreous silica and if its annealing behavior is the same. Then from the annealing expansions shown in Fig. 7(d) using the vertical scale of the figure as a unit of length, the axial expansions of 100 units parallel to the *c* axis and 500 units perpendicular to it represents a volume change of 1100 units cubed on total annealing, corresponding to a dilatation of 4% and hence caused by 27 500 units cubed of quartz. For about $\frac{1}{3}$ the annealing range of vitreous silica[11] the linear expansion is 50 units, hence corresponding to a volume change of 450 units cubed. If there is a 2% expansion on annealing, there are involved 22 000 units cubed of amorphous silica. Even with the reasoning given by Klemens,[16] allowing a 10–15% dilatation, 10–20% of the body would have to be amorphous. This is unreasonable in view of the fact that, after total annealing, the properties are so closely those of ordered quartz. Neither does it correspond to the behavior of the other properties. According to this hypothesis, the refractive index would be expected to decrease because of the expansion and the decreasing ultraviolet absorption, but it does not change; the rotatory power and birefringence, since they are given in per unit length of the specimen in Figs. 7(j) and (l), would be expected to decrease, and they increase instead. Thus, the hypothesis of the presence of two phases must be abandoned. Instead it is suggested that during annealing there are readjustments of the kind that occur in the rapid inversions of silica, small movements of the silicon-oxygen tetrahedra with respect to each other. These improve the long-range order and make only small changes in the local configurations. Thus the thermoelastic phenomena in the thermal spike seem to accommodate the disorder by favoring a closer packing of the local configuration sacrificing some long-range order, while slow annealing at low temperatures favors a little greater long-range order at the expense of lesser packing in the local configuration, and a small dilatation of the solid results. Because of the increase in long-range order, the birefringence and the rotatory power increase. The increased polarizability of the oxygen ions must about compensate for the alterations in the absorption spectrum and the change in density, and thus the refractive index is left nearly unchanged.

The changes of annealing are observed at quite low annealing temperatures. Indeed, a definite expansion perpendicular to the *c* axis was apparent even after the 200°C annealing. It may therefore be expected that the effects will be sensitive to the temperature of irradiation. Although Wittels and Sherrill's[8] dosage data are not believed to be as reliable as the data given here, an effect of this sort may be responsible in part for the differences between the two sets of results. The irradiation temperatures they quote are about 100°C. The data presented here are probably (they were not measured but were estimated from test-hole coolant temperatures and reasonable temperature rises within casings) in most part for irradiation temperatures 40°C to 70°C lower. The greater extension of I which Wittels and Sherrill observed could be explained in this manner. Some of the observations given here confirm qualitatively the existence of such an effect. These are the strains found within a single irradiated quartz specimen, the variations in rotatory power and birefringence in

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[35] E.g., G. R. Hennig and J. E. Hove, *Proceedings of the Conference on the Peaceful Uses of Atomic Energy, Geneva, 1955* (United Nations, New York, 1957), Vol. 7, paper 751.

some specimens, and the different densities found for specimens irradiated simultaneously in the same can. The only reasonable explanation for these phenomena is that they were caused by temperature gradients in the specimens and cans during irradiation.

The behavior in I can be discussed in terms of the original crystal symmetry, but in II it is no longer possible to do this as is illustrated by the behavior of the axial ratio. The ratio $Q=(1+\Delta a/a)/(1+\Delta c/c)$ becomes stationary in II while the isotropization proceeds almost as $Q(1+\Delta a/a_0)$ (as shown in Fig. 9) a behavior which cannot be justified in a simple way. It would seem that with the greater destruction of long-range order and the increased accommodation of displaced atoms, there are local anisotropic configurations formed which are rotated with respect to the original axes. The material which in IB was in a state which Klemens[3] dubbed a "dilute glass" could similarly in II be dubbed a "dilute crystal," but since there is probably a continuity of (thermodynamic) states (with no sharp physical boundaries) present in the solid, the nomenclature is no more desirable than the similar one for a glass criticized by Warren long ago.[25] With the peculiar behavior shown in II and with the possibility that elastic phenomena may be involved, it is no longer necessary that the fractional expansions form an ellipsoid. Even the finding (see below, the discussion of the refractivity of quartz) that the density computed from the expansions parallel and perpendicular to the c axis does seem to correspond to the actual density does not prove that the fractional expansions do not form an ovaloid or a surface of trigonal symmetry (like Young's modulus), and they should therefore be investigated further.

This writer has not made any observations in the midst of II, but Wittels *et al.* have published some density, axial ratio, x-ray diffraction, and annealing behavior determinations which are from this stage. The experimental work is unreported in detail as yet. They repeatedly mention that, on annealing irradiated quartz, cryptocrystalline[‡] quartz is obtained. The writer has not seen any evidence of this phenomenon in I or III, and hence it seems reasonable to attribute it to II, but this should be confirmed by independent observation. It would be explained by the phasal relations between the local configurations becoming so greatly disturbed that the long-range order can no longer be re-established throughout the specimen, and so the local configurations form nuclei for the devitrification of the disordered quartz. However, the anisotropy of quartz would not permit annealing to form an unstrained mass of randomly oriented ordered quartz crystallites. Wittels has mentioned the observation of a porous structure. Another possible result would be small crystals in a vitreous matrix. It would be desirable to obtain more detailed experimental information of annealing in this stage.

In III there still are ordered local configurations present as is shown by an appreciable rotatory power and birefringence; and since the rotatory power is observed in approximately the direction of the original c axis, at least some of these local configurations must be vestiges of the original structure. However, they have become so small and disoriented that they can no longer remain nuclei for recrystallization during the local adjustments to establish better long-range order. They are deformed, and the general disorder of a glass results. The product is amorphous as suggested by the loss of rotatory power and birefringence and as definitely shown by x-ray diffraction pictures; but, at least after heating to 1100°C for a short period, it is not identical with vitreous silica, as shown by the x-ray diffraction low-angle scattering and by small differences in density, until late in IIIB. Evidently the product of the annealing from IIIA, although essentially amorphous and vitreous, does possess slightly greater short-range order than ordinary vitreous silica does. Thus if one accepts the cryptocrystalline silica reported by Wittels as being the product of annealing from IIB, then it would appear that the product of annealing specimens of increasing irradiation dosage contains decreasingly smaller crystallites until, eventually, in the annealing product of III these are too small to be termed crystallites, and the product must be considered vitreous. After further irradiation (late in IIIB) the annealing products eventually become indistinguishable from ordinary vitreous silica.

There is an uncertainty in applying the usual treatment of the refractivity to quartz because of its anisotropy. Since the refractivity represents an ionic volume, it should be the same whatever polarization of light is used to determine it. The Lorentz-Lorenz calculation is therefore performed for an ellipsoidal cavity whose axes are in the ratio $(1+S)$, the quantity S being determined by the condition that R be the same for n_ϵ and n_ω. Following Mueller,[27] $F=E+\frac{4}{3}\pi J\beta$, where $\beta=1-0.8S$ for the extraordinary ray and $\beta=1+0.4S$ for the ordinary ray, and hence $R=(n^2-1)/\rho[3+\beta(n^2-1)]$. For the case of quartz S is found to be 0.0358 and $R=0.1206$, which is nearly a mean value for the results obtained by inserting the respective indices of refraction in the usual expression in which β is unity. The refractivity calculated by this *ad hoc* procedure (Fig. 8) increases gradually on irradiation with a very slight sigmoid shape to the value for irradiated vitreous silica. However, to get this result it is necessary to use as the density for specimen 752 that which is computed from the expansion of specimens 752 and 753, rather than the smaller density of the small fragments 410 which were also present in this irradiation can. If the latter density is used, the refractivity calculated at this point greatly exceeds the value for unirradiated vitreous silica, a result which would be most extraordinary. It is therefore

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[‡] *Note added in proof.*—Consisting of small randomly oriented crystallites. See, e.g., *Dana's Textbook of Mineralogy*, 4th ed. by W. E. Ford (John Wiley and Sons, Inc., New York, 1938), p. 204.

concluded that the densities calculated from the expansions are correct for these specimens and that the smaller specimens show a larger property change for a given dosage. This is explained by the larger specimens having been at a higher temperature during the irradiation, and is further evidence of a sensitivity of at least some of the effects to the temperature of irradiation.

Some of the complexity present in this description of the radiation disordering of quartz and the subsequent annealing of the disordered product implies that simultaneous and competing processes occur. Thus, the simplest explanation for a sensitivity of the radiation-induced property changes to the irradiation temperature is the simultaneous occurence of damaging and annealing. The formulation of different annealing processes in the several stages implies competing processes in specimens irradiated for intermediate dosages. Thus it may be expected that differing irradiation conditions and differing annealing programs will give variations in results.

Comparisons with other Insulators

In the disordering of siliceous minerals by metamictization, the phenomena of the damaging seem to follow a course similar to that found here for quartz. The metamictization is caused by the alpha particles and the recoiling decaying natural radioactive species present.[36] The former, having energies of about 3–4 Mev, produce scattered displacements (in a nuclear reactor scattered displacements are formed in the scattering of low-energy neutrons) while the latter have energies from 0.05 to 0.1 Mev. They therefore possess energies of the order of magnitude of the energetic atoms formed by neutron scattering in nuclear reactors. However, because of their greater mass, the recoiling radioactive atoms are more effective in displacing atoms, and the thermal spikes associated with them should be somewhat larger and of somewhat longer duration over their effective lifetimes; but yet the phenomena should not be tremendously different from those found here, and indeed this seems to be the case. The course of the disordering of zircon was found by Holland and Gottfried[37] to possess a number of the features of the disordering of quartz as discussed here. There are similar sigmoid damage dosage curves, and similar behavior of the axial ratios. The damage can therefore be discussed as occurring in 3 stages. Much earlier work[38] showed complexities in annealing behavior. In I a return to the properties of unirradiated zircon occurs; but in II this is no longer possible. The effects therefore seem to be controlled by the sluggish transformations and rapid inversions shown by silica structures, much as has been hypothesized here for quartz. However, the presence of the other ionic species introduces a complication which appears both in the metamictization and in the annealing. Holland and Gottfried[37] reported for zircon that during II there appeared new x-ray diffraction lines. Evidently some new local configurations developed, and this is here suggested to be the result of a kind of crystallization which occurred in the thermal spike. Crystallization of such a new phase can also occur during annealing as shown by Pabst[39] for metamictized thorite, and it is suggested here to take place on favorable local configurations which act as nuclei.

The disordering of quartz in a nuclear reactor is thus presented here as the simplest example of a metamictization. It is a prototype for one of a number of classes of radiation damage which can now be delineated among those found to occur in insulators. The cases of molecular and ionic crystals are discussed by Seitz and Koehler.[40] Results published for diamond and silicon carbide suggest that in these cases the interstitial atoms are accommodated by a homogeneous elastic deformation, and the structure is so rigid that long-range order is maintained until a very high concentration of interstitial atoms is reached. The high melting point and high thermal conductivity are probably contributing factors to decreasing the effects of thermal spikes of energetic displaced atoms. In the case of diamond, the x-ray patterns remain sharp until several times the dosage required to completely disorder quartz. In the case of graphite the interstitial displaced atoms seem to be accommodated by a local elastic deformation. In both the graphite and the diamond classes, the interstitial atoms remain, at least in part, only loosely bound to the lattice; and large amounts of energy is stored thereby. In the case of quartz, the interstitial atoms seem to be accommodated by a local permanent deformation and a disorientation which recall the rapid inversions; in the thermal spikes vitrification does not occur, despite temperatures above the melting point, because of the firm bonding, and this recalls the sluggishness of the reconstructive transformations. Little if any energy is stored, and it must be assumed that the displaced atoms are bonded in the local configuration in much the same ways as their neighbors. The refractory-ionic-metal oxides seem to form a class in which recrystallization is very rapid, so that it can occur in the thermal spikes, and hence extensive structural disorder is not readily observed. Probably much of what is observed is due to the accumulation of defects from extensive displacement and recrystallization. However, the effects become apparent in some cases. A spectacular case was recently found by Klein and reported by Wittels and Sherrill[41]: Klein observed the formation of a high-temperature phase of ZrO_2 during irradiation in a neutron reactor,

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[36] H. D. Holland, *Nuclear Geology* (John Wiley and Sons, Inc., New York, 1954), p. 178.

[37] H. D. Holland and D. Gottfried, Acta Cryst. **8**, 291 (1955).

[38] E.g., Von Stackelberg *et al.*, Z. Krist. **95**, 230 (1936); **97**, 252 (1937); **102**, 173 (1939); **102**, 207 (1939).

[39] A. Pabst, Am. Mineralogist **37**, 137 (1952).

[40] F. Seitz and J. S. Koehler, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 1, p. 308.

[41] M. C. Wittels and F. A. Sherrill, J. Appl. Phys. **27**, 643 (1956).

which the latter investigators associated with thermal spikes. The metamictization of minerals is dominated by the behavior of the silica structure; but there are also present some effects which are related to the class of the refractory-ionic-metal oxides, and a phase separation seems to occur at least in some cases. Small amounts of stored energy are found on annealing metamictized minerals in calorimeters, and it is suggested here to be due mainly to chemical reaction between the separated phases and to recrystallization.

APPENDIX

The paper by Simon[42] appeared after the writing of the present paper. His data seem to agree with the interpretations given here.

The deposit of about the density of cristobalite found by Stewart[43] on the walls of a discharge tube was probably radiation-damaged vitreous silica.

The variability in the density of quartz found in nature has usually been attributed to impurities. That it may in part be due to radiation damage from cosmic rays and radioactive inclusions should be considered.

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[42] I. Simon, J. Am. Ceram. Soc. **40**, 150 (1957).

[43] R. W. Stewart, Can. J. Research **26**, 230 (1948).

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Theory of an Experiment for Measuring the Mobility and Density of Carriers in the Space-Charge Region of a Semiconductor Surface

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The use of galvanomagnetic experiments to determine the mobility and density of carriers in the space-charge region of a semiconductor surface is considered. In part I an approximate model is used: it is a single crystal composed of two regions, a surface region of thickness of the order of a Debye length and a bulk region. Expressions for the resultant Hall coefficient are given for three experimental configurations by use of circuit analysis. The sensitivity of each configuration is derived, and by also considering experimental desirability, one is selected for study. It has the magnetic field perpendicular to the surface and the Hall voltages of surface and bulk are in parallel. Changes in Hall voltages of 1 to 50% are expected by using ambients to change the surface potential.

In part II the model is assumed to be a single crystal with continuous variation of the potential in the direction perpendicular to the surface. Rigorous expressions are derived for the Hall coefficient and magnetoresistance by use of the one-dimensional Boltzmann equation. A feature of the derivation is its independence of a specific model of the surface region. The resulting expressions contain surface densities and mobilities which can be evaluated from experimental data of Hall coefficient and conductivity. Conversely, the expressions can be used with theory based on specific surface models to predict values of conductivity, Hall coefficient, and magnetoresistance.

INTRODUCTION

THE interpretation of many experiments relating to the surface region of a semiconductor depends upon a knowledge of the density and mobility of carriers in the space-charge region as a function of surface potential.[1] The density of carriers has been calculated by solving Poisson's equation.[2,3] A theoretical study of the mobility of carriers in the space-charge region has been made by Schrieffer.[4] His study indicated that the mobility is a function of the surface potential and, for commonly obtained values of the surface potential, is lower than the bulk value. This general picture has been successful in interpreting a large number of experiments, including measurement of conductivity, field effect, and capacity.[1] However, a more direct measurement of the density and mobility of carriers in the space-charge region is desired to establish firmly the basic picture of the semiconductor surface and because of intrinsic interest in the scattering process.

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[1] For a review of the current state of surface physics and an extensive bibliography see R. H. Kingston, J. Appl. Phys. **27**, 101 (1956); and *Semiconductor Surface Physics*, edited by R. H. Kingston (University of Pennsylvania Press, Philadelphia, 1957).

[2] R. H. Kingston and S. F. Neustadter, J. Appl. Phys. **26**, 718 (1955).

[3] C. G. B. Garrett and W. H. Brattain, Phys. Rev. **99**, 376 (1955).

[4] J. R. Schrieffer, Phys. Rev. **97**, 641 (1955).