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Extrusion of quartz on ion bombardment: Further evidence for radiation-induced stress relaxation of the silica network*

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It is shown that although crystal quartz shows a highly aeolotropic uniaxial radiation expansion when it is disordered with energetic neutrons, plates of crystal quartz oriented on either principal axis exhibit a perpendicular expansion equivalent to the total volume expansion without developing porosity when subjected to bombardment with protons, deuterons, or helium ions having ranges about a micron. Thus a plastic flow must occur during ion bombardment. A mechanism for these courses of transformation is given: that the crystal structure breaks up into a mosaic of units elongated parallel to the optic axis in a vitreous matrix. The elongated units could account for the relative behavior of various aeolotropic properties, and the vitreous matrix could facilitate plastic flow.

INTRODUCTION

Hines and Arndt[1] subjected quartz to bombardment with ions and interpreted the reflectivity changes as being caused by the radiation-induced transformation to a vitreous product described by Berman *et al.*, Primak *et al.*, Wittels, Simon, and others[2] for quartz exposed in nuclear reactors. From their reflectivity data Hines and Arndt calculated an effective depth and average refractive index. They did not consider the dimensional changes which must have occurred.

The dimensional changes caused by 140-keV protons and helium ions were reported by Primak.[3] He was uncertain of the ranges of the particles, and he had to contend with a film depositing during bombardment, but the dimensional changes occurring during the irradiation of quartz are so large and so aeolotropic that there could be no question that, at least in approximation, vertical expansion corresponding to the total volume expansion was being observed; and for vitreous silica also, for which the volume change is some five times smaller, the total volume contraction appeared to be manifested vertically. In the interference microscope, pits were observed on bombarded quartz; and these were attributed to dust particles protecting parts of the surface during bombardment. A few curious features were observed that appeared to be pipes pushed up out of the surface. In the case of vitreous silica, the stress could be observed photoelastically; and hence the phenomena were termed, collectively, a radiation-induced stress relaxation. In other cases these phenomena have been referred to as a radiation creep. The effect may also be referred to as a plastic flow occurring during irradiation.

The probable mechanism by which dimensional changes can occur in silica is described by Primak[4] as involving the thermal movement of segments of the silicon-oxygen network facilitated by breaks in the network caused by the presence of impurities or by some agent as radiation, heat, shock, etc. Such breaks would be present in abundance during ion bombardment.

Since the presentation of this early work on the ion bombardment of quartz, the techniques of measurement have been greatly refined. Reflectivity measurements have been extended to measurement of the chromatic fringes produced in reflection, and the crude calculations made by Hines and Arndt have been extended so that the reflectivity of the bombarded surfaces can be interpreted with greater certainty. Our precision in measuring surface dimensional changes has been increased by an order of magnitude. Many other materials have been studied, and the vertical expansion appears in most cases to be associated with the development of porosity caused by segregation of trapped gas implanted by the ion bombardment.[5] It has therefore seemed desirable to reexamine the case of ion-bombarded crystal quartz.

MATERIALS, MEASUREMENTS

Crystal quartz used in the present studies was acquired from the Sawyer Research Products, Inc., in the early 1960's. Z-cut plates were oriented optically by the interference figure seen in convergent polarized light; X and Y cuts were oriented with respect to crystal planes with an autocollimator. They were lapped and polished to optical specification by usual optical techniques.

Chromatic fringes were obtained by two techniques. In the first, the specimen was viewed in a metallurgical microscope illuminated by the vertical illuminator used with a monochromator. A photomultiplier was mounted on the photographic tube of the microscope. The output of the photomultiplier electronics unit (Photovolt Corp.) was placed on the Y axis of an X-Y recorder, and the output of a potentiometer mounted on the wavelength dial of the monochromator was placed on the X axis. Resolution of the spectra with the customary settings was about 2 mμm. It is readily shown that the effect of this resolution is but to cause a small decrease in the contrast of the fringes. The advantages of this microscope arrangement were that the area being measured was readily identified and the reflectivity of several areas of the plate could be compared to within a few percent of the reflectivity. The wavelength range of the instrument was rather limited: from about 0.4 to 0.75 μm. In the second technique, the specimen was mounted in a special fixture and placed in the sample compartment of a Beckman DK-2A spectrophotometer. In this fixture, the beam was limited by a small aperture which was focused on the plate with a spherical mirror, and the reflected beam was collected by another spherical mirror and reflected to the detector. The angle of incidence and reflection on the plate was a mean of about 11°. The advantage of this arrangement was the large wavelength range of the instrument. Its disadvantage was that the beam could not be located as precisely on the specimen and/or the detector; hence the absolute values of the reflectivity were uncertain. With neither technique were the wavelength scales uniform nor were the reflectivity scales constant with wavelength. The graphs were digitized, suitable scaling was performed by computer, and the data were replotted on a wave-number scale.

Several kinds of optical interference measurements were made. In the Fizeau interferograms ΔND is observed where N is the refractive index and D is the thickness; in the Twyman-Green interferograms ΔD is observed; and in the Twyman-Green transmission interferograms (where the plate is placed between the mirrors rather than being one of the mirrors) $\Delta(N-1)D$ is observed. The interferograms were photographed on 35-mm film and enlarged onto high-contrast projection paper. The technique of measuring such interferograms is described in detail elsewhere.[6] However, in many of the interferograms, the steps were so large, they could be read with a pointer and scale.

CAUSE OF THE GROWTH

The primary question to be resolved here is whether the growth of the bombarded quartz surface is, like that of many other materials,[5] caused by porosity from the implantation of gas by the ion bombardment. To resolve this, the optical behavior of a layer of radiation-vitrified quartz and of a porous layer on quartz are considered.

The vitrified product of the irradiation of quartz has a refractive index about 1.48, considerably lower than that of quartz, 1.55. The chromatic fringes produced in reflection from such a layer on quartz should lie everywhere below the reflectivity of quartz. It was pointed out by Hines and Arndt[1] that, during the course of the vitrification, the refractive index would be nonuniform in depth in this layer, and that for such a nonuniform layer the reflectivity could rise above the reflectivity of quartz. Their work antedated modern computational facilities and were based on laborious approximate calculations of the system, two films on a substrate. With present day computational facilities exact calculations of this system can be performed readily. It is hardly necessary to use a more complex model because this simple model will show the major features of such a transformation.

The first case considered is that of an internal layer being transformed and growing toward the surface. The thickness of the final layer is taken as 1.89 μm, that observed for a long bombardment with 140-keV deuterons. Since the density of quartz is 2.648 and the density of the vitrified product is about 2.26, the transformation began at a depth 1.61 μm in the quartz. The refractive index of quartz was taken as

$$1.5324 + 0.004\,07\,\lambda^{-2} ,$$

where λ is the wavelength in μm. The refractive index of the vitrified product was taken as that observed for sodium light, and its dispersion the same as that of vitreous silica:

$$1.4586 + 0.003\,55\,\lambda^{-2} .$$

The dispersions were calculated from data given by Sosman.[7] The calculations were made with the corrected formulas from Heavens.[8] The chromatic fringes plotted by the computer are shown in Fig. 1. For most of the transformation, the fringes lie about the reflectivity of quartz. Near the end of the transformation some fringes may be completely above the reflectivity of quartz; but then, as the transformation proceeds further, they drop until, at the end, they are completely below it.

The second case considered is for the introduction of a gas layer beneath the vitreous layer, the inevitable result of the introduction of porosity. These results are shown in Fig. 2. Here the fringes keep rising in amplitude, eventually reaching amplitudes near 0.3 compared to the normal reflectivity of quartz 0.045.

The experimental results are shown in Fig. 3.

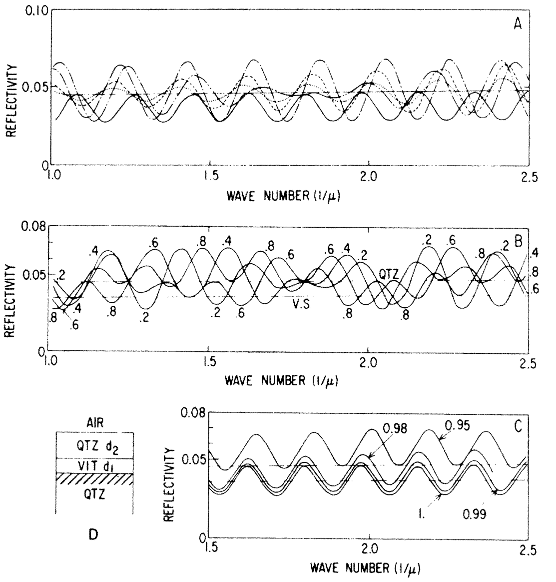

FIG. 1. Calculated reflectivity of a layer of quartz being vitrified. (A) Early stages of the transformation; solid line reflectivity of quartz; solid curve completely vitrified, $\alpha = 1$; dotted, $\alpha = 0.01$; dashed, $\alpha = 0.02$, dot-dash, $\alpha = 0.05$; dash-double dot, $\alpha = 0.1$. (B) Reflectivities for the intermediate stages of transformation, $\alpha = 0.2$–0.8. The two lines are the respective reflectivities for quartz and vitrified quartz. (C) Final stages of transformation, $\alpha = 0.95$–1.0. The two lines are the respective reflectivities of quartz and vitrified quartz. (D) The system of two films on a quartz substrate.

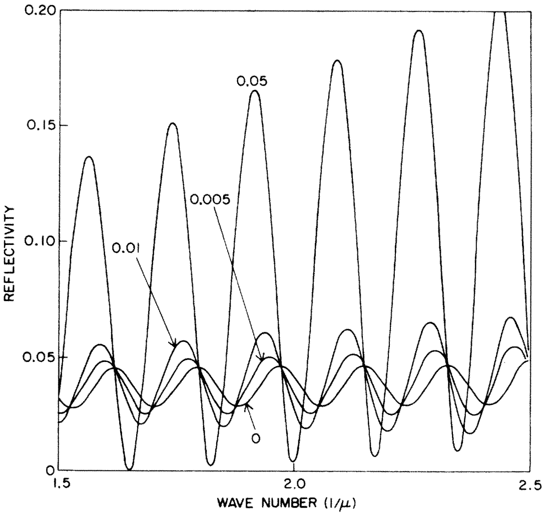

FIG. 2. Reflectivity calculated for quartz covered with a 1.57-μm layer of vitrified quartz with an intervening gas layer of the thickness (in microns) given on the respective curves.

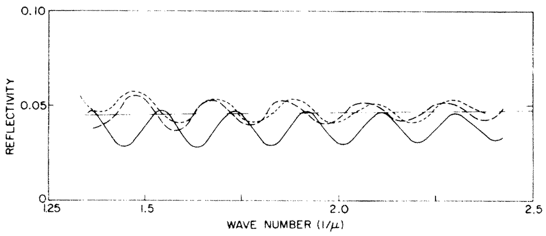

FIG. 3. Experimental measurements of the reflectivity of 140-keV deuteron-bombarded quartz relative to unirradiated quartz scaled to the reflectivity assumed in Figs. 2 and 3. Plate orientation parallel to the optic axis. Solid line, assumed value for unirradiated quartz; solid curve, 240 mC/cm^2; dotted line, 3 mC/cm^2; dashed line, 12 mC/cm^2.

It is clear that they do not correspond to the introduction of porosity. They do correspond to the formation of a vitreous layer which, to begin with, is nonuniform in depth and which has become nearly uniform for the longest bombardments studied.

AEOLOTROPY OF THE RADIATION EXPANSION OF QUARTZ

The fractional volume change (dilatation) in the neutron irradiation of quartz calculated from the density change data given by Primak[9]

$$\Delta V/V = (\Delta d/d)(1 - \Delta d/d)^{-1}$$

and the dilatation calculated from measurements of linear expansion of parallel (optic axis) and perpendicular-cut specimens irradiated in the same cans, on the assumption that a quartz sphere would be deformed to an ellipsoid on irradiation,

$$\Delta V/V = (1 + \Delta a/a)^2 (1 + \Delta c/c) - 1$$

are plotted in Fig. 4. These two curves do not conform to each other; hence, a question was raised as to the aeolotropy of the radiation expansion. To answer this question, a group of discs about 1-cm diameter and 2-mm thick were cut, and a circle was enscribed on each. The plates were irradiated to different dose, one laevo- and one dextro-rotatory plate to each dose, and after irradiation the diameter of the enscribed circle was determined with a spectrum plate comparator[10] to within a few microns at 15° intervals. The figures were, of course, no longer circles, and the measurements were then of various axes. The measurements did not deviate significantly from those calculated for deformation to an ellipse. The dilatation was therefore calculated from the linear expansions of the major and minor axes as given in Table I. These results are also plotted in Fig. 4. It is seen that they conform to the results for

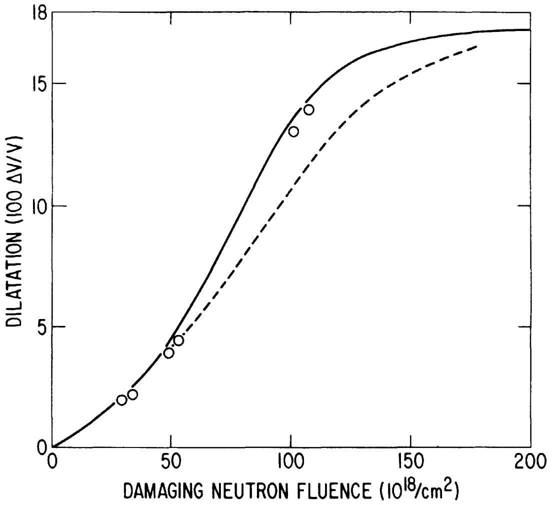

FIG. 4. Dilatation of quartz exposed in nuclear reactors; dashed line, from linear expansion of parallel and perpendicular cut plate; circles, from the linear expansion of the major and minor axes of circles enscribed on parallel cut plates.

the density changes found originally. The difference from the original linear expansion results must be attributed to some peculiarity of the original plates or the conditions of the irradiation. Possibly it was an effect of temperature, because the original irradiation was of a variety of tightly packed specimens in a double walled irradiation assembly, and the later irradiations were performed in the reactor CP-5 with the specimens bathed in coolant water.

It is concluded that unstressed quartz specimens, uniformly irradiated, show a uniaxial radiation expansion.

TABLE I. Radiation expansion of quartz in the reactor CP-5.

Fluence[a]	Percent expansion[b]				Mean dilatation
(10^{18} neutrons/cm^2)	"a"	"c"	"a"	"c"	$100\,\Delta V/V$
29	0.86	0.20	0.92	0.20	1.96
	0.86	0.20	0.86	0.18	
34	0.90	0.23	1.07	0.43	2.18
	0.97	0.26	0.83	0.20	
49	1.82	0.35	1.71	0.33	3.96
	1.84	0.39	1.76	0.33	
53	1.94	0.37	2.02	0.32	4.43
	1.97	0.42	2.08	0.37	
101	5.23	2.07	5.28	2.07	13.08
	5.22	2.04	5.30	2.07	
107	5.57	2.30	5.50	2.29	14.02
	5.56	2.32	5.70	2.22	

[a] Damaging neutrons, W. Primak, Nucl. Sci. Eng. 2, 320 (1957).

[b] Two sets of measurements are given for each of two plates, one laevo-rotatory and the other dextro-rotatory.

GROWTH ON ION BOMBARDMENT

The heights of steps at the boundaries of small ion-bombarded areas on quartz plates have been determined in this laboratory over a period of many years. Results obtained with 140-keV protons, deuterons, and He^+ ions are plotted in Fig. 5. It was recognized for a long time that there was some difficulty in determining the ions incident on the target, but only recently was it shown that the problem was the voltage bias produced by charging of the insulating surface was affecting the secondary emission contribution to the current measurement.[11] The relative values for a particular experiment were quite consistent because a number of areas of different dose were obtained on each bombarded plate. With the proper application of external bias, the results have become quite reproducible and correspond to what is obtained in a proper Faraday cup configuration against which they have been calibrated. These results are the left-most ones in which a residual uncertainty remains from nonuniformity of the beam. It is obvious that the bombardment in each of the cases has progressed to saturation of the effect and that at least over the range which has been observed, from about 17% of the total effect, no difference has been observed for the several plate orientations employed. There appears to be *no* aeolotropy in the expansion on bombardment with ions having ranges about a micron.

It is quite remarkable that although a definite step is seen in reflection in the Twyman-Green interferometer when the plate replaces one of the mirrors, there is no step seen at large dose when the plate is placed into one leg of the interferometer and viewed in transmission. There is but the slightest step seen at some intermediate doses. Typical examples are shown in Fig. 6. The transmission result may be expressed as

$$\Delta L/L = (N_u - 1)/(N_b - 1) - 1 \; .$$

Since N_b, the refractive index for the bombarded area must be about 1.47 at large dose and N_u is the value for quartz, about 1.55, this requires a growth of 17%, the total volume expansion of quartz on irradiation being manifested vertically. This may be compared with the actual thicknesses calculated from the chromatic fringes and from the steps seen in reflection in the Twyman-Green interferometer. These results for four cases are given in Table II. Within the precision of these results, it is confirmed that the total volume expansion is manifested vertically.

HOMOGENEOUS METAMICTIZATION OF QUARTZ

The amorphous state which we now know to be caused by irradiation has been termed metamict

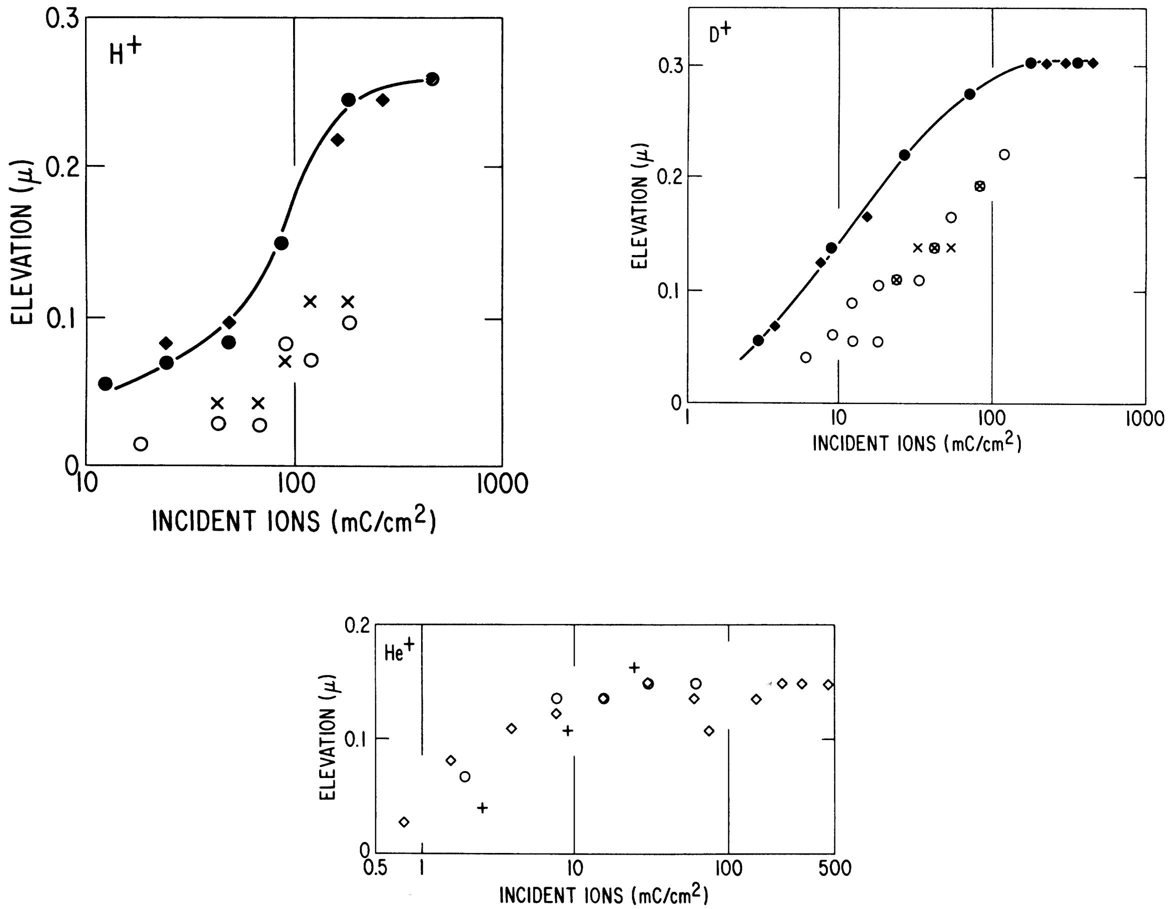

FIG. 5. Elevations of 140-keV ion-bombarded areas of quartz plates. Solid points are the most recent data when these differed on the dose scale from earlier data. Circles, *Z*-cut plates; diamonds, parallel-cut plates; crosses, *Y*-cut plates; ×'s *X*-cut plates.

by mineralogists. The course of this transformation has again become a subject for discussion in recent papers.[12] It has been discussed for the disordering of quartz, a particularly simple case because of its simple composition, from the earliest investigations of fast neutron radiation damage in this material.[2] An insight into the course of the transformation can be obtained by examining the behavior of several of the properties of quartz during the course of the transformation. A selection of such data is given in Table III, and it is plotted on a percent of total change basis in Fig. 7. From the fact that these properties do not change in a simultaneous fashion, it may be concluded that the transformation does not consist of blocks of the material becoming amorphous; some kind of progressive change is involved.

The rotatory power depends on intact units along the optic axis. Both it and the expansion along the optic axis transform more slowly than the other properties. The birefringence depends on units parallel to the optic axis. Both it and the expansion perpendicular to the optic axis transform more rapidly than the other properties. Thus it would seem that the crystal structure is breaking up to leave relatively intact units elongated parallel to the optic axis separated by relatively disordered regions. This condition persists until about $(8-10)\times 10^{19}$ *nvt* of damaging neutrons, by which time the relatively ordered regions have become quite small in either direction so that the optical anisotropy is practically gone. Yet the irradiation has to be extended at least half again as long before the density changes are nearly completed. Measurements of refractive index made in this laboratory have shown a scattering much greater than the precision of the instruments used to determine it. These measurements have

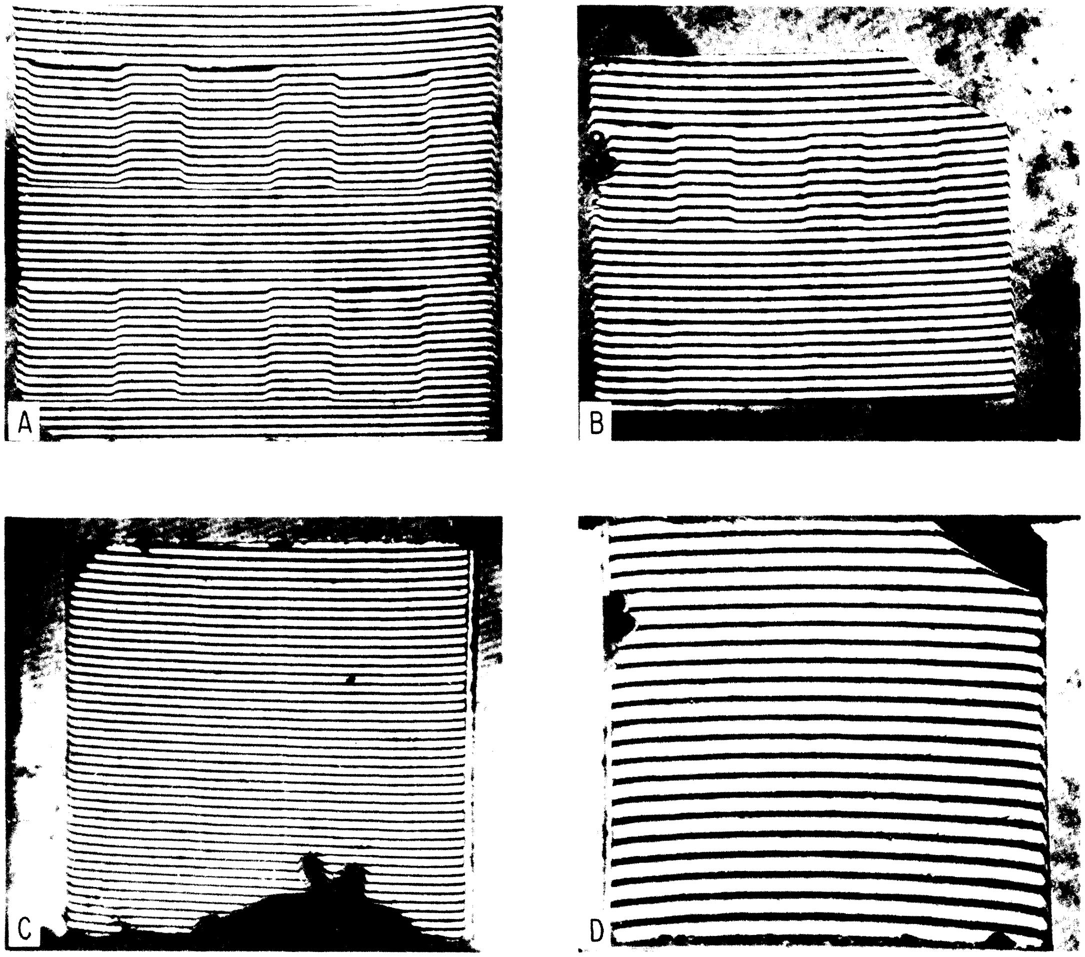

FIG. 6. Reflection (*A* and *B*) and transmission (*C* and *D*) Twyman-Green interferograms of 140-keV D^+ bombarded *Z*-cut quartz. Notice the steps in the reflection interferograms, and their absence in the transmission interferograms. For the reflection interferograms the measured incident charge (mC/cm^2) for the respective areas reading from left to right, top and then left to right bottom was for *A*: 120, 84, 54, 42, 33, 24; for *B*: 18, 12, 9, 6, 3, 1.5. Interferogram *D* corresponds to *B*, but *C* is reversed left to right compared to *A*.

TABLE II. Extrusion of quartz on 140-keV ion bombardment.

Specimen	3830	3824	3831	3833
Cut	$\parallel$	$\perp$	$\parallel$	$\parallel$
Ion	H^+	H^+	D^+	He^+
Dose (mC/cm^2)	208	180	240	180
Chromatic fringe thickness (N=1.47)(μm)	1.50	1.56	1.89	0.99
Step height (μm)	0.25		0.30	0.15
Percent growth[a]	20	19	19	18

[a] 100 times [step height/(chromatic fringe thickness −step height)].

depended on determining the angle for total reflection by laying the irradiated quartz plate upon a prism. It was long thought that the variations in the results were caused by warping of the plates. Perhaps such differences in measurements of parallel and perpendicular cut plates are caused by the way in which the crystal structure breaks up in the respective directions.

Behavior similar to that of the optical properties was found by Wittels[13]: The lattice spacing calculated for the maxima in the x-ray diffraction peaks changes more rapidly than the density. Comes *et al.*[14] explained this effect as indicating the presence of two phases, a crystalline phase undergoing a more rapid expansion than an amorphous

TABLE III. Effect of neutron irradiation on optical properties of quartz.

Fluence [a] (10^{18} neutrons/cm^2)	Rotatory [b] power (deg/mm)	Birefringence (mμm/mm)	Ord. Index [c]
29	23.6	7518 [d]	1.5360
34	24.4	7445	
49	20.1	5956	
53	18.6	5415	1.5211
63		5105	
101	2.28	725	
107	1.47	477	
None	25.54	9176	
None [e]		9088	1.5443
49	16.1	5429	
50	16.3		1.5198
50		5310	1.5262
108	2.5	1014	1.4904
180	0.013		1.4697
180		91	1.4701
Final [f]	0	0	1.4686

[a] Damaging neutrons.
[b] Green light.
[c] Sodium light.
[d] Next 8 measurements white light.
[e] Remaining data from W. Primak, Phys. Rev. 110, 1240 (1958).
[f] Assumed.

one. They attempted to calculate the ratios of the phases and relative expansions from the diffraction intensities. The implications of this argument are stranger than the effect because the agent, the energetic neutrons, sweeps a constant volume of the material, and the transformation impoverishes the crystalline phase in linear proportion. That a simple exponential saturation does not take place appears to require that the process introduces another transformation route or agent.

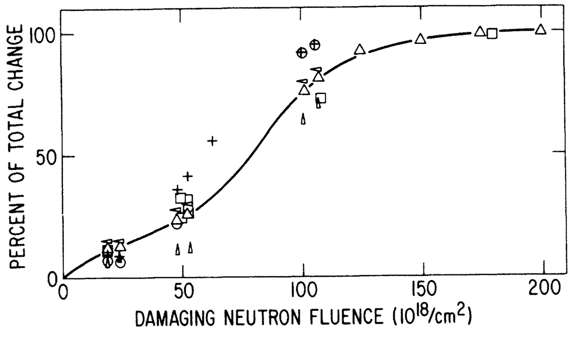

FIG. 7. Percent of total change of several properties of quartz compared with the dilatation encountered on exposure in a nuclear reactor; triangles, dilatation; crosses, birefringence; squares, refractive index; circles, rotatory power; horizontal arrow heads, permanent linear expansion perpendicular to optic axis; vertical arrow heads, parallel linear expansion.

Klemens[15] suggested that the additional agent was large stresses developed in the material. Wittels[13] rejected this hypothesis because he did not find evidence for high stresses in his x-ray diffraction patterns. The evidence for plastic flow under stress during irradiation which is presented here would preclude the development of large stresses. Strain is usually thought of as the reversible strain developing under stress. However, if the permanent strain, as in a permanent dilatation, is considered, this may be the additional agent. The suggestion made originally, that the agent was a thermal spike associated with the slowing down of the energetic particle[9] has been reinvestigated and the thermal spike was found not to exist in the sense in which it was proposed originally; but a massive transformation, associated with momentary bond rupture in the wake of the energetic particle, appears to be a viable mechanism for transformation of disordered silica,[16] if not for quartz.[17] In an earlier paper it was suggested that the components of the mosaic of relatively ordered regions become rotated with respect to each other during the transformation in order to explain the more rapid transformation of some of the properties as compared to others. This is hardly necessary if the mosaic blocks are elongated: i.e., if the breaking up of the crystal structure is finer in one direction than the other. Comes *et al.*[14] favor a disorientation by Dauphine twinning. These become fine points when the behavior under ion bombardment is considered.

Wittels's[13] observations of coesite and the author's calculation of the effects of ion bombardment on vitreous silica and quartz[17] offer an insight into microscopic aspects of the transformation. Wittels found that coesite was much more resistant to radiation damage than quartz. The author found evidence that the transformation of vitreous silica was much more rapid than that of quartz and that the threshold energy for the transformation of quartz was about 25 eV, while it was very low or nil for vitreous silica. The transformation of the vitreous silica appeared to proceed by the relative movement of silicon-oxygen tetrahedra within segments of the silicon-oxygen network which had fragmented momentarily in the wake of the energetic particle.[16] Such motion and the quenching of a new configuration which occurs in vitreous silica is hardly possible in the crystalline quartz and would be impossible in the more closely packed coesite. Thus the breaking up of the crystal structure of quartz into a mosaic of crystalline material in a disordered matrix provides conditions which can facilitate further disordering.

Some of the radiation effects in vitreous silica appear to be cooperative thermal and radiation effects. Thus data for irradiation of quartz at different temperatures may be useful in separating effects in the crystalline and amorphous regions, but such information is not available.

TRANSFORMATION BY ION BOMBARDMENT

The relatively homogeneous transformation which occurs during neutron irradiation cannot take place under ion bombardment where a twofold condition of stress is engendered. There is the stress of the expanding material being in contact with the adjacent and underlying untransformed material, and there is the stress associated with the transformation varying in depth. The fact that the growth of the parallel and perpendicular cut plates seems to be the same indicates further that the transformation is not proceeding in an orderly fashion and that the material is being extruded without regard for direction. This implies a plastic flow.

We do not have any information about plastic flow of crystal quartz. However, it does not seem possible for plastic flow to occur without seriously affecting the optical anisotropy of the crystal. Unfortunately, we have not yet succeeded in measuring optical properties which might elucidate this behavior, but it is expected that they will show a greater rate of change relative to growth than was the case for the relatively homogeneous transformation by neutron irradiation. There is an abundance of evidence for the plasticity of vitreous silica under a variety of conditions and at surprisingly low temperatures.[4] It has been attributed to relative motion of segments of the Si-O network. It appears that segmentation of the quartz network, which would be part of the mechanism of the disordering (other parts would be trapping of displaced atoms, vacancy and void formation, relative motion of the segments), requires a large deposition of energy, of the order of magnitude required to displace atoms.[17] However, segmentation and/or motion of segments of vitreous silica can occur with all of the energy available in the irradiation, both the ionization and the energy deposited in atomic scattering. It therefore seems reasonable to attribute most of the extrusion to effects occurring in vitreous islands in the partially transformed material. Then the extrusion process itself, the plastic flow, must become a further mechanism for the disordering of the material.

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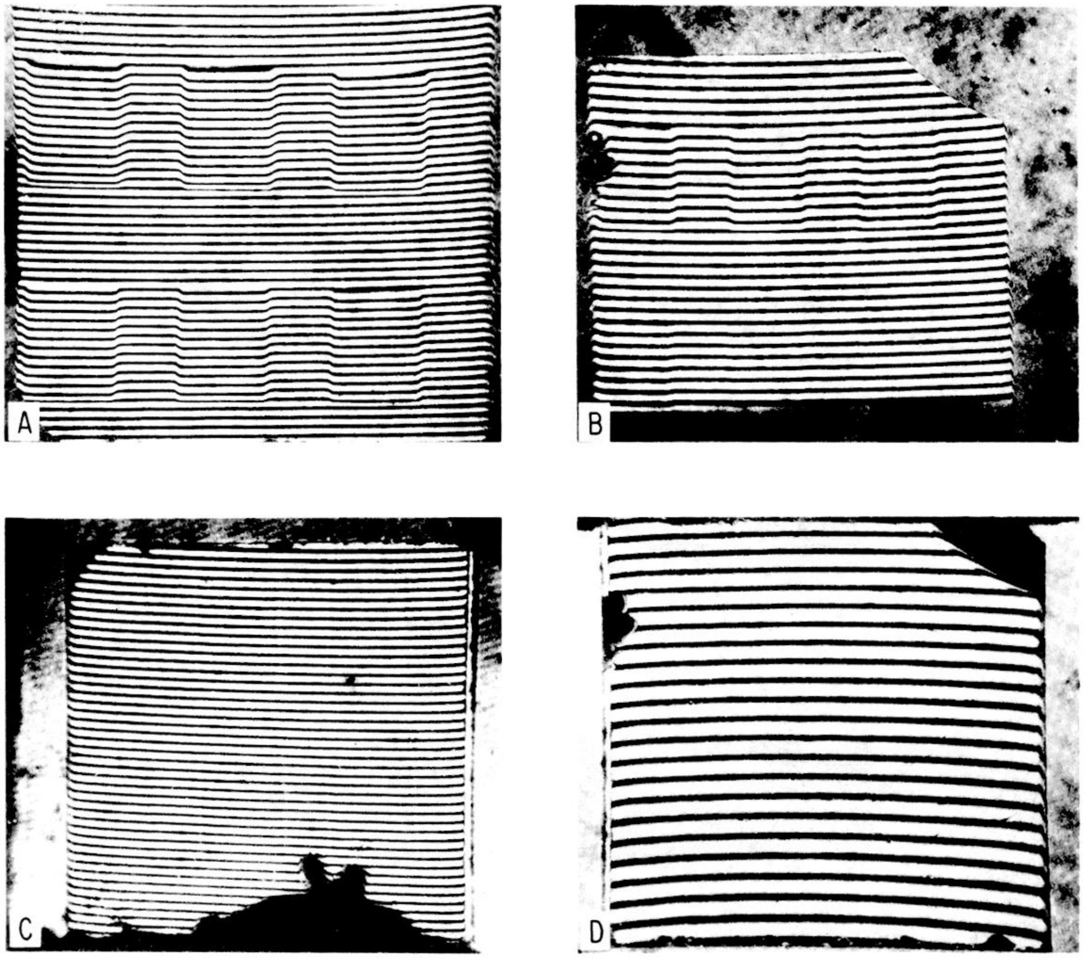

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