

Color Centers and Radiation-Induced Defects in Al_2O_3 ^{†*}

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(Received April 5, 1961)

The peak energy E_0 and full width U , in ev, of the color centers in Al_2O_3 before irradiation are: $E_0=5.45$, $U=0.6$; $E_0=4.84$, $U=0.54$; with an indication of a band at $E_0>6.2$, $U>0.4$. Irradiation of 3×10^4 r produces saturation of the gamma-ray-induced bands which occur at $E_0=5.45$, $U=1.25$; $E_0=3.08$, $U=1.50$; and probably an additional band at $E_0=4.28$, $U=0.70$. Reactor irradiation produces bands at $E_0=6.02$, $U=0.60$; $E_0=5.35$; $U=0.40$; $E_0=4.85$, $U=0.54$; $E_0=4.21$, $U=0.80$; $E_0=3.74$, $U=0.88$; $E_0=2.64$, $U=0.64$; and $E_0=2.00$, $U=0.44$.

Curves of color-center concentration versus irradiation time for the reactor-induced bands at $E_0=6.02$, $E_0=5.35$, and $E_0=4.85$ can be accurately represented by a saturating exponential plus a linear increase. This behavior is predicted by a simple theory which assumes that the color centers are formed by the coloring of defects present prior to and increased by irradiation and possibly by the coloring of additional centers formed only by radiation damage. The measured rate of defect formation could be consistent with current radiation damage theories; however, several inaccurately known parameters preclude a meaningful comparison.

INTRODUCTION

IRRADIATION of single crystals of aluminum oxide by reactor, i.e., fast neutron and purely ionizing radiation, produces numerous color centers. Interest in these stems from two points of view. First, this is an almost untouched area for research in pure color-center physics. Second, energetic radiations, particularly fast neutrons, will produce lattice defects. The details of the defect-production mechanism, the number and kind of defects, their dependence on the energy of the bombarding particle, and numerous other features are all fundamental to understanding the radiation-damage mechanism. It would be desirable, before investigating the damage mechanism, to begin by completely characterizing the various color centers; especially useful would be a correlation between the nature of the defects and the optical absorption bands. However, radiation-damage information can be obtained even without this information. This paper will describe the more prominent absorption bands produced by reactor and gamma-ray irradiations and the dependence of the height or intensity of these bands on radiation dose. In particular, the growth kinetics of these bands will be related to the rate of formation of defects during the radiation-damage process.

EXPERIMENTAL DETAILS

All the measurements described below were made on single crystals of synthetic sapphire or $\alpha\text{-Al}_2\text{O}_3$ (corundum) obtained from the Linde Company. These crystals are grown by the Verneuil process and only samples appearing water clear and relatively free from strain were used. The samples were oriented with their largest

surfaces perpendicular to within 4° of the c axis by optical methods and occasionally orientations were verified by x-ray measurements. The optical transmission between 3 and 6 ev varies somewhat with different samples, and small variations occur occasionally between different parts of the same sample.

Almost all optical absorption measurements were made with a Beckman DU spectrophotometer, and all spectra were determined at room temperature. The range of this instrument is from 6.18 to about 1 ev, which is unfortunate since Al_2O_3 is transparent from approximately 9 ev to about 5μ . Optical bleaching from ordinary room illumination was not detected. This is reasonable since most of the absorption is in the far ultraviolet. Consequently, samples were occasionally exposed to room light, but this was minimized.

Reactor irradiations were performed in various facilities of the BNL graphite reactor, particularly in the pneumatic tubes, or "rabbits," where the maximum temperature was approximately 70°C . Neutron flux measurements were made with uncovered and Cd-covered gold and cobalt foils. The total fast- and slow-neutron flux in the tube used for most of the exposures was roughly 2.9×10^{12} nv and the Cd ratio was 2 with Au and 10 with Co. One crystal was irradiated with Ta^{128} gamma rays whose average is roughly 0.56 Mev, but all other gamma-ray irradiations utilized tubular Co^{60} gamma-ray sources. Gamma-ray dose measurements were made with calibrated ionization chambers. The dose given is the measured value in air at the point where the sample is located, not the ionization in the sample. The gamma rays emitted by Co^{60} are 1.1 and 1.3 Mev, but since a large number of gamma rays undergo degrading Compton scattering in both the cobalt and lead shield before striking the crystal, the average energy is less than this. During gamma-ray irradiation, the maximum crystal temperature was approximately 30°C .

Absorption spectra were always plotted versus photon

[†] Work performed under the auspices of the U. S. Atomic Energy Commission.

* Preliminary reports appeared in the following: P. W. Levy and G. J. Dienes, *Report of Bristol Conference on Defects in Crystalline Solids* (The Physical Society, London, 1955)—referred to as I; P. W. Levy, *Bull. Am. Phys. Soc.* 1, 136 (1956); 3, 116 (1958).

energy using an ordinate which is proportional to the concentration of color centers. In every case the observed spectra showed that several different bands were superimposed on one another. To accurately separate the spectrum into different bands, it is essential to know the precise shape of each band at the temperature of the sample during the absorption measurement. This information is not available for Al_2O_3 and it is necessary to "guess" the band shape or to assume that it is Lorentzian, Gaussian, etc. The absorption bands observed so far seem to be Gaussian, or very close to it, at room temperature, and in resolving spectra into component bands it was assumed they are accurately Gaussian. The procedure used to accomplish this has been discussed previously.¹ The parameters describing each band are E_0 , the energy of the maximum, and U , the full width at half-maximum intensity, both in ev.

ABSORPTION SPECTRA OF UNIRRADIATED Al_2O_3

When received from the supplier, all crystals appeared to be water clear. However, when examined with a polariscope, a small amount of strain was usually seen to be present. The optical transmission measurements of the untreated crystals indicated a small amount of absorption in the 3–6-ev region. To separate the volume absorption from the surface reflection, the expected reflection "loss" as a function of wavelength was computed from the index of refraction. In the 4.7–0.22-ev region the experimentally determined values of Malitson, Murphy, and Rodney² were used. Indexes for wavelengths above and below these were computed from Sellmeier's equation in which the constants had been obtained by fitting to the measured values. The

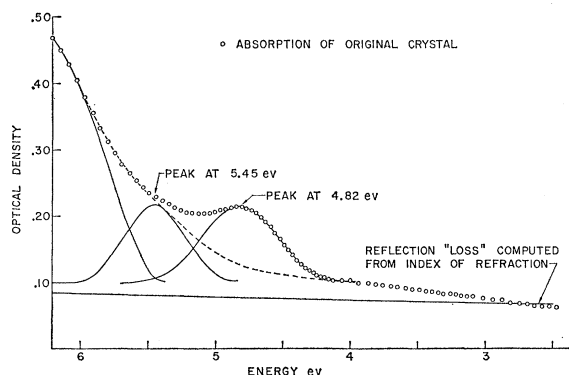


FIG. 1. The observed optical absorption, which was much greater than usual, of an Al_2O_3 single crystal when received from the supplier. Different ways of separating this spectrum into component bands are indicated. Its general shape is typical of this material; however, the intensity of the band at 4.82 ev is, relative to the other bands, unusually high.

¹ P. W. Levy, J. Phys. Chem. Solids **13**, 287 (1960); J. Am. Ceramic Soc. **43**, 389 (1960).

² I. H. Malitson, F. V. Murphy, and W. S. Rodney, J. Opt. Soc. Am. **48**, 72 (1958).

optical density of a crystal that showed unusually high absorption is shown in Fig. 1, as well as the apparent absorption due to the surface reflection. The general shape of this absorption spectrum is typical of untreated crystals. Obviously, there are one or more bands in the region of 6 ev and another at 4.82 ev. The observed spectra can be resolved into these two bands or equally well into three bands. That there is a band at 5.45 ev is suggested by the appearance of a band at this energy in the coloring induced by gamma rays. Also, annealing experiments to be described in a later paper show the presence of a band at this energy.

In numerous crystals the measured optical density from 3 to 1 ev was *less than* that expected from the computed surface reflection. Also, the annealing experiments usually resulted in samples that were more transparent after irradiation and annealing than when received. This would imply that the crystal used for the index-of-refraction measurements was atypical in one or more respects.

GAMMA-RAY-INDUCED COLORING

Typically, when Al_2O_3 single crystals are irradiated with gamma rays, a dose of $3\text{--}5 \times 10^4$ r brings the induced coloring to saturation. The absorption spectrum in Fig. 2 was obtained by computing the difference between the absorption of the original crystal and the absorption after an irradiation of 1.09×10^9 r. However, very nearly the same spectrum was obtained at various doses. The two larger bands are undoubtedly the same as those reported by Hunt and Schuler.³ Even if it was not assumed that these two bands have Gaussian shape, it was difficult to resolve the observed spectrum into just two bands. Thus, it is probable that one or more additional bands occur near 4.28 ev. This conclusion is supported by the observation that there is a relatively sharp discontinuity in the data at 4.8 ev and the sug-

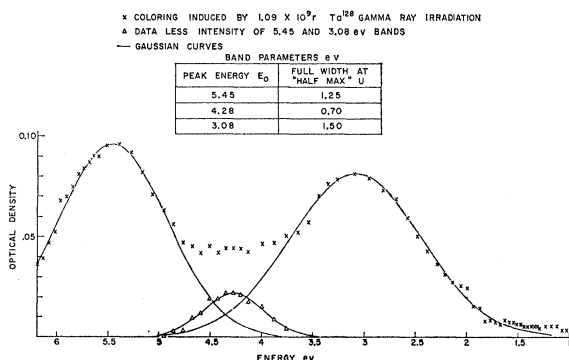


FIG. 2. Gamma-ray-induced absorption spectrum of Al_2O_3 . The spectrum obtained by an irradiation of only 3×10^4 r remains unchanged by additional gamma-ray irradiations even up to 10^9 r. Obviously, the existence of a band at 4.28 ev can be questioned, and the parameters given for it are subject to large error.

³ R. A. Hunt and R. H. Schuler, Phys. Rev. **89**, 664 (1953).

gestion of a discontinuity near 3.6 ev. The total amount of gamma-ray induced absorption was so small that reliable growth curves could not be obtained for any bands.

ABSORPTION BANDS INDUCED BY REACTOR IRRADIATIONS

When irradiated in a reactor, besides being exposed to ionizing radiation, crystals will be exposed to energetic particles, principally fast neutrons, which will eject atoms from their normal lattice positions, creating numerous defects. The defects are converted to color centers by capturing electrons or holes produced by the ionizing field. Thus, it is not surprising that reactor irradiation produces several strong absorption bands. An example of the reactor-induced spectrum, i.e., the difference between the observed absorption before and after irradiation, determined with a recently obtained Cary spectrophotometer, is shown in Fig. 3. Clearly there are peaks near 6, 5.4, and 4.8 ev, and a very slight indication of a peak at 6.5 ev which could be spurious. The spectrum from 6.18 to 1 ev agrees very well with numerous measurements made with the Beckman DU spectrophotometer.

One such absorption spectrum is plotted in Fig. 4 which includes two different resolutions of the spectrum into component absorption bands. Actually, conclusive evidence is lacking to clearly indicate which of these is more nearly correct. Both the annealing experiments and the gamma-ray induced coloring curves indicate there is a band at 5.4 ev, and on the basis of this the resolution given by the dashed curves seems more probable. The possibility remains, however, that the observed spectra contain one or more additional bands that have not been detected.

The intensity below 4 ev in Fig. 4 is not great enough to make a reasonable resolution into component bands. The spectrum of a crystal irradiated approximately 100 times that used for Fig. 4 is plotted in Fig. 5. In this

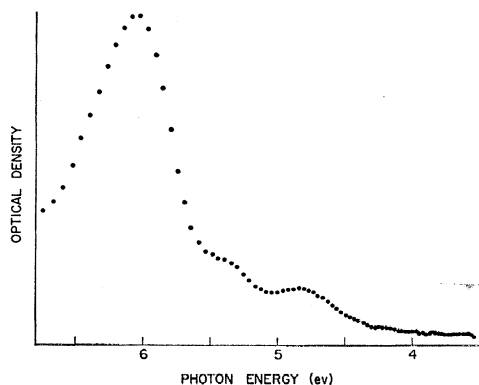


FIG. 3. The optical absorption spectrum produced by reactor bombardment of Al_2O_3 . The very slight indication of a separate band near 6.5 ev could be spurious.

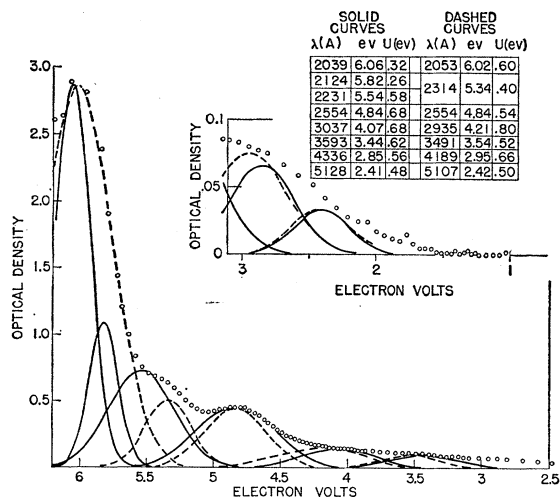


FIG. 4. A reactor-radiation-induced absorption spectrum of Al_2O_3 resolved into two sets of component Gaussian-shaped absorption bands. The set shown with dashed curves appears to be more probable. The values of E_0 and U are those actually obtained by the resolution procedure, i.e., no attempt has been made to fit this and other data with a consistent set of band parameters. The parameters quoted for bands below 4.5 ev are subject to large errors—see Fig. 5.

case it is possible to make reasonably reliable resolutions, and the parameters obtained should be much more accurate. Incidentally, in Figs. 4 and 5, the peak energy and full width of the bands is that obtained from the original analysis of each set of data. No attempt has been made to fit the data given throughout this paper with a consistent set of absorption band parameters, in order to indicate the degree of uncertainty present in the resolutions of the spectra into individual bands.

Most of the bands described above, and tabulated in Table I, have been investigated by Mitchell, Rigden, and Townsend⁴ who have made a detailed study of their anisotropic absorption. They did not detect bands at 5.8 or 5.5 ev, which supports the conclusion that the resolution given by the dashed curve in Fig. 4 is the more probable. Also, Gibbs, Cutler, and Bates⁵ report that the band at 4.8 ev is formed by heating in oxygen and removed by heating in hydrogen. This would account for its prominence in the sample having unusually high absorption when received; presumably this sample had been prepared under oxidizing conditions.

GROWTH OF RADIATION-INDUCED ABSORPTION BANDS

During reactor irradiation, defects, impurities, etc., present before exposure can be converted into color

⁴ E. W. J. Mitchell, J. D. Rigden, and P. D. Townsend, *Phil. Mag.* **5**, 1013 (1960).

⁵ P. Gibbs, I. B. Cutler, and J. L. Bates, *Bull. Am. Phys. Soc.* **2**, 300 (1957).

centers by electron or hole trapping. Also, the concentration of some of the original defects will be increased by neutron bombardment, and in addition, different kinds of defects may be created. The rate of formation of color centers by carrier trapping on defects both originally present and produced by bombardment, can be described by the following equation:

$$dN_i/dt = f_i(N_{0i} + K_i t - N_i), \quad (1)$$

where N_{0i} is the concentration of the i th defect before irradiation, t is the time, K_i is the rate of formation of new defects of the same type, N_i is the concentration of color centers formed by carrier trapping on the $(N_{0i} + K_i t)$ defects present at time t , and f_i is the fraction of uncolored defects colored per unit time. This equation is expected to accurately apply where the trapping of carriers is small compared to electron hole recombination. A detailed derivation of this equation, and a discussion of the conditions when it is expected to apply, will be published separately.⁶ The extended treatment shows, and it is also reasonable to assume, that an equation of this type applies independently to each defect. The solution of this equation is

$$N_i = N_{0i}(1 - e^{-f_i t}) + K_i \left(t - \frac{1}{f_i}(1 - e^{-f_i t}) \right) \quad (2.1)$$

$$= \left(N_{0i} - \frac{K_i}{f_i} \right) (1 - e^{-f_i t}) + K_i t. \quad (2.2)$$

Experimental curves are written as

$$(\text{O.D.})_i = C_{1i}(1 - e^{-C_{2i}t}) + C_{3i}t, \quad (2.3)$$

where "O.D." means optical density.

The first term in (2.1) represents coloring of defects present in the sample prior to irradiation, and the second

TABLE I. Absorption bands in Al_2O_3 . Independent determinations of the parameters defining what could be the same band are grouped together. When one determination is clearly the most reliable, it is marked with an asterisk.

Peak energy E_0 (ev)	Full width U (ev)	Formation conditions
> 6.2	> 0.4	In unirradiated samples
6.02	0.60	Reactor-induced
5.34	0.40	Reactor-induced
5.45	1.25	Gamma-ray-induced
5.45	0.6	In unirradiated samples
4.84	0.54	Reactor-induced
4.82		In unirradiated samples
4.28	0.70	Gamma-ray-induced
4.21*	0.80	Reactor-induced
3.54	0.52	Reactor-induced; short irradiation
3.74*	0.88	Reactor-induced; long irradiation
3.08	1.50	Gamma-ray-induced
2.95	0.66	Reactor-induced; short irradiation
2.64*	0.64	Reactor-induced; long irradiation
2.42	0.50	Reactor-induced; short irradiation
2.00*	0.44	Reactor-induced; long irradiation

term arises from coloring of defects formed during the irradiation. Equation (2.2) demonstrates that the observed growth will be a saturating exponential plus a linear growth. If more than one absorption band overlaps, the observed growth will be a superposition of equations such as (2.1). In the case of two bands,

$$N_i + N_j = (N_{0i} - K_i/f_i)(1 - e^{-f_i t}) + K_i t + (N_{0j} - K_j/f_j)(1 - e^{-f_j t}) + K_j t, \quad (3.1)$$

which will be nearly a saturating exponential plus a straight line unless f_i is very different from f_j . If $f_i = f_j$,

$$N_i + N_j = \left(N_{0i} + N_{0j} - \frac{K_i + K_j}{f_i} \right) (1 - e^{-f_i t}) + (K_i + K_j)t, \quad (3.2)$$

which is precisely a saturating exponential plus a straight line. From Figs. 3 and 4 it is apparent that prominent reactor-induced bands occur at 6.02, 5.35, and 4.85 ev. To study the growth of these bands, a series of 1-hr irradiations was carried out in one of the "rabbits" and the absorption spectrum measured after each irradiation. However, before the reactor irradiations were started, the sample was colored to saturation with gamma rays, and, subsequently, all growth curves were constructed by taking the difference between the saturation gamma-ray coloring and the absorption after each reactor irradiation.

Growth curves for these three prominent bands were obtained in three different ways. The first set of curves was obtained from the observed optical absorption at the peak of each band. These data are shown in Fig. 6 which was used to obtain the values of the constants in

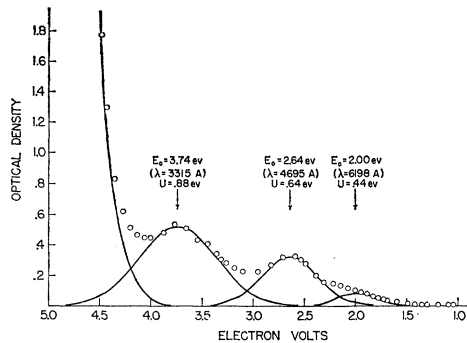


FIG. 5. Absorption spectrum of an Al_2O_3 sample, reactor-irradiated to an extent roughly 100 times that used for Fig. 4. The values of E_0 and U for the peaks in the 4.5–1 eV region obtained from this figure should be much more reliable than those shown in Fig. 4—provided they are the same bands.

⁶ P. W. Levy, Bull. Am. Phys. Soc. 1, 136 (1956); and to be published.

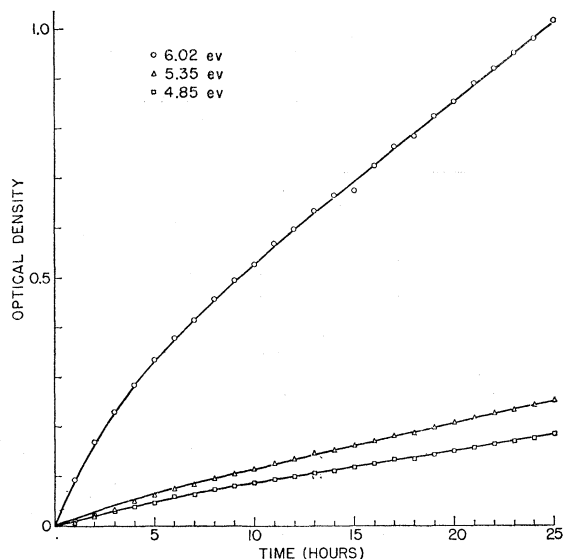


FIG. 6. Growth of the three most prominent reactor-induced bands, as a function of irradiation time determined from the observed optical density of the indicated photon energies. The constants C_{1i} and C_{3i} in Eq. (2.3) obtained from this graph are tabulated in Table II(a). They and C_{2i} , see Fig. 7, were used to compute the theoretical curves.

Tables II(a) and III(a). The solid lines were computed from Eq. (2.2) using the parameters in Table II(a). To determine these parameters, the K_i are taken from

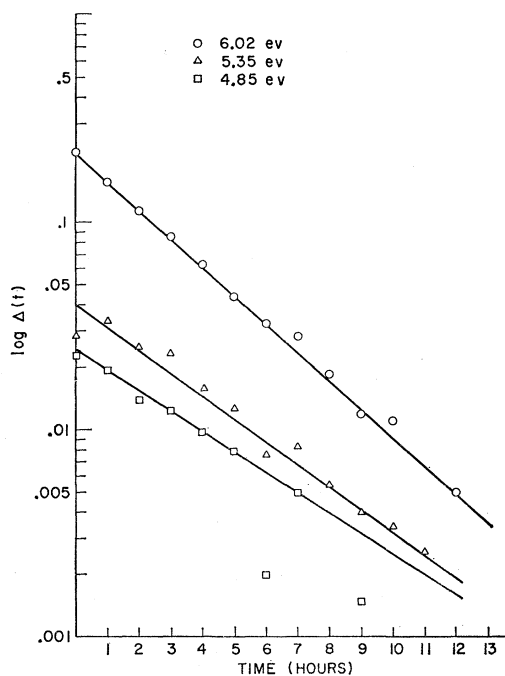


FIG. 7. Demonstration that each of the data curves in Fig. 6 can be represented by the sum of a saturating exponential and a linear term. The constants C_{2i} in Table II(a) were obtained from the solid lines. All of the experimental errors accumulated in this figure.

the linear portion of the curve above 15 hr. The linear region for each band is extrapolated to $t=0$, and from the difference between each line and the data, Fig. 7 was constructed. Also, the intersection of the straight-line extrapolation and the $t=0$ axis is the value of $(N_{0i} - K_i/f_i)$. These two figures demonstrate conclusively that the growth curves for the bands at 6.02 and 4.85 eV follow the anticipated behavior. The other band at 5.35 eV does not deviate markedly from this behavior; this is not surprising since it is superimposed on the 6.02-eV band. The f_i are obtained from the slope of the straight lines drawn in Fig. 7. The bands at longer

TABLE II. Experimentally determined parameters in the equations plotted in Figs. 6 and 8. $(O.D.)_i = C_{1i}(1 - e^{-C_{2i}t}) + C_{3i}t$.

Bands (ev)	C_{1i}	C_{2i}	C_{3i}
(a) Constants used in Fig. 6—obtained from the observed optical density at the indicated band maxima of spectra not resolved into component bands.			
6.02	0.214	0.316	0.0320
5.35	0.028	0.251	0.0089
4.85	0.024	0.226	0.0064
(b) Constants used in Fig. 8—obtained from spectra resolved into Gaussian-shaped absorption bands.			
6.02	0.230	0.267	0.0305
5.35	0.058	0.062	0.0052
4.85	0.049	0.141	0.0050

TABLE III. Constants in the equation $N_i = (N_{0i} - K_i/f_i)(1 - e^{-f_i t}) + K_i t$.

Band (ev)	$N_{0i}f_{0i}$	f_i	$K_i f_{0i}$
(a) Unresolved spectra			
6.02	4.94×10^{16}	0.316	1.39×10^{12}
5.35	0.69×10^{16}	0.251	0.267×10^{12}
4.85	0.81×10^{16}	0.226	0.274×10^{12}
(b) Spectra resolved into Gaussian-shaped bands			
6.02	5.39×10^{16}	0.267	1.33×10^{12}
5.35	1.52×10^{16}	0.062	0.155×10^{12}
4.85	1.30×10^{16}	0.141	0.213×10^{12}

* f_{0i} = oscillator strength = 1; $N_{0i}f_{0i}$ in units of color centers/cm²; f_i in units of fraction of uncolored centers colored per hour; $K_i f_{0i}$ in units of uncolored centers/cm² formed per second.

wavelengths behave in a similar fashion but their total intensity is not enough to make a precise analysis.

The growth characteristics described above for each band were made without resolving the observed absorption spectra into component bands. From such a resolution, however, it should be possible to obtain much more reliable growth curves. This would be especially so if the total number of bands contributing to each spectrum and their precise shape were known. Since these are not known, a second analysis was made by resolving numerous spectra into component bands assuming each was Gaussian and using the parameters given in Table I. The peak intensities obtained in this

way are shown as data points in Figs. 8 and 9. The parameter obtained for each band, using exactly the same procedures used with Figs. 6 and 7, are given in Tables II(b) and III(b).

A third analysis was made using the observed intensities at the absorption peaks and the computed "reflection loss" curve as the absorption of the crystal before reactor irradiation instead of the saturation gamma-ray coloring curve. This third analysis resulted in values of $N_{01}=6.16$, $N_{02}=1.19$, $N_{03}=1.18$ (in units of 10^{16} color centers per cm^3); the K_i were unchanged

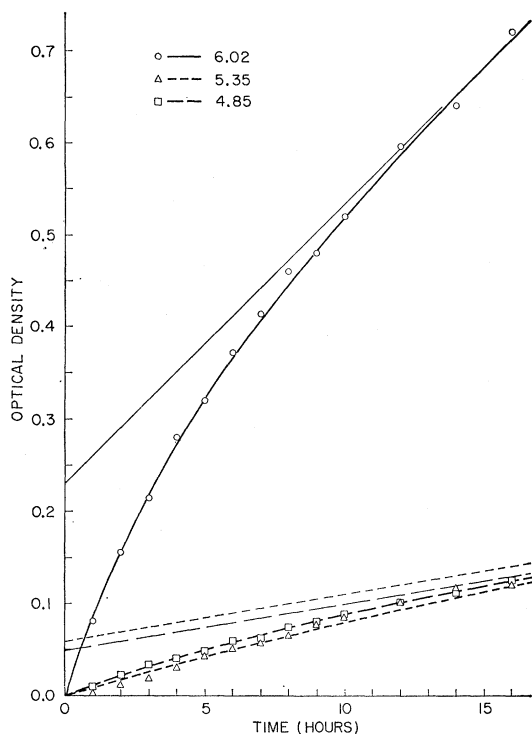


FIG. 8. Growth of the three most prominent reactor-induced bands, as a function of irradiation time, determined from spectra resolved into Gaussian-shaped absorption bands. The narrow straight lines were extrapolated from data points (not shown) between 20 and 80 hr, which is linear to within experimental error, e.g., see Fig. 10. The heavy lines are theoretical curves computed from Eq. (2.3) using C_{1i} and C_{3i} obtained from this plot, and C_{2i} from Fig. 9. These constants are tabulated in Table II(b).

but plots similar to Figs. 7 and 9 did not result in satisfactory straight lines. This third type of analysis was attempted since there is a possibility, supported by annealing studies now underway, that a large fraction of the absorption of the unirradiated crystal is due to the presence of the 6.03-eV band, and possibly in addition, the 5.35- and 4.85-eV bands.

Comparison of the parameters obtained by the three different methods of analysis indicate that the same qualitative behavior is obtained using all three methods but that different values of the constants in Eq. (2.2)

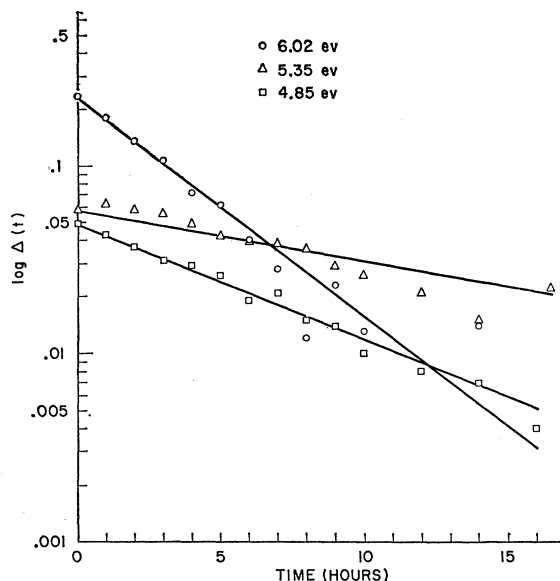


FIG. 9. Demonstration that each of the data curves in Fig. 8 can be represented by the sum of a saturating exponential plus a linear term. The constants C_{2i} in Table II(b) were obtained from solid lines. All of the experimental errors accumulated in this figure.

are obtained. The values obtained by resolving the spectra into component Gaussian-shaped bands should be the most reliable.

The rate of formation of defects by the reactor radiation is given by the constants K_i in Eq. (1). The magnitude of K_i should be proportional to the fast neutron flux assuming that the fast neutron distribution

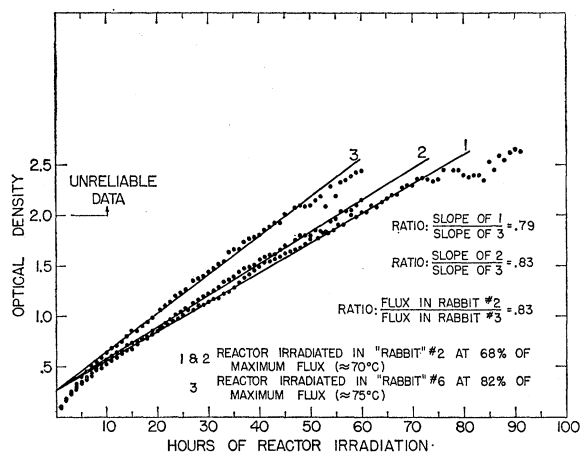


FIG. 10. Demonstration that the K_i , i.e., the slope of the linear part of the growth curve, of the 6.02-eV band (2040 Å) is proportional to fast-neutron flux. Note also that there is an indication that the growth curve deviates from the linear behavior near 80–100 hr. This would occur if defect recombination is taking place. Even though the data for optical density above 2 is "unreliable," additional, more reliable, measurements show the curvature. The 4.85- and 5.35-eV bands show the same linear behavior.

is always the same. To test the dependence of K_i on flux, Al_2O_3 crystals were irradiated in two different irradiation facilities in which the flux was different but the temperature was roughly the same. A comparison of the growth curves obtained under these conditions is shown in Fig. 10. Obviously, the data are in agreement with this hypothesis, but the slopes do not differ sufficiently to provide a really good test.

COMPARISON WITH RADIATION DAMAGE THEORY

From the data given in Table II, the concentration of various centers could be calculated from Smakula's formula if the oscillator strength f_0 were known. Since it is not known, the computed concentrations will leave it unspecified. A value near one is not unreasonable, but much smaller values cannot be ruled out. In making these computations all the absorption bands were assumed to be Gaussian, the indexes of refraction were either those reported or taken from Sellmeier's equation, and the crystals were all approximately 0.5 mm thick.

The pertinent results are summarized in Table III. Currently, there are two theoretical treatments concerned with the calculation of the number of atoms displaced from their normal lattice positions by energetic particles, e.g., fast neutrons. One is by Kinchin and Pease⁷; the other by Seitz and Koehler.⁸ These do not differ much in principle; a detailed comparison of the two is given by Dienes and Vineyard.⁹ The Kinchin and Pease treatment is easier to handle computationally and has been used to compute Table IV. The number of displacements predicted by theory depends very strongly on the threshold displacement energy E_d , which is the minimum energy which must be transferred to the lattice atom to eject it from its normal position. Also, the number of displacements depends on the energy of the incident neutron; for neutrons above 1 Mev the number of displacements is relatively independent of neutron energy, while for neutrons somewhat below 1 Mev the displacements are proportional to neutron energy. Thus, if the fast-neutron flux is predominantly above 1 Mev, knowledge of the flux distribution is not essential, while if a large fraction of the fast neutrons is below 1 Mev, knowledge of the flux distribution is absolutely necessary. In Table IV both values obtained for the fast flux have been used. It is reasonable that these span the range of the fast flux. Also, it is assumed that the same value of E_d applies to both the Al and O atoms. It is unlikely that this is the case, since the oxygen atoms are large and are on a close-packed hexagonal lattice in which they occupy every other layer. The aluminum atoms occupy two

TABLE IV. Displacements formed in Al_2O_3 by 1-Mev neutrons—according to Kinchin and Pease.

Threshold energy (ev)	Atoms displaced ($10^{12}/\text{cm}^2 \text{ sec}$)			
	Fast flux = $0.3 \times 10^{12} \text{ nv}$		Fast flux = $1.5 \times 10^{12} \text{ nv}$	
	Cd ratio = 2		Cd ratio = 10	
	Al	O	Al	O
25	174	234	35	47
50	87	117	17	23
100	43	58	9	11
200	21	29	4	5

out of every three sites on layers between the O layers and are considerably smaller. Perhaps it is easier for the Al atoms to be ejected, but it would also be easier for them to diffuse back to their normal lattice positions. It appears that the vacant Al sites would be the natural place for ejected atoms to come to rest.

The minimum energy required to produce the 6.02-ev band by electron bombardment has been determined by Arnold and Compton.¹⁰ Since it is not known if this band is due to a defect formed by the ejection of an Al or O atom, they give $E_d = 50$ ev for Al or $E_d = 100$ ev for O. They also find that roughly ten times more defects are formed by electron bombardments at 77°K than at room temperature. From this observation, it would appear that the number of defects formed, as they suggest, would be roughly this factor greater than the measured number of defects, especially since reactor bombardments were carried out near 70°C. Obviously, the combination of such a large amount of annealing and an oscillator strength near 0.5 would bring the measured defect concentration in agreement with the calculated values.

There is another possibility which must be considered. The optical transmission of Al_2O_3 extends to approximately 9 ev, which is well beyond the range of our spectrophotometer. If the defects responsible for the observed bands are multiple, e.g., divacancies, another band attributed to a single Al or O vacancy could exist and not have been detected. The concentration of multiple defects would be considerably below that of single vacancies, thus again causing the measured number of defects calculated in Table III to be low.

A direct determination of the total number, i.e., vacancies plus interstitials, of the defects formed by reactor irradiation of Al_2O_3 has been made by Antal and Goland.¹¹ This was done by measuring the long-wavelength neutron transmission of an Al_2O_3 crystal before and after a 240-day reactor bombardment. The number of defects they obtained was approximately 40 times less than that predicted by Kinchin and Pease. Obviously, if a large amount of annealing occurs immediately after the radiation-damage event, involving defects from the same recoil, this would account for

⁷ G. H. Kinchin and R. S. Pease, *Reports on Progress in Physics* (The Physical Society, London, 1955), Vol. 18, p. 1.

⁸ F. Seitz and J. S. Koehler, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1956), Vol. 2.

⁹ G. J. Dienes and G. H. Vineyard, *Radiation Effects in Solids* (Interscience Publishers, Inc., New York, 1957).

¹⁰ G. W. Arnold and W. D. Compton, *Phys. Rev. Letters* 4, 66 (1960).

¹¹ J. J. Antal and A. N. Goland, *Phys. Rev.* 112, 103 (1958).

a part of the discrepancy. However, if vacancy-interstitial recombination occurs via diffusion from one damage event to another, a process discussed elsewhere,⁶ the total concentration of defects would tend to be increasingly different from the expected linear growth. There is an indication in Fig. 8 that this may occur for irradiations of approximately 100 hr as shown by the "bending over" of the growth curves.

CONCLUSION

Two, three, or even four absorption bands are found in single-crystal Al_2O_3 before irradiation, two or three are formed by gamma-ray irradiation, and five or six by exposure to the fast-neutron and ionizing radiation in a reactor. Curves of color-center concentration vs irradiation time for the most prominent reactor-induced bands can be accurately represented by the addition of a saturating exponential and a linear increase. This behavior is in accord with a simple theory describing the coloring of a defect which is present in the crystal prior to irradiation and is also produced by a radiation-damage process. In paper I (see footnote to title) a different mechanism, based on annealing of centers during irradiation was proposed which also leads to a linear plus exponential growth curve. However, the

mechanism described in detail here and which was described briefly in I, is more likely to be correct. Also, these coloring curves, at a particular wavelength, could arise from the superposition of two, or more, absorption bands. One band might be formed by the coloring of defects originally present and the other band by the coloring of defects produced during the irradiation. Assuming that the linear increase is due to the coloring of only one defect, the formation rate can be determined with good accuracy. This rate could be in agreement with theoretical estimates of the rate of formation of defects if all the following are true: (1) The optical oscillator strengths are 0.5 or less; (2) the minimum energy required to eject an Al or O atom from its normal lattice position is 50 or 100 eV; (3) roughly nine-tenths of the defects produced at room temperature anneal out immediately; and (4) the fast-neutron flux lies somewhere between the measured extremes. It is possible, however, that the rate of formation of defects is correctly estimated by the theories of Kinchin and Pease, and Seitz and Koehler, but that recombination of defects, perhaps from separate radiation damage events, occurs to the extent that at a reactor exposure of only 5×10^{17} *nvt*, the number of defects accumulated is less than that expected.