all carriers are generated right near the illuminated surface. The solutions for this case are the limiting forms of the expressions just derived, in which $k\rightarrow\infty$. Alternatively, the problem may be defined in terms of the differential equation (B.8) in which $\mathcal{G}=0$, and the new boundary conditions:

$$\begin{aligned} &\text{at}\quad y=0,\quad D_T dp_f/dy=s_1p_{f1}-Q;\\ &\text{at}\quad y=t,\quad D_T dp_f/dy=-s_2p_{f2}.\end{aligned}\tag{B.14}$$

The results are

$$p_f=Q\Lambda[s_2\sinh\lambda(t-y)+\lambda D_T\cosh\lambda(t-y)],\tag{B.15}$$

$$J_y{}^+=eD_TQ\Lambda\lambda[s_2\cosh\lambda(t-y)+\lambda D_T\sinh\lambda(t-y)],\tag{B.16}$$

$$I^{sc}=eD_TQ\theta\Lambda[s_2\sinh\lambda t+\lambda D_T(\cosh\lambda t-1)],\tag{B.17}$$

$$\Delta G=e\mu(b^{-1}+\Gamma)Q\Lambda\lambda^{-1}[s_2(\cosh\lambda t-1)+\lambda D_T\sinh\lambda t].\tag{B.18}$$

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Radiation Effects in Silica at Low Temperatures

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Optical absorption bands induced in fused silica and crystalline α quartz of low impurity content at 77°K by fast electrons or x-rays bleach slowly at room temperature. The presence of OH$^-$ ions in fused silica inhibits the formation of such radiation-induced absorption. Comparison of the number of centers produced at 215 mμ (C band) in Corning 7943 fused silica (OH$^-$ free) for equal absorbed dose when irradiated with electrons and x-rays indicates that displacements are not involved in the initial formation of the color centers. A defect model requiring simple ionization seems adequate to explain most of the observed phenomena in this pure fused silica. No simple model can be proposed which adequately describes the data in the case of the Corning 7940 fused silica (OH$^-$ bearing).

INTRODUCTION

IRRADIATION of fused silica or crystalline quartz with x-rays, gamma rays, fast electrons, or fast neutrons creates defect centers. These defect centers alter the properties of the original material in many ways. For example: (1) absorption of electromagnetic energy occurs at optical frequencies where the material was formerly transparent; (2) an appreciable number of paramagnetic centers is produced; (3) the thermal conductivity at low temperatures is altered; (4) the density is changed; (5) the crystalline structure is altered or even destroyed; and (6) the average separation among atoms is changed. Many of the property changes are related, for a given defect type may contribute to several of them. It is thus of considerable interest to determine, if possible, the nature of the defect centers that are responsible for the macroscopic property changes.

Information concerning specific models can often times be gained by studying the damage produced by x-rays and by fast electrons of various energies. For example, if a threshold energy for the production of the defect can be established, then the defect model requires the direct displacement of atoms to form vacancies and interstitials. This can be determined by measuring the optical absorption arising from the defect as a function of the incident energy of a fast electron. Furthermore, x-rays would not be expected to produce this type of damage. On the other hand, defects which can be formed by simple ionization of the lattice atoms would be expected to be produced by both x-rays and by fast electrons. The number of centers formed by fast electrons should be directly proportional to the stopping power of the material for electrons. A comparison of the optical absorption in fused silica for equal absorbed doses of electron and x-irradiation can also establish which of these two models more nearly describes the observed effects. This paper presents data on the damage induced in fused silica and crystalline α quartz by x-rays and by fast electrons of energies between 0.5 and 2.0 Mev. These data are then used to examine the models of the radiation-induced defects that give rise to the color centers in this material.

Some very definite models for the defects giving rise to optical absorption maxima have been proposed. These models and the experimental factors which bear on them are discussed in the following section.

PRESENT MODELS OF THE DEFECTS

A, *C*, and *E* Centers

The model of the center giving rise to the A_1 (620 mμ) and A_2 (450–477 mμ) bands in crystalline quartz has been firmly established as a result of combined optical[1]

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[1] Ditchburn, Mitchell, Paige, Custers, Dyer, and Clark, *Report of Bristol Conference on Defects in Crystalline Solids July, 1954* (The Physical Society, London, 1955), p. 92.

and electron spin resonance measurements.[2,3] The center consists of a hole trapped at an aluminum ion that has substituted for a silicon ion. The hole spends about 3% of the time on the aluminum ion and 97% of the time on a neighboring oxygen ion.

Although a correlation seems to exist between the magnitude of the A band (540 mμ) in fused silica and the aluminum content of the sample,[4,5] the evidence that the center is the same as in crystalline quartz is much less complete. The random orientation of the Si—O bonds in the fused silica does not allow for a unique establishment of the model by electron spin resonance measurements.

The two A centers in crystalline α quartz are formed by a simple ionization process when an electron-hole pair is formed and the hole is trapped by the substitutional aluminum and a neighboring oxygen ion. It is only required then that some trap exist for the electron and that the aluminum ion be substitutional.

The C band (215 mμ) has probably received more attention than any of the defect bands. It has been found that the C band in pure fused silica can be generated to only a negligible extent by extensive x-irradiation at room temperature.[6] In contrast, fast neutrons (plus the associated gamma field) produce a C band that grows with increased exposure time and saturates at quite high levels.[7] The appearance of the band in crystalline quartz for gamma-ray exposure and low neutron fluxes is a subject of some controversy. Ditchburn *et al.*[1] and Mitchell and Paige[4] identify a C band after an irradiation with less than 10^{17} *nvt* fast neutrons. Nelson and Crawford[8] and Nelson *et al.*[9] contend that the C band does not appear in crystalline material at these low fluxes. Only when the crystal has been irradiated with sufficient fast neutrons ($>10^{20}$ *nvt*) to appreciably decrease the crystalline order does the C band appear.[10]

Bleaching results imply that the C center is an electron trapped at a defect. Mitchell and Paige[11] observed that irradiation with C-band light bleached both the C and A bands. Since the A bands arise from trapped holes, then the C band could, indeed, arise from a trapped electron.

Considerable information on the microscopic nature of the C center has been gained by electron spin resonance measurements. Weeks[12] first examined the electron spin resonance of irradiated crystalline quartz and fused silica. He found two resonance lines in fused silica —a narrow line with $g=2.0013$ and a broad line with $g=2.0090$—which he ascribed to defects in the SiO_4 tetrahedra. The magnitude of the spectroscopic splitting factor, g, indicated that the narrow line probably arose from a trapped electron and the broad line from a trapped hole. In the crystalline material two groups of lines were found. A summation of each of these groups over random crystallographic directions relative to the magnetic field gives the two lines found in the fused silica. After extensive neutron irradiation ($>10^{20}$ *nvt*), the groups of lines in the crystalline material are replaced by two single lines which resemble those found in fused material after a similar irradiation.

A qualitative correlation between the optical and paramagnetic resonance work leads to the conclusion that the center giving the narrow resonance is probably responsible for the optical C band in fused silica.[8,12–14] However, the detailed correlation is not very good.

The observation that fast neutrons or high-energy gamma rays are apparently essential to produce a C band that grows with exposure time has led most workers to consider the defect to be produced only when displacement of a lattice ion occurs. Mitchell and Paige[4] postulate that the C band arises from an electron trapped at an oxygen vacancy, whereas Nelson and Crawford[8] suggest that the center may arise from a partial valence bond localized either at a silicon or oxygen atom. The latter authors argue that the crystalline nature of the material is very important and that only after a breakdown of the crystalline structure can an appreciable number of stable broken valence bonds be produced that can give rise to the C band. The Mitchell and Paige model requires that enough energy be transferred to the oxygen atom to remove it from its site. For example, if the binding energy were 25 ev an electron energy of about 0.16 Mev would be required for displacement by an elastic collision. The valence bond model, however, requires only the removal of an electron from a strained Si—O bond to form the defect, i.e., energies of the order of the band gap should be sufficient.

Mitchell and Paige[4] were the first investigators to examine changes in the transmission of quartz or fused silica for wavelengths shorter than 185 mμ. They

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[2] Griffiths, Owen, and Ward, see reference 1, p. 81.

[3] M. C. M. O'Brien and H. M. L. Pryce, see reference 1, p. 88.

[4] E. W. J. Mitchell and E. G. S. Paige, Phil. Mag. **1**, 1085 (1956).

[5] A. Kats, *Proceedings of the Fourth International Glass Conference*, Paris, July, 1956, 1957 (unpublished), p. 400.

[6] A. J. Cohen, J. Chem. Phys. **23**, 765 (1955).

[7] C. M. Nelson, Oak Ridge National Laboratory Report ORNL-2413, August 31, 1957 (unpublished), p. 58.

[8] C. M. Nelson and J. H. Crawford, Jr., Symposium on Defect Structure of Quartz and Glassy Silica at Mellon Institute, 1957 (to be published).

[9] Nelson, Weeks, Lide, and Pegram, Oak Ridge National Laboratory Report ORNL-2614, August 31, 1958 (unpublished), p. 25.

[10] M. Wittels and F. A. Sherrill, Phys. Rev. **93**, 1117 (1954) observed that the single-crystal x-ray reflections disappear after an irradiation of about 1.2×10^{20} neutrons/cm^2 and conclude that the crystalline state is destroyed by this irradiation. W. Primak, Phys. Rev. **110**, 1240 (1958) points out that some long-range order still exists after this dose as is evidenced by the presence of appreciable birefringence and rotatory power.

[11] E. W. J. Mitchell and E. G. S. Paige, Proc. Phys. Soc. (London) **B67**, 262 (1954).

[12] R. A. Weeks, J. Appl. Phys. **27**, 1376 (1956).

[13] J. S. van Wieringen and A. Kats, Philips Research Rept. **12**, 432 (1957).

[14] Iu. N. Molin and V. V. Voevodskii, J. Tech. Phys. U. S. S. R. **28**, 143 (1958) translation: Soviet Phys. (Tech. Phys.) **3**, 125 (1958).

identify an E band (163 mμ) in both quartz and fused silica that grows with fast neutron irradiation. They found that x-rays induce this band in fused silica but not in crystalline quartz.

Since optical irradiation into the C band bleaches both the C and E bands, Mitchell and Paige presume that the centers are complementary and that the E centers consist of a hole trapped at a defect. They further suggest that the hole is trapped by an interstitial oxygen ion making it O^{-1}.

As noted above, electron spin resonance on irradiated material gives evidence for a hole trapped by a defect.[12,13] If one tacitly assumes that the same defects occur in fused silica and crystalline quartz, then one can conclude that the center giving the hole resonance also gives rise to the E band. The evidence for this is the following. Weeks[12] finds that a 550°C anneal of a neutron-irradiated specimen of Corning 7940 fused silica eliminates all of the resonance of the trapped electron, but only about half of the resonance of the trapped hole. Mitchell and Paige[4] find that a 500°C anneal of a neutron-irradiated quartz sample bleaches all of the C band but only about two-thirds of the E band. Simultaneous measurements of the optical absorption and paramagnetic resonance have not been reported on a heated fused silica sample.

The model of the E center[4] as a hole trapped at an interstitial oxygen is certainly complementary to the model of the C center as an electron trapped at an oxygen vacancy. That is, a displacement of an oxygen ion from its lattice site can produce the defects responsible for both bands. The subsequent trapping of an electron and hole could thus give the two defect bands. The same complementary relation exists with the model of Nelson and Crawford.[8] A partial valence bond localized on a silicon atom might be expected to give a resonance characteristic of a trapped electron while a partial bond localized on an oxygen atom might be expected to give a resonance characteristic of a trapped hole. Thus, the breaking of an Si—O bond can form both centers.

Nelson and Weeks[15] have shown that the ratio between the C and E bands varies widely depending upon the material examined. It can thus be said that no direct relationship exists between these bands. Thus, other defects must be present which can trap electrons or holes but remain nonparamagnetic.

Other possibilities also exist for the C and E centers. A silicon vacancy could act as a hole trap. Mitchell and Paige[4] argue that this is not the defect giving rise to the E band. They find that the A bands produced by neutron irradiation of a crystalline quartz sample are greater if the sample has been annealed at 950°C prior to irradiation. They argue that the high temperature allows aluminum ions to substitute for existing silicon vacancies, thus increasing the A bands. If silicon vacancies are thus assumed to exist in the lattice and if they are hole traps, then one would expect to see an E band with ionizing radiation. Since an E band is not found after x-irradiation of crystalline quartz, they conclude that the E center is not a hole trapped at a silicon vacancy. This argument is not applicable to fused silica, since an E band is generated by x-rays in this material.

Another possible model of the C center is an electron trapped at an interstitial silicon. A silicon ion that is displaced by an incident particle would act as an electron trap. There is, however, no evidence which bears on the validity of this model.

The number of centers giving rise to an absorption band can be determined by applying Smakula's equation if the oscillator strength of the center is known. A comparison of the optical absorption band and the absorption in magnetic resonance led Weeks to suggest that the C band has an optical oscillator strength of 0.1.[16] Mitchell and Paige[4] estimate that the lower limit of the oscillator strength for the C band is 0.05 and for the E band is 0.2. This estimate is made from a calculation of the number of displacements that are produced by a known flux of incident neutrons.

Other Centers

In addition to the above centers, various authors have reported radiation-induced absorption bands at other wavelengths in a variety of materials.

A B_1 band (about 300 mμ) is found in fused silica after neutron, gamma, or x-irradiation. This band has been identified as arising from an impurity although the impurity has not been identified.[17]

A B_2 band (between 238 and 243 mμ) has been found in fused silica. Mitchell and Paige[4] find it after neutron or x-irradiation, Levy[18] finds it after neutron irradiation, but Levy and Varley[19] failed to observe it after gamma, neutron, or x-irradiation of high boron content material. Cohen[20] contends that a band at 242 mμ is produced in fused silica only after neutron bombardment. This divergence in results on apparently similar material leads one to suspect that it is characteristic of an impurity. This, however, has not been proven.

Mitchell and Paige[4] find a D band in crystalline quartz (173 mμ) and in fused silica (172 mμ) after irradiation with 50-kv x-rays. It is not known whether the band grows with neutron bombardment because of the overlap of the C and E bands. No model has been suggested for this center.

A small band at about 250 mμ has been observed by

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[15] C. M. Nelson and R. A. Weeks, Bull. Am. Phys. Soc. Ser. II, 4, 158 (1959).

[16] R. A. Weeks, Bull. Am. Phys. Soc. Ser. II, **2**, 136 (1958).

[17] See, for example, references 1 and 4 and E. S. Dainton and J. Rowbottom, Trans. Faraday Soc. **50**, 480 (1954).

[18] P. W. Levy, J. Chem. Phys. **23**, 764 (1955).

[19] M. Levy and J. H. O. Varley, Proc. Phys. Soc. (London) **B58**, 223 (1955).

[20] A. J. Cohen, Phys. Rev. **105**, 1151 (1957).

Nelson *et al.*[7–9] in neutron-irradiated fused silica. This appears as a shoulder on the C band. No model has been proposed for this center.

Nelson *et al.*[9] observe a small band at 230 mμ in Corning 7940 fused silica if the sample is annealed at 550°C following a neutron bombardment of 1.1×10^{18} *nvt*. This band may be present immediately after irradiation, but it cannot be seen because of the large C band that overlaps it. The origin of this band is not known.

Mitchell and Rigden[21] observe a band to grow at 2.79 microns in crystalline quartz following pile irradiation. It is not developed by x-irradiation. They suggest that this band arises from the combination of hydrogen impurity and the products of atomic damage giving O—H bonds whose resonant frequency is at 2.79 microns.

EXPERIMENTAL PROCEDURE AND RESULTS

Electron Irradiation

Electron irradiations were carried out by means of a Van de Graaff generator in which the accelerating voltage could be varied from 2.0 Mev to 0.5 Mev. The sample was fixed by the geometry of the holder at a distance of 3 in. from the window of the generator and was cooled both by conduction through the walls of the holder and by a jet of helium gas which was cooled by flowing through 50 feet of copper tubing immersed in liquid nitrogen. The portion of the irradiated samples seen by optical measurements was only $\frac{3}{16}$ in. in diameter and irradiation flux over this area was essentially uniform. Back reflection of electrons was avoided by absorbing the beam transmitted through the sample in graphite some distance below the sample. A graphite disk with a beam aperture was also used above the sample to absorb stray electrons reflected from the walls of the sample holder.

The Van de Graaff generator was calibrated by measuring the charge collected in a Faraday cup after the electron beam passed through the area normally occupied by the sample. This was done for several beam currents at each generator voltage used. Beam current was then plotted against electron flux in electrons/cm^2 minute for various accelerating voltages.

Transfer from the Van de Graaff accelerator to the spectrophotometer used for optical measurements was made under liquid nitrogen. Optical measurements were made in a liquid nitrogen Dewar especially designed for the Cary Model 14M spectrophotometer.

The choice of sample thickness was dictated by (1) the requirement that the optical density be less than 2.0 for the flux value in question, and (2) that the total energy loss of the electrons be small. With respect to the latter, Table I shows the energy loss per electron in two thicknesses of fused silica for the energies used in this investigation. Irradiations at 2.0 Mev and 1.0 Mev, for which the flux was greater than 10^{15} e/cm^2 (see Fig. 6), were made on thin samples (0.140–0.165 mm). Below this flux value thicknesses of 0.635–0.681 mm were used. At 0.5 Mev only the thin samples were irradiated.

TABLE I. Energy loss per electron passing through fused silica.[a]

Incident energy (Mev)	Energy loss in Mev/electron 0.127-mm thickness	 0.635-mm thickness
2.0	0.0433	0.217
1.0	0.0427	0.214
0.5	0.0460	0.230

[a] Stopping power values from *Energy Loss and Range of Electrons and Positrons*, National Bureau of Standards Circular No. 577 (U. S. Government Printing Office, Washington, D. C., 1956), using $Z=11$ as the Z equivalent to silica. No correction has been made for the effect of electron scattering.

Most of the experimental data were obtained using Corning 7940 fused silica, a glassy silica with low impurity content. In the course of this investigation a new product, Corning 7943 fused silica,[22] was made available which is comparable to the 7940 material in all respects except that the OH$^-$ content of the 7943 silica is extremely low. The 7943 material has no measurable 2.72-μ OH$^-$ absorption for a sample thickness of 0.940 mm while a 7940 sample 0.673 mm thick has an optical density of 0.19. The two materials also differ markedly in their response to irradiation (see, e.g., Fig. 2). In addition, a fused silica microscope slide which develops the blue coloration associated with irradiated impure silica glass was examined. Most of the crystalline α quartz was grown by the Clevite Corporation on a Y-bar seed[23] and the samples were taken from the Z-growth portion of the finished crystal. This section of the crystal developed little visible coloration[24] under irradiation. Data similar to those obtained with this material have also been obtained using synthetic quartz grown on Z-cut seeds by the General Electric Company, Limited. The data shown in Fig. 5 were obtained using a cerium-activated silicate glass prepared by R. J. Ginther of this laboratory.

Figure 1 compares the optical absorption of Corning fused silica 7940 when electron-irradiated and measured at 77°K and when irradiated at room temperature and measured at 77°K. Negligible absorption was induced in the visible region so the data are given only between 360 mμ and 190 mμ. The two absorption maxima observed are located at 215 mμ and 257 mμ. These are the same bands found by Nelson *et al.*[7–9] in the 7940 material for fast-neutron bombardment at pile temperature. The two bands are comparable in magnitude when the silica is irradiated and measured at 77°K. If the

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[21] E. W. J. Mitchell and J. D. Rigden, Phil. Mag. 2, 941 (1957).

[22] The authors acknowledge the gift of the 7943 silica by the Corning Glass Works, Corning, New York.

[23] Patent Application U. S. Serial No. 459, 052 of October 29, 1954.

[24] Hammond, Chi, and Stanley, Engineering Report E-1162, November 3, 1955, U. S. Army Signal Corps Engineering Laboratories, Ft. Monmouth, New Jersey (unpublished).

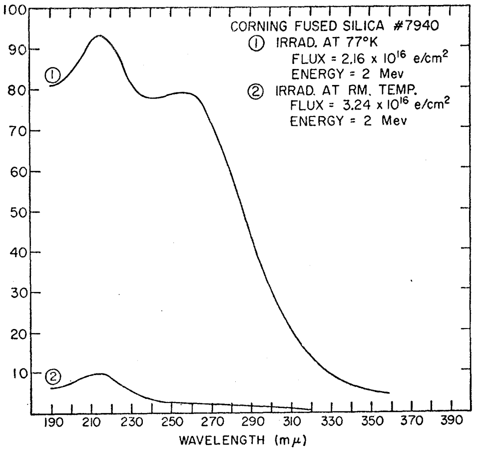

FIG. 1. Absorption coefficient *vs* wavelength for electron-irradiated Corning 7940 fused silica. Energy = 2 Mev. (1): Irradiated at 77°K; measured at 77°K. Flux = 2.16×10^{16} *e*/cm^2. (2): Irradiated at room temperature; measured at 77°K. Flux = 3.24×10^{16} *e*/cm^2.

sample is warmed to room temperature following the low-temperature irradiation and then immediately remeasured at 77°K, the 215-mμ and 257-mμ absorptions are reduced to about half their value. Further loss in absorption takes place slowly at room temperature and approaches the value obtained when the irradiation is initially made at room temperature. This latter case is illustrated by curve 2 in Fig. 1 in which the 215-mμ absorption is about one-tenth as great as when irradiated at 77°K. The 257-mμ band is extremely small when the irradiation is made at room temperature.

Figure 2 shows a comparison of the behavior under electron irradiation of the 7940 (OH$^-$ bearing) and 7943 (OH$^-$ free) silicas for equal flux values and 2.0-Mev energy. Irradiations and measurements were at 77°K. The 7943 material is seen to have about 3.4 times more absorption at 215 mμ than does 7940. The 257-mμ absorption in 7940 is at least a factor of 10 greater than in 7943. Similar behavior with respect to the visible and ultraviolet centers produced by 150-kv x-rays in OH$^-$ bearing and OH$^-$ free impure silicas has been reported by van Wieringen and Kats,[25] i.e., "wet" silica is less affected by radiation than is "dry" silica. A comparison of 50-kv x-ray data for the two materials is shown in Fig. 8 in the next section. Nelson *et al.*[9] have made comparisons of the behavior of the 7940 and 7943 silicas under neutron bombardment. They find that the absorption at 215 mμ and the electron paramagnetic resonance signal believed to be associated with this band are increased by about a factor of 7 in the 7943 material with respect to values observed in 7940. Observations at this laboratory showed that the two types of fused silica exhibit a different emission when warmed to room temperature. The 7940 silica has a reddish glow while the 7943 material luminesces blue. Only visual observations of the emission have been made.

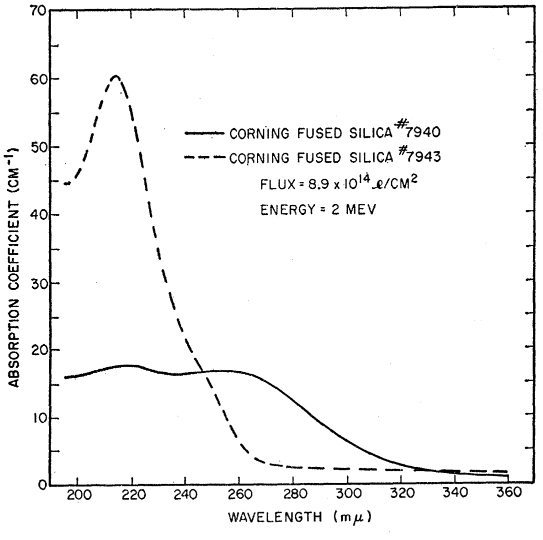

FIG. 2. Absorption coefficient *vs* wavelength for electron-irradiated Corning fused silica 7940 and 7943. Energy = 2 Mev, flux = 8.9×10^{14} *e*/cm^2. Solid line, 7940; dashed line, 7943.

Crystalline α quartz is much less affected by irradiation than is either of the fused silicas investigated. Figure 3 shows the absorption produced in Clevite synthetic α quartz by an electron flux which is almost 200 times that given the silicas in Fig. 2. The absorption is down by a factor of 3 from that for 7940 silica. There is a small absorption peak near 270 mμ which bleaches when the sample is warmed to room temperature. The 215-mμ absorption is reduced by almost one-half as was the case for the silicas. The maximum at about 200 mμ is reduced by a greater factor than the 215-mμ band. Similar results have been obtained for General Electric, Limited, synthetic quartz. Neither of these materials develop appreciable visible color. A sample of Clevite synthetic quartz in which the impurity content was sufficient to cause significant visible coloration under electron bombardment was also investigated. The electron energy was 2 Mev and the flux was 1.18×10^{17} *e*/cm^2. When irradiated and measured at 77°K, the chief visible color centers were at 510 mμ

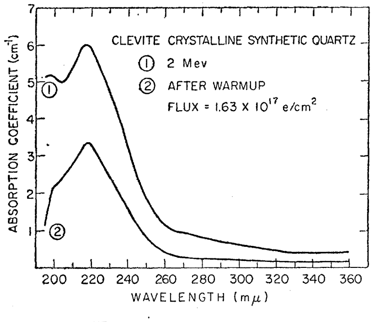

FIG. 3. Absorption coefficient *vs* wavelength for electron-irradiated Clevite crystalline synthetic α quartz. Energy = 2 Mev, flux = 1.63×10^{17} *e*/cm^2. (1): Irradiated and measured at 77°K. (2): Warmed to room temperature; remeasured at 77°K.

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[25] J. S. van Wieringen and A. Kats, Philips Research Repts. **12**, 432 (1957).

($\alpha=9.5$ cm^{-1}) with two subsidiary maxima at about 550 mμ and 590 mμ. Bands were also developed at 335 mμ ($\alpha=9.38$ cm^{-1}) and two bands of about equal intensity ($\alpha\sim18$ cm^{-1}) at 204 mμ and about 218 mμ. Warming to room temperature and remeasuring at 77°K resulted in little change in absorption except for a slight loss in the 218-mμ and 335-mμ centers. When the irradiation was made at room temperature and the measurement at 77°K, the center at 510 mμ was less intense ($\alpha=7.95$ cm^{-1}) and no maxima at 590 mμ, 335 mμ, and 218 mμ (*C* band) were observed. A new small maximum at about 265 mμ was discernible. The absorption rose rapidly below 210 mμ indicating the presence of a band beyond the range of measurement. The 205-mμ band was present as a shoulder on the tail of this band. It should be particularly noted that a distinct *C* band was developed only by irradiating at the low temperatures.

In the case of fused silica, appreciable impurity content causes visible coloration when irradiated at low temperatures. A fused silica microscope slide which develops a blue color after irradiation was investigated. The features observed are shown in Fig. 4. Irradiation and measurement at 77°K gave maxima at 550 mμ, 270 mμ, and 215 mμ (*C* band), with some absorption between 300 mμ and 350 mμ. Warm-up to room temperature and re-measurement at 77°K resulted in the disappearance of this visible color and most of the 270-mμ absorption. The 215-mμ band was reduced by a little more than half its original value. If the irradiation was made at room temperature (measurement at 77°K) the band at 550 mμ was of nearly the same intensity as that obtained for the low-temperature irradiations. The band, however, was stable under these conditions. The 215-mμ band was not as intense as for the low-temperature irradiation ($\alpha=16.3$ *vs* $\alpha=20.2$ cm^{-1}).

It was considered desirable to obtain data on another form of silica to see if the optical absorption features persist, as they should if they are intrinsic to the SiO_2 network. For this reason, a cerium-activated silicate glass was electron irradiated and measured at 77°K. The results are shown in Fig. 5. This glass contains about 4% boron and 96% SiO_2. Absorption maxima due to irradiation are located at about 215 mμ and near 260 mμ. Curve 2 shows that both bands bleach upon warming to room temperature in a manner similar to the two bands in 7940 and 7943 fused silica.

The appearance of two ultraviolet bands at about the same wavelengths in three glassy silicas and in crystalline α quartz suggests that the defect responsible for the short-wavelength band is related to the basic SiO_2 structure and that the long-wavelength band is related to the hydroxyl ion in all of these materials.

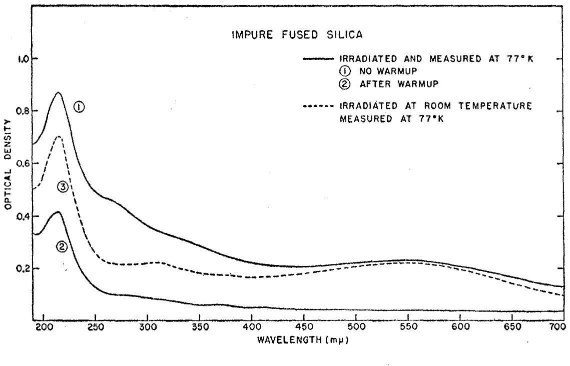

FIG. 4. Optical density *vs* wavelength for electron-irradiated impure fused silica (microscope slide). Energy=2 Mev, flux=1.78 $\times10^{15}$ *e*/cm^2, thickness=0.99 mm. (1): Irradiated and measured at 77°K. (2): Warmed to room temperature; remeasured at 77°K. (3): Irradiated at room temperature; measured at 77°K.

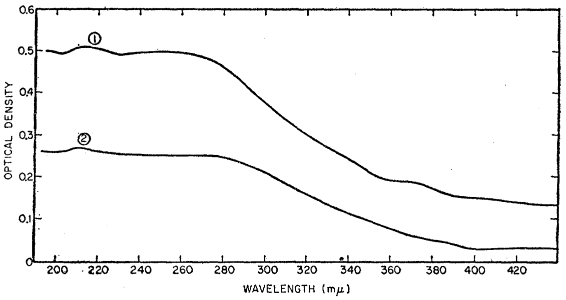

FIG. 5. Optical density *vs* wavelength for electron-irradiated cerium-activated silicate glass. Energy=2 Mev, flux=3.24×10^{16} *e*/cm^2, thickness=0.102 mm. (1): Irradiated and measured at 77°K. (2): Warmed to room temperature; remeasured at 77°K.

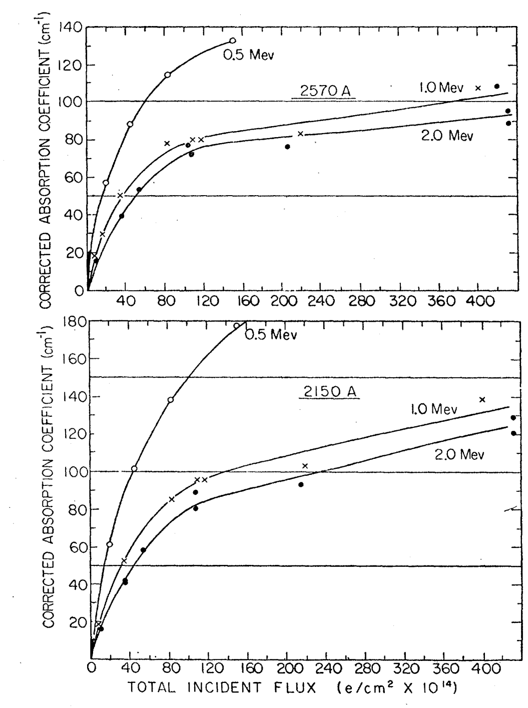

FIG. 6. Corrected absorption coefficients at 257 mμ and 215 mμ *vs* total incident electron flux. Corning 7940 fused silica. ●: 2 Mev, ×: 1.0 Mev, ○: 0.5 Mev.

TABLE II. Calculated percent increase in absorption coefficient in fused silica due to multiple scattering.

Incident energy (Mev)	Percent increase in measured absorption coefficient 0.165-mm thickness	0.66-mm thickness
2.0	2.3	9.2
1.0	7.4	29.6
0.5	23.5	93.9

Growth curves of the 215-mμ and 257-mμ bands in Corning 7940 fused silica, at 77°K, have been obtained at 2.0 Mev, 1.0 Mev, and 0.5 Mev. These are shown in Fig. 6. The measured absorption coefficients have been modified to take into account the effective increase in thickness of the sample. This results from an increase in path length because of multiple scattering events as the electron traverses the sample. These corrections have been made using the theory developed by Yang.[26] As can be seen from Table II, this correction is not negligible, especially at lower energies and for thick specimens. The data in Fig. 6 have also been corrected for reflection losses, neglecting the small change in refractive index between 700 mμ and 190 mμ. No effect was found for dose rate change. The curves established by the experimental points are believed to be accurate within ±5%.

The two absorption centers at 215 mμ and 257 mμ are not related as can be seen from the diverging growth rates with increasing electron flux. It was experimentally impractical to obtain data at higher flux values than shown because of the time required for irradiation.

As mentioned at the beginning of this section, most of the data have been obtained on Corning fused silica 7940 because the 7943 material was not available when the investigation began. The amount of material finally obtained was insufficient to establish complete growth curves as was done for 7940. Data were taken on 7943 at various energies at the same total flux. This is shown in Fig. 7 for the 215-mμ band compared with data on 7940 for the same flux. The probable error in the 7943 data is ±10%. The 0.75-Mev point for 7940 silica is subject to this same error because a complete growth curve was not established at this energy.

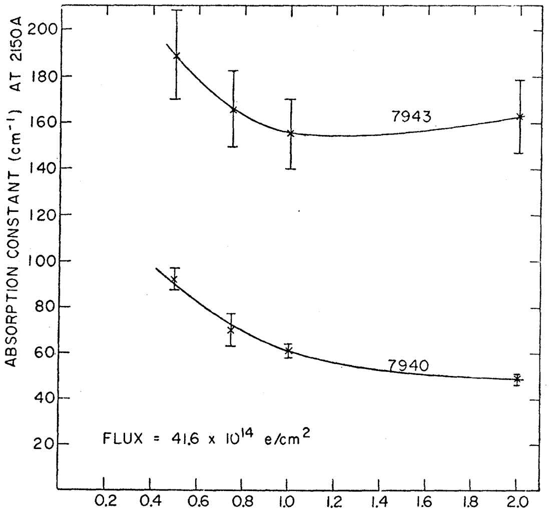

FIG. 7. Absorption coefficient at 215 mμ for various primary electron energies (flux$=41.6\times10^{14}$ e/cm^2) for Corning fused silica 7940 and 7943.

X-Ray Irradiation

X-irradiations were made with an OEG-60 Machlett x-ray tube (W target; Be window) operated at 50 kv (constant potential) at 6.2 ma plate current. The energy absorbed in silica was obtained by calibrating the tube output by means of the optical density changes in a silver-activated phosphate glass.[27] A check on the accuracy of this calibration was made by comparing the absorbed x-ray dose with an equivalent absorbed dose under electron bombardment on a material that is damaged primarily by excitation processes. This was done by comparing the number of F centers produced in a NaCl sample by equivalent amounts of the two irradiations. Satisfactory agreement was obtained.

As in the electron irradiations, all x-ray exposures and measurements were made at 77°K. The results obtained for Corning 7940, 7943, and Clevite synthetic crystalline α quartz are shown in Fig. 8. The x-ray exposure time chosen was 5 hours and the absorbed dose in the fused silica was 1.71×10^7 rad and about 10^7 rad in the crystalline quartz. Corning 7943 silica (non-OH$^-$ bearing) has approximately 6 times the absorption at 215 mμ as does 7940 silica and nearly 56 times the absorption at this wavelength as in Clevite synthetic crystalline quartz. This comparison of the magnitudes

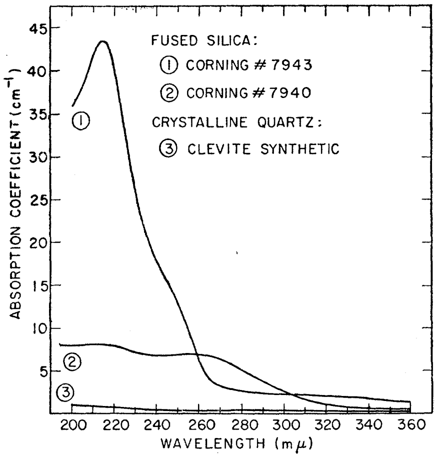

FIG. 8. Absorption coefficient *vs* wavelength for x-irradiated fused silica and crystalline quartz. 50 kv at 6.2 ma. (1): Corning fused silica 7943. (2): Corning fused silica 7940. (3): Clevite crystalline synthetic α quartz.

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[26] C. N. Yang, Phys. Rev. **84**, 599 (1951).

[27] Schulman, Klick, and Rabin, Nucleonics **13**, 30 (1955).

of the 215-mμ absorption in the two fused silicas and the similarity of the ratio of the 215-mμ absorption coefficient to the 257-mμ absorption coefficient for the two types of irradiation (x-rays and fast electrons) suggests that the same processes are operative in producing the optical effects. Table III summarizes the comparison with respect to the 215-mμ absorption for the fused silica materials. Absorption coefficients could not be entered at energies other than 2 Mev for 7943 silica because no growth curves were obtained at other energies.

For low absorbed doses (3.42×10^6 rad) in the 7940 fused silica the agreement between the measured absorptions at 215 mμ is excellent. For higher doses (1.71×10^7 rad) the electron-irradiated material shows more damage than does the x-irradiated silica. In the case of 7943 silica the agreement is very good even at the higher dose.

Since about 99.9% of the energy of an incident fast electron is expended in excitation and ionization processes, the magnitudes of the optical effects produced by a given electron flux and by an equivalent absorbed x-ray dose should be about the same if defects produced by Coulomb encounters with the atoms of the lattice are not present in significant numbers. The data of Table III suggest that this is the case, especially for 7943 silica. If excitation and ionization processes are the dominant factor in producing the observed damage, the experimental data can be compared with the calculated energy losses of fast electrons due to ionization and excitation.[28] This is done in Fig. 9 for 7940 and 7943 silica for a common electron flux value of 41.6×10^{14} e/cm^2. The agreement is quite good for 7943 silica with the damage computed on the basis of defects formed by excitation processes. No such correlation can be made with the 7940 silica data.

The necessity for making irradiations and measurements at low temperatures is well illustrated by comparing the x-ray data obtained here with those of Cohen[6] who worked with fused silica at room temperature. Cohen x-irradiated Corning 7940 silica for an absorbed dose of approximately 1.4×10^9 rad, i.e., about 100 times the largest dose given here, and obtained an absorption coefficient of only about 0.6 cm^{-1}.

Table III. A comparison of the 215-mμ absorption coefficients produced by x-rays and fast electrons.

	X-ray (50 kv)		Electrons		
Material	Absorbed dose (rad)	215 mμ (cm^{-1})	Absorbed dose (rad)	215 mμ (cm^{-1})	E (Mv)
7940	1.71×10^7	8.2	1.71×10^7	12.5	2
				16.4	1
				20.5	0.5
	3.42×10^6	2.6	3.42×10^6	2.5	2
7943	1.71×10^7	43.2	1.71×10^7	44.0	2

Annealing

The defects induced by neutron bombardment in α quartz and fused silica may be, according to Mitchell and Paige,[4] completely annealed by heating at 950°C. They also found that if the heating of fused silica was done in vacuum prior to irradiation, virtually no change was observed in the visible and 215-mμ bands on subsequent irradiation but that heating in air caused a slight decrease in these centers upon irradiation. Heating at 520°C removed the visible and 215-mμ (*C* band) centers but left the band at 163 mμ (*E* band). Nelson *et al.*[7,8] found that γ-ray irradiation of a neutron-bombarded sample of Corning 7940 silica which had been annealed at 700°C gave a more intense *C*-band absorption than for an untreated sample given the same γ-ray flux. This implies that the neutron-induced damage was not removed at 700°C.

Figure 10 shows the effects of annealing in air at 950°C on electron-irradiated Corning 7940 fused silica (2 Mev, flux$=3.56\times10^{15}$ e/cm^2). Curve 1 is for no annealing prior to irradiation. Curve 2 shows the effect of prior annealing. The absorption level is somewhat less than in the untreated sample in agreement with the observation of Mitchell and Paige given above. Curve 3 is the result of (a) irradiation of an untreated sample; (b) annealing at 950°C for 24 hours; (c) reirradiating. In this case the 215-mμ and 257-mμ centers are about 2.6 times less intense than if originally untreated. All irradiations and measurements were at 77°K.

In Fig. 11 is a similar group of curves where the annealing temperature was chosen as 400°C. Electron energy and flux values were as in Fig. 10. Curve 1 of this group shows the results for no treatment prior to

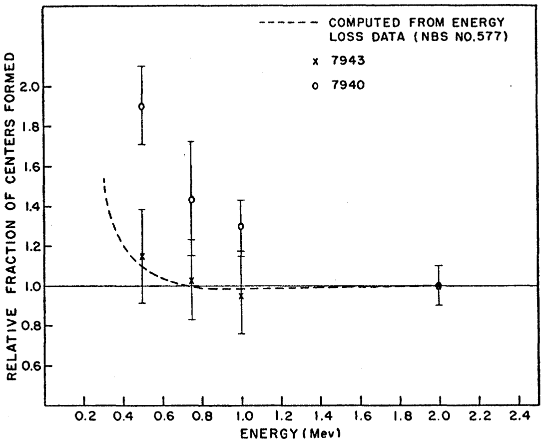

Fig. 9. Relative fraction of *C*-band defects formed *vs* incident electron energy. Dashed line computed from electron stopping power data from NBS circular No. 577.[28] ○ : Corning fused silica 7940. × : Corning fused silica 7943.

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[28] A. T. Nelms, *Energy Loss and Range of Electrons and Positrons*, National Bureau of Standards Circular 577 (U. S. Government Printing Office, Washington, D. C., 1956).

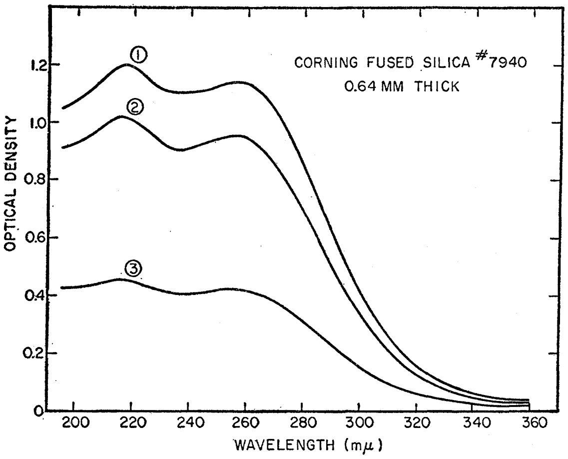

FIG. 10. Optical density *vs* wavelength for Corning fused silica 7940 annealed at 950°C. (1): No annealing prior to 2-Mev electron irradiation. (2): Annealed at 950°C for 24 hours prior to 2-Mev electron irradiation. (3): 2-Mev electron irradiation followed by anneal at 950°C for 24 hours; re-irradiated with 2-Mev electrons. Electron flux $=3.56\times10^{15}$ e/cm^2. All irradiations and measurements at 77°K.

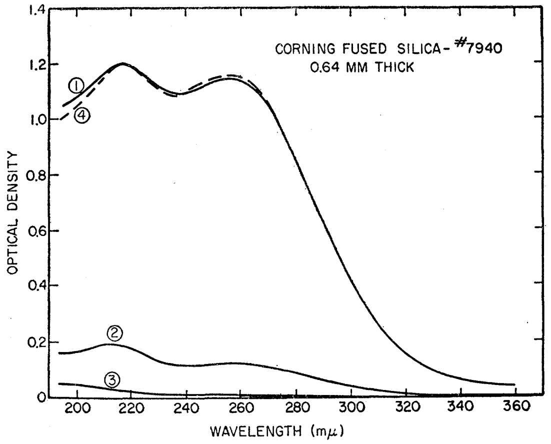

FIG. 11. Optical density *vs* wavelength for Corning fused silica 7940 annealed at 400°C. (1): No annealing prior to 2-Mev electron irradiation. (2): Same as (1) after 7 days at room temperature. (3): After anneal at 400°C for 3 days. (4): Re-irradiated with 2-Mev electrons. Electron flux $=3.56\times10^{15}$ e/cm^2. All irradiations and measurements at 77°K.

irradiation. Curve 2 is the absorption remaining after a room temperature anneal for 7 days. Curve 3 is the result after further annealing at 400°C for 3 days. Curve 4 shows the effect of re-irradiation after this anneal. Curves 1 and 4 are practically identical.

The data in Fig. 11 for the 400°C anneal clearly show that the defects responsible for the 215-mμ and 257-mμ centers were removed by the heat treatment. Since the far ultraviolet region could not be examined, it is not known if the *E* band also disappeared. The evidence of Mitchell and Paige[4] indicates that it is not completely removed after a 520°C anneal. If this is the case, then the *E* and *C* bands cannot be complementary defects as proposed in the Mitchell and Paige model. This view has been convincingly demonstrated by the work of Nelson and Weeks[15] who have shown that the *C* and *E* bands develop and bleach independently of each other.

DISCUSSION

The comparisons made of the damage produced by fast electrons and x-rays in fused silica (see Table III and Fig. 9) have shown that the color centers responsible for the optical absorption maxima at 215 mμ and 257 mμ are produced by excitation and ionization processes. The agreement between experimental data on 7943 silica and computed energy losses due to excitation processes, shown in Fig. 9, is excellent. No such agreement is obtained for the 7940 material. The differences in the behavior of the two silicas is attributed to the differences in OH^- content, but the role of OH^- in influencing the observed damage is not known.

The electron flux which is equivalent to the x-rays in terms of total energy absorbed by the sample corresponds to an early state in the formation of color centers as can be seen from the growth curves of Fig. 6. An absorbed dose of 1.71×10^7 rad can be obtained with a flux of only 6.89×10^{14} e/cm^2. The growth curves suggest a two-stage process of defect formation. The fast initial rise might correspond to trapping of electrons or holes at defects already present, while the later, nearly linear, portion of the growth curves may correspond to creation of the defects. Insufficient data have been obtained on x-irradiated silica to establish a growth curve. From such a curve one might be able to determine if defects are produced by x-rays or whether x-rays are effective only in providing electrons or holes for already existing defects. If the growth curve for x-rays is equivalent to that for the electrons for large doses, then it is probable that defects are being produced by the x-rays.

In considering the question of defect formation, it is interesting to determine the energies required to form a center in fused silica. In the 7940 material (for the 215-mμ absorption) the energy required varies from about 2000 ev/center at 2 Mev to about 1200 ev/center at 0.5 Mev in the early stages of coloration. In the 7943 silica, at 2 Mev, the value is about 570 ev/center. Rabin and Klick[29] have studied *F*-center production in alkali halides at low temperatures and have determined that a value of as little as 30 ev is required to fill an already existing vacancy whereas several thousand ev are required to form the defect. While no specific analogies can be drawn between the alkali halides and fused silica, the large energy values for defect formation in fused silica suggest that defects are being created during the irradiation even at the low fluxes. Thus, it seems likely that the defects are being produced by the x-rays. The broken-bond model proposed by Nelson and Crawford[8] should require only a simple ionization process for forma-

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[29] H. Rabin and C. C. Klick (to be published).

tion and, as such, would seem to be a definite possibility for representing the actual damage situation in fused silica. If it is further assumed that one or both of the C and E centers arise from a trapping of an electron or hole by the defects arising when an Si—O bond is broken, then the lack of correlation between the number of C and E centers remaining after a thermal anneal[15] can be explained in terms of the trapping of charges by impurities. That is, impurities compete with the defects for the free charges. This also could explain the small C-band coloration and the presence of the additional absorption band at 257 mμ which appears to be associated with the hydroxyl-ion in the less pure silica (7940).

The broken-bond model requires strained regions so that the broken bond will relax quickly and not reform. This mechanism is probably not operative to any large extent in crystalline α quartz and could explain the relatively small damage observed in this material.

In terms of this broken-bond model one can understand the reduced damage in fused silica when an anneal at 950°C precedes the irradiation. The strained regions already present in the glass would be relieved and would thus reduce the number of broken bonds formed as a result of irradiation. It is not clear, however, why there is decreased sensitivity when the sample in question has been irradiated prior to the 950°C anneal. It may be that the larger number of broken bonds allows greater freedom of re-arrangement of the lattice constituents than is possible during the anneal of the previously unirradiated material.

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Test of Spin Hamiltonian for Iron^{3+} in Strontium Titanate

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The applicability of a conventional spin Hamiltonian to the paramagnetic spectrum of Fe^{3+} in strontium titanate is investigated. The work was inspired by a paper by Müller who finds deviations from a conventional spin Hamiltonian which he attributed to covalent bonding. The spectrum is remeasured and compared with the more general theory of Koster and Statz. It is found that the conventional Hamiltonian describes the spectrum about as well, in this case, as the improved theory. The remaining discrepancies vary from crystal to crystal and are due to random distortions of the Fe^{3+} site. A rather good agreement with theory was obtained for one crystal which apparently was more perfect than the other measured samples. From perturbation theory, it is concluded that the deviations from a conventional Hamiltonian should be about 0.1 Mc/sec if covalency and exchange effects can be neglected. The experimental errors in the present experiments are about 1 to 2 Mc/sec. Even though for the present example it is unnecessary to resort to the improved theory, it is shown that, even in the absence of covalency, measurable deviations from a conventional spin Hamiltonian are expected in substances where the zero-field splittings and the applied magnetic field are large.

I. INTRODUCTION

IN the literature, one sometimes finds statements that the spin Hamiltonian[1,2] is not completely satisfactory in describing the energy levels of paramagnetic ions as a function of magnetic field. For example, in connection with maser studies, attention has been called again to the fact that gadolinium ethyl sulfate diluted in lanthanum ethyl sulfate shows a spectrum at low frequencies and lower temperatures not consistent with a spin Hamiltonian.[3] Müller stated in a recent paper[4] that Fe^{3+} in strontium titanate showed deviations from a spin Hamiltonian. Geusic[5] stated that he observed deviations from a spin Hamiltonian of the order of one percent for Cr^{3+} in Al$_2$O$_3$ crystals.

Observed deviations from spin Hamiltonian may have many reasons. First of all, the approximations underlying a spin Hamiltonian may introduce errors which are larger than the experimental uncertainties.

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[1] B. Bleaney and K. W. H. Stevens, *Reports on Progress in Physics* (The Physical Society, London, 1953), Vol. 16, p. 108.

[2] K. D. Bowers and J. Owen, *Reports on Progress in Physics* (The Physical Society, London, 1955), Vol. 18, p. 304.

[3] Bleaney, Scovil, and Trenam, Proc. Roy. Soc. (London) **A223**, 15 (1954).

[4] K. A. Müller, Helv. Phys. Acta **31**, 173 (1958).

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