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**RADIATION DAMAGE IN
DIAGNOSTIC WINDOW MATERIALS
FOR THE TFTR**

by

William Primak

FUSION POWER PROGRAM

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9700 South Cass Avenue
Argonne, Illinois 60439**

**Prepared for the
U. S. Department of Energy
under Contract W-31-109-Eng-38**

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Fusion Power Program/
Solid State Science Division

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July 1981

32b
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FRONTISPIECE: The Low Energy Electron Bombardment Machine for Testing Materials at the High Ionization Dose Levels which will be Encountered in the TFTR.

The electron gun is enclosed in a plastic box and is biased at the required energy. The gun is mounted at an angle to the beam line to prevent evaporated materials from impinging on the target. The electron beam is brought on axis by the electrostatic deflection plates integral in the gun assembly. Further control of the beam is provided with the two sets of external quadrupoles. The beam is focused by an electrostatic lens in the gun and further focusing is provided by the large iron encased solenoid magnet at the top of the drift tube. Below the drift tube is a solenoid operated gate valve and the Faraday cup assembly beneath. The sample is mounted on the bottom flange. Both the gate valve and the Faraday cup assemblies are insulated from ground and from each other by means of Kel-F gaskets to permit them to be biased if it is desired to explore the secondary emission. Partially in view, mounted above the turbomolecular pump, is a chamber for coating the samples which are studied.

Part of the system and all the electronics were assembled by Emmet Monahan. He also performed all of the electron bombardments and many of the measurements in the tests described here.

PREFACE

The reader will realize that the evaluation of radiation effects is a very complex problem which is intimately intertwined with the engineering of the particular application. The writer emphasized this when, in early 1977, through S. Harkness (ANL, Fusion Power Project), K. Young (PPPL) requested this writer's advice on the subject of the radiation damage which would be anticipated in a large vitreous silica window from the neutron flux calculated for the TFTR. The interrelationship with the engineering appears never to have been fully appreciated, for the progress in engineering design was communicated only fragmentally and intermittently.

Following the initial contact, consideration of other radiations which would be incident on the vitreous silica window was requested. Computations were made utilizing data which had been obtained in This Laboratory, over the preceding 25 years, most of which has been published, but some of which was yet in our files. When these calculations had been completed, questions remained which were investigated experimentally. Finally, as the design of the TFTR progressed, new sets of radiation specifications were supplied, and reevaluations were made. Other materials were added for consideration: crystal quartz, sapphire, zinc selenide, lithium fluoride, and magnesium fluoride. The author established mechanical failure of the window material as the primary concern; and, then, its functioning as a diagnostic window. For the first, the properties of interest were dilatation, internal stress, fracture; and for the second, optical absorption, luminescence. The results were reported briefly, in summary, piecemeal, in a series of internal memoranda. Here, present evaluations and recommendations are assembled and made available for circulation. As this report was being prepared, the writer was advised that the tank wall would rise to a temperature of about 100°C after a few pulses and that this would be the ambient temperature for the rest of the day, the cycle being repeated each day. This thermal specification was not considered in the evaluations presented here. Additionally, some of the windows, possibly the quartz window and probably the zinc selenide window, would be placed on tubes $\frac{1}{2}$ m long and thus be exposed to an estimated fortieth the radiation flux at the tank wall. It seems likely that such an arrangement will be necessary for the functioning of a fluoride window. The thermal specification for this mounting was not stated. The evaluations presented here deal almost entirely with the radiation specification for the tank wall.

As is true for most technical reports, it is only possible to give a brief resume here of the work which was done. This work fills 6 large notebooks and the better part of 100 computer files. Some of the material has been published as scientific articles; this work is referred to briefly. Some of the later work, not so treated, is described in fuller detail here. A large bulk of the work dealt with the vitreous silica window, for which there was a special concern because of its size and its being mounted at the tank wall. It was during these considerations that most of the codes

were written. They are quite complicated, involving stages of multiple integration, as it is quite evident from the nature of the data. Unlike published articles, which are checked and reviewed through an extensive processing, the present report could not be so treated for it had to be prepared on a budgeted time scale. It is hoped that no major errors have slipped through, for these can appear even in published articles which have been checked and reviewed; witness the incorrect formula for the dilatation as a function of ionization dose, and an error in an application of the LSS theory through the application of an incorrect integration limit in one of our codes, both of which were corrected for This Report. The original calculations were checked by applying them to experimental results for materials with which there was extensive experience in This Laboratory and by making "order of magnitude calculations" with simplifying assumptions. It was not possible to recheck the calculations or the codes at this time, and it is hoped that none of the graphical output from these codes, some written over four years ago, presented in the figures, have been misinterpreted in the captions. The writer would have greater confidence in the quantities given in the text as the final results, because these were copied from the original internal correspondence.

The radiation specifications were furnished originally by K. Young and later modifications were furnished by G. Taylor. E. Monahan assisted by performing the cantilever measurements and the optical absorption measurements. He also assembled the electron bombardment machine and performed the electron bombardments. A. Youngs performed the ion bombardments. The x-ray irradiations were performed with aid from C. Delbecq and P. Yuster. They collaborated in measuring the luminescence spectra. Arrangements for the preparation of this report were made by C. C. Baker.

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RADIATION DAMAGE IN DIAGNOSTIC WINDOW MATERIALS

FOR THE TFTR

ABSTRACT

The general problem of evaluating diagnostic window materials for the TFTR at the tank wall location is described. Specific evaluations are presented for several materials: vitreous silica, crystal quartz, sapphire, zinc selenide, and several fluorides: lithium fluoride, magnesium fluoride, and calcium fluoride; and seal glasses are discussed. The effects of the neutrons will be minimal. The major problems arise from the high flux of ionizing radiation, mainly the soft x rays which are absorbed near the surface of the materials. Additionally, this large energy deposition causes a significant thermal pulse with attendant thermal stresses. It is thus desirable to protect the windows with cover slips where this is feasible or to reduce the incident radiation by mounting the windows on long pipes. A more detailed summary is given at the end of this report.

INTRODUCTION

1. Exposure and Dose. There is no simple relationship between the incident radiation and the radiation damage. The radiation damage is not caused by the incident radiation, but rather by the energy which is absorbed from the incident radiation. The radiation specification gives the incident radiation. From this must be calculated the local absorbed energy which is termed the dose. The radiation damage consists of the property changes which may result from the dose. The changes may be transient, labile, or permanent. Further alterations frequently occur if the temperature is raised. Each material behaves in a unique manner; hence, the materials must be investigated individually. Since the radiation spans a broad range of energies, the calculations must be made for each energy, and the results integrated; then the effects for the various radiations must be summed. Thus, the calculations involve the energy spectra for the radiation, the cross sections for absorption, and a yield function for the effect. The result can be given in some unit of energy or of some property change. The two most important processes at the energies where radiation damage is usually of concern are the displacement of atoms from their normal positions in the solid and ionization of the atoms of the solid. The first is the major concern for the absorption of particulate energy (e.g., neutrons, accelerated ions); the second for x rays, gamma rays, etc. The first will be described here in terms of either property change or of the density of displaced atoms (which in the calculation is frequently a unit in the neighborhood of 30 eV); and the second will be given in R, a unit which is about 83 ergs/g for the lighter atoms. It is somewhat higher for hydrogen, making it 92 ergs/g for water; and it tends to rise somewhat less toward the middle of the periodic table. The value 83 ergs/g will be used for all of the materials described here.

2. Radiation Exposure for the TFTR Diagnostic Windows. Neutron and prompt gamma flux were supplied by K. Young¹ and were taken from the TFTR Conceptual Design.² The calculation requested was for a $1/2$ second pulse with 4000 total such pulses in a 4-year period of operation. The data were obtained from a group calculation. The neutron data were supplied in tabulated form, and the gamma flux in graphical form. Since our calculations are performed in lethargy units, the data had to be plotted, digitized, converted to flux in an interval of $\ln E$, and plotted against $\log E$, smoothed, and redigitized in equispaced intervals of $\log E$ for calculation purposes. The original data are shown in Fig. 1 and Table I, and the curves of the functions used in the calculations are shown in Fig. 2 and Fig. 3.

Following the calculations performed for these radiations, K. Young³ added a soft x-ray component comprising 0.1 W/cm^2 in a $1/2$ sec pulse having the spectrum $0.02 e^{-E/5}$. This is a Brehmstrahlen spectrum. Finally, a soft x-ray impurity emission spectrum was added,⁴ a uniform distribution from 100 to 500 eV of 10 W/cm^2 per pulse.

A further understanding of the behavior of such machines followed from experience with PLT and PDX; and G. Taylor⁵ refined the low energy x-ray spectrum, and a recalculation was based on it. He described the low energy

Table I. Neutron Flux Spectrum

Group	Energy at lower bound (eV)	Flux (cm ⁻² sec ⁻¹)
	15x10 ⁶	
1	10x10 ⁶	7.75x10 ¹²
2	6.7x10 ⁶	3.90x10 ¹¹
3	4.49x10 ⁶	5.19x10 ¹¹
4	3.01x10 ⁶	7.77x10 ¹¹
5	2.02x10 ⁶	1.33x10 ¹²
6	1.35x10 ⁶	2.07x10 ¹²
7	9.07x10 ⁵	2.64x10 ¹²
8	5.50x10 ⁵	4.78x10 ¹²
9	3.34x10 ⁵	4.79x10 ¹²
10	2.02x10 ⁵	4.40x10 ¹²
11	1.23x10 ⁵	3.42x10 ¹²
12	4.09x10 ⁴	3.68x10 ¹²
13	1.17x10 ⁴	9.56x10 ¹²
14	3.35x10 ³	1.50x10 ¹²
15	7.49x10 ²	1.87x10 ¹²
16	1.67x10 ²	4.90x10 ¹¹
17	3.73x10 ¹	6.93x10 ¹¹
18	8.32x10 ⁰	2.74x10 ¹¹
19	1.85x10 ⁰	1.74x10 ¹¹
20	4.14x10 ⁻¹	5.33x10 ¹⁰
21	Thermal	3.23x10 ⁹
Total Flux		5.12x10 ¹³

Fig. 1. The prompt gamma ray flux anticipated at the wall of the TFTR.

Fig. 2. The neutron energy spectrum at the TFTR wall: The logarithm of the flux in an interval of $\ln E$ (eV) plotted against the common logarithm of the energy (MeV).

Fig. 3 The prompt gamma ray spectrum at the TFTR wall: the energy (MeV) in an interval of $\ln E$ (eV) plotted against the common logarithm of the energy (MeV).

spectrum as: 2 W/cm² uniformly distributed between 0 and 50 eV in the pulse start-up; then the rest of the pulse: 30% between 0 and 50 eV, 40% between 50 and 500 eV, 20% between 500 and 1000 eV, and 10% above 1 keV. The pulse shape was described graphically, but for most purposes it is not of interest here since the concern was largely with accumulated effects; the pulse was still about 1/2 sec long with a repetition rate of 5 min. Since its length was but 0.2% of the repetition rate, the exact shape was not even of concern for the instantaneous heating problem. The above distribution was not convenient for calculation purposes as its logarithmic representation was inconvenient. It was therefore redescribed in power functions as shown in Fig. 4.

Two additional modes of operation were added⁵ as following the original specification of 1/2 sec pulses. These three pulse forms were integrated graphically, and it was found that the first was a 10 W pulse of approximately 1/2 sec duration. It will be termed the 5 J pulse in This Report. The additional modes of operation were called the TFM and the TFM Extended modes of operation. The pulse lengths were about twice as long as the original specification and on integration correspond to the respective values 17.2 J and 24.3 J. The quantity of such pulses anticipated per annum was 40,000.

In connection with the above additional modes of operation, effects caused by a neutron dose 6-fold greater than the original specification was to be considered.

The final specification of the 5 J pulse is presented in Table II and in Fig. 4.

Table II. Energy specification for the 5 J pulse.

Energy Range (ev)		Taylor's Specification (W/cm ²)	Power Function [a exp(-E/c)]	Energy in Power Function (W/cm ²)	
From	To		a	c	
0	50	2+2.4	30	0.1233	3
50	500	3.2	400	0.01678	4
500	1000	1.6	900	0.00909	2
1000	∞	0.8	5000	2.443x10 ⁻⁴	1

To check the correlation of the calculations for vitreous silica with the actual behavior within a Tokamak device, a sample was exposed in PLT. This sample was found to have developed a stress pattern which could not be explained in terms of the radiation exposure to which it was supposed to have been subjected. The stress pattern corresponded to that caused by a substantial exposure to x rays in the 10 keV region, and such a radiation

Fig. 4. The soft x ray-spectrum: impurity x rays and brehmstrahlen; The common logarithm of the energy (W/cm^2) in an interval of $\ln E$ (eV) plotted against the common logarithm of the energy (eV). The dashed curves were suggested by G. Taylor. The solid curves were used because of ease of calculation and greater continuity.

field was not known to have been present. Irradiation of a second sample, which had been planned, was never done. A large vitreous silica window, 12 in. diameter by 2 cm thick, which had been used in PLT to cover a rectangular opening in several orientations, was examined and found to possess a lamellar stress pattern with a maximum stress 2 to 3 mm beneath the exposed surface. The possibility that these stress patterns resulted from the radiation-induced stress relaxation of the thermal pulse is discussed in Section 5 of the behavior of vitreous silica (below).

3. Radiation Dose for the Window Materials: The radiation dose for particulate and for electromagnetic radiations are very different calculations. The latter is the simpler and is presented first.

The gamma ray dose presents the complication that the most part of the energy is absorbed by the Compton effect, which means that only part of the energy is removed from the primary beam which then becomes degraded in energy. This is a severe problem when dealing with thick bodies, as in shielding calculations. With thin bodies, such as these windows, it is sufficient to use a fraction of the mass absorption coefficient in making the calculations.⁶ Since it will be found that the effect of the gamma component of the radiation will be small, no further consideration need be given to this problem.

The x rays are absorbed by the photoelectric effect. This means that the energy removed from the primary beam is completely transformed into electrons with the energy of the x ray less the energy of ionization. Since the range of the electrons is small compared to the distances the x rays traverse the material except for the softest x rays (which have very large mass absorption coefficients), it can be assumed that their effect is local. For the softest x rays, the absorption is so close to the surface that a large fraction of the photoelectrons must be expelled from the surface, and hence their energy is not expended in the material. Thus the surface effect (at less than 0.2 μ) will have to be reduced substantially, perhaps 30 to 50%. No further attempt was made to estimate this surface effect. The energy absorbed was estimated from the mass absorption coefficients (taken largely from two sources)^{7,8} and the composition. The mass absorption plotted against the energy on dual logarithmic paper consists of quite straight line segments, hence are readily fitted segmentally with power functions. Such functions were utilized for the calculations. They are given for the individual materials below. The product of the mass absorption coefficients and the incident flux was used to calculate a local dose in R, and this was integrated over the spectrum numerically to obtain the local dose, which could then be plotted as a function of depth from the surface of the window.

The calculation of the neutron dose is a more complicated matter because the neutrons per se do not do anything. Their effect on the material is caused by the scattering of atoms. The scattering is isotropic for the lower energy neutrons. For the present purposes this means that in each scattering event there is an equal probability of the scattered atom having any energy up to the value $\frac{4M}{(1+M)^2}$ where M is the mass of the scattered atom. A spectrum of scattered atoms can thus be calculated.

From this point, the calculation of the effect may proceed in either of two ways:

- (1) the energy which is available to cause an effect can be calculated, which is thus a dose; or
- (2) the spectrum may be multiplied by a yield function and integrated to obtain the property change, thus circumventing the calculation of a dose.

For some effects in some materials the second is the more convenient, for others, the first. Both methods will be used here for particular cases. Recall that the scattered atoms lose their energy mainly by two processes in the high energy region which will produce radiation effects of the kind of concern here: by ionization, and by displacing atoms of the solid. Thus there are two doses associated with the neutron scattering. The significance of this is discussed below. Finally, at the upper end of the neutron spectrum calculated for the TFTR, non-isotropic processes become significant. These are mostly of two kinds:

- (1) the scattering becomes distorted in the forward direction, which means that there is a depression of the high energy portion of the spectrum of scattered atoms; and,
- (2) inelastic scattering processes begin to appear, which means that scattered atoms of much higher energy than given by the limit presented above may appear.

The contributions of these two processes were tested for two materials, graphite and silica, and did not seem to be significant.⁹ The major finding was that the effects produced by neutrons at high energies are depressed by the falling scattering cross sections at these energies. Isotropic scattering was assumed in the calculations presented here.

The scattering cross sections for neutrons were taken from standard tables.¹⁰ Where elastic scattering cross sections were not available, the total cross sections were used, neglecting the major resonances. Thus, over-estimates may have been obtained.

If the change in any property of interest were linear with dose, this change in property could itself constitute a dose scale for the effect. In general, however, the rate of radiation-induced changes in properties tend to decline with increasing dose. A method for obtaining a linear scale for such a case is given by Primak and Fuchs.¹¹ The linear dose is given by:

$$w = z(1-bz)^{-1}$$

where z is the property change observed at some point and b is the intercept on the inverse property axis obtained when the inverse property change is plotted against the inverse of any measure of the radiation received, favoring the later data if the graph is not quite linear. The procedure was used in checking the effect of high energy neutrons on

0

vitreous silica when graphite was used as a comparison material. It was also used to estimate the actual change in zinc selenide from an initial rate of change. Some few materials will increase in the rate of property change on irradiation. A notable example is the behavior of crystal quartz. Particular optical absorptions may show an induction period. Typically, this occurs when the center is formed from other centers in the crystal and cannot develop until a sufficient concentration of the primary center is formed.

4. Assembling the Radiation Data. The amount of direct information about radiation effects is rather limited, and care must be exercised in using it because it has rarely been obtained in the radiation fields related to or duplicating conditions of interest. Often the irradiation conditions were not described adequately to utilize the data for quantitative purposes. Typically, when testing is initiated, behavior over periods of time much longer than the time available for evaluation is desired, which mandates investigation of radiation fields which do not duplicate the conditions of interest. In addition, the data, particularly for neutron irradiation, are not easily obtained. The experiments are lengthy because radioactivity has to be handled, and the changes are apt to be complex, requiring many observations. Suitable sources are not available as desired and are usually operated for other purposes; hence, conditions required for the desired experiments are difficult to obtain. The doses of interest for the TFTR are small ones, and it is difficult to get these in the operating procedures used for nuclear reactor sources; yet they are long ones for accelerator sources. In reference to the electromagnetic radiation exposure anticipated for the TFTR, the dose is extremely large compared to that available from conventional gamma or x-ray sources. The problem is simplified by the fact that for both atoms and electrons the energy loss is heavily weighted toward small energy losses. Thus, their energy is, for the most part, frittered away in small quantities; hence, it makes little difference for what energies we obtain the radiation data which is employed in the calculations, just as long as the cross sections or absorption for the particular energies of the original radiation are available. Thus the yield functions for the neutron radiation damage can be obtained from the behavior of accelerated ions; this will be done here when neutron irradiation data are not available. Such information can be obtained in a matter of days, whereas information about the behavior of neutrons obtained directly may take months to procure. Similarly, in reference to the effects of electromagnetic radiation, since its effect is to produce electrons, the effects of electrons can be used to estimate them. In electron bombardment it is possible to obtain doses of the required magnitude in hours, whereas months and years may be required with available electromagnetic radiation sources.

It should be understood that the reason it is possible to obtain the required doses so quickly with ions and electrons is that their ranges are short compared to the much lower absorption cross sections of neutrons and electromagnetic radiation. Thus the dose (the energy absorbed per unit volume) achieved in ion and electron bombardment is high. But, also, it is possible to measure and control very small charges, hence the effects of small doses can also be studied with them.

A Cockcroft-Walton machine for the acceleration of ions had been developed and utilized for radiation damage studies here for many years. Procedures for utilizing it have been described.¹² Electron bombardment studies had been conducted with a 3 MeV van de Graff machine in This Laboratory. However, even at the lowest energies available from this machine, about 0.2 MeV, the heating would have been too great to permit the accumulation of the doses required in any reasonable length of time. Since no lower energy machine was available locally, a 30 keV machine was constructed to serve the present studies. For most of the studies it was convenient to use it at energies between 11 and 16 keV, for a few at about 25 keV. At these energies, the depths irradiated corresponded to the depths affected by the very large doses of the impurity x rays anticipated in the TFTR, which, it will be seen, presents the major radiation problem for the TFTR diagnostic windows.

5. Physical Property Changes in Window Materials. In regard to the mechanical integrity of the windows, the major problems arise from stress caused by differential dilatations. These are brittle materials and fracturing has to be viewed as caused by the growth of flaws. Thus, the duration of the stresses as well as their magnitude and the temperature of the materials must be considered. All of the stresses must be combined and the window evaluated by procedures customary in fracture mechanics.¹³ Such an evaluation will not be attempted in this report. Radiation-induced dilatations will be compared with thermal dilatations to indicate their magnitude. Stresses from radiation-induced dilatations may arise from either non-uniform absorption of the radiation or non-uniformity in the radiation field (including shadowing). The major shadowing problem will be of the soft radiation by the supporting member.

Dilatations are determined in This Laboratory by a number of methods. Density changes in nearly uniformly irradiated samples can be measured to 10^{-4} ;^{14,15} dimensional changes in nearly uniformly irradiated blocks or plates can be measured to 10^{-5} on ruled line standards,^{16,17} to 10^{-6} interferometrically on end standards (blocks whose ends are figured to interferometric specifications);¹⁸ by the deformation of plates, interferometrically,¹⁹ through strain birefringence,^{20,21} or by the deflection of cantilevers,¹⁹ to 10^{-7} or better in suitable cases, for radiations whose penetration is through only part of the depth of the plate, or which can be shadowed. All but the shadowing technique were employed in various cases to obtain results reported here.

Electrical stresses resulting from charging will be mentioned in connection with vitreous silica. The possibility of their arising occurs in connection with the absorption of soft radiation, discussed above.

Optical absorption was determined with a DK2A spectrophotometer by conventional methods. The question of determining the optical absorption in the vacuum ultraviolet was mentioned in connection with fluoride windows but was not pursued because these windows were rejected on other grounds. Optical absorption in the infra-red was discussed in connection with the zinc selenide windows but was not done because this appeared to have been resolved by data in the literature; also, relative to the behavior of crystal quartz, but the estimated damage to this material appeared to be small enough that it would not be a problem.

All of these materials will luminesce, and with the radiation intensities present in the TFTR, they will shine like electric light bulbs. The luminescence spectra for alumina and silica were determined under soft x-ray irradiation, and then the intensity was determined under electron bombardment which could provide the ionization intensity anticipated in the TFTR. Unfortunately, it was not appreciated at the time that appreciable heating of the samples occurred during the electron bombardment; this was determined later. Thus the results are not suited for detailed scientific analysis, but they may be a more realistic presentation of what may be expected in practice, because similar heating will be experienced in the TFTR. Although the luminescence will be intense for some materials, it was adjudged as causing no difficulties because chopping techniques will be used for the observations.

6. Material Selection and Fabrication. Both radiation effects and mechanical integrity are quite variable in brittle transparent materials, hence the items should be purchased under special specifications and, likewise, fabricated to special specification. Particularly, optical absorption and luminescence are often associated with impurities. Fracture is usually associated with flaws which can be present a priori or may be formed during fabrication. Problems which have been found in specific materials in our experience will be described in connection with them. Several general principles of fabrication are described here and should be discussed with the fabricator prior to placing the order for the material. Materials should be sliced and cut by gentle means and not pushed through diamond saws. With materials for which this is possible, cut blanks should be etched after initial lapping. Corners should be chamfered and polished with a radius specification (which may have a large tolerance), and the edges should be finished and polished. To prevent stresses from electrical charging, all good insulating windows should have their edges around to the exposed surfaces metallized and grounded. If sealing glasses are used for mounting, their inner surfaces should be metallized up to the required optical aperture.

Since the flaws grow under stress according to kinetic laws, those flaws which will develop in a specified lifetime can be discovered by overstressing for a much shorter time according to these laws.¹³ Such procedures are recommended for these windows.

Windows can be protected from surface radiation effects by using shutters to avoid exposure when their use is not needed, by choppers to reduce the exposure, and by providing replacable cover slips. Stresses can be reduced and the machine protected from damage by the fracturing of a window by utilizing a double window (the outer window could be sealed with elastomers such as Kel-F or Teflon) with an evacuated space between. Such protection is particularly recommended for weaker materials, such as the fluorides, and for large area windows. However, some special provision will have to be made for the removal of heat from the window face in this case. Heat flux will be some 20 to 80 mW/cm² which will have to be removed from the face of the window to prevent a progressive temperature rise.

7. Thermal Stresses. The very soft x rays will be absorbed, largely, within a few microns of the window surface. For thermal conduction this is

a surface absorption of heat. During the pulse, the heat will diffuse into the window and give a temperature distribution which will be a maximum at the internal face of the window and fall to near the original ambient temperature of the window within a few millimeters. Associated with this temperature distribution there will be a lamellar thermal stress pattern. Since the window will be sealed, a portion of it will not be exposed to the radiation, and hence there will also be a radial stress pattern. The calculation of the thermal distribution is a problem in the diffusion of heat which is discussed in detail and calculations are presented in the section on vitreous silica, below. The solutions for each of the materials is discussed under that material.* The stress problem for the infinite window is a problem in plane stress and strain and can be solved exactly at least for amorphous materials and cubic materials along principal axes. From the extensive photoelastic studies made in This Laboratory, all of them with plates much smaller than these windows, it is clear that these solutions may be used in the present case. From them it is readily shown that the maximum stress S_T will be at the window face and that it will be:

$$S_T = \Delta T \delta_T R \frac{2}{3} \left(\frac{1+\nu}{1-\nu} \right)$$

where δ_T is the thermal dilatation (cm^3/deg), R is the modulus of rigidity (or shear modulus) (psi), ν is Poisson's ratio, and δ_T is the temperature rise. The calculations were made for the radiation at the tank wall. Because of its small coefficient of thermal expansion, the stresses are least for vitreous silica despite its high temperature rise because of its low thermal conductivity and ranges from 460 psi for the Initial operation to 1290 psi for Extended TFM operation. For the respective crystals quartz, sapphire, zinc selenide, and magnesium fluoride the values in 10^3 psi are: 2.9--9.1, 3.5--11, 1.5--4.8, (2.2--7 or 1.4--4.5). The uncertainty in the last value arises from our lack of knowledge of the thermal conductivity of the magnesium fluoride. These, clearly, are serious stresses. It will be seen below that in the case of the vitreous silica they become manifest in the radiation-induced stress relaxation. What they will do to the crystals and their seals is uncertain.

8. Applicability to the TFTR. It will be seen that the radiation effects consist of a diverse list of small effects which have to be combined with other effects such as the thermal and mounting effects to determine the design specifications. A complete set of specifications for the windows were not available when this work was started. In particular, the thermal conditions were not specified, and these would affect the behavior of the windows significantly. Some of the radiation-induced changes are decreased by raising the temperature, others (e.g., in magnesium fluoride) are increased. Some of the changes will be annealed during the bakeouts. None of these operating procedures for the TFTR were considered when the present evaluations were halted. All of the evaluations were made for the specification of radiation at the tank wall. At the last, as this report was being prepared, a decision to place some of the windows on pipes extended 50 cm from the wall was transmitted, which would reduce the ionization specification 40-fold.

*Or the Addendum.

II. SPECIFIC MATERIALS

A. Vitreous Silica

1. General. Pure vitreous silica when subjected to any of the kinds of radiation considered here, exposure to neutrons, x rays, or gamma rays, or bombardment by electrons or ions, undergoes a contraction.²² The contraction may be as much as near 3%; and, in the case of neutron irradiation in a nuclear reactor, it may subsequently relax by a few tenths percent on further irradiation. The contraction is nearly linear to begin with and then saturates according to a typical exponential saturation function on neutron irradiation or on bombardment with ions heavier than protons. Ionization (electrons, x rays, gamma rays) causes a contraction at about the 0.7 power of dose. The rate may be less for soft x rays than for electron bombardment,^{2,3} but this has not yet been verified. Some impurities, probably aluminum, a common impurity in vitreous silica, may introduce an element of expansion which saturates, whereupon the ongoing contraction becomes evident.²⁴ Optical absorption is introduced in the ultraviolet, causing the "cut-off" in transmission to extend from about 0.18 μ to about 0.31 μ . There is a small optical absorption peak formed in the red at about 0.63 μ in pure vitreous silica; but in impure vitreous silica the absorption is much more general in the visible region, giving the material a dirty violet color. Differential stresses in non-uniformly irradiated vitreous silica should be sufficient to cause fracturing, and this has been reported. However, irradiation causes a plastic flow stress relaxation so that the stress reaches some maximum value and then declines despite continuing radiation damage and volume change.²²

2. Neutron Yield. The volume changes experienced by vitreous silica under various conditions are treated as a fundamental property by Primak.²² To calculate the volume changes under neutron irradiation, it is necessary to know the property change caused by neutrons having energies within the neutron spectrum specified. Such data are not available and would be very difficult to obtain. A function for this purpose was formed from the LSS calculations and the ion bombardment data. Three points from the LSS calculations for the fraction of the energy expended in elastic collisions are shown in Fig. 5. These are extrapolated to 8% at 2.5 MeV. From the three points, 100% at zero energy, 56% at 0.1 MeV and that at 2.5 MeV, the following equation is obtained:

$$y = 0.0362 + (1.0375 + 8.7154 x)^{-1}$$

which fits the curve shown in Fig. 5 quite well. Since the dilatation experienced at energy (E) 100 keV is 2.47×10^{-20} according to our experimental data, the negative dilatation function is

$$\delta = AE \cdot y; \text{ hence, } A = 4.411 \times 10^{-19}$$

Since, in the neutron scattering in which the highest energy scattered atom has the energy E , the scattered atoms are uniformly distributed up to this energy, the function must be integrated as follows:

Fig. 5. A bi-logarithmic graph of the total energy (large dash, small dash), that expended in elastic scattering (circles, dashed), and the fraction expended in elastic scattering (crosses), for neon ions traversing vitreous silica. The points are from the LSS theory; the curves beyond are an extrapolation.

$$\delta_E = \frac{A}{E} \int_0^E E \cdot y \, dE$$

which gives the result:

$$\delta_E = A [0.018095 E + 1/8.715415 - \frac{1.037549}{(8.715415)^2 E} \ln \left(\frac{8.715415}{1.037549} E + 1 \right)],$$

and this can be expressed in terms of the neutron energy $\mathcal{E}$ because the mean maximum energy atom which it can scatter is about 0.18 E; and, hence,

$$\delta_{\mathcal{E}} = 4.411 \times 10^{-21} [0.3257 \mathcal{E} + 11.47 - (7.589/\mathcal{E}) \ln(1.512 \mathcal{E} + 1)].$$

This function was combined with our earlier calculations for the radiation damage experienced in CP-3^{25,26} and gave a result about 9% higher than the experimental results. This is very good agreement for such calculations and such data.

The dilatation for the neutron spectrum and a single 5 J pulse is shown in Fig. 6. When this is integrated, the total negative dilatation per pulse is 3.6×10^{-8} . This gives the linear dilatation δ_L ; the actual dilatation δ is

$$\delta = \delta_L (1 + 25 \delta_L)^{-1}$$

by the procedure described above in the section on dose (linearization of dose). Thus, for 4000 pulses, the calculated negative dilatation is 1.4×10^{-4} . A thermal dilatation of this magnitude would be caused by an 84 deg temperature rise. If part of the window were shadowed from the radiation, the differential stress across it would be about 600 psi.

3. Ionization. The effects of ionization are described by Primak and Kampwirth²⁷ and corrected by Primak²⁸ as possessing the following dependence on dose $\mathcal{D}$ (megaR):

$$10^6 \delta = 0.762 \mathcal{D}^{0.647}$$

It should be noted that since the ionization field is a volume field, and the dose is given in a unit of per gram, there should be a small correction based on the volume change. This is insignificant compared to our knowledge of the constants over the range of the energies of electrons and electromagnetic radiation. The change does saturate eventually, and this may be incorporated. Assuming this occurs at -0.028, the negative dilatation becomes:

$$\delta = 0.028 [1 - \exp \left(- \frac{0.762 \times 10^{-6}}{0.028} \mathcal{D}^{0.647} \right)]$$

Fig. 6. The negative dilatation of vitreous silica caused by neutrons in an interval of $\ln E$, at the tank wall, during 1 sec (2 pulses).

The mass absorption coefficients are given in Fig. 7. When combined with the above dose dependence and the spectrum, and integrated over the spectrum, the dependence of dilatation on depth shown in Fig. 8 was obtained. The surface energy deposition is enormous, and the material could not possibly tolerate the stresses unless stress relaxation occurred.

4. Surface Fracturing, or crazing (a network of surface fractures such as occurs on old pottery glazes) was observed by Primak²⁹ on vitreous silica following bombardment with protons or helium ions with ranges in the few micron region. For the present studies, those plates were reexamined, and the residual surface stress was measured. The crazed plates showed stresses from 9,400 to 20,700 psi, with one at 35,100 psi, several times the normal breaking strength. Since the lower part of this range corresponds to dilatations of about $\frac{1}{4}\%$ and this would be reached at the depths for which crazing was found in about 7 TFTR pulses, it was expected that such crazing would occur in TFTR windows. Crazing was therefore sought by providing the ionization with electron bombardment.

Two samples were bombarded, the first for 10^6 megaR, four spots with respective ranges 2, 3, 5, and 7 μ ; and the second with one spot, 10^7 megaR, range 5 μ . No crazing was found on any spot. No significant stress developed. The negative dilatation calculated from the above formula at 10^6 megaR is 0.52% and for 10^7 megaR it is 1.7%. For the first sample, a depression was measured and found to be 0.4 to 0.6% of the range and for the second 2.2% of the range. Although no significant stress (as indicated by the birefringence) was found, surface conduction of light indicated a marked change in refractive index. It is evident, therefore, that a plastic flow stress relaxation took place and that the whole dimensional volume change was experienced vertically.

Such a plastic flow stress relaxation had been observed in ion bombardment, but not at such great depths. It had not been observed with electron bombardment. This raises questions about the crazing which had been observed in ion bombardment.

- (1) Was stress associated with charge storage involved?
- (2) Is the distribution of dissipated energy along the range a factor? In ion bombardment it drops abruptly toward the end of the range, less so in electron bombardment and even less so for the TFTR spectrum.
- (3) Is temperature a factor? The ion bombardments would have been near room temperature. For the electron bombardments, a 60 °C temperature rise was estimated for the gradient in the sample. However, the thermal behavior of the assembly was tested by placing a strip of fusible alloy in it and observing the time required for melting; and from the calculations based on Newton's cooling law, it was estimated the temperature of the assembly might have been as much as 50 °C above room temperature. Calculations presented below indicate that in the TFTR there may be a surface temperature rise of 65 °C in the initial state, 145 °C in the TFM stage, and 185 °C in the extended TFM stage during

Fig. 7. Logarithm of the mass absorption coefficients used in calculating the absorption of soft x rays in vitreous silica: The last segments of the curve are not quite right, but not sufficiently different from the best data available to affect the results significantly.

Fig. 8. The negative dilatation of vitreous silica which has experienced the ionization from 40,000 of the 5 J pulses at the tank wall, as a function of depth from the face of the window. Note that the dilatation is nearly saturated for the first few tenths of a micron.

the pulse. Thus the present findings may be more applicable to the TFTR conditions than the earlier work with ion bombardment.

The present indications are that a general crazing may not be a problem for the TFTR windows, assuming that the same grade of vitreous silica used in these tests is employed for the TFTR windows. This grade is the commercial product "Suprasil." If a cover slip is employed to protect the window, even greater security should be attained, especially if it is mounted in such a manner so that its temperature is permitted to rise.

While a general crazing of the surface of the window may not occur, the tests described here do not preclude the possibility of crazing in selected areas of the window if it is not protected with a cover slip. Vulnerable areas would be: in the vicinity of the shadowed area where the intensity of ionization is decreasing, and in the vicinity of the seal where the temperature rise may be less than in the central area. Here fracturing could lead to failure of the seal. It is therefore recommended that the seal area be shadowed from the intense soft x-ray emission.

5. Thermal Pulse. The original specification for the incident energy was between that for the Initial operation and the TFM operation described in Table II. This was over 10^4 cal/g deposition in the first 0.1 μ of the window. It is not worth repeating the calculations for the first stage of the argument for the revised specification because a correction of several-fold, an insignificant factor here, would take care of the range of conditions given in Table II. The concern was about the state of the material under these conditions. The basic unit of the silica network may be considered to be 18 atoms, 6 SiO_2 units. There would be 281 atoms in a cylinder of these dimensions and 0.1 μ thick. The energy dissipation (neglecting the surface re-radiation of photoelectrons) would be about 100 eV/atom sec, hence about 3.5 ionizations. Thus, even for relatively long lifetimes of ionized states, the material is essentially non-ionized, and hence we are dealing with what is essentially a classical thermal conduction problem.

Most of the energy which is absorbed by the window is the soft x radiation, and most of it is absorbed in the first few microns of the window. As mentioned above, from the point of view of thermal conduction, this is a surface deposition. The thermal problem is considered in two stages. First, during the pulse there is a heat flux on one face. It may be assumed that the heat loss through the faces is small. Second, during the ensuing 5 min between the pulses there is heat flow in the disc, with no flow through the face facing the vacuum, and the worst condition, little flow through the opposite face. The solutions for these respective problems are given by Carslaw and Jaeger.³⁰ The thermal constants were taken from Goldsmith, Waterman, and Hirschhorn.³¹ For the initial conditions and the TFM conditions, the mean values of the constants between 300 and 400 °K were used; for the extended TFM conditions, the mean values between 300 and 500 °K. The data introduced into the equations are shown in Table III, and some of the results are given there also. The solutions to the equation is given in Fourier series which are only slowly converging, and nothing sophisticated was done to improve them; the series were truncated

Fig. 9. Temperature distributions calculated for a vitreous silica window following the heating by the 23 J pulse (Extended TFM operation): The oscillations in the first curve (highest) result from truncating the Fourier series at too few terms. The times (sec) for the succeeding curves are: 0.5, 1, 2, 5, 30, 60, 120, 300.

Table III. Thermal Behavior of Vitreous Silica (Density 2.2 g/cm²)

Thermal Constant						
Temperature (°K)	Heat Capacity (10 ⁻² cal g ⁻¹ deg ⁻¹)			Thermal Conductivity 10 ⁻⁴ cal sec ⁻¹ cm ⁻²)		
300	10.5			22		
400	13			30		
500	16			36		

Pulse Characteristics						
Mode	Pulse (J)	Duration (sec)	Mean Rate (cal/sec)	Mean Heat Capacity (10 ⁻² cal g ⁻¹ deg ⁻¹)	Mean Thermal Cond. (10 ⁻⁴ cal sec ⁻¹ cm ⁻²)	Max. Face Temp. Rise (deg)
Initial	5	0.63	1.90	11.8	26	66
TFM	17.2	1.5	2.74	11.8	26	146
Extended	24.3	1.5	3.87	13.3	29	184

Cooling Characteristics: Temperature Rise (deg)
in a 1.9 cm Thick Window at Several Depths (Face at 1.9 cm)

Time (sec)	Initial			TFM			TFM Extended		
	1.9 cm	1.6 cm	0 cm	1.9 cm	1.6 cm	0 cm	1.9 cm	1.6 cm	0 cm
Duration (0)	66	0.19	nil	146	6.2	nil	184	7.7	nil
0.5	29	1.83	nil	84	11.0	nil	106	14	nil
1	23	4.0	nil	69	17	nil	87	21	nil
2	17	6.4	nil	54	23	nil	68	28	nil
5	11.3	7.4	nil	37	25	nil	46	31	nil
30	4.7	4.4	0.48	15.7	14.6	1.7	20	18	2.0
60	3.4	3.2	1.5	11.2	10.9	5.1	14.2	13.7	6.3
120	2.6	2.6	2.2	8.7	8.6	7.5	11.0	10.9	9.4
300	2.4	2.4	2.4	8.1	8.1	8.1	10.2	10.2	10.2

when a term was reached which was below a specified limit. The final temperature distribution of the heating cycle at 13 equispaced points of the first 3 mm was fitted to 20 term Fourier series. This and the integral of the points by Simpson's rule were taken as the initial conditions for the cooling cycle, and the distribution through the whole window was then calculated for various times in the 5 min cooling cycle. This procedure causes a degradation of the original data, making the initial temperatures of the cooling cycle somewhat lower than the final temperatures of the heating cycle. This is a matter of little consequence for the demonstration of the effect here. Typical curves for the cooling cycle are shown in Fig. 9, and numerical values are given in Table III.

In addition to the thermal problem of the whole window, the effects which would occur in a 2 mm thick cover slip were also calculated. The initial condition is hardly different from the first 2 mm of the window, a maximum temperature but a few °C higher. The final cooling temperature is, of course, somewhat greater.

The lamellar thermal pattern described here causes a lamellar stress pattern. Since radiation relaxes the stress in the material by a plastic flow mechanism, this stress pattern will be partially relaxed during the heating cycle. Since the mean volume thermal expansion is about $1.7 \times 10^{-6}/^{\circ}\text{C}$, a 100°C temperature rise corresponds to a thermal dilatation, (positive) of 1.7×10^{-4} . For vitreous silica, the stress in psi is 4.33×10^6 times the dilatation, hence the stress is some 700 psi. Since part of this will be relaxed during the irradiation or heating cycle, a negative dilatation should be evidence when the plate is cooled, with a distribution over a few tenths of a millimeter. Since this is the range of x rays having energies in the 10 keV region, the pattern may be misinterpreted as indicating such a radiation component. Such stress patterns were seen in vitreous silica plates exposed in PLT, both in a large window and in a small test sample, but the cause was not ascertained.

It is unlikely that the stress will be completely relaxed in each cycle, hence there should be a progressive deformation of the plate. In the simple semi-infinite case, this should continue until the cold stress is nearly the negative of the high temperature stress if the lifetime of the plastic flow condition is short compared to the cooling rate, as seems likely. It is difficult to predict what will occur in the more complex geometry of a practical window where a portion is shadowed from the radiation and where a seal conducting the heat will exist. However, it may be anticipated that the effect will lead to deformations and stresses in the seal which have not been planned, and the possible failure of such a seal should be considered. It should be realized that these effects will be minimized, and possibly insignificant, if a cover slip is employed, because most of the heating will occur in the cover slip.

If the front face of the window is not cooled, it will rise in temperature on each pulse. The heat removal required for the respective three modes of operation (mW/cm^2) are about: 20, 60 and 85.

6. Radiation-Induced Stress Relaxation in Vitreous Silica. Evidence for the phenomenon in samples exposed in a nuclear reactor was presented by

Primak and Edwards.³² It was thought to be associated with the neutron radiation damage, but this cannot be considered settled at this time because of the other radiations present. The effect was found in ion bombardment by Primak.²⁹ The behavior of quartz, and the vertical appearance of the total volume change occurring during ion bombardment of small areas of a target have been presented in detail.³³ The similar effect for vitreous silica was more difficult to establish because the volume changes are so much smaller. The results presented here clearly demonstrates the effect occurs also in vitreous silica and appears on electron bombardment for the particular material studied here (Suprasil) and under the conditions of electron bombardment used here, somewhat above room temperature. It may be presumed it will occur with x rays also. The phenomenon is a rheological one, and the rheological aspects have not been investigated. Thus, many questions about it remain: the temperature dependence, dependence on the intensity of ionization, and the values of the rheological constants. It may be inferred that the ionization lowers the rheological moduli. How long this state persists after the ionization is terminated is not known. Experimental investigation of the problem is complicated because the ionization may rapidly alter the state of compaction caused by other radiation,^{31,34,35} thus introducing a state of stress in a relatively stress-free plate.

The behavior recounted above, the appearance of a stress associated with a thermal pulse, and the explanation presented above that it is caused by a radiation-induced stress relaxation, suggests that any stress may be relieved by the radiation. Since there are mechanical stresses associated with the mounting and atmospheric pressure, it would be expected that there would be a plastic flow associated with them. If the plastic flow stress relaxation is a rheological phenomenon, as suggested here, there should be a progressive deformation of the plate. If the rheological constants are dependent on the temperature and the intensity of ionization, as seems reasonable, the rate of relaxation, hence of deformation will not be uniform, and a state of stress will result which will depend on all of the factors considered here. Most of the effect should appear in the first few millimeters of the plate because the ionization intensity falls so rapidly in the thickness of the plate. As stated above, a major concern at this time is that the expansion characteristics of the seal material under consideration may not be appropriate for a plate undergoing such changes. The most desirable precaution would be the use of a freely mounted cover slip to absorb the radiation. In the absence of such a cover slip, the plate used for the window should be increased in thickness by several millimeters.

In ion bombardment with deuterons or heavier ions, the negative dilatation calculated from the stress developed in the non-uniformly irradiated specimen increases linearly before stress relaxation is observed at 20,000 to 40,000 psi.³⁶ EerNisse's data indicates values as high as 130,000 psi, but this writer has never seen such values in his own experiments.³⁷ In ionization compaction, the calculated negative dilatation increases non-linearly from the start, according to the writer's data, nearly with a 0.7 power dependence on dose. In proton bombardment, the dependence is about the 0.8 power of dose. The question arises whether these reduced power dependencies are associated with stress relaxation. Primak and Kampwirth²⁷

found that in gamma irradiated specimens, where stress would have been very small, the rate of compaction appeared to be smaller than in electron bombardment, but the power dependence was the same. Thus, the reduced power dependence does not appear to be caused by a macroscopic rheological phenomenon. Approximately the same dependencies were found in experiments in which the compaction was secured over a period of weeks as when the ionization intensities were increased to obtain them in a period of hours. It must be concluded that, even in the slowest experiments, the compaction rate was much greater than the relaxation rate under the conditions employed.

Only one of the electron bombardments of thin plates was carried on long enough to observe the stress relaxation. The residual energy was 10.81 keV, range of electrons 1.17 μ . The current density was about 2 $\mu\text{A}/\text{cm}^2$. Stress relaxation was observed after 6 days of irradiation at 9.2×10^5 megaR when a mean dilatation of 3.55×10^{-3} had been experienced. The maximum mean stress reached was therefore about 15,000 psi. This was much less than the maximum mean stresses found in ion bombardments. However, ion bombardment is much more effective in producing dilatation, and the stress relaxation there was found within a few hours.

7. Optical Absorption. Optical absorption was tested only for samples having the neutron dose about that for the original specification. It was anticipated that 4000 pulses (5 J) would cause a negative dilatation 0.014%. Samples $\frac{1}{2}$ in. thick were available which had been exposed in a nuclear reactor (CP-5) in 1964, which possessed negative dilatations 0.017 and 0.018%. Transmission began to fall significantly below 0.4 μ reaching 50% at 0.33 μ and 10% by about 0.31 μ . There was a small absorption peak between 0.55 μ and 0.69 μ in which the transmission was reduced about 10%. A transmission curve is shown in Fig 10.

The above results are for the grade of silica, Suprasil. Other grades may show other results.

No measurements were made of samples subjected to ionization.

8. Luminescence. The x-ray luminescence spectrum of a sample of the vitreous silica, Suprasil, was measured and was found to consist of a peak near the cut-off at 0.32 μ with a tail extending through the visible and a more definite peak just above the small red absorption peak extending from about 0.61 to 0.7 μ . The luminescence in light emitted (W) per electron energy absorbed (W) was 2.9×10^{-10} with no filter and 1.3×10^{-11} with a red filter. The luminescence measurements were described in greater detail for alumina (sapphire). The luminescence of neutron irradiated vitreous silica is stronger, but no measurements were made of it.

9. Fabrication. Although it would appear that large stresses will not develop in the TFTR vitreous silica window, moderate stresses will be applied for long periods of time, months or more. Since some of the effects of the radiation are not known, it would be desirable to take the precaution of fabricating this window with minimal flawing. The specification should therefore include slow cutting (the window should be cut with

Fig. 10. Optical transmissivity of 1 cm thick sections of the vitreous silica Suprasil after exposure near fuel in a thermal nuclear reactor for a fluence comparable to that anticipated at the TFTR wall after 4000 pulses.

abrasive rather than with diamond saws and taking only light cuts). The material should be bubble free and of low birefringence. All edges should be polished, chamfered and rounded, completely chip free. After abrasive lapping, the blank should be etched prior to final fine lapping and polishing. All surfaces should be polished out. The stresses introduced by grinding and lapping are discussed by Primak.³⁸ Careful processing can give plates having birefringence less than $\frac{1}{4}$ $\mu\text{p}/\text{cm}$.

To avoid stresses from charging, it is recommended that the edges and the unused aperture of the faces be metallized and connected to ground.

Testing the plates by the techniques of fracture mechanics¹³ may be desirable.

The major experience in This Laboratory has been with the grade of vitreous silica, "Suprasil," available from the Amersil Company. Persons specifying vitreous silica should become familiar with the various commercial grades manufactured and their characteristics. A classification of grades available some years ago is reproduced by Primak³⁹ and is given in Appendix I. Suppliers should be required to furnish melt number and date of the blanks, and fabricators should be required to maintain and furnish documentation relating to cutting, grinding, and polishing procedures so that the source of any problems which arise can be traced.

B. Crystal Quartz

1. General. Although its composition is the same, the radiation behavior of crystal quartz is very different from that of vitreous silica. To begin with, the rate at which changes occur in crystal quartz is very much slower than in vitreous silica.¹⁰ As the radiation damage progresses, after an exposure of about 3×10^{19} damaging neutrons,²⁶ vitreous islands develop and the rate of change begins to increase. Eventually the structure is disrupted, and now there are crystalline islands in the vitreous matrix; and many of the phenomena which are observed in vitreous silica begin to appear. The final result of the changes is a material apparently indistinguishable from irradiated vitreous silica. To begin with, the changes are aeoleotropic, change in the direction of the optic axis being less than in the transverse direction. The properties associated mainly with the parallel direction change at a different rate from those associated mainly with the transverse direction. Primak explained this as caused by the crystalline islands being elongated in one direction.³³

For the TFTR, only the initial stages of the radiation damage process are of concern. Here the changes associated with particulate bombardment are quite well described in the work of this author and others. Effects of small doses of ionizing radiation are recounted in work with oscillator crystals performed during World War II.⁴¹ There did not seem to be any data for the large doses of ionizing radiation which would be encountered in the TFTR.

2. Radiation Damage by Neutrons. There are not available for crystal quartz (which hereinafter will be referred to simply as "quartz") the extensive data which have been obtained for vitreous silica; and, indeed, most of the data which are available for quartz are for much greater exposures than the windows in the TFTR will receive. It therefore seems best to utilize those data in which the effects of quartz and vitreous silica were compared in the same irradiation and reference the data to the vitreous silica. The only data available to us in the range of interest were those obtained in This Laboratory in 1952 and 1953 and published in part in 1955.⁴⁰ These data cover the range of fluences 2.65×10^{17} to 2.8×10^{18} . They are shown in Fig. 11. It is seen that in this region the negative dilatation of vitreous silica is nearly linear, but the dimensional changes of quartz are not. The mean dilatation calculated for the Initial neutron exposure of vitreous silica was 1.43×10^{-4} . This can be converted to a neutron exposure by the procedure given by Primak.²⁶ The result is 8×10^{16} damaging neutrons/cm². As well as the results shown in Fig. 11 can be extrapolated, there will be a positive dilatation of 1.1×10^{-4} . Note that the expansion perpendicular to the optic axis is about twice that parallel to the optic axis. Changes in crystallinity in this region would be very small. The lowest exposures reported by others in the files in This Laboratory are those of Mayer and Gigon,⁴¹ 3.8×10^{18} to 2.2×10^{19} neutrons/cm².

The other specification for neutron exposure requested was 6 times the exposure of the Initial condition, hence 4.8×10^{17} . Again referring to Fig. 11, there should result a positive dilatation of 3.8×10^{-4} .

It is instructive to compare these dilatations with the thermal dilatations of quartz. At 25 °C the Initial and the 6-fold exposures would correspond to the respective dilatations caused by 3.1 and 10.8 deg temperature rises; and at 100 °C to 2.7 and 9.5 deg temperature rises.

It is not anticipated that these small changes would be significant unless part of the window were shielded from the neutrons. In that case, stresses amounting to some hundred of psi would develop in the window.

3. Selection of Quartz; Flaws; Optical Absorption. Unless there is a special reason for another orientation, the window should be specified cut within several degrees of the optic axis (nearly Z-cut) to minimize mounting stresses and stresses which may develop from the aeolotropic expansions. Fractures, once initiated, may propagate rapidly because the material is a crystal. It should therefore be selected to be as flaw-free as possible. Since the quartz is intended as a window for 100 μ to 1 mm electromagnetic radiation, the ordinary optical absorption is not of direct concern. However, it is of interest because it is indicative of impurity which tends to precipitate in particular planes of the crystal and induce twinning and other flaws. The material should not be acquired from oscillator manufacturers since the material which they use may be acquired under a specification of 60% free from twinning. Material for this purpose must be selected under an optical specification. The window itself should be specified as 100% free from twinning; and, in addition, it should show no banding when exposed sufficiently long in a gamma source. Fabrication arrangements should include an etch pit examination and a polarimeter examination with monochromatic light (e.g., a low pressure mercury arc source

Fig. 11. Progressive fractional changes in vitreous silica and quartz after successive exposures in a thermal nuclear reactor near fuel: estimated fluence at the tank wall after 4000 pulses of $\frac{1}{2}$ sec duration is between the dash-small dash lines; triangles, the negative dilatation of vitreous silica; squares and cross, fractional length increase perpendicular to the optic axis for quartz; circles, fractional length increase parallel to the optic axis for quartz. The cross is from a report of G. Mayer; the remainder, from the early work of W. Primak and L. H. Fuchs.

with interference filter). Correspondence relative to the selection of quartz is presented in Appendix I.

4. Effects of Ionization. Other than descriptions of color centers, the only reports in this writer's file on the effects of ionization on crystal quartz are those of Frondel⁴¹ on adjustment of the frequency of quartz oscillator plates by x irradiation. The maximum changes (saturation) varied greatly among the oscillator plates, from 0.003 to 0.125%, but typically were about 0.018% with plates changing more than 0.025% being rare. Accompanying the change in frequency, he reports a coloration. It seems likely, therefore, that the aluminum centers were involved. Apparently, the change must have been long lived, or it could not have been used for the purpose of adjusting the frequency of commercial oscillator plates. However, it annealed at relatively low temperature. He states that annealing would start by 180 °C and that the coloration was discharged in the process.

Since the mechanism of the change in frequency cannot be determined from his work (in particular, the density, which would have contributed to the frequency, was not measured), we cannot relate it to the dimensional stability, of interest here. According to Mayer,⁴² in neutron irradiation, the two major compliances, the axial and the equatorial, show changes opposite in sign, the first positive, the second negative, despite an expansion occurring in both directions, the expansion in the second direction being much greater than in the first. The change in Young's modulus would, of course, be opposite in sign to the change in compliance. Thus axial Young's modulus decreases on neutron irradiation, but equatorial Young's modulus increases. Frondel reports only a decrease in oscillator plate frequency, hence a decrease in Young's modulus.

To determine the effect of ionization, a thin cantilever plate was mounted and bombarded with 16.3 keV electrons to a dose of 3×10^5 megaR. To understand the results, it is necessary to know some of the details of the experiment. The quartz was coated on each face with aluminum and mounted above an electrode which formed a capacitor, the other plate being the metallized quartz cantilever. This capacitor was an element of an oscillating circuit whose frequency was measured. A dilatation of the bombarded layer of the quartz would cause a deflection of the cantilever, hence causing the frequency of the oscillating circuit to change. The deflection was calculated from the frequency change, and from this the mean dilatation of the bombarded layer. As soon as the beam impinged on the sample, the frequency would change by some 70 Hz. The subsequent changes were small at first, but over the period of a day the change was about 100 Hz more. The respective dilatations calculated for these changes are 4×10^{-5} and 1.1×10^{-4} . When the electron beam was stopped, there was a frequency change which saturated in about 30 sec and corresponded to a negative dilatation of 3×10^{-5} . The initial change could be caused by a small thermal effect, or possibly an inverse piezoelectric effect caused by charge storage. The subsequent changes which took place over many hours could have been (or could have included) drift due to the circuitry. Thus it appears that even at this large radiation dose, there is no certain evidence of a significant dilatation. Even if the changes were real, they should not be of concern

because the maximum changes seen correspond to the dilatation experienced by quartz in but a 3 deg temperature change.

5. Thermal Pulse. The thermal pulse in crystal quartz will be smaller than it is in vitreous silica because of the much greater thermal conductivity of quartz. The calculations presented here are for a Z-cut plate (heat flow parallel to the optic axis). The thermal data were taken from Sosman⁴³ and are given in Table IV. The calculations were performed as described for vitreous silica except that 23 points covering most of the thickness of a 1.4 cm thickness of the plate were used to describe the initial conditions for the cooling cycle, and more terms of the Fourier series were used to calculate the results. The characteristics of the machine employed for the calculations would not permit calculations of the temperature distribution in the cooling cycle beyond 14.2 sec. A few significant data from these calculations are given in Table IV, and the temperature distributions at several times following the heating by the Extended TFM pulse are shown in Fig. 12. As described above for silica, the actual temperatures should be a little higher than shown because of the degradation of the data in the calculation procedure used for the initial conditions for the cooling cycle.

6. Thermal Stress. A solution for the thermal stress equations for quartz is not at hand. The solution for the amorphous solid is given by Love.⁴⁴ The solution for the cubic crystal oriented on the crystal axes can be adduced from the solution for the photoelectric equations given by Primak.²⁰ However, since it was shown by Primak and Luthra⁴⁵ that the combination of elastic constants which appear in the solutions are so little different for different materials, it may be anticipated that the same will be true for quartz relative to vitreous silica. The problem in the case of quartz is that, although the thermal pulse is smaller, the thermal dilatation is an order of magnitude greater. It is estimated that the thermal stresses at the termination of the thermal pulse for the Extended TFM operation will be about 8000 psi. It will be about 1/3 of this for the Initial conditions. We have not investigated the possible consequences of such stress pulses in quartz. Among them will be charging effects, because the material is piezoelectric. The precaution of having metallized polished edges, suggested above for the vitreous silica window, may be even more important for the quartz window. Fracture mechanics techniques for stress testing each window are also recommended. Increasing the diameter to provide an enlarged rim beyond the seal will decrease the stress concentration in this region.

As in the case of the vitreous silica window, these problems with the quartz window will be avoided by placing a thin cover over the window if the heat can be removed from it during the 5 min cooling period.

C. Sapphire

1. General. Considerations of this material have been various, ranging from a small window 2 in. diameter to one 8 in. diameter and over an inch thick. The crystals are considered to be quite radiation resistant.

Table IV. Thermal Behavior of Crystal Quartz
(Density 2.65 g/cm²)

<u>Temp.</u> <u>(°C)</u>	<u>Heat Capacity</u> <u>[10⁻²(20° g cal)g⁻¹deg⁻¹]</u>	<u>Thermal Conductivity</u> <u>(10⁻³ cal sec⁻¹ cm⁻²)</u>	
		<u>Parallel</u> <u>axis</u>	<u>Perpendicular</u> <u>axis</u>
0	16.6	32	17
50	18.7	25.5	14.9
100	20.4	21	13.1
150	21.9		
200	23.2		

Pulse Characteristics (Parallel Axis)
(at 100 °C, Heat Capacity 20.4x10⁻², Conductivity 21x10⁻³)

<u>Mode</u>	<u>Pulse</u> <u>(J)</u>	<u>Duration</u> <u>(sec)</u>	<u>Mean</u> <u>Rate</u> <u>(cal/sec)</u>	<u>Max. Face</u> <u>Temp. Rise</u> <u>(deg.)</u>
Initial	5	.63	1.90	16
TFM	17.2	1.5	2.74	36
Extended	24.3	1.5	3.87	50

Cooling Characteristics of a 1.4 cm
Crystal Quartz Window Z-cut., Face at 1.4 cm

<u>Time</u> <u>(sec)</u>	<u>Initial</u>			<u>TFM</u>			<u>TFM Extended</u>		
	<u>1.4 cm</u>	<u>1 cm</u>	<u>0 cm</u>	<u>1.4 cm</u>	<u>1 cm</u>	<u>0 cm</u>	<u>1.4 cm</u>	<u>1 cm</u>	<u>0 cm</u>
<u>Duration (0)</u>	16	0.56	nil	36	5.3	nil	50	7.5	nil
.5	7.2	1.9	nil	21	7.9	nil	29	11.2	nil
1	5.6	2.5	nil	17	8.9	nil	24	12.6	nil
2	4.2	2.7	nil	13	9.0	0.3	19	12.7	nil
5	2.8	2.3	0.5	9.1	7.6	2.0	12.9	10.7	2.9
10	2.0	1.8	1.2	6.8	6.3	4.1	9.6	8.8	5.8
14.1	1.8	1.7	1.4	6.0	5.8	4.8	8.5	8.2	6.8

Fig. 12. Temperature distributions calculated for a crystal quartz window mounted at the tank wall following heating by the 23 J pulse (Extended TFM operation). The irregularities in the first curve are from truncating the Fourier series. The following curves, descending from the initial distribution, are for times (sec) 0.5, 1, 2, 5, 10, 14.2. The numerical capacity of the computer was insufficient to compute longer times.

However, material grown by different manufacturers shows considerable variation in forming color centers, and even more in luminescence.

Most of the applications of aluminum oxide in radiation environments have been for electrical insulation purposes. Investigations of engineering applications in reactor environments have been concerned with dimensional changes, changes in mechanical properties, and changes in electrical insulation properties (e.g., electrical resistance and break-down). The material is highly impervious to gases, and this is the material in which the radiation blistering effect was first observed⁴⁶; there are several investigations of gas trapping and blistering caused by the implantation of gaseous ions.^{47,48,49} Chemical effects caused by ion implantation have been studied.⁵⁰ The original scientific investigation of the radiation effects were of the optical absorption in the ultraviolet found after irradiation.⁵¹ A tail from these bands may extend into the visible region, or there may be another band in this region. There may be impurity absorptions in the visible.

2. Radiation-Induced Dilatations. Radiation-induced volume swelling in nuclear reactors is reported as being about 1% at a fluence (neutrons) $1 \times 10^{21}/\text{cm}^2$.^{52,53} It appears to be rising proportionately to fluence at these fluences. If this rate can be extrapolated to lower fluence, it would correspond to 6.3×10^{-7} as the dilatation for the initial condition and 3.8×10^{-6} for the 6-fold condition. Since this last value corresponds to the thermal dilatation experienced in a fraction of a degree, this is clearly negligible. However, it should be noted that data for these low neutron fluences are not available.

In bombardment with helium ions (140 keV He^+ , range 0.56μ) an expansion of 0.01μ was noted at incident charge 0.03 C/cm^2 (the reported charge may have been a factor of 2 low). If this is the volume expansion, it is comparable to that reported for neutron irradiation for displacing an equivalent number of atoms by elastic collisions. On the other hand, if it is the linear expansion, part of it must be caused by the introduction of porosity by segregation of implanted gas. At incident charge three times as great there is a marked increase in the growth rate, and this certainly must be associated with the segregated gas because visible blistering can be seen under the microscope in monochromatic light. For further information about the gas segregation problem, the reader is referred elsewhere.⁴⁸

This writer is unfamiliar with any reports of dilatation resulting from ionization (electrons, x rays). There do not appear to be any reports of ionization effects for the dose levels anticipated in the TFTR.

3. Optical Absorption. Particulate and high energy electron irradiation is reported to form an absorption band at 0.204μ . Arnold⁵⁴ gives the optical absorption up to 0.36μ , and the curves for the different radiations for which he reports are not similar. Levy and Dienes⁵¹ found a subsidiary band at 0.26μ and reported its ratio to the 0.204μ band to be constant. They also reported measurements into the visible region for what appears to be a tail from these bands. They reported a band at 0.4μ produced by gamma ray irradiation (Co-60 source). They say this band was saturated at 3000 R and that no further increase was seen up to

100 megaR. The saturation value taken from their text and figures (the figures are incompletely labelled) appears to be an optical density (OD) of 0.7 per cm at 0.4 μ and 0.6 per cm at 0.6 μ (70% transmission per cm). The absorption in the visible associated with particulate radiation is supposed to be larger. Grains, fragments, and parallelipeds of sapphire irradiated in nuclear reactors in the early 1950's were examined in This Laboratory in 1978 and found to be a moderately dark brown color. C. Delbecq and P. Yuster advised the writer that they have not found any sapphire which did not color on irradiation.⁵⁵

Concerning the 0.204 μ band, Arnold states it is produced by proton bombardment, by neutron, and by 2 MeV electron irradiation; that ultra-violet light, soft x rays, and Co-60 gamma ray irradiation do not produce it. It should be noted that the ionization dose corresponding to his proton bombardment is 1.1×10^3 megaR, and that it would be difficult to achieve such doses with customary soft x ray or Co-60 sources.

4. Luminescence. C. Delbecq and P. Yuster⁵⁵ advised the writer that they had not found any sapphire which did not luminesce on irradiation. In particular, luminescence occurred where the red ruby lines are located (about 0.69 μ) because of traces of chromium. One sample which had been acquired from Crystal Systems, Inc., and which had been represented as being of good quality, did not show magnetic resonances associated with chromium and iron impurities known to have been present. This material luminesced intense blue under x-irradiation, and a weak red luminescence was visible through a red filter. In polarized light, the specimen was found to consist of a number of intergrowths showing biaxial birefringence at the boundaries of the intergrowths. It was concluded that the material was too imperfectly crystalline to show the magnetic resonances associated with the impurities. A sample of sapphire from another source showed no blue luminescence, only the weak red luminescence. A third sample of sapphire borrowed from J. C. Thompson⁵⁶ seemed to show both the red and blue luminescence and exhibited a strong afterglow.

A quantitative determination of the luminescence was made of two samples of sapphire, one obtained from Crystal Systems, Inc. (CS, a different sample from the one described above) and one from Union Carbide Corporation (UCC) in collaboration with P. Yuster and C. Delbecq. The luminescence obtained with soft x rays was scanned with recording monochromators. Then the samples were bombarded with electrons to obtain dose rates comparable to those anticipated in the TFTR, and the emission at the major luminescence bands was measured through filters. The x-ray source was calibrated by means of a deep Fricke dosimeter.²³ The electron accelerator was checked with calibrated meters, and the voltages from the power supplies were found to be at least as accurate as the meters. A mercury arc lamp was used to calibrate the wavelength scale of the monochromator. The light calibrations were referred to quaternary sources. The calibrated ternary source was an incandescent lamp which the supplier had calibrated photometrically against a National Bureau of Standards calibrated lamp (secondary source). The ternary source was used to calibrate a number of incandescent lamps of various sizes (quaternary sources) photometrically. One of these quaternary sources was used to calibrate the spectrophotometers utilizing the manufacturer's grating efficiency curve, the

photomultiplier sensitivity curve, the temperature of the lamp, and the Planck radiation curve multiplied by de Vos' emissivity data for tungsten. Similar use of the tungsten lamp characteristics with the filter and window transmissions and the detector sensitivity curve were utilized to calibrate the luminescence measurements made during electron bombardment. The final results were calculated in watts on the assumption that the luminescent output in the photopic sensitivity curve for the eye is 680 lumens/W. The details of these calibrations are given in Appendix II.

In the original report of the results, figures were shown which purported to show luminescence exhaustion at high electron dose and a variety of hysteresis effects. It has now been found that appreciable heating must have occurred during those measurements. The present interpretation is that the luminescent output decreases at higher temperature and that part of the luminescence observed may have been thermoluminescence. The luminescence spectra are shown in Figs. 13-16, and the calculated results are given in Table V.

The blue peak from the CS sapphire has been identified by others as luminescence arising from F-centers. The red line, so prominent in the UCC product, is associated with chromium impurity. Side bands are always found with it. The luminescent power in these side bands appears to be about equal to that in the red line. This line is a very narrow line. It appears so broad in the figures because the monochromator slits were opened quite wide. The red line is quite weak in the CS material, but there appears to be an appreciable amount of power in the red band which is associated with the red line. The magnetic resonance studies, referred to above, indicate that this behavior, the low intensity of the red line relative to the side bands is associated with imperfect crystallization. This material showed evidence of twinning or lineage. The relative behavior of the blue and red emission for x-ray irradiation and electron bombardment was discussed in the original report as indicating saturation of the blue band on electron bombardment. This would now be interpreted as a greater temperature sensitivity, quite reasonable if the blue band is associated with an F-center.

A physical picture of the luminescence can be obtained by comparing it with the surface brightness of a 100 W bulb. Typically such a bulb is a 100 candle power source and the bulb is 3 in. in diameter. Since a foot candle is a lumen/ft², the brightness at the bulb surface is 6400 lumens/ft². Since 1 W of light is 680 lumens, the surface brightness of the bulb envelope is 1.1×10^{-2} W/cm². According to Table V, the most intense output is the blue band of the CS material, 1.6×10^{-5} W/W, hence, for the Initial condition, 10 W operation, the brightness of the window, if it were in the midst of the visible, would be about 1.5% of the brightness of the 100 W bulb surface. The efficiency of lower wattage incandescent lamps is markedly lower than that of the 100 W lamp; thus the luminescence of the window would be about 7.5% of the brightness of a 40 W bulb. The brightness of the window would be twice this under TFM Extended operation.

Figs. 13-14. Luminescence spectra for the UCC sapphire: the upper curve in Fig. 14 is for a back face silvered sample, the lower curve for an unsilvered sample.

Fig. 15-16. Luminescence of GS sapphire: the specimen used for Fig. 16 was silvered, hence the actual luminescence was more than a factor of two less. Note how small the chromium line is. The irregularity beyond is undoubtedly mainly noise, as described above.

Table V. Luminescence

	4047,4054	4048	4049
	Sapphire	Sapphire	Silica
	(UCC)	(CS)	(Suprasil)
Absorbed x rays (W/cm^2)	5.16×10^{-4}	5.16×10^{-4}	4.98×10^{-4}
X-ray luminescence ^a (W/cm^2)			
Ruby line	1.14×10^{-8}		
Side bands	1.05×10^{-8}	1.02×10^{-9}	
Total	2.19×10^{-8}	1.02×10^{-9}	
LE ($W_{\text{light}}/W_{\text{ioniz}}$)	4.24×10^{-5}	1.97×10^{-6}	
F-band (W/cm^2)		1.14×10^{-7}	
LE (W/W)		2.21×10^{-4}	
UV peaks (W/cm^2)			
0.251 μ	8.9×10^{-9}		
0.34 μ (tail to 0.6 μ)			1.2×10^{-11}
0.6 to 0.72 μ			1.37×10^{-11}
Absorbed electrons,			
low current (W/cm^2)	3.54×10^{-2}	0.35	2
Red light (W/cm^2)	5.71×10^{-7}	4.49×10^{-8}	
LE (W/W)	1.61×10^{-5}	1.27×10^{-7}	
Blue light (W/cm^2)		1.9×10^{-6}	
LE (W/W)		^b 1.12×10^{-6}	
No filter (0.3 μ - ?)(W/cm^2)			6×10^{-10}
LE (W/W)			2.9×10^{-10}
Red filter (W/cm^2)			2.5×10^{-11}
LE (W/W)			1.3×10^{-11}

^aCorrected for increase caused by silvering.

^bLight efficiency (LE) is reduced by over an order of magnitude by an exposure of several minutes at 400 megaR/sec (i.e. $\sim 10^5$ megaR).

D. Zinc Selenide

1. General. A plate of the zinc selenide of interest, about 3 in. diameter and $\frac{1}{4}$ in. thick, was examined. The material was presumed to have been made by compressing crystalline material. It was an amber colored disc, very transparent. There was a strain pattern of small rectangular areas, dimensioned $\frac{1}{8}$ to $\frac{1}{4}$ in. on a side. The strain birefringence corresponded to a few degrees rotation of a de Senarmont compensator. If this material did not color too severely on irradiation, radiation-induced dilatation could be measured by photoelastic methods.

The most significant prior work on zinc selenide is the study by Watkins⁵⁷ of the zinc vacancy-zinc interstitial identified and studied with EPR measurements after high energy electron irradiation at low temperature. The optical absorption is in the midst of the visible region. It was identified as a V-center by D. Dunstan, et al.⁵⁸ Spitsyn, et al.⁵⁹ appear to have made the same center by irradiation in a thermonuclear reactor, but their report is not detailed enough to determine how the center arose. If their results are to be explained by an exponential saturation, it is readily demonstrated that saturation is seen by a fluence of about 10^{18} neutrons/cm². The TFTR exposures will be about 10 times greater.

No information about dimensional changes was found.

2. Neutron Radiation Damage. There was no possibility of obtaining the information desired in any reasonable length of time utilizing neutron sources. Estimates were therefore made on the basis of ion bombardment data which could be and was secured quickly. These estimates are based on the assumption that the effects are proportional to the number of atoms displaced from lattice positions in neutron scattering and the subsequent cascades produced in the slowing down of the scattered atoms. It is assumed that the size of the cascade is proportional to the quantity in the Lindhard, Scharff, and Schiott (LSS)^{60,61} range calculations which they call the "nuclear energy," the energy expended in scattering atoms, for energy transfers greater than a threshold. The threshold was assumed to be 30 eV, and the proportionality factor was assumed to be 1/30. This method was employed because the nuclear energy greater than a threshold is given in one of our codes. The scattering was assumed to be isotropic; i.e., that the distribution of scattered atoms is uniform over the energy range 0 to $4/(A+2)$ times the energy of the neutron, where A is the atomic weight of the scattered atom. Thus, the cascade yield has to be integrated over this energy range, and the result has to be integrated again over the neutron spectrum times the scattering cross section. The calculation is ad hoc in three regards:

- (1) the neutron cross sections of zinc and selenium include inelastic scattering, perhaps to the extent of 1/3, and whether this would enhance the number of displacements would depend on the lifetime of the capture state as discussed below;
- (2) the assumption of the LSS calculation that the ionization is proportional to velocity probably underestimates it for high energies; and,

- (3) the assumption above that the proportionality factor is the inverse of the threshold probably overestimates the yield because some of the higher energy secondary scattering involves some dissipation of energy through ionization processes.

Before presenting the calculation, the problems with it are discussed. The problem of the inelastic scattering of the neutrons is that in elastic scattering the maximum energy of the scattered atom is but 5% of the neutron energy, and the times involved in the slowing down are of the order of magnitude 10^{-15} sec. If the lifetime of the capture state is long compared to this, then, during all of this time, all of the neutron energy less whatever is used in nuclear excitation is present as kinetic energy. The implication of this for the final result is discussed below. Regarding the calculation as a whole, the only material for which there is enough data to offer an experimental estimate of the number of displacements is graphite because of the abundance of data gathered during the years in investigating the moderator used in the first nuclear reactors. An LSS calculation for this material using a threshold of 25 eV, made some years ago,⁹ was found to give an excessive result. It was reexamined and was found to have an error in integration. When this was corrected, the yield function was found to correspond to the Seitz function at low energies and to the James cut function at high energies, both presented in the same place, hence about 30% too high in the high energy region where the experimental data corresponded to the James cut function. This is really quite good agreement for such a calculation. Although the appropriate correction would be to take proper account of the ionization losses, the simplest ad hoc procedure would be to use a slightly higher threshold value, and probably 31 eV would give a result close to the experimentally determined yield. It should be noted that the effect of ionization would be smaller for zinc and selenium because of their much greater atomic weights, but then the appropriate threshold for this material is not known. The value 30 eV for the present calculations is an arbitrary choice.

The cascade yields were calculated separately for zinc and for selenium incident on zinc selenide. The result for zinc is shown in Fig. 17. Because the intervals coded into the neutron scattering calculation are different from those used in this calculation, it was necessary to interpolate these cascade yields, and the simplest procedure was to use fourth order polynomial fits:

For Zn:

$$\log E_{v>30} = -0.1198 + 1.223 L_z - 0.2667 L_z^2 + 0.1221 L_z^3 - 0.0205 L_z^4$$

For Se:

$$\log E_{v>30} = -0.1218 + 1.224 L_s - 0.2640 L_s^2 + 0.1212 L_s^3 - 0.02004 L_s^4$$

Fig. 17. The "nuclear energy" for energy transfers exceeding 30 eV, from the LSS calculations for a zinc ion incident on zinc selenide.

where L_z and L_s are the respective logarithms of the energies of the incident zinc and selenium ions. The scattering cross sections were fitted sectionally by power functions of the form:

$$\sigma = a(E/b)^c$$

and the curves are shown in Fig. 18. The displaced atom yield as a function of neutron energy is shown in Fig. 19. When this curve was integrated, the result was 2.86×10^{19} displacements for each pulse in the initial operating mode, and for the specification of 4000 pulses it is 1.14×10^{19} .

For the specification 6-fold greater it is 6.9×10^{19} displacements. The results were used to scale the practical consequences of the irradiation. To estimate the stress in the window, ion bombardment data were utilized; and to assess the effect on the optical absorption, the data of Spitsyn, et al.⁵⁹ were used.

Thin plates of zinc selenide were mounted as cantilevers and subjected to ion bombardment, one with 140 keV He⁺ ions, and another with 160 keV Kr⁺⁺ ions. The dilatations calculated from the deformation of the cantilevers assuming the respective ranges 1.3 and 0.18 μ are shown in Fig. 20. There was no evidence of blistering, but this would have to be confirmed on uncoated plates as it is difficult to make a detailed examination of metalized plates. The results are a little strange and may indicate complex phenomena because the slope of the curve for the helium ion bombardment is the 1.2 power of dose and that for the krypton ion bombardment is the 0.7 power of dose. The number of displacements per incident ion was calculated from the LSS code, and the respective results 267 and 8533 were obtained for the ions helium and krypton. Thus, at the beginning of the krypton data, the calculated number of displacements is 3.4% of the atoms of the crystal. This is a large percentage. For the helium data, the rise begins when the calculated displacements are about 1.1% of the atoms in the solid. The mean dilatation is about 1.5×10^{-25} per displacement/cm³ near the beginning of the krypton data and about 7×10^{-26} in the midst of the helium ion data. For the following calculations the value 9×10^{-26} was used as the mean dilatation per displacement/cm³.

When the last result is combined with the result of the neutron calculation, the dilatation calculated for the initial 4000 pulses is 1×10^{-7} and for the 6-fold condition it is 6×10^{-6} . These values are less than the thermal expansion per degree. Even if the enhancement of the inelastic scattering were to increase the neutron yield by an order of magnitude, hardly reasonable, dilatation would still be insignificant.

Spitsyn, et al.⁵⁹ state that in their nuclear reactor exposures considerable optical absorption was introduced in the visible, but no effect was found in the infrared. Only the crudest estimates are possible for this Russian work because their radiation data are inadequate. If it is assumed that the fluence they give, 1.84×10^{18} , is to be associated with a mean neutron energy 10^5 eV (in the typical thermal neutron reactor most of the radiation damage is associated with a 2-decade energy range at the upper end of the slowing down spectrum),²⁶ then the mean energy of the scattered atoms is about 0.025 times this; and using a scattering cross

Fig. 18. The neutron scattering cross sections which were employed in estimating the neutron radiation damage in zinc selenide; upper curves for selenium, lower for zinc.

Fig. 19. The estimated displacement yield distribution curve for zinc selenide in 2 pulses (1 sec) of the TFTR neutron spectrum at the tank wall.

Fig. 20. The dilatation of zinc selenide on bombardment with helium and with krypton ions.

section of 5 barns, an atomic density of 4.4×10^{22} atoms/cm³, and assuming that half the energy is expended in ionization, the number of displacements is about 2×10^{19} /cm³. This number is comparable to the number calculated for the TFTR. The greatest ambiguity lies in the interpretation of the quantity which the Russian workers give for the fluence. If it is the total neutron fluence, it should be appreciated that it covers some 8 decades in the lethargy plot of the neutron energy spectrum, only two of which are typically effective in producing the radiation damage associated with the scattering of atoms by high energy neutrons.²⁵ Distant from fuel this spectrum is nearly constant in the slowing down region and has a peak in the thermal region near 0.025 eV. Close to fuel there is a peak in the high energy region, and this may shift the effective energy of the damaging neutrons to nearly 10^6 eV, thus increasing the yield significantly. With these considerations, the estimates above for the yield in the Russian experiments may be in error by a factor as large as 4. It should also be noted that they report an effect by thermal neutrons. They do not indicate how well thermalized that spectrum was. If it was truly a thermal spectrum, it may indicate that some of the effect which they report was caused by the introduction of impurities formed by transmutation or ionization. It should also be noted that the absorption which they found in the visible region has been reported for zinc selenide doped with impurities.

3. Ionization Dose. The ionization dose for the initial condition was calculated in the same manner as described above for vitreous silica appropriate mass absorption coefficients. These were fitted with a logarithmic equation and with power functions as follows:

0.1 to 0.45 keV:	$\log A = 3.04795 - 3.5 \log E - 1.833 (\log E)^2$
0.45 to 1.04 keV:	$A = 1.15 \times 10^4 (E/0.45)^{-2.131}$
1.04 to 1.44 keV:	$A = 5.9 \times 10^3 (E/1.04)^{-1.88}$
1.44 to 9.6 keV:	$A = 5.9 \times 10^3 (E/1.44)^{-2.582}$
9.6 to 12.7 keV:	$A = 145 (E/9.6)^{-2.037}$
12.7 to 70 keV:	$A = 145 (E/12.7)^{-2.928}$
70 to 150 keV:	$A = 0.98 (E/70)^{-1.898}$

where the units are cm²/g. As before, it was assumed that the dose was the attenuation of the primary beam. This should be a good approximation except for the highest energy x rays which contribute only little to the dose. The results are shown in Fig. 21. A line drawn through a similar set of points for vitreous silica is shown for comparison. The R unit which is used is 83 ergs absorbed in a gram of material. There should be some mild surface attenuation compared to the calculated results because the range of photoelectrons is comparable to the smallest depths shown.

4. Ionization Effects. A thin plate of zinc selenide was mounted as a cantilever plate and subjected to bombardment with 16 keV electrons, range 1 μ . When allowance was made for the thermal effects in the equipment, the changes observed were smaller than those found for quartz, given above. Then the plate was bombarded with 25 keV electrons, range about

Fig. 21. The ionization dose in several materials exposed to the soft x-ray spectrum at the tank wall. No correction has been made for surface photoemission. The circles are for lithium fluoride; diamonds, zinc selenide; line, vitreous silica.

2 μ . There was evidence of a small contraction in this second phase of irradiation, but the amount was so small that this result must be considered uncertain at the present time. It would not be of practical concern.

E. Fluorides

1. General. Lithium, magnesium, or calcium fluoride was of interest as a candidate material for a window with a transmission in the far ultraviolet. For the unirradiated materials, the transmission is in the inverse order given here; but on irradiation, the absorption bands developed both in rate and in intensity, are also in this inverse order. The mechanical strength is in the order given. Lithium fluoride will flow plastically under rather small stresses, developing dislocations and twin zones. As a result of preliminary reports on these materials, and work at Princeton on the problem of making a seal to lithium fluoride, evaluation of this material was halted. Work on calcium fluoride, the one which has the best promise of the three for radiation resistance had not begun when the evaluation project was halted. The most complete evaluation was thus of the magnesium fluoride.

The general behavior of these materials under irradiation is to form positive and negative ion vacancies and electron and hole centers. The vacancies may aggregate. These centers have optical absorption spectra in the ultraviolet and in the visible. Luminescence occurs. The best known center is the F-center having an absorption band at 0.25 μ for both lithium fluoride and magnesium fluoride, and at 0.38 μ for calcium fluoride. Alpha and beta centers are close to the UV absorption edge and may form shoulders on it. The exciton bands are in this region. The V-bands may lie between the F-band and the absorption edge, or may be located at longer wavelengths. The F-aggregate bands, like the M-band and the R-band lie at wavelengths 1.5 times to twice that of the F-band. Mobility of some of the species which are found occurs well below room temperature, which explains the aggregation process. The efficiency with which the centers form depends markedly on temperature. At low temperatures, close pairs are formed; and, as the temperature rises, these become mobile and recombine. As each of the species becomes mobile, the production rate is affected, and thus there may be several increases and decreases in the production rate over the temperature range: liquid helium to elevated temperature.⁶² Typically, the final of these stages is reached well above room temperature. The production and stability of the centers may be mediated by impurities which may form traps for holes or electrons and otherwise participate in the processes. In the work done in This Laboratory with lithium fluoride, expansions as large as 0.1% were noted in deuteron irradiations.⁶³ There are reported values 3 to 4.5 times as great in thermal neutron reactor exposures up to 3×10^{17} nvt.⁶⁴ In gamma ray exposures (Co-60 source) values up to 0.012% have been noted in This Laboratory,⁶⁵ but this differed by half an order of magnitude depending on the crystal and its prior treatment. Dimensional changes comparable to these were found when a crystal was placed into contact with a hot plate for a few seconds, presumably caused by plastic deformation associated with non-uniform thermal expansion.⁶⁶ Heating a crystal in an annealing cycle

diffuse and recombine. It is doubtful that the windows will reach the temperatures for this last condition. These matters will be dealt with in further detail below.

2. Ionization Dose in Lithium Fluoride. This was calculated by the procedures described above for other materials utilizing the mass absorption coefficients from the same sources. The mass absorption coefficients were fitted to power functions and a logarithmic function as follows:

$$0.1 \text{ to } 0.68 \text{ keV: } A = 1.07 \times 10^5 (E/0.1)^{-2.493}$$

$$0.68 \text{ to } 4 \text{ keV: } A = 1.18 \times 10^4 (E/0.68)^{-2.727}$$

$$4 \text{ to } 20 \text{ keV: } A = 94 (E/4)^{-2.946}$$

$$20 \text{ to } 150 \text{ keV: } \log A = 4.5123 - 5.1257 \log E + 1.2178 (\log E)^2$$

in units of cm^2/g . The results of the calculations are shown in Fig. 21.

3. Effect of Neutrons on Magnesium Fluoride. The direct determination would require a lengthy series of irradiations, the handling of radioactive material at each step of the irradiation, and the measurement of radioactive material. Such a project would require many months of investigation. An attempt was therefore made to estimate the effects of neutron irradiation from ion bombardment data. Two irradiations were conducted, one with 140 keV helium ions, and the second with 160 keV Ne^{++} ions. The latter were used because such an ion behaves like a 320 keV singly charged ion and has the corresponding range. The problem in interpreting the ion bombardment data is that it may be contaminated with effects caused by the trapping of the gases. Since it would be expected that the radiation damage resulting from the ion bombardment would cause an expansion of the material, the effect of the trapping of the gas would be to cause an even greater expansion. If the gas segregated, this would become immediately apparent, as this causes very large changes in the reflectivity and is noted by interference effects seen in monochromatic light. Such effects were not seen. Only a very small interference effect was found, what would be expected for a small change in the refractive index of a surface layer, and this was used to determine the range of the neon ions, 0.49μ , about that calculated from LSS theory. The samples which were irradiated were thin plates mounted as cantilevers; and from their deformation, the dilatation as a function of dose was calculated. The results are shown in Fig. 22. A very small initial contraction was followed by an expansion whose rate fell as the irradiation progressed. The small initial contraction was seen in two experiments, hence it does not appear to be an experimental error; but it could be other than a radiation expansion. It may be a thermal effect or the release of stress induced in the sample preparation: the grinding and polishing.

Magnesium fluoride is anisotropic and these samples were oriented with the optic axis at a slight angle to the normal to the surface.

The procedure which was used to calculate the neutron dilatation was that employed previously for the vitreous silica. It was assumed that the effect of neutrons would be to scatter magnesium and fluorine atoms, and that the radiation effect would result from the energy dissipated by these

increased the defect production rate on irradiation by a factor 2.⁶⁵ Whether this redistributed impurities, introduced vacancies, inhibited annealing of defects, or promoted production of V_k -centers is not known.

An important center in these materials is the V_k -center which consists of a pair of halide ions which have trapped a hole. When this hole combines with an electron in a radiationless transition, the energy may be propagated along the close packed directions of the crystal to form separated vacancy pairs which then may trap charge. This is the mechanism for the efficient production of F-centers in the alkali halides with relatively low energy photons or during ionization. This method is not effective for calcium fluoride because the closed packed directions are not present in its crystalline form. The mechanism is less effective in magnesium fluoride than in the alkali halides.

The important point which is made here is that the species which are responsible for the radiation effects in these materials are not formed directly, in general, under the conditions in the TFTR. Their formation and trapping in the crystal lattice is mediated by the presence of other species and by the condition of the crystal lattice. Thus, the production rate of the F-band varied from 1.5 to 6% of the calculated number of ionizations during irradiation with either gamma rays or 21 MeV deuterons in the experiments performed many years ago in This Laboratory. Despite the low efficiency of this process, it exceeded by far the rate of vacancy production by displacement, and thus the rate was dependent on the ionization. Associated with the formation of vacancies which are stabilized by the trapping of charge, there is a physical expansion which is close to the volume which would have been preempted by the lattice point had an ion been present.^{66,63} The worst experience which has occurred with lithium fluoride has been the aggregation of defects in the cleavage directions of the crystal with subsequent massive disintegration.^{67,64} However, this was observed in thermal neutron reactors where lithium is lost by nuclear fissioning and free fluorine segregated in the crystal.

Although calcium fluoride was among the first materials in which radiation effects were observed, having been noted by one of Humphrey Davies' assistants,⁶⁸ relatively less is known about it. The usual method of producing F-centers in calcium fluoride is to color it additively, but these centers have been introduced at low temperature by irradiation. They do not appear to accumulate at room temperature.⁶² However, there is no information for the dose rates which will be encountered in the TFTR. No information about dimensional changes was found. F-centers have been produced by high energy electrons (1 MeV) at room temperature, but no information about their production with lower energy radiation was encountered.

The information on magnesium fluoride⁶² may be summarized briefly for present purposes as the interplay of two effects: the freezing in of the centers at very low temperature, and the diffusion of the positive and negative components of the complementary centers at higher temperatures. Thus, at low temperatures close pairs are formed which anneal readily on heating, but at high temperature more stable centers are formed because the complementary centers have diffused away from each other. At still higher temperatures the diffusion is rapid enough so that the trapped centers then

Fig. 22. The dilatation of magnesium fluoride on bombardment with doubly charged 160 keV neon ions: triangles, first run; arrowheads, second run. Apices pointed upward indicate expansion; downward, contraction.

scattered atoms. Since neon has the mean atomic mass of magnesium fluoride, the effect of the neon ions should be the same as that for scattered magnesium and fluorine atoms. The problem is that the neon ions all have the same energy, but the magnesium and fluorine atoms scattered by neutrons of any energy have all energies from nil to about 0.18 times the energy of the neutrons, and are nearly equally distributed over this energy range. Thus, for the comparison of the ion bombardment effect with the neutron effect, it is necessary to construct a yield function which will give the dilatation as a function of neutron energy. This function can then be integrated from nil to 0.18 times the neutron energy. The ion yield function was assumed to be proportional to the fraction of the ion energy expended in scattering atoms as given by the LSS theory, since that gave approximately the correct result for the dilatation of vitreous silica. Over the range of energies E of interest, this yield function is fitted sufficiently precisely for our purposes by a function of the form:

$$y = (aE+b)^{-1} + c$$

where E is the energy and a , b , and c were calculated from three points over the range of interest as: 6.7421, 1.1421, and 0.0244 respectively. The remainder of the curve was adequately described by the above function except for a depression in the keV region, associated with the threshold energy for displacement of an atom and which becomes significant when the threshold energy is high. The threshold energy for magnesium fluoride is not known, but may be in the range 5-30 eV. Fortunately, because of the high energies of the neutrons in the TFTR, this could hardly cause an error of more than 1%, and it was neglected. Note that this neglect would lead to a slight over-estimate. This function now has to be integrated over the energies of interest:

$$\delta_E = \int_0^E AEy dE / \int_0^E dE$$

Again, the integration should be from the threshold energy, not from nil; and the present simplification leads to a small over-estimate. This integration is over the energy of the scattered atom, but this is easily converted to the energy of the neutron $\mathcal{E}$ from the formula:

$$E = \gamma \mathcal{E} = 0.177 \mathcal{E};$$

and the final result becomes,

$$\delta_{\mathcal{E}} = A[2.163 \times 10^{-3} \mathcal{E} + 0.1483 - (0.1418/\mathcal{E}) \ln(1.045 \mathcal{E} + 1)],$$

where A is the dilatation yield per unit energy of the scattered atoms. This quantity can be evaluated from the ion bombardment data by the formula

$$\delta_E = AEY.$$

The ion bombardment data show that the dilatation is declining from the beginning of the bombardment. The constant required here is the initial linear yield, and this is obtained from the formula based on Novick's law,

described above. The dilatation which would have been obtained had the rate been linear with the initial slope is

$$\delta_L = \delta / (1 - 230.96)$$

and the converse, given the linear dilatation, the observed dilatation is:

$$\delta = \delta_L / (1 + 230.96 \delta_L).$$

The data now are: at 0.32 MeV where the LSS nuclear energy is 0.31 of the total energy, after a bombardment of $400 \mu\text{C}/\text{cm}^2$, the observed dilatation is 9.7×10^{-4} . The linear dilatation is thus 1.25×10^{-3} , and it has occurred in a depth of 0.49 μ . Thus, in the equation $A = \delta_E / EY$ the value of A becomes 2.46×10^{-22} and the neutron dilatation yield function becomes:

$$\delta_E = 2.46 \times 10^{-24} [0.2163 E + 14.83 - (14.2/E) \ln (1.045 E + 1)].$$

This has to be multiplied by the neutron scattering cross section and the number of atoms/cm³ and integrated over the neutron spectrum. The cross sections which were used were taken from the total cross sections (BNL 325) neglecting some of the prominent resonances in the intermediate energy region. The curve for magnesium and for fluorine are so nearly the same that a single curve sufficed and is shown in Fig. 23. The calculations were made with the same code used for the vitreous silica calculations, replacing the yield function and the cross section functions with the present ones. The result for the dilation per pulse was 1.5×10^{-10} . Thus, for the initial condition of 4000 pulses, the dilatation should be 6×10^{-7} and for the 6-fold specification it is 3.6×10^{-6} . This may be compared to the thermal dilatation which is reported to be $3.3 \times 10^{-5}/^\circ\text{C}$.

The behavior of the magnesium fluoride appears to be similar to the behavior which was found long ago in This Laboratory for lithium fluoride: radiation causes the introduction of F- and other centers which cause an expansion. The problem with the above calculation is that the centers are introduced by ionization as well as by displacement, hence the assumptions in calculating the neutron effect from the ion bombardment data may be faulty in this regard. However, the efficiency for production of centers by ionization in magnesium fluoride, according to Sibley, is much lower than it is for lithium fluoride. If the non-nuclear or ionization component of the ion energy dissipation contributes to the dilatation and to the introduction of centers, the constant A which has been calculated here would be smaller, but then the effect of the high energy neutrons compared to the neon ions would be greater and more than compensate for the reduction in the value of A , hence the neutron yield would be greater than calculated. It would be difficult to imagine that this effect would be greater than several-fold, hence the dilatation effect should still be negligible in reference to mechanical problems. Except for this matter of the contribution of the ionization, all the other components of the calculation should have given an overestimate. Hence, the conclusions about the mechanical problems seem quite secure.

4. Optical Absorption of Magnesium Fluoride: Ion Bombardment and Neutron Irradiation. After the ion bombardments were completed, some of

Fig. 23. The neutron scattering cross sections used in estimating the effect of neutrons on magnesium fluoride.

the samples were set face down on molten wax to protect the bombarded surface, and the metalizing which had been placed on the back surface to permit the measurements utilized to calculate the dilatation was removed with dilute sodium hydroxide solution. The sample plate was then removed from the wax and cleaned, and the relative reflectivity was determined for both the irradiated and the unirradiated portions of the surface. The reflectivities are shown in Fig. 24 and the ratio of the reflectivities in Fig. 25. It is not clear whether the rise in the reflectivity on irradiation is caused by a change in the dispersion or by the deposition of a superficial coating during the bombardment. The ratio of the reflectivities shows four small nearly equally spaced peaks, and one peak which would be superfluous to those which would be caused by interference in a surface layer. The four widely spaced peaks correspond to a layer of the thickness of the anticipated range of the neon ions in magnesium fluoride, 0.49μ . The superfluous peak is close to that given by Sibley for a satellite of the F-peak, possibly an M-peak. This would be suggestive of a very high F-peak in this sample. The reflectivity peaks correspond to about a 1.5% change in reflectivity, assumed to be an increase, which corresponds to an increase of 1.8×10^{-3} in refractive index. Such a change seems an appropriate magnitude when compared with the results found in This Laboratory for lithium fluoride.⁶³ A transmission curve was obtained for this plate, and it showed a small decrease in transmission at 0.258μ , about 2%, just where Sibley places the F-peak. Since the layer thickness is 0.49μ , this corresponds to an optical density of $17.6/\text{mm}$. Since the linear dilatation for the 6-fold condition is 3.6×10^{-6} , the corresponding optical density would be $0.036/\text{mm}$ which would correspond to an 8.7% decrease in transmission at the peak of the F-band in a 1 mm thick section.

This estimate for the magnitude of the F-band absorption is a very crude one because the precision of measurement of an effect in so thin a layer is low. However, if the effect were as much as 50% greater, this could easily have been seen. Thus in a typical window, which might be 4 to 5 mm thick, an appreciable absorption is anticipated in the region of the F-band. Exactly what this might be would be difficult to predict from the present data because the yield is temperature dependent, as described above. Further complications may arise from the thermal pulse and cause a peculiar depth distribution. Additional complications may arise from the absorption of light in the absorption bands, as this may make the centers mobile and cause bleaching.

If the absorption will be significant, thermal annealing tests should be made.

In addition to the introduction of absorption at the F-band, it would be anticipated that some absorption will be encountered near the absorption edge, as a variety of complementary and other centers usually have their absorptions there.

5. Heavy Ion Extended Ion Bombardment. Thick plates of magnesium fluoride were bombarded with 160 keV Ne^{++} ions and with 140 keV Ne^{+} ions to much greater incident charge than was possible for the thin cantilever plates. Neon was trapped, segregated, and formed blisters at these doses.

Fig. 24. The relative reflectivities of magnesium fluoride (dashed) and of the same sample bombarded with doubly charged 160 keV neon ions, $0.28 \times 10^{15}/\text{cm}^2$.

Fig. 25. Ratio of the reflectivities of the two curves shown in Fig. 24. The small irregularities are caused by the irregularities of the data and the sectional smoothing operation performed on them.

The effects at the lower incident charge values used in the cantilever plate bombardments is not known. However, the total effects calculated above for particulate bombardment were so small, it is not anticipated that the conclusion these will be negligible for the TFTR is to be changed.

6. Ionization Effects. The effects of ionization on magnesium fluoride were determined by electron bombardment of a thin plate mounted as a cantilever to determine the dilatation and by bombarding small areas of a 1/8 in. thick plate with electrons to determine effects at large dose levels. The latter results are presented first.

The surface of the plate was prepared by coating with a thin gold layer (160 Å) to provide a conducting surface to remove charge. This coating was quite transparent with a blue tinge, but it was electrically conducting. The plate was placed in a stainless steel holder with a viewing aperture beneath and covered with an aperture plate possessing 4 rectangular openings 2 mm square which could be covered individually with stainless steel cover plates. The scheme was to bombard the assembly with all of the apertures uncovered and then to cover the apertures in turn when they had received the desired dose. Two plates were bombarded in this manner, the first with electrons having a residual energy (i.e., beyond that dissipated in the gold film) of 26.84 keV, hence a range of 4 μ; and the second with electrons having a residual energy of 18.08 keV, hence a residual range of 2 μ. The first 3 bombardments at the higher energy were for the respective cumulative doses 2×10^4 , 2.2×10^5 , and 2×10^6 megaR. At the last, the two areas still exposed had turned black, hence further bombardment was discontinued. The doses for the second plate were 1×10^4 , 3×10^4 , 1×10^5 , and 3×10^5 megaR respectively. The first bombardments were performed with successively increased currents in order to reach the desired doses in a reasonable time; they were 20, 50 and 90 μA, respectively. The second plate was bombarded at 20 μA since it was not intended to reach such high doses, and because the black color of the first plate indicated the formation of colloid centers (which are formed more readily at higher temperature). The bands produced typically are an F-band, peak at 0.26 μ, and a subsidiary band (which may be an M-band) centered at 0.37 μ. The band found for the second area of the first plate was a broad one centered at 0.3 μ, again suggesting heating had occurred. Also, the optical density at the peak of this band was several times as great as that of the last area of the second plate, which had received a greater dose; and since the band was broader, the number of centers involved must have been even greater. This, too, indicated that the first plate had been heated, because the efficiency of center production in magnesium fluoride has been reported to increase when the temperature is increased in this temperature range.

Other evidence for heating of the first plate was a change in the color and intensity of luminescence during irradiation at the higher currents as the irradiation progressed. When the plate was examined under the microscope after irradiation, it was observed that disintegration of the surface had begun for the two longer irradiations. The bombarded areas were elevated, and the elevations were greater by a factor of 7 than would have been predicted from the cantilever experiment, even if the whole volume expansion had been experienced vertically.

The optical absorption data are given in Table VI and are shown in Fig. 26.

7. Electron Bombardment Heating. No value for the thermal conductivity of magnesium fluoride could be found. However, typical values for this class of materials are 0.02 cal/cm deg. From the formula for the spherical diffusion of heat in the steady state, it is apparent that the maximum difference in temperature between the bombarded area and the rest of the plate was less than several degrees at the greatest energy input used here. Further, the maximum temperature rise within the cubic volume of the aperture dimension was less than 6 deg. Thus, heating could not have been local heating; the whole assembly of holder, sample, aperture plate, etc. must have been heated. This whole assembly weighed about 10 g and was mainly stainless steel. It sat on a glass window with which it did not make good thermal contact and was held in place in a cylindrical portion of the flange by 4 thin spring clips which would have made point contacts. Since the specific heat of stainless steel is about 0.11 cal/g deg, it would have risen about 18 deg/min during the last bombardment of the first plate if no heat were being conducted from the assembly. The actual temperature was estimated by placing a thin sliver of Woods metal (melting point determined to be 71 °C) beneath a plate in the assembly, bombarding it, and determining the time required to observe melting at currents of 65 and 90 μ A with 27.5 keV electrons. This was 10 and 11.5 min respectively. The problem is a Newton's law problem whose solution is an exponential rise in temperature to some final temperature T_m .

$$T = T_m[1 - \exp(-\alpha t)]$$

The equation has two constants, the final temperature and the conduction constant α . These constants can be evaluated from the initial condition that when no temperature rise has yet occurred, all of the heat must be used to raise the temperature, the quantity being given by the mass of the assembly and the specific heat; and the second constant from the time to observe melting of the Woods metal. It is readily seen from these data that if the time to observe melting is greater than a few minutes, the final temperature is less than a few degrees above the melting temperature of the Woods metal. The question then is: why did it take as much as 10-12 min to melt the Woods metal? The obvious reason is that the assembly is not a unitary one. The upper member, the aperture plate is not in good thermal contact with the rest of the assembly. It weighs 5.2 g. By the same mode of calculation, it can be shown that within 2 min it is within 5 deg of the maximum temperature. In 3 min it is within 1.8 deg of the maximum temperature. Thus, it would take several minutes to communicate its temperature to the lower plate on which the sample is mounted. The sample is also in poor thermal contact with the lower stainless steel member, but it is definitely in contact with it rather than with the upper member, the aperture plate. Since the sample rested on the Woods metal, this must also have rendered the sample in poorer contact with the lower stainless steel member. Since each of these members in turn must have required several minutes to reach the melting temperature, the 10-12 min time is accounted for. The conclusion is that the aperture plate may have been as much as 40-50 deg above the temperature of the sample mounting plate, the lower

Table VI. Bombardment of Areas of First Plate (4210)
with 26.84 keV Electrons (Range 4 μ)

Areas	1	2	3 & 4
Current (μ A)	20	50	90
Dose (megaR)	2×10^4	2.2×10^5	2×10^6
Estimated maximum temperature ($^{\circ}$ C)	<35	54	78
Gold coating	Intact	Intact	Partially lifted
Surface	Intact	Some small circular fractures, some crossed	Small portions ejected
Appearance (after stripping gold coat) ^a		Light tan	Black, irregular
Elevation (μ)	Not observable	~ 0.027	~ 0.4
Transmission at peak (0.3 μ)(%)	64	2.8	nil
O.D. above surroundings ^b (for 4 μ thickness)	0.04	1.39	

^aGold stripped by mercury contact.

^bTransmission near bombarded areas 69%; absorption caused by x rays,
probably mainly from the stainless steel aperture plate.

Fig. 26. The optical absorbance of electron bombarded magnesium fluoride (the second plate): circles, at 0.26 μ (F-band peak); diamonds at 0.37 μ (M-band peak?); and squares, at 0.4 μ .

member, but the sample cannot have been more than 50 deg above the temperature of the flange. To this would have to be added the temperature rise in the bombarded area, perhaps 5 deg. Thus the temperature of the sample may have been 75-85 °C during the latter part of the bombardment of the first plate. The conduction constant was calculated as 0.01, and from this it may be concluded that the temperature of the second plate may have reached 35 °C during the latter part of its bombardment; and since the time for this bombardment was about 20 min, the temperature would have been rising during much of it. Since the increase in optical density of the F-peak in the bombardments of the second plate is greater than linear with dose, it is apparent that the efficiency of production of centers in the magnesium fluoride is a sensitive increasing function of temperature in this temperature range. This is in accord with the discussion of the production of centers in this material presented above.⁶²

8. Ionization Dilatation. A thin plate was coated with 238 Å of aluminum on each face, on the one to serve as the conducting coating for the cantilever-capacitor method of determining dilatation from the deflection of a cantilever, and on the other face to conduct the charge in electron bombardment. The temperature of the plate during irradiation is not known, but these irradiations are conducted at very low currents, 6.5 µA, and the energy was only 16.2 keV. The dilatation calculated as a function of dose (megaR) is shown in Fig. 27. The gross features of the data are presented by the equation:

$$\delta = (1.35 \times 10^{-4} + 8.4 \times 10^{-10} D) [1 - \exp(-3.33 \times 10^{-5} D)]$$

where D is the dose in megaR (83×10^6 ergs/g), which is rather odd because it is a growth curve to an increasing saturation value, indicating a multiplicity of processes are occurring. Another feature of the data is a decrease in dilatation when irradiation is interrupted. This could be caused by aggregation, annihilation, or bleaching of centers.

At the end of the curve shown in Fig. 27, the expansion is about 5×10^{-4} after only 5×10^5 megaR. At the surface this would be reached in about 1200 pulses, at the 1 µ level in about 5000 pulses. The expansion is that which would occur in a 15 deg temperature rise. The lamellar differential stress would be about 2600 psi. This stress would also be contributed radially across the seal area, to which would have to be added the seal stress. There is no indication of any saturation of the effect. The effects should be more severe at a higher temperature.

The extreme effects of temperature are seen when comparing these data with the elevations of the areas produced when the thick plates were irradiated. This is discussed above. It was seen when the 3×10^5 megaR area of the second thick plate (2 µ range electrons) was compared with the 2×10^5 megaR area of the first thick plate (4 µ range electrons). For the last areas of the first plate (2×10^6 megaR bombarded at 90 µA) there were ejected areas and other signs of surface disintegration.

Fig. 27. The dilatation of magnesium fluoride on bombardment with 16.2 keV electrons: the steps occurred when the sample stood unbombarded overnight.

F. Seal Materials

1. General. When this evaluation was begun, application of the windows with gasket arrangements were mentioned. Later it was decided that the windows were to be attached with sealing glasses of the kind employed in the electronics industry. These are low melting glass or glass-crystalline compositions whose composition is adjusted to meet thermal expansion requirements for the materials with which they are to be used. They may be borosilicate flint glasses with oxide additions. These compositions are generally regarded as proprietary information.

The radiation behavior of these materials is very complex, much more complex than that exhibited by the simple compounds used for the windows themselves.⁶⁹ Such materials have been under investigation in This Laboratory for some years for other applications in the energy programs.^{48,70,71} It has become clear that they cannot be evaluated by any simple means. Although some studies have been made at temperatures other than near room temperature,⁷² there do not appear to be any studies which would give information about the radiation behavior of these materials under the thermal conditions which will be experienced in the TFTR. It was planned to determine the compositions of the specific materials planned for the seal glasses as the first step in their radiation evaluation when the evaluation project was halted.

2. Radiation Behavior of Silicate Glasses. Evidence for all of the behaviors described above for silica, oxides, and alkali halides is observed in the silicate glasses. There are elements of expansion and contraction which occur at different rates and saturate at different points. Centers are formed, valence changes occur, mobile species form. A typical radiation behavior for a silicate glass is to show expansion for a period, and then contraction occurs to yield a net contraction which eventually saturates. For some compositions, the expansions and contraction nearly balance, in others, one dominates. Commonly, the alkali becomes mobile even at room temperature.⁷³ When it reaches the surface it combines with atmospheric moisture to give alkali hydroxides which are deliquescent, and thus liquid droplets form on the surface. These eventually combine with carbon dioxide from the atmosphere to give a crystalline deposit on the glass. This alkali migration persists after irradiation ceases. Many of the glasses darken on irradiation, some even with ultraviolet light from the sun; thus, the purple color of old white bottle glass.⁷⁴⁻⁷⁷ This solarization of glass is one of the earliest reported radiation effects in solids. A more specific effect is that of protons on lead glasses.⁷⁸ The behavior toward different kinds of radiation may be quite different. Among the observations in This Laboratory was that of a glass which showed only a small dimensional change on ion bombardment, but showed large progressive contraction on electron bombardment. Another glass showed significant dimensional changes, as described above, during ion bombardment and little change on electron bombardment.

3. Thermal Changes of Irradiated Silicate Glasses. Just as the radiation behavior shows great variations, so, too, do the annealing behaviors. The radiation-induced coloration of soda lime glass fades even at room temperature. Other radiation-induced changes begin to decline during

irradiation well below 200 °C in crown glass. For most of the glasses they diminish to nil by 400 °C.⁷² However, it should not be assumed that all of the sealing glasses will behave in this manner, because some of them contain oxide additions which may possess much more stable radiation effects. The internal stress which may occur in such materials has not been investigated.

4. Recommendations. Since the sealing glasses have not been evaluated for their radiation behavior, the best procedure would be to protect them from the radiation. The simplest procedure would be to design the joint so that it can be shadowed from the soft radiation by a metal sleeve or shield. This would also serve to protect the seal from the thermal pulse.

III. Summaries

1. Vitreous Silica. Irradiation of "pure" vitreous silica (e.g., Suprasil) causes the material to contract; i.e., it causes a negative dilatation. Over the region of interest for the TFTR this change is linear for neutron irradiation, and it varies as about the $2/3$ power of dose for ionizing radiation. Radiation also causes a stress relaxation so that there will be permanent deformations with relatively low final stresses in the plate eventually. In some plates fracturing was observed during the course of this process during ion bombardment, but attempts to obtain such fracturing for the conditions which it was thought would maintain for the TFTR were unsuccessful. However, the phenomena are not completely understood, and although such fracturing is not currently anticipated for TFTR service, its occurrence remains a possibility. Since no tests or evaluations of the seals were made, the several effects on them are not known.

Vitreous silica transmits light below 0.2μ , but after irradiation absorption becomes great up to about 0.33μ if the material is "pure," and there is another much smaller absorption band at about 0.63μ . There is a faint blue luminescence on irradiation which was measured. After considerable irradiation the luminescence increases markedly. However, this luminescence was not measured.

Because of the low thermal conductivity of vitreous silica, the temperature rise at the face exposed to the plasma will be considerable, 60 to 180 deg by the end of the pulse. Because of the radiation-induced stress relaxation it is anticipated that the effects seen in the plate will be complex, eventually resulting in a distribution of permanent negative dilatation in the plate. This is discussed in detail in the section on vitreous silica.

2. Crystal Quartz. Pure crystal quartz appears to be quite unaffected by ionization. Neutron irradiation causes an expansion which is aeolotropic. The total effect is small, about as great as that in vitreous silica for the exposures anticipated in the TFTR. Although radiation-induced stress relaxation is seen in crystal quartz when it has become considerably disordered, it is not anticipated at the small dose which will be seen in the TFTR. The neutron-induced dilatation is anticipated as being 1×10^{-4} to 5×10^{-4} , comparable to that observed in a 3 to 11 deg rise in temperature. The thermal pulse will be under 50 deg, much smaller than for vitreous silica; but because of the much greater thermal expansion, it will generate much larger stresses, 3000-9000 psi. These are significant stresses, hence it may be desirable to move the window from the tank wall.

3. Sapphire. Mechanical changes in sapphire on irradiation are considered to be small. All sapphire which has been irradiated in This Laboratory was observed to color in the visible. Optical absorption bands observed in the ultraviolet have been around 0.2 and 0.24μ , but tails from these are observed nearly to the visible. All of the material examined in This Laboratory luminesced at the ruby red line (0.69μ) with side bands of variable proportions. One sample showed a blue luminescence centered at about 0.42μ . This was the most intense luminescence; and if located in

the visible, a plate at the tank wall would be 1.5 to 3% the brightness of a typical 100 W incandescent lamp. The thermal stresses caused by the pulse heating are very high for a plate on the tank wall because the modulus of rigidity is so large. These stresses may range to 11,000 psi.

4. Zinc Selenide. As well as could be determined, the effects of irradiation on this material will not be significant for infrared measurements. At the tank wall, the thermal stresses might range to 4,800 psi, which may be severe, for zinc selenide fractures easily. Special concern should be given to fabrication and testing of these windows. If placed on a pipe extended from the tank wall, the thermal pulse stresses should be negligible.

5. Fluorides. All of the fluorides: lithium fluoride, magnesium fluoride, and calcium fluoride will develop an F-band and other optical absorption bands in the ultraviolet and visible. Of these, lithium fluoride is the most sensitive and calcium fluoride, the least. Lithium fluoride would be objectionable also because it flows plastically under relatively low stress forming dislocations and twin zones. When a twin zone is formed, the surface is deformed with the emplacement of a strip oriented at a small angle to the original surface; and the contour may be altered additionally. There is little data on calcium fluoride and no investigation of it was requested. Dimensional changes and optical absorption of the magnesium fluoride were determined. Radiation effects are more severe when the temperature is raised. For neutron irradiation at the tank wall, if it is maintained near room temperature, the neutron-induced dilatation is an order of magnitude less than the thermal dilatation per degree. The effect of the ionization at the tank wall, even at room temperature, would be objectionable. After only 5×10^5 megaR, the ionization dilatation would be 5×10^{-4} which would correspond to the dilatation observed in a 15 deg temperature rise and cause a differential stress of some 2,500 psi. A plate at the tank wall and at the tank wall temperature may develop surface blackening and surface destruction. It is recommended that this material be used only on a long tubulation which can be cooled during exposure to radiation from the plasma.

6. Seal Materials. The materials planned for these are proprietary glass compositions whose radiation behavior was not evaluated. It is therefore recommended that the seals be shadowed or otherwise protected from the radiation, particularly the soft electromagnetic radiation. Dimensional changes, negative or positive, comparable to those predicted for vitreous silica, may be anticipated from the neutron and hard gamma radiation, but some of this should be annealed by the baking procedures. Differential stresses of hundreds of psi arising from these changes should be anticipated for units mounted at the tank wall.

APPENDIX I

- A. Grades of Vitreous Silica
- B. Correspondence relative to the acquisition of crystal quartz.
- C. Specifications for crystal quartz.

A. Classification of Commercially Available Vitreous Silicas

Type	Source	Melting	Metallic impurity ^b (ppm)	OH, etc. ^a	Cl	Examples
I	Quartz crystal powder	Electric furnace	Like quartz mainly Al 30-100 Na 4	Nil	Nil	I.R. Vitreosil, Infrasil, Purasil
II	Quartz crystal powder	Flame	Less than type I	0.015 - 0.04 wt. %	Nil	O.G. and O.H. Vitreosil, Herasil, Homosil, Ultrasil
III	Vapor phase hydrolysis of pure silicon compounds e.g., SiCl ₄	Flame	Nil	0.1 wt. %	If from SiCl ₄ ~ 50 ppm	Corning 7940, Spectrosil, Suprasil
IV	Oxidizing pure silicon compounds	Water free flame or electric furnace	Nil	Nil	Several hundred ppm	Corning 7943 Spectrosil WF

^aAll vitreous silica which contains hydroxyl exhibits strong absorption at 2.73 μ by the Si-OH stretching vibration and weaker bands at 2.6, 2.22, and 1.38 μ , among others, identified as overtones or combinations involving Si-O vibrations.

^bIncreasing metallic impurities shift the ultra-violet 'cut-off' at ~ 0.18 μ to longer wavelengths. Thus, types III and IV have the best ultra-violet transmissions.

^cAll vitreous silicas made from quartz crystal by either electric fusion or flame fusion exhibit absorption at 0.24 μ , and associated with this are fluorescence emission bands at 0.28 and 0.39 μ ; the latter is visibly excited by a 0.254 μ mercury source. Both this fluorescence and the 0.24 μ absorption are removed by an oxidising heat-treatment. In fused quartz type I containing no hydroxyl, removal is very slow and is governed by diffusion of oxygen through the solid. For fused quartz containing hydroxyl, oxidation is much faster and occurs by the reaction

thus, its rate is governed by diffusion and removal of hydrogen. Garino-Canina showed that the 0.240 μ absorption and the 0.39 μ fluorescence were also removed by electrolysis at 1080°C under a potential gradient of ~1000 V/cm. Absorption and fluorescence occur simultaneously and require the silica to be in a chemically reduced state. There is some doubt about the nature of the centres. They re-occur when types I and II vitreous silicas, fully oxidised by heat-treatment or electrolysis, are reduced by heating in hydrogen. Types III and IV do not show fluorescence or 0.24 μ absorption when manufactured, and they are not introduced by hydrogen treatment. The presence of metallic impurities seems essential; germanium and aluminium have been suggested.

^dTypes I and II vitreous silicas when subjected to x-ray, γ -ray, or nuclear pile irradiation are coloured brown-violet and show three absorption bands at about 0.55, 0.30, and at a lower wavelength given variously as 0.221, 0.220, 0.223, and 0.215 μ . Type II materials, because of metallic impurity or greater hydroxyl content, or both, show less optical absorption than similarly irradiated type I silicas. In types III and IV synthetic vitreous silicas the 0.55 and 0.30 μ bands are absent, but they show a 0.215 μ absorption. Lell ascribed coloration to the simultaneous presence of aluminium and alkali impurities. Type IV vitreous silica, shows a much higher 0.215 μ absorption. The 0.215 μ absorption in type IV synthetic silica is reduced progressively as hydroxyl is introduced.

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS
BOULDER LABORATORIES
BOULDER, COLORADO

CRYOGENIC ENGINEERING LABORATORY
CENTRAL RADIO PROPAGATION LABORATORY
RADIO STANDARDS LABORATORY

December 12, 1958

IN REPLY
REFER TO FILE NO.

84.20

AIR MAIL

Dr. William Primak
Chemistry Division
Argonne National Laboratory
Box 299
Lemont, Illinois

Dear Dr. Primak:

Re your letters Nov. 11 and Nov. 28, and yours of
Nov. 28 to J. B. Saunders

Very little really good optical grade quartz is to be found in the hands of commercial quartz oscillator manufacturers. From the enclosed specifications you will see that there are two recognized grades of oscillator quartz and that optical grade quartz is to be selected from the best portion of Grade I. The amount of optical grade probably will not generally exceed one per cent of the total. Most manufacturers should be able to detect optical twinning and avoid it in cutting. However, it should be remembered that the more sensitive the testing equipment, the more imperfections there will be seen. The equipment specified in the enclosed Raw Quartz Specifications was chosen to yield a considerable quantity of relatively good quartz and not be so sensitive that practically all quartz would fail to pass. Further it is considerably more difficult to see imperfections in ground specimens than in polished or in uncut specimens even when the liquid is a nearly perfect match for the quartz, probably due to air film retained in the abrasive grain pits. If in addition the liquid does not match too well, which frequently is the case in oscillator unit manufacturing plants (many use a mineral oil with $n_D =$ about 1.48), it would be easy to miss seeing some twinning. This may account for the twinning found in your specimens. As stated in our letter of August 9, 1957, we did not make any careful examination of your specimens for imperfections but only measured the orientation. Casual inspection of one or two of the larger pieces in the oil bath (HB-40, $n_D=1.54$) did not disclose any optical twinning, and neither did a light etch in HF. I suspect you might get better quality quartz if you were to have your specimens prepared by one of

the manufacturers of optical equipment such as: Bausch & Lomb Optical Co., 635 St. Paul St., Rochester 2, New York; O. C. Rudolph & Sons, P. O. Box 446, Caldwell, N. J.; Crystal Optics Co., Dr. Karl Lambrecht, Pres., 3618 N. Greenview Avenue, Chicago 3, Ill., or any others you may know.

In regard to your question about the etching method to detect optical and/or electrical twinning, we know of no other feasible method of examining for electrical twinning. While it is possible in some cases that the twinning might not reach the surface in pieces of the size under consideration, it is highly improbable that it will not do so, as this type of twinning usually is of considerable extent when it occurs in otherwise good quartz. If you decide to purchase quartz and have it cut I suggest that you make it a condition of the purchase that it be tested by the U. S. Testing Laboratory, 1415 Park Avenue, Hoboken, N. J., and that you contact Mr. Joseph Zito and tell him just what you want. Mr. Zito was one of the key men in our Quartz Testing Laboratory at Washington, D. C., and when the work of testing quartz was transferred, under contract, to U. S. Testing Laboratory, Mr. Zito took charge of their quartz testing department. The last we bought was from Murray American Corporation, 15 Commerce Street, Chatham, N. J. We paid a little over 50 dollars per pound for 2000/3000g size with no extra charge for sending it through U. S. Testing. Also, a recent letter from the Diamond Drill Carbon Co. (B. Rhodes), 244 Madison Avenue, New York 16, N. Y., states that they now have some large size good quality quartz on hand. The 1000/2000g size was the smallest size from which we could satisfactorily cut precisely oriented cubes 1-1/2x1-1/2x1-1/2 inches (finished size). We also would suggest that you buy considerably more than just enough, since the commercial testing will take no account of electrical twinning and this has to be allowed for.

It is now possible under a recently enacted law, for this bureau to make some types of tests for the general public as well as for government agencies, such as AEC, on a reimbursable basis, which in the past we were not allowed to do. So, it might be possible, if you so desire, to work out a way for our quartz crystal laboratory to prepare and test samples in such a way as to insure that they are free from defects and have the correct orientation. Also, it might be possible to do some work on a joint project basis if our interests are found to have sufficient in common. We are interested in the properties of quartz, primarily those having a bearing on its uses for frequency control. This leads to

Dr. William Primak

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December 12, 1958

interest in structural and other imperfections, natural or induced. We have developed an optical method of testing for residual strains which is perhaps several orders more sensitive than the usual oil bath and polaroids and which is very useful in connection with evaluating the quality of synthetic quartz as affected by variations of growth conditions. It might be interesting to examine and photograph bombarded specimens before and after (provided they are not radioactive) in this equipment. As set up at the present time, it will accept specimens up to about 2mm thick, cut normal to the optic axis and polished.

Very truly yours,

A handwritten signature in cursive script, reading "F. P. Phelps". The signature is written in dark ink and is positioned below the typed name.

F. P. Phelps, Physicist
In Charge, Quartz Crystal Laboratory
Radio Broadcast Services Section
Radio Standards Laboratory

Enclosure: Raw Quartz specification

Raw Quartz
NBS Specification 941C
As Revised 26 June 1951

MIL-C-15729A

18 OCTOBER 1951

**SUPERSEDING
MIL-C-15729(SHIPS)
1 October 1950**

MILITARY SPECIFICATION

CRYSTALS, QUARTZ, RAW

This specification was approved by the Departments of the Army, the Navy, and the Air Force for use of procurement services of the respective Departments.

1. SCOPE

1.1 Scope.—This specification covers raw quartz crystals for optical and electronic use.

1.2 Classification.—Quartz crystals furnished under this specification shall be classed as faced (F) or unfaced (U), and shall be of one or more of the grades hereinafter designated. (See 3.2.)

2. APPLICABLE SPECIFICATIONS, STANDARDS, DRAWINGS, AND PUBLICATIONS

2.1 The following specification and standard, of the issue in effect on date of invitation for bids, forms a part of this specification:

SPECIFICATIONS

NAVY DEPARTMENT

General Specifications for Inspection of Material.

STANDARDS

MILITARY

MIL-STD-129—Marking of Shipments.

(Copies of specifications, standards, and drawings required by contractors in connection with specific procurement functions should be obtained from the procuring agency or as directed by the contracting officer.)

3. REQUIREMENTS

3.1 Definitions.—For purposes of this specification, the definitions in 3.1.1 to 3.1.7.1, inclusive, shall apply.

3.1.1 Optical quartz.—Optical quartz shall, in general, consist of crystals 500 grams and over in weight, and shall have the following percentage limits of usability: 45 to 60 and 60 to 100. It shall, in general, surpass oscillator quartz in quality, and in addition shall be, as far as practicable, free from strain and give good definition when used with monochromatic light.

3.1.2 Facing.

3.1.2.1 Faced crystals. — Faced crystals are crystals each of which must have at least one identifiable natural face; this may be a side (prism) face or a cap (pyramid) face. Faced material 100 to 200 grams in weight shall have at least one identifiable natural face with an area not less than $\frac{1}{4}$ square inch. Faced material 200 grams and over in weight shall have at least one identifiable natural face with an area not less than $\frac{3}{4}$ square inch.

3.1.2.2 Unfaced crystals. — Unfaced material 200 grams and over in weight is that material which does not have an identifiable natural face with an area exceeding $\frac{3}{4}$ square inch.

3.1.3 Usable portion.—The term "usable portion", as applied to crystals weighing less than 5,000 grams, shall be defined as the

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largest single continuous volume conforming to the requirements of a given grade. This term, as applied to crystals weighing 5,000 grams or more, shall be defined as the total usable volume conforming to the requirements of a given grade; this total usable volume may be the sum of several single volumes conforming to one grade in a single crystal. In determining the usable portion of irregularly shaped crystals, the size and general form of the individual crystal must be taken into consideration in establishing the usability. Those portions terminating in a thin section from which a quartz plate of $\frac{1}{2}$ inch cross section cannot be cut, are considered defective in calculating the usable portion of crystals.

3.1.4 Optical defects.

3.1.4.1 Optical twinning.—Optical twinning is a detrimental defect readily discernible when the crystal is submerged in an oil bath and examined with polarized light. All strained and twinned volumes shall be considered defective, and such volumes shall be subtracted from the total volume of the crystal when estimating the usable portion.

3.1.4.2 Other defects.—Other defects are all those that can ordinarily be detected when a crystal is submerged in an oil bath and examined by moderate arc-lamp illumination. (See 3.1.5 and 3.1.7.) Under these conditions, the defects will deflect some of the light and thereby become luminous and detectable.

3.1.5 Moderate arc-lamp illumination.—Moderate arc-lamp illumination shall be defined as the light furnished by a $4\frac{1}{2}$ ampere d.c. arc lamp such as that made by Bausch and Lomb and listed as catalog No. 31-33-81-02 and 31-33-81-03, or equal.

3.1.6 Polarized light.—Polarized light shall be defined as light derived from a type EH-4, 100-watt reflector flood, mercury vapor lamp, transmitted through the polarizing device on the inspection oil bath.

3.1.7 Oil bath.—The oil bath shall consist of a tank of satisfactory design and of sufficient size so that the crystal may be completely submerged in oil during examination. The tank shall be equipped with a polarizer and an analyzer which shall be adjustable in order to obtain maximum light extinction.

3.1.7.1 Inspection oil.—The oil in the bath shall be free from color (a yellow color absorbs the blue of the arc light, making it more difficult to pick up defects which scatter blue light) and shall have a refractive index as near as practicable to the refractive index of quartz.

3.2 Weight, grade, and classification.

3.2.1 Crystals weighing 200 grams or more.—Quartz crystals weighing 200 grams or more shall be graded as follows:

3.2.1.1 Grade 1.—Grade 1 quartz is quartz which, in the usable portion shall be free from all defects that can ordinarily be detected in an oil bath, when examined with polarized light and with moderate arc-lamp illumination. (See 3.1.5 to 3.1.7, incl.)

3.2.1.1.1 Classification.—Grade 1 quartz crystals shall be classified as faced (F) and unfaced (U), divided into percentage limits of usability, and designated as follows:

Designation	Limits of usability Percent
13 -----	30 to 45
14 -----	45 to 60
16 -----	60 to 100

The first figure in the designation indicates the grade; the second, the lower percentage limit of usability, except that the figure "4" is used to indicate 45 to 60 percent usability.

3.2.1.2 Grade 2.—Grade 2 quartz is quartz which does not meet the requirements of grade 1, but which in the usable portion shall be free from all defects that can ordinarily be detected in an oil bath when examined

with polarized light (see 3.1.6 and 3.1.7) and with moderate arc-lamp illumination, except that when examined with moderate arc-lamp illumination (see 3.1.5), the following inclusions are permitted in the usable portion:

- (a) Hard blue needles (all types, except when large or present in great numbers).
- (b) Soft blue needles (all types, except when present in great numbers).
- (c) Color (including color phantoms), provided the light absorption is not so great as to materially interfere with the examination.
- (d) Tyndall effect.
- (e) Scattered fine or small inclusions (often referred to as "specks" or "points").

3.2.1.2.1 Classification.—Grade 2 quartz crystals shall be classified as faced (F) and unfaced (U), divided into percentage limits of usability, and designated as follows:

Designation	Limits of usability Percent
23 -----	30 to 45
24 -----	45 to 60
26 -----	60 to 100

The first figure in the designation indicates the grade; the second, the lower percentage limit of usability, except that the figure "4" is used to indicate 45-60 percent usability.

3.2.2 Crystals weighing less than 200 grams but not less than 100 grams.—Each crystal weighing 100 to 200 grams shall have a median length of not less than 2 inches in a direction parallel to the optic axis and an average diameter of not less than 1 inch in a direction perpendicular to the optic axis. It shall be faced and shall have a continuous usable volume, comprising not less than 60 percent of its total volume, equal to or better than grade 2 material as specified in 3.2.1.2.

3.2.2.1 Classification.—Crystals weighing 100 to 200 grams shall be designated as follows:

Designation	Limits of usability Percent
L6 -----	60 to 100

The letter "L" indicates the grade of the crystals and the number "6" indicates the lower percentage limit of usability.

3.2.3 Minimum weight.—Crystals weighing less than 100 grams and unfaced crystals weighing less than 200 grams will not be acceptable under this specification.

3.2.4 Other grades.—No other grade of quartz will be acceptable under this specification.

4. SAMPLING, INSPECTION, AND TEST PROCEDURES

4.1 Inspection.—Each and every crystal shall be subjected to inspection to determine compliance with the applicable requirements of 3.2 to 3.2.4, inclusive. Any crystal failing to meet the applicable requirements shall be individually rejected. The inspection agency shall be as specified by the purchaser or its designee, or the bureau or service concerned.

4.1.1 Inspection procedures.—For Naval purchases, the general inspection procedures shall be in accordance with General Specifications for Inspection of Material.

5. PREPARATION FOR DELIVERY

5.1 Packaging by supplier.—Each box shall contain material of only one weight class.

5.1.1 Quartz crystals shall be packaged in wooden boxes of such construction as will withstand rough handling. Each crystal shall be suitably protected by padding to prevent damage by contact with other crystals or with the box itself. Crystals shall be packed sufficiently tight in the box to prevent shifting. Individual boxes may be of any size usual with the supplier of the material, but all boxes in any given shipment shall be of the same size, and acceptable for shipment by common carrier.

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5.2 Packaging and marking by inspection agency.—A crystal weight-class designation shall be marked on each box to indicate the weight-class of the crystals contained, as follows:

<i>Weight-class (in grams)</i>	<i>Crystal weight designation</i>
100 to 200 -----	1
200 to 300 -----	2
300 to 500 -----	3
500 to 700 -----	5
700 to 1,000 -----	7
1,000 to 2,000 -----	10
2,000 to 3,000 -----	20
3,000 to 4,000 -----	30
4,000 to 5,000 -----	40
5,000 to 7,000 -----	50
7,000 to 10,000 -----	70
10,000 and over -----	100

After grading and classifying, boxes shall be marked to indicate the contents, as follows, and in the order given: Weight-class, grade, percentage limit, facing, and serial box number (of that grade classification).

EXAMPLE: (a) 2-13F-9 indicates that the box so marked contains quartz crystals weighing not less than 200 grams but less than 300 grams of grade 1 quality, usability 30 to 45 percent, all faced material, and that this is the ninth box of that particular size and grade packed.

(b) 1-L6F-9 indicates that the box so marked contains quartz crystals weighing

not less than 100 grams but less than 200 grams of grade L quality, usability 60 to 100 percent, all faced material, and that this is the ninth box of that particular size and grade packed.

5.3 Marking.—In addition to any special marking required by the contract or order, packages and shipping containers shall be marked in accordance with Standard MIL-STD-129.

6. NOTES

6.1 Rejected crystals.—Rejected crystals may be packed together in the same case and need not be marked for cause of rejection.

Notice.—When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

Custodian:

Navy—Bureau of Ships

Other interest:

Army—OSigT
Navy—AMCOrS
Air Force.

APPENDIX II

Calibrations for Determining Luminous Efficiency

1. Note on Units. It will be convenient here to utilize the energy absorbed in a square centimeter of window. This will be given in watts.

The radiant output is given in watts on the assumption that the luminous output in the photopic sensitivity curve for the eye is 680 lumens/watt. Detector sensitivity curves are usually given in electrical output (or property change) per watt of incident light. One of our own photometric sources was calibrated with the aid of a sensitive thermopile, and this result is proportional to energy.

2. Calibration of the Monochromators. These monochromators are Bausch and Lomb 33-86-40 grating monochromators, one fitted with a grating blazed at 0.3μ , and the second with a grating blazed at 0.5μ . They were fitted with a motor driven cam which caused the monochromator to scan the wavelength range, and the spectrum was detected with a photo-multiplier whose output was recorded on a continuously moving chart. Two light sources were utilized to calibrate the monochromators. For the wavelength calibration, an Ultra-Violet Products, Inc. Pen-Ray mercury arc lamp was used. The chart was read with a digitizing stage accurate to several mils, calibrated against a steel scale. The spectral line positions and spectral data were fitted with polynomial least squares. The UV monochromator calibration curve did not deviate significantly from a straight line, but the visible monochromator chart was fitted better by a parabola with a small second degree term. These functions were used to rectify the data.

The energy calibration was obtained by scanning the spectrum of an incandescent lamp, nominally 5 watts, which had been compared photometrically with a calibrated lamp, as described below, placed 17 in. from an aperture ($3/8$ in.) of the same size used for the luminescence determinations. All of the spectra were digitized and converted by the data logger into detector output current at 240 equally spaced wavelength intervals covering the monochromator scanning range. The monochromator efficiency curve and the photomultiplier sensitivity curves were digitized similarly. Thus the energy input to the monochromator could be obtained by dividing the first data set by the other two in turn. This was compared with the Planck radiation curve for the calculated lamp temperature multiplied by de Vos' emissivity of tungsten.¹⁹ The calculation of the Planck radiation curve is described below. The problems of the monochromator efficiency curves and the detector sensitivity curves are discussed here.

The monochromator efficiency curve for the 0.3μ blazed grating supplied by the manufacturer was available. The efficiency was given for several wavelengths, and we sketched a smooth curve through them corresponding to the general form for such curves published by the manufacturer. It should be realized that in addition to local irregularities, such as the Woods anomaly which occurs when the angle between the incident and reflected light from the blaze surface is 90 deg, there are other problems,

such as films forming on the gratings as they age. The latter tend to affect the wings of the curve, and particularly the short wavelength side. Fortunately, there was little that was significant in the luminescence spectra in these regions. A calibration curve for the 0.5μ grating was not available. For this instrument we drew an efficiency curve similar to one which we had for another instrument for which such a calibration was available and which had been used with a thermopile detector.

The detectors had not been calibrated individually. For the detector sensitivity curve we used the manufacturer's typical curves for detectors of these types. In the case of the UV monochromator, we adjusted the detector sensitivity curve so that the spectrum of the lamp corresponded closely to the curve in relative proportions. Its absolute value was taken from the luminous intensity of the lamp (the integral of the lamp emission multiplied by the photopic sensitivity curve of the eye). In the case of the visible monochromator we adjusted the monochromator efficiency curve in a similar manner because we had no reliable data for it.

The efficiency and sensitivity curves are shown in Figs. 28 and 29.

The luminous output of incandescent lamps vary markedly one from another and for different viewing directions. All of our calibrated lamps are marked for viewing direction and for voltage of operation. They will also vary considerably in operating temperature, current etc., even for the same size and taken from the same carton. Because the resistance of tungsten is so steep a function of temperature, it is possible to calculate the temperature of a lamp within a degree by measuring the current and voltage to 3 digits. For the present purposes, the equation given in the ICT was used,⁸⁰ but the T^3 term was made negative because the values then corresponded better to the curve given by Goldsmith, *et al.*⁸¹ The function used was the following:

$$r_t = 5.00 + 2.619 \times 10^{-2} t + 3.5 \times 10^{-6} t^2 - 3.1 \times 10^{-10} t^3,$$

where t is in °C and r_t is the resistivity at that temperature.

Because the Planck radiation curve changes so greatly in the visible region, the ratio of the spectral intensities at 0.68, 0.5, and 0.46 can be used to fix the apparent temperature of the filament within 5 or 10 deg. Since these temperatures corresponded to those calculated from the above equation, the resistivity equation procedure, being simpler, was used. A further check was made by dismantling a lamp and measuring the filament. The characteristics of the second lamp from the same package of two corresponded to the dimensions of the filament from the first. This was a 40 W lamp. It had a coiled filament 4.2 cm long made of wire 0.0033 cm diameter, coil diameter 0.0190 cm, turns spaced 0.0045 cm. The cold resistance of the second lamp was determined with a digital ohmmeter. The length of wire calculated from the dimension measurements was 45.9 cm, and calculated from the resistivity was 46.88 cm. The calculated area of the wire was about $\frac{1}{2} \text{ cm}^2$. If this were a 40 W lamp at 120 V, its operating temperature would be 2192 °K by our resistivity equation, and the luminous efficiency would correspond to that calculated from the Planck Radiation Law multiplied by the emissivity and half the filament area (about half is

Fig. 28. and 29. Monochromator efficiency (lower) and detector sensitivity (upper) curves: for the 0.3 μ blazed grating monochromator and detector (above); and for the 0.5 μ blazed unit (below).

blocked by the coil). Therefore, the procedure which was used was the following one.

The filament resistance of the lamps were determined cold with a digital ohmmeter. The lamp was then operated at the desired voltage as read on a digital voltmeter, and the current was read with a digital milliammeter. These data were used to calculate the lamp temperature. The luminous output was compared with our calibrated lamp using a Vactek selenium cell covered with a light blue filter connected to a digital voltmeter. The spectral sensitivity of this combination had been determined and was similar to the photopic sensitivity curve. The voltage output of this cell is not proportional to illumination. Therefore the cell distance from the lamp was altered to obtain a fixed reading, and the intensity of the lamps were assumed to be inversely proportional to their squared distance from the cell. The Planck radiation function,

$$3.743 \times 10^{-16} \lambda^{-5} [\exp(1.4388/\lambda T - 1)]^{-1} \text{ W}/\mu \text{ cm}^2$$

where λ is the wavelength (cm) and T is the temperature ($^{\circ}\text{K}$) of the lamp, was multiplied by de Vos' emissivity values⁷⁹ and the photopic sensitivity curve. This function was plotted and integrated with a planimeter to obtain the luminous energy output. This was compared with the luminous intensity of the lamp assuming 680 lumens/W to obtain a factor containing the effective filament area and lamp bulb losses. It was assumed that the curve multiplied by this factor represented the spectral distribution of the lamp. This curve was used to calibrate the monochromators and the silicon photodiode. The characteristics of the lamps employed are given in Table VII.

The monochromator scanings for the mercury arc lamp are shown in Figs. 30 and 31. The width of these lines represents the slit width employed, as the line obtained with the slits reduced to minimum opening are narrow lines. It will be realized that two kinds of data are obtained from the monochromator scanings. If the line is sharp, then all of it is within the slit, and the peak value is the energy present at that wavelength. If a broad peak is being examined, then the energy must be obtained by integrating over the wavelength range, and the calibration is in W/ μ . These results are summarized in Table VIII.

3. The Silicon Photodiode. The silicon photodiode used to measure the electron excited luminescence was a United Detector Technology (UDT) PIN-10 Shottky detector. The relative sensitivity curve was checked with a monochromator whose output had been determined with a thermopile and found to correspond to the data for the 15 W lamp which is described in Table VII. The detector was used with a Keithley electrometer 610A in fast mode. The calibration was made with a window matching the one used in LEE with an IR+red filter and an IR+blue filter. The transmissivities of these combinations determined with a Beckman DK2A spectrophotometer are shown in Fig. 32. The sensitivity of the detector was not quite linear with inverse distance squared. The spectral lamp output was combined with the transmissivities of the filters and the spectral sensitivity of the detector to obtain the sensitivity curve for the detector in these combinations. The dependence on intensity is given closely by:

Table VII. Calibration Lamp Characteristics

Nominal Size (W)	Cold Resistance (ohm)	Operating Voltage (V)	Operating Current (mA)	Calculated Operating Temperature (°K)	Distance for Vactek Cell Reading (cm)	Luminosity (CP)
40	24.5	115.4	331	2496	159	(32.5) ^a
New 40	29.0	121.1	310	2391	135.7	23.68
15	90.0	121.8	115.4	2145	64.6	5.37
7 1/2	156.0	121.8	65.2	2181	43.2	2.40

^aStandard.

Fig. 30. The mercury arc scanned by the 0.3 μ blazed grating monochromator.

Fig. 31. The mercury arc scanned by the 0.5 μ blazed grating monochromator.

$$w = 7.795A^{1.088}$$

for the red; and for the blue

$$w = 15.43A^{1.094},$$

where A is the current reading by the Keithley 610A in amperes. The IR filter was not used for measuring the electron excited luminescence.

Table VIII. Monochromator Calibration Summary

	U.V. (0.3 μ blaze)	Visible (0.5 μ blaze)
Wavelength equivalent to slit width (μ)	0.0127	0.0117
Power in slit width in the photopic region (W) with 2.4 CP lamp at 17 in. from 3/8 in. aperture	1.30×10^{-7}	1.19×10^{-7}
Absolute calibration: factor to multiply rectified readings ^a to get power in a narrow line (W/A)	8.1×10^{-3}	1.33×10^{-2}
Broad band calibration: factor to get distributed power ^b (W/ μ per amp)	0.638	1.13

^aRectification consists of dividing by the detector sensitivity and monochromator efficiency at that wavelength.

^bFrom the integral of the rectified^a readings.

Fig. 32. The silicon photodiode relative sensitivity curve (uppermost) and the transmissivity curve for the red (right) and the blue (left) filters used in combination with the indium oxide coated window (middle curves). The lowermost curves are the transmissivity curves with the addition of the infrared filter to the respective combinations.

ADDENDUM

Thermal Stress

Heating by the absorption of soft x rays in and near the surface of a window has been mentioned in several places in This Report and is treated in some detail for the vitreous silica window. For most of the materials, the thermal conditions and the physical constants of the materials required to make a precise calculation are not available. No value could be found for the heat capacity of zinc selenide. An average value was obtained (as described above) by measuring the temperature rise when a heated piece was dropped into water. No value could be found for the thermal conductivity of the magnesium fluoride in this temperature range, and a value given for pressed material 0.13 cal/cm deg at 454 °C in a 1965 report seems large compared to values given for other fluorides. Thus, the calculations made here can only be considered indicative rather than definitive. The calculations of the thermal cycle involve established theory and equations. The thermal stress is calculated on a model based on the photoelastic work which has been done in This Laboratory. This model is based on a small thickness of the material experiencing a permanent dilatation. Then it can be shown that the mean stress $\bar{S}$ in this region is related to the mean dilatation $\bar{\delta}$, which this region would show when it is separated from the material, by the following equation:

$$\bar{S} = \bar{\delta} R \frac{2}{3} [(1+\nu)/(1-\nu)]$$

where R is the modulus of rigidity and ν is Poisson's ratio. From this we make the assumption that the differential stress between any such layer and the portion of the medium which has not experienced a dilatation is given by the same equation applied to the dilatation involved. The results of the calculations for the conditions at the tank wall are given in Table IX. As described above, a suitable value for the thermal conductivity of magnesium fluoride was not at hand, hence calculations were made for two values at the extremes of the range in which it was believed its thermal conductivity would fall; however, as also mentioned above, the one value which was found for a compact of this material is somewhat higher. Additional calculations were made to determine the effects of altering the thermal constants and the thermal data. Altering the thermal conductivity or heat capacity produces effects which are difficult to describe simply, because the thermal distribution is altered. Some indication of this effect can be gathered by intercomparing the results for the different materials and, particularly, the curves shown for vitreous silica and for quartz (Figs. 9 and 12). Altering the thickness of the plate has little effect; the distribution from the face remains little changed, but the final temperature is lower if the plate is thicker. If the energy incident on the window is altered (but the pulse length is unchanged), the thermal distribution is directly proportional to the incident energy. Thus, the thermal stress is altered in the same proportion. Since the stresses

experienced at the tank wall are significant in propagating fractures, even a several-fold reduction would be very beneficial. Therefore, it is recommended that extending the windows from the tank wall should be considered seriously.

Table IX. Thermal Pulses and Stresses

Item	Vitreous Silica	Quartz	Sapphire	ZnSe	MgF ₂	MgF ₂
Density (g/cm ³)	2.2	2.65	3.987	5.42	3.17	3.17
Heat capacity (cal/g deg)	0.13	0.20	0.22	0.083	0.25	0.25
Thermal conductivity (cal/cm deg)	0.0030	0.025	0.05	0.026	0.02	0.05
Thickness (cm)	1.9	1.4	1	1	0.5	0.5
Maximum temperature rise (deg)						
Initial pulse	66	16	8.1	15.7	13.5	8.5
TFM	146	36				
Extended TFM	184	50	25.5	49.5	42.5	26.9
Thermal dilatation (10 ⁻⁶ /deg)	1.7	38	18	22.5	33	33
Modulus of rigidity (10 ¹¹ d/cm ²)	3.1	3.3	18.6	2.94	2.72	2.72
Maximum thermal stress (10 ³ psi)						
Initial	0.46	2.9	3.94	1.51	2.23	1.4
TFM	1.03	6.6				
Extended TFM	1.29	9.1	12.4	4.76	6.55 ^a	3.06 ^a

^aCorrection made for backface temperature.

REFERENCES

1. K. Young to W. Primak, 6/17/77 (PC-C-024; 9C1)
2. TFR Conceptual Design, Vol. III A (1976); Vol. III, previous edition (1975).
3. K. Young to W. Primak, 8/5/77 (PCC-C-027; 9C1).
4. K. Young to W. Primak, phone 10/21/77.
5. G. Taylor to W. Primak, 2/26/80.
6. W. Primak, *J. Appl. Phys.* 27, 54 (1956).
7. B. L. Henke and E. S. Ebsu, *Advances in X-Ray Analysis*, C. L. Grant, et al., eds., (Plenum Press, N. Y.). Vol. 17, pp. 188-190.
8. W. H. McMaster, N. Kerr del Grande, J. H. Mallett, and J. H. Hubbell, Report UCRL 50174R1, Section 2 (May 1969).
9. W. Primak, *Nucl. Science and Eng.* 73, 29 (1980).
10. D. I. Garber and R. R. Kinsey, *Neutron Cross Sections*, BNL-325, 3rd ed. Brookhaven National Laboratory (1976).
11. W. Primak and L. H. Fuchs, *Nucl. Sci. and Eng.* 2, 49 (1957).
12. W. Primak, *J. Nucl. Materials* 74, 84 (1978).
13. *Fracture Mechanics of Ceramics*, R. C. Bradt, D. P. H. Hesselman, and F. F. Lange, eds. (Plenum Press, N.Y., 1974).
14. W. Primak and P. Day, *Anal. Chem.* 26, 1515 (1954).
15. W. Primak, *Rev. Sci. Instrum.* 29, 177 (1958).
16. W. Primak, *Phys. Rev.* 110, 1240 (1958).
17. F. S. Tomkins and M. Fred, *J. Opt. Soc. Am.* 41, 641 (1951).
18. W. Primak and E. Edwards, *Phys. Rev.* 128, 2580 (1962).
19. W. Primak and E. Monahan, *Rev. Sci. Instrum.* (in press).
20. W. Primak, *Surface Science* 16, 398 (1969).
21. W. Primak and E. Monahan, *Rev. Sci. Instrum.* 50, 738 (1979).
22. W. Primak, *The Compacted States of Vitreous Silica* (Gordon and Breach, New York 1975).
23. W. Primak, *Rad. Effects* 45, 29 (1979).
24. W. Primak and R. Kampwirth, *J. Appl. Phys.* 39, 6010 (1968).
25. W. Primak, *Nucl. Sci. and Eng.* 2, 117 (1957).
26. W. Primak, *Nucl. Sci. and Eng.* 2, 320 (1957).
27. W. Primak and R. Kampwirth, *J. Appl. Phys.* 39, 5651 (1968).
28. W. Primak, *J. Appl. Phys.* 49, 2572 (1978).
29. W. Primak, *J. Appl. Phys.* 35, 1342 (1964).
30. H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, 2nd ed., (Oxford University Press, London, 1959), Eqs. 3.4(6) and 3.8(3).
31. A. Goldsmith, T. E. Waterman and H. J. Hirschhorn, *Handbook of Thermo-physical Properties of Solid Materials*, (Pergamon Press, New York 1951), Vol. III.
32. W. Primak and E. Edwards, *Phys. Rev.* 128, 1580 (1962).
33. W. Primak, *Phys. Rev.* B14, 4679 (1976).
34. W. Primak and R. Kampwirth, *J. Appl. Phys.* 40, 685 (1969).
35. W. Primak and R. Kampwirth, *J. Appl. Phys.* 40, 2565 (1969).
36. W. Primak, *Phys. Rev.* B12, 4846 (1972).
37. W. Primak (unpublished).
38. W. Primak, *Phys. and Chem. of Glasses* 22, 43 (1981).
39. Reference 32, p. 35.
40. W. Primak, L. H. Fuchs and P. Day, *J. Am. Ceram. Soc.* 38, 135 (1955).
41. C. Frondel, *Amer. Mineralogist* 30, 432 (1945).
42. G. Mayer and J. Gigon, *Phys. et Rad.* 18, 109 (1956).

43. R. B. Sosman, The Properties of Silica (Chemical Catalogue Co., New York, 1927).
44. A. E. H. Love, A Treatise on the Mathematical Theory of Elasticity, 4th ed (Dover Publications, New York, 1944).
45. W. Primak and J. Luthra, Phys. Rev. 150, 551 (1956).
46. W. Primak, J. Appl. Phys. 34, 3630 (1963).
47. W. Primak and J. Luthra, J. Appl. Phys. 37, 2287 (1966).
48. W. Primak, J. Appl. Phys. 48, 1556 (1977).
49. W. Primak, J. Nucl. Materials 74, 84 (1978).
50. D. M. Gruen, B. Siskind and R. B. Wright, J. Chem. Phys. 65, 363 (1976).
51. P. W. Levy and G. J. Dienes, Defects in Crystalline Solids (The Phys. Soc., London, 1955) p. 225.
52. E. W. Salmi, C. E. Backus, T. G. Franck and C. D. Sutherland, IEEE Thermionic Conversion Specialist Conf., Miami (1970).
53. T. G. Franck and G. E. Backus, 3rd Int. Conf. on Thermionic Electric Power Generation (Jülich, Germany).
54. G. W. Arnold, CONF-740402-P2 (San Diego, April 1974), Vol. II, p. 500.
55. Private communication.
56. University of Texas, Austin, Texas.
57. G. D. Watkins, Phys. Rev. Letters 33, 223 (1974).
58. D. J. Dunstan, J. E. Nicholls, B. C. Cavenett, J. J. Davies and K. V. Reddy, Solid State Comm. 24, 677 (1977).
59. V. I. Spitsyn, A. I. Ryabov, N. S. Stel'makh and G. N. Pirogova, Izvestiya Akademii Nauk SSR, Neorg. Mat. 13, 27 (1977).
60. J. Lindhard, M. Scharff and H. E. Schiott, Kgl. Danske Videnskab. Selskab. Mat.-Fys. Medd. 33, 14 (1963).
61. J. Lindhard, V. Nielsen and M. Scharff, ibid. 36, 10 (1968).
62. W. A. Sibley and D. Pooley, Treatise on Materials Science (Academic Press, New York, 1974), Vol. 5, p. 45 et seq.
63. W. Primak, Phys. Rev. 112, 1075 (1958).
64. M. Lambert, Etude des Imperfections de Structure du Fluorure de Lithium Irradié, Thesis Report CEA 1080, Centres d'Etudes Nucléaire de Saclay (1959).
65. W. Primak and G. Wolfe, Phys. Rev. 132, 1612 (1963).
66. W. Primak, C. J. Delbecq and P. Yuster, Phys. Rev. 98, 1708 (1955).
67. P. Berge, Effet des Radiations Sur les Propriétés Electriques et Optique du Fluorure de Lithium, Thesis, Université de Paris (1961).
68. T. J. Pearsall, J. Royal Inst. 1, 77, 267 (1830).
69. W. Primak, ERDA Report CONF-770102, p. 157 (1977).
70. W. Primak, J. Nucl. Materials 63, 313 (1976).
71. W. Primak, J. Nucl. Materials 74, 84 (1978).
72. W. Primak and E. Monahan, unpublished.
73. W. Primak, J. Electrochem. Soc. 122, 1002 (1975).
74. M. J. Pelouze, Compte Rend. 64, 53 (1867).
75. M. Faraday, Ann. Chem. Phys. 25, 99 (1825).
76. A. Splittgerber, Ann. Physik 47, 166 (1839).
77. T. Gaffield, Am. J. Sci. Arts 97, 244, 316 (1867).
78. W. Primak, Nucl. Instrum. and Methods 127, 21 (1975).
79. J. C. deVos, Physica 20, 690 (1954).
80. International Critical Tables (McGraw Hill, New York, 1929) Vol. VI, p. 136.
81. Reference 31, graph I-T-7.

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