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Photoconductivity and charge trapping in α-Al_2O_3

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An electron trap which strongly affects the photoconductivity of colored α-Al_2O_3 has been investigated from 10 to 300 K. The trap, which also causes the 260-K thermoluminescence peak and makes possible the interconversion of F and F^+ centers by optical means, was studied in thermochemically-reduced samples as well as in samples which had been irradiated with high-energy electrons, reactor neutrons, or γ rays. The activation energy for thermal release of the electron from the trap has been measured as 0.73 ± 0.03 eV from the photoconductivity, thermoluminescence, and phosphorescence. The absorption band for optical release of the electron has been observed in the excitation spectrum of the photoconductivity near 5 eV, with a half-width of ~ 0.6 eV. The possible identity of this and other traps is discussed.

I. INTRODUCTION

Recent measurement strongly suggest that the F center in α-Al_2O_3 absorbs at 6.1 eV and that the F^+ center absorbs at 4.8 and 5.4 eV.[1-3] A possible third F^+ band near 6 eV has been observed in the excitation spectrum of the 3.8 eV F^+ emission band but the corresponding absorption is usually hidden in the general optical density around 6 eV. An F^+ center consists of an oxygen ion vacancy which has trapped one electron and an F center consists of an F^+ center which has trapped a second electron. The local symmetry of an oxygen ion vacancy in α-Al_2O_3 is C_2, the effect of which has been detected as dichroism in the F^+ absorption bands[3] and lifetime effects in the 3.0 eV emission of the F center.[4]

In this paper we are mainly concerned with the physical processes accompanying the interconversion of F and F^+ centers by optical means.[5] This kind of experiment, which was originally performed on a neutron-irradiated sample,[1] contributed significantly to the identification of the F and F^+ absorption bands. The measurements showed that the intensity of the F band was diminished by bleaching with 6-eV light but could be restored by subsequent bleaching with $\sim$5-eV light, whereas the reverse was true for the F^+ bands. The interpretation of this result is that 6-eV light excites one of the two electrons in the F center into the conduction band which allows it to be trapped elsewhere in the crystal. An F^+ center is thus formed. Subsequent bleaching with $\sim$5-eV light releases the trapped electron and its recombination with an F^+ center reforms an F center. The efficiency of this interconversion is highest in some thermochemically-reduced samples[2] and is temperature dependent. The motion of the free electron in the process can also be detected as photoconductivity, which we describe below.

Hughes[6] has measured the time dependence of the x-ray excited electrical conductivity in α-Al_2O_3 over the time range $10^{-9}-10^3$ s. the lifetime for intrinsic conductivity is only a few nanoseconds after which the mobility is trap modulated. Hughes's measurements suggested that the conductivity was due to the motion of electrons, although hole motion could not be entirely ruled out. The effect of three different traps was detected. The activation energy for release from the second of these was 0.75 eV which is close to the value found by Lehmann and Gunthard[7] by measuring phosphorescence in as-grown samples. We are particularly concerned here with the nature of this trap and its effect on photoconductivity and thermoluminescence.[8]

There have been several studies of thermoluminescence in α-Al_2O_3, the most recent by Cooke *et al.* which was directed towards the potential use of the material as an x-ray or ultraviolet dosimeter.[9] The measurements described here were aimed at investigating the 220- and 260-K peaks in high-purity α-Al_2O_3, which had been subjected to different treatments, in order to gain information about the nature of the traps responsible. It will be seen that these traps have the largest affect on the

F to F^+ center conversion which was described above.

II. EXPERIMENTAL

Samples of ultraviolet grade single crystal α-Al_2O_3 were obtained from several manufacturers including Crystal Systems, Inc., Adolf Meller, Inc., and Linde, Inc. Additional samples were purchased from Insaco, Inc. who had obtained their boules originally from Meller. Chemical analyses supplied by the manufacturers showed the impurity content of all the samples were comparable, with most impurities present in less than 10 parts per million (ppm). Additional analyses were done for iron-group metals and all gave levels of at most a few ppm of these ions. It is worth noting that the iron-group ions have strong charge transfer transitions in the region of 5 – 7 eV which makes them apparent from optical-absorption measurements at concentrations of a few tens of ppm.[10] Samples from Crystal Systems, Meller, and Insaco had an optical-absorption band at 6.1 eV characteristic of F centers. It is usual to grow α-Al_2O_3 under a reducing atmosphere which often has the effect of thermochemically coloring the samples. The Linde samples showed no F band when received. The samples had dimensions of $\sim 10 \times 5 \times 1.5$ mm^3 and were polished to a fine optical finish. Samples cut parallel to and perpendicular to the c axis were available but no orientation effects in the measurements presented here were detected.

dc photoconductivity measurements were made over the spectral range from 4 – 6.5 eV and over the temperature range from 6 – 300 K. A sample holder based on a configuration which has been described elsewhere[11] was used. The holder was inserted into the exchange gas chamber of an Oxford Instruments CF201 continuous flow helium cryostat. Light from a deuterium lamp was dispersed by a McPherson 218 grating monochromator and fell on the sample in the same direction as the applied electric field, which varied up to 3 kV cm^{-1}. Maximum photocurrents of about 10^{-11} A were detected using a Cary 401 vibrating reed monochromator. The system had a leakage current under typical use of $\sim 10^{-16}$ A.

Thermoluminescence measurements were made over the temperature range 70 – 300 K, and light could be detected over the spectral range from 1.5 – 6.0 eV, although only F band light near 3 eV was actually detected in these measurements. The heating rate used was ~ 5 K min^{-1}. Optical-absorption measurements could be made at 10, 77, and 300 K using a Cary 14 spectrophotometer.

III. RESULTS

A. Optical absorption

In Fig. 1 is shown the interconversion of F and F^+ centers caused by preferential optical bleaching of a thermochemically-reduced sample at room temperature. The measurements were made on the same sample used to make similar measurements at 10 K in Ref. 2, which are shown here as an insert in Fig. 1 for convenience. The general features of the results are that the F band is reduced by bleaching with 6.4-eV light, curve a, while the F^+ bands at 4.8 and 5.4 eV are increased. The reverse is true following bleaching with 5-eV light, curve b. The conversion of F to F^+ centers is about four times more efficient at 10 K than at room temperature, and is not fully reversible even at room temperature; that is, once the sample has been

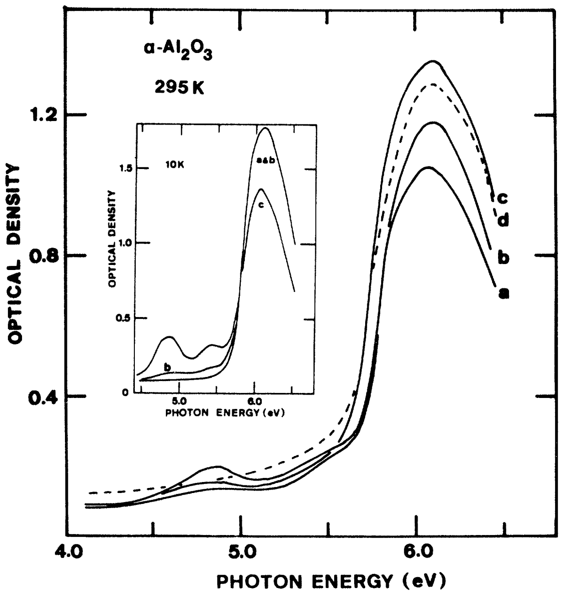

FIG. 1. Optical-absorption spectra of type-I thermochemically-colored α-Al_2O_3 at 295 K. Curve a, after bleaching with 6.4-eV light; curve b, after bleaching with 5.0-eV light; curve c, after heating to 500 °C for 30 min; curve d, after irradiation with 1 Mrad of 70-kV x rays. Insert: optical spectra at 10 K; curve a, after several months at 300 K; curve b, after bleaching with 5.0-eV light; curve c, after bleaching with 6.4-eV light.

bleached with 6.4-eV light, it is not possible to subsequently bleach with 5-eV light and fully remove the absorption at 4.8 eV. However, if the sample is left in the dark at room temperature for several months, the absorption below 5.7 eV disappears leaving only the *F* band (see insert to Fig. 1, curve *a*).

The interconversion process cannot be effected in all thermochemically-colored samples even at low temperature; for example, one sample with an optical density of 0.6 at the peak of the *F* band showed no noticeable change ($\Delta_{\mathrm{OD}} < 0.005$) following 15 minutes irradiation with 6.4-eV light. Those samples in which the interconversion process occurred are referred to below as type-I samples, whereas those in which no change could be effected are called type-II samples.

In some samples the 6.1-eV band was reduced by as much as 20% when the sample was left standing at room temperature. The absorption could be restored by heating the sample to 500 °C for 30 minutes, Fig. 1, curve *c*. The heating is accompanied by a blue thermoluminescence characteristic of *F* centers.[12] Following subsequent irradiation at room temperature to a dose of $\sim 10^6$ rad of 70-kV x ray the 6.1-eV band is slightly reduced, whereas the absorption over the range 4.0–5.5 eV was generally increased, although no noticeable increase in the F^+ bands was apparent, Fig. 1, curve *d*. It was not possible to repeat these experiments on particle-irradiated samples because in these samples *F* centers anneal out near 400 °C.[13]

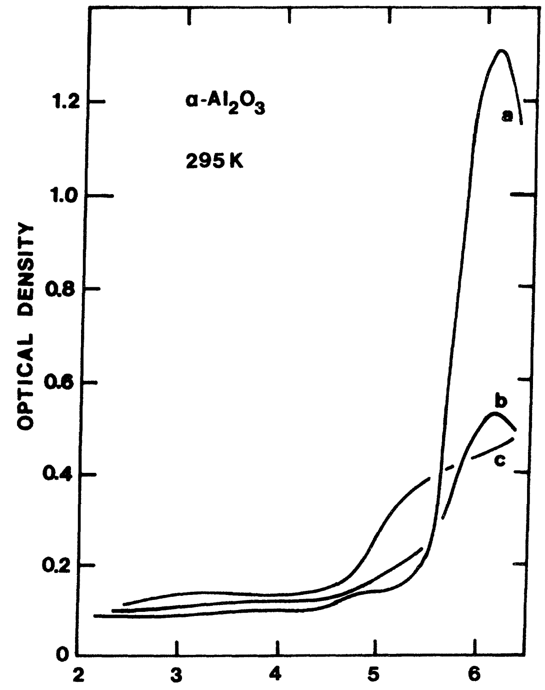

FIG. 2. Optical absorption of type-I thermochemically-reduced α-Al$_2$O$_3$ at 295 K. Curve *a*, before heating; curve *b*, after heating at 1250 °C in air for 12 hours; curve *c*, after heating to 1500 °C in air for 12 hours.

In a previous publication[2] it was reported that anion vacancies anneal in thermochemically colored α-Al$_2$O$_3$ when the sample is heated over 1300 °C. We show in Fig. 2 the optical-absorption curves which result from annealing in air at 1250 °C for 12 hours, curve *b*, and 1500 °C for 12 hours, curve *c*. Notice that following this treatment a broad band near 5 eV is formed.

B. Photoconductivity

For a photoconductor in which the mean range $\omega_0 E$ of the charge carriers in the direction of the applied electric field E is small compared to the thickness of the sample d, the photocurrent I_ϵ can be written[14]

$$I_\epsilon = N_\epsilon (\eta\omega_0)_\epsilon \,|\, e \,|\, E/d , \qquad (1)$$

where N_ϵ is the incident photon flux with energy ϵ, e is the charge on an electron, and η is the free carrier yield, i.e., the number of free-charge carriers produced per incident photon. This equation is usually rearranged to give

$$(\eta\omega_0)_\epsilon = (I/N)_\epsilon (d/\,|\, e \,|\, E) \qquad (2)$$

where the product $(\eta\omega_0)_\epsilon$, which is proportional to the photocurrent, is called the photoresponse per incident photon of energy ϵ. The photoresponse per absorbed photon $(\eta_a\omega_0)_\epsilon$ is obtained by dividing $(\eta\omega_0)_\epsilon$ by the fraction of incident photons of energy ϵ absorbed in the sample. An experimental test of the validity of Eq. (1) is that the photocurrent is directly proportional to both the applied electric field and the intensity of the incident light.

The photoresponse of two thermochemically-reduced samples of α-Al$_2$O$_3$ at 77 K is shown in Fig. 3. Curve *a* is for a type-I sample which was 1.58 mm thick and which had an absorption coefficient α at 6.1 eV of 18 cm^{-1}. Curve *b* is for a type-II sample which was 1.0 mm thick and for which α was 10 cm^{-1} at 6.1 eV. Using these data it is found that $(\eta_a\omega_0)$ for the carriers excited from the 6.1-eV band was 3.2×10^{-9} cm^2 V^{-1} for the type-I sample and 5.7×10^{-8} cm^2 V^{-1} for the type-II sample, respectively. The value for the type-II sample is comparable to those found by

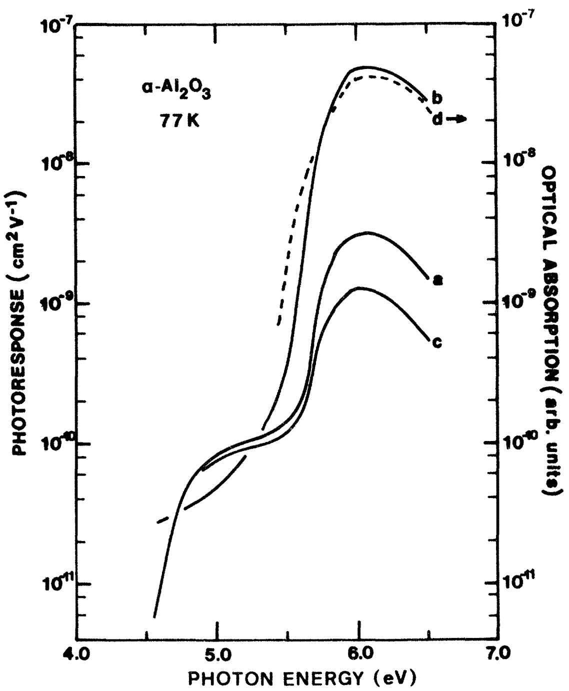

FIG. 3. Photoresponse of thermochemically-reduced αAl_2O_3 at 77 K. Curve *a*, type-I sample after one scan; curve *b*, type-II sample; curve *c*, type-I sample after six scans. Curve *d*, spectrum of light absorbed in the type-II sample at 77 K.

Hughes[6] in Linde samples, i.e., $8-30\times10^{-8}$ cm^2V^{-1}. The charge carriers in type-I samples can be seen to have a relatively shorter mean range which we discuss below. In uncolored Linde samples the photoresponse was immeasurably small over the spectral range considered here. In both type-I and type-II samples the photocurrent was similar for both directions of the applied electric field and was proportional to both the applied electric field up to 3 $kV\,cm^{-1}$ and the incident light intensity for short exposures up to $\sim5\times10^{13}$ photon s^{-1}. Curve *d* in Fig. 3 shows the spectral dependence of the photons absorbed in the type-II sample used for curve *b*. The similarity of curves *b* and *d* near 6 eV shows that the photoresponse is due to charge carriers released by excitation of *F* centers.

It was found that the photocurrent excited by a short pulse of 6.1-eV light decayed with a time constant shorter than a millisecond at 10 K in both type-I and type-II samples. Near room temperature the lifetime of the type-I samples is longer because of trapping effects as we see below.

When 6.1-eV light fell on a type-I sample for a few seconds, the photoresponse due to *F* centers generally decreased. However, illumination for several minutes had the opposite effect, i.e., that of slightly increasing the *F* band photoresponse over its original value. Bleaching the sample with 5.0-eV light decreased the photoresponse across the whole spectrum slightly. All of these effects were much smaller in type-II samples.

The photoresponse at 6.1 eV for both type-I and type-II samples decreased with increasing temperature, Fig. 4. The magnitude of the photocurrent at each temperature was made while a short pulse of 6.1-eV light fell on the sample and the measurements were repeated several times to ensure reproductibility. Notice that in Fig. 4 both curves have been normalized at low temperature although the type-II photoresponse is actually over an order of magnitude greater than that for the type-I sample (Fig. 3). It can be seen that up to 200 K the temperature dependence of the photoresponses is similar, but near 240 K the normalized photoresponse of the type-I sample increases significantly above that of the type-II sample. The increase is due to thermal extension of the mean range of the charge carriers at this temperature due to emptying of an electron trap. Lehmann and Gunthard[7] apparently observed phosphorescence in their samples due to this trap and they deduced from the time dependence of the intensity that a second-order process was involved. However, in our samples the phosphorescence was almost first order. The effect can

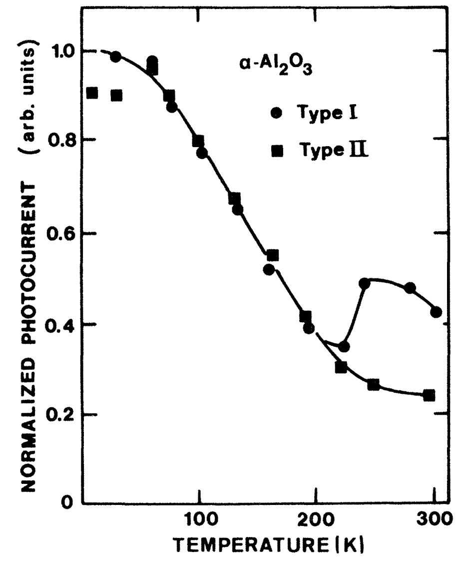

FIG. 4. Temperature dependence of the normalized photoresponse from the 6.1-eV band in thermochemically-reduced α-Al_2O_3.

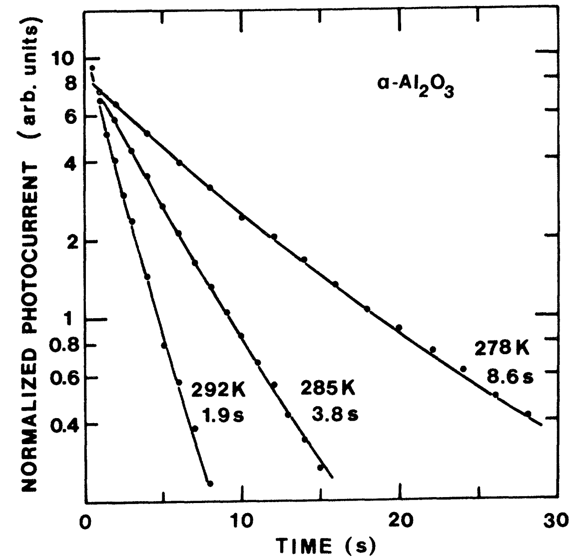

FIG. 5. Time decay of the photocurrent excited by a pulse of 6.1-eV light in type-I thermochemically-reduced α-Al$_2$O$_3$.

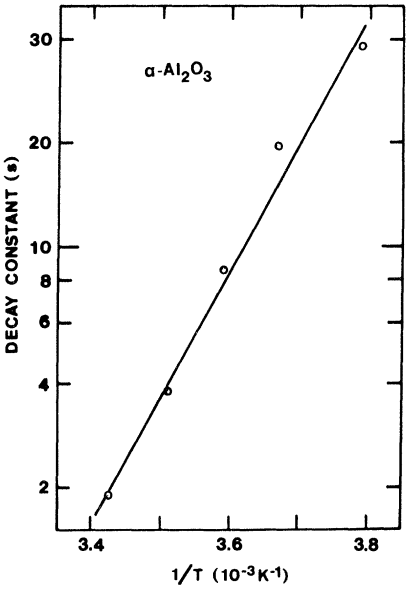

FIG. 6. Semilogarithmic plot of the time constant for the decay of photocurrent in type-I thermochemically-reduced α-Al$_2$O$_3$ excited by a pulse of 6.1-eV light vs inverse temperature $1/T$.

also be followed in the decay of the photocurrent excited by a pulse of 6.1 eV light. Typical curves obtained in this way are shown in Fig. 5. It is not possible to determine accurately the order of the decay kinetics from these measurements because the crystal tends to polarize when dc photocurrents are allowed to flow for a long time, which makes determination of the base line uncertain. The best fit to the curves in Fig. 5 could be made using

$$I(t)=I(0)\exp[-t/\tau(T)]+C, \tag{3}$$

where $I(t)$ is the current at time t, $\tau(T)$ is the time constant for temperature T, and C is a constant which allows for the uncertainty in the base line. C does not imply that there is any current which is independent of t. In all cases C was less than 1% of $I(0)$ and is, therefore, not significant. The values of $\tau(t)$ obtained from these plots can be compared to an Arrhenius-type dependence, in which

$$\tau(T)=\tau(0)\exp(E_a/k_BT), \tag{4}$$

where E_a is the activation energy for release of an electron and k_B is Boltzmann's constant. $\tau(T)$ is plotted against $1/T$ in Fig. 6, where the straight line is a fit of Eq. (4) to the data points with $E_a=0.73\pm0.02$ eV and $\tau(0)=4\times10^{-13}$ s. A similar analysis on the phosphorescence data gave $E_a=0.72\pm0.02$ eV and $\tau(0)=8\times10^{-13}$ s.

C. Thermoluminescence

In this section thermoluminescence measurements are described which were directed towards determining the possible nature of the trap associated with the phosphorescence and long-lived photocurrents found near room temperature in Sec. III B. This trap produces a well-known thermoluminescence peak near 260 K during which 3.0-eV F emission occurs. An additional peak or shoulder is also usually observed near 220 K as we shall see. Previous measurements on uncolored samples showed that 3.8-eV F^+ emission occurred at this temperature,[9] but in our samples 3.0-eV emission was dominant apparently because of the relatively large concentration of F centers.

Care was taken to place the sample in the same position for each experiment and the gain of the detection system was kept the same for all measurements. Although the absolute magnitude of the emission intensities presented below was not determined, the relative magnitude of the individual measurements is accurate to about 15%.

In Fig. 7 are shown the thermoluminescence curves for a type-I (curve a) and for a type-II (curve b) sample, respectively. These data were taken after the samples had been cooled to 77 K

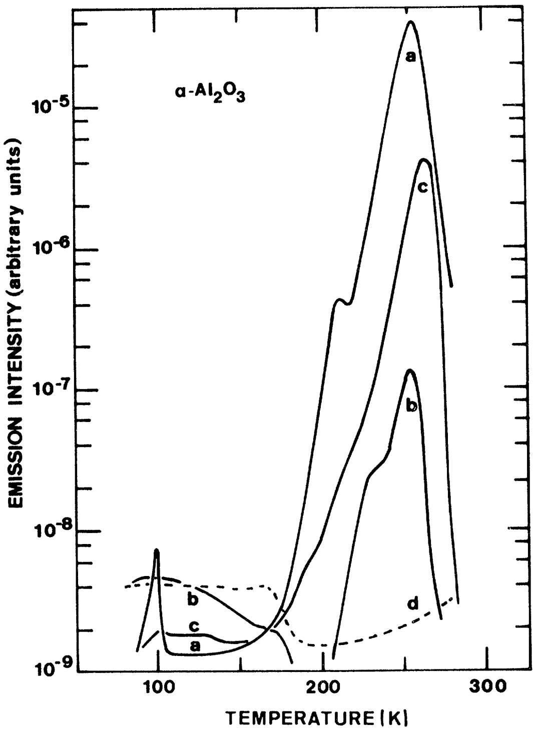

FIG. 7. Thermoluminescence spectra of α-Al_2O_3. Curve a, thermochemically-colored type I; curve b, thermochemically-colored type II; curve c, irradiated with $\sim 10^{17}$ reactor neutrons; curve d untreated.

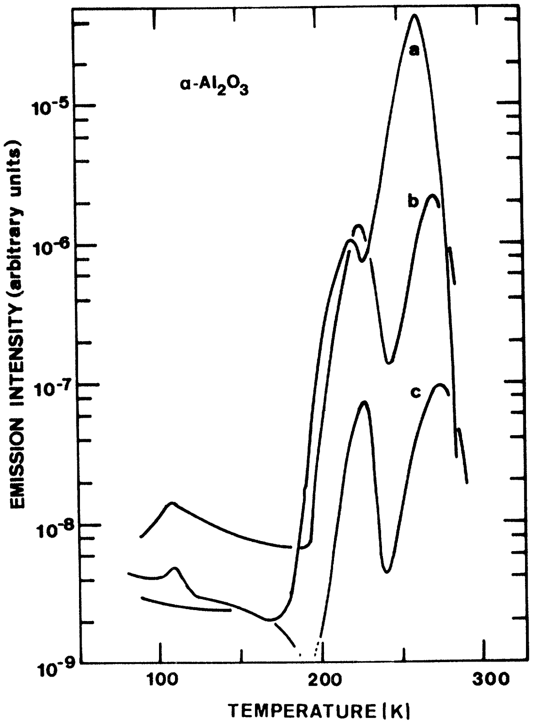

FIG. 8. Thermoluminescence spectra of Linde α-Al_2O_3. Curve a, after irradiation at 77 K with 1.5-MeV electrons to a dose of $\sim 5\times10^{17}$ electrons; curve b, one hour after γ irradiation; curve c, three weeks after γ irradiation.

and then illuminated with 6.1-eV light for five minutes. Notice that the intensity of the luminescence is plotted on a logarithmic scale so that the intensity of the 260-K peak in the type-II sample is ~ 300 times weaker than the equivalent peak in the type-I sample. Since the number of F centers is only a factor of 2 larger for the type-I sample, this implies that the number of traps in the type-II sample is at least 2 orders of magnitude less than in the type-I sample. Analysis showed that the 260-K peak is first order and that the activation energy determined from a "leading-edge" calculation was 0.72 ± 0.03 eV. This value is in agreement with previous measurement.[9]

F centers can be produced in α-Al_2O_3 by particle irradiation[15] but not by γ irradiation, so the different effect of these treatments on the thermoluminescence was investigated. Before irradiation an uncolored sample shows no significant thermoluminescence, Fig. 7, curve d. Following irradiation with $\sim 1\times10^{17}$ reactor neutrons curve c was obtained. This sample which is 1 mm thick had an optical density at 6.1 eV of ~ 3. However, the intensity of the 260-K peak is smaller by an order of magnitude than in the type-I sample, which contained about one-half the number of F centers. The reason for this is that neutron irradiation produces damage in cascades and the close proximity of the F centers formed leads to concentration quenching of the luminescence.[16] Alternatively the damage can be done using high-energy incident electrons, which produce mostly isolated vacancies. In Fig. 8, curve a, is shown the thermoluminescence curve for a sample which had been irradiate at 77 K with $\sim 10^{17}$ 1.5-MeV electrons. This sample was 1 mm thick and had an optical density of 0.4 at 6.1 eV. It can be seen that the intensity of the 260 K peak is comparable to that of the type-I samples.

The F centers introduced by electron irradiation annealed out over the temperature range 100–500 °C. The intensity of the thermoluminescence in an experiment following the isochromal anneals was compared with the number of F centers present measured from the height of the 6.1-eV band. The results are shown in Fig. 9 where it can be seen that the normalized intensity of the 260-K peak falls on the isochromal anneal curve. The 220-K thermoluminescence peak an-

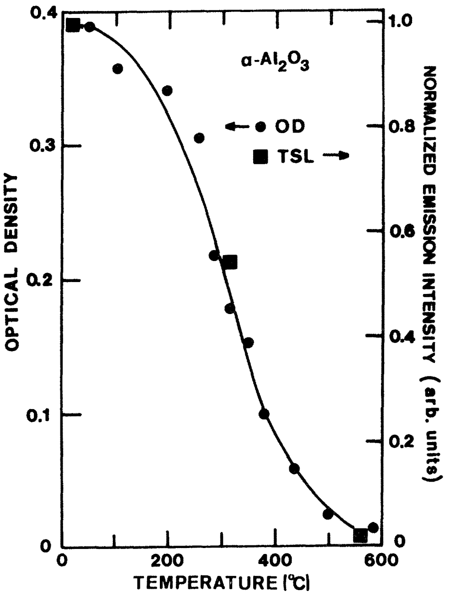

FIG. 9. Normalized intensity of the 6.1-eV F band in electron-irradiated α-Al$_2$O$_3$ following 10-min isochronal annealing at successively higher temperatures. The squares indicate the normalized intensity of the 260-K thermoluminescence peak following the relevant isochronal anneal.

nealed at a slightly lower temperature than the 260-K curve.

During electron irradiation the sample is also subjected to intense γ irradiation. The effect of γ irradiation alone was studied by allowing the electrons to strike a copper target positioned 45° to the direction of the incident beam. The sample was maintained at 77 K and located about 2 cm away from the copper target. The time taken to prepare the sample for the thermoluminescence measurements was similar to that for an electron irradiated sample. In Fig. 8 the thermoluminescence curve measured one hour after the irradiation is shown (curve *b*) and also the curve after the sample had been stored at room temperature from three weeks (curve *c*). It can be seen that γ irradiation produced the 220 and 260 K peaks with approximately equal intensities and that they both decay at the same rate.

IV. DISCUSSION

It is clear from the temperature dependence of the efficiency of the F-F^+ center interconversion process that an electron trap is involved which is operative at 10 K but which is not operative at room temperature. The measurements presented here suggest that this trap, which is responsible for about 80% of the possible interconserversion observed at 10 K, is also responsible for the 260-K thermoluminescence peak, since in type-I samples the relative intensity of the 260-K peak is more than 2 orders of magnitude more intense than in type-II samples. It is worth noting that the trap in question is by far the most effective electron trap below room temperature since all other thermoluminescence peaks are much weaker.[9]

The presence of this trap is also responsible for the lower photoresponse observed at low temperatures in type-I samples compared to type-II samples. The fact that the photoresponse of F centers in both types of material is highest at the lowest temperature indicates that the electronic state into which the electron is excited by 6.1-eV light is in or very close to the conduction band either before or after the center relaxes, so that there is a high probability of escape (and hence interconversion if there is an available trap) even at helium temperature.[2] We can assume then, that the free-electron yield η_a for F centers is unity at all temperatures. Diffferences in photoresponse are, therefore, due to differences in the mean range per unit field ω_0 between samples. If η_a is taken as unity, the values for type-I and type-II samples at 77 K are 3.2×10^{-9} and 5.7×10^{-8} cm, respectively. These values are typical for ionic insulators, e.g., MgF$_2$ (Ref. 11) and KCl.[17] Figure 4 indicates that ω_0 decreases with increasing temperature. ω_0 depends on the effective mobility μ_{eff} and the trapping time τ through $\omega_0=\mu_{\text{eff}}\tau$. The effective mobility is expected to decrease with increasing temperature due to scattering by, for example, LO phonons, but the actual temperature dependence of ω_0 will depend on many factors, including the ratio of the trapping time to the reemission time. It is the rapid decrease in the latter quantity which causes the increase in photoresponse of type-I samples near 260 K. Since the photoresponse-temperature curves for both type-I and type-II samples below 200 K are similar, it appears that the general decrease observed is due to an intrinsic property of the lattice, e.g., scattering by lattice vibrations.

The unusual changes in the magnitude of the F-center photoresponse when the sample is under prolonged illumination also appears to be related to the presence of electron traps. The initial drop in photoresponse is very efficient since the decrease in photoresponse shown in Fig. 3, curve *c* was produced by scanning only six times the energy of the incident light from 4 to 6.5 eV using the 60-W deuterium lamp-monochromator system. However, apart from the main electron trap there also appears to be shallow traps in the samples which produce a phosphorescence-like effect in the 3.0-eV *F* emission even at low temperatures.[18] In addition, the bleaching of *F* centers introduces F^+ centers into the sample which are also efficient electron traps. It appears, then, that the increase in photoresponse which occurs after prolonged illumination results from a spatial redistribution of effective electron traps as the exciting light falls on the sample. The effect would not be expected if the main trap were not present and is not observed in type-II samples. The details of the process outlined above are being investigated further and will be reported later. Notice that the production of F^+ centers when *F* centers are bleached prevents the complete interconversion of centers. In our samples only about one-third of the *F* centers present could be bleached (see the inset in Fig. 1).

Not much is known about electron traps in α-Al_2O_3. Hughes[6] has confirmed the effect of Cr^{3+}, which is a relatively deep trap and is not responsible for the effects discussed here. Cox[19] has discussed the properties of samples doped with both Mg^{2+} and Ti^{4+} in which the Mg^{2+} assists in trapping a hole and Ti^{4+} is possibly an electron trap. However, Cooke *et al.*[12] have shown that the thermoluminescence of α-Al_2O_3 doped with titanium was not significantly different than undoped material; in particular, no correlation was found with the magnitude of the 260-K peak. However, the 220-K peak, which is introduced by γ irradiation or electron irradiation but not neutron irradiation, appears to be due to a chemical impurity which might be Mg^{2+}. Cooke *et al.*[9] have shown that there is considerable F^+ emission in the thermoluminescence which is consistent with a hole recombining with an *F* center.

Since hydrogen seems to play an important role as a trap in oxides,[20] we checked to see if the type-I samples contained a significant concentration of hydrogen. The concentration was estimated by looking for the 3280 OH^- stretching mode. Engstron *et al.*[21] have estimated that an absorbance of 0.025 at this energy through a path length of 12.7 mm of material corresponds to a concentration of about 2.6×10^{16} cm^{-3}, which was actually observed in Linde material. We are looking for a trap which is present at a concentration 2 orders of magnitude larger in type-I samples than in type-II samples. The crystals used here were only one-tenth the thickness of Engstron *et al.*'s samples and the noise on the chart corresponed to 0.001 absorbance. No absorption band at 3280 cm^{-1} was observed in the spectra of either sample from which we estimate the concentration of OH^- ions was less than 1×10^{16} cm^{-3} in both. It appears then that OH^- is probably not the trap responsible for the effects discussed here. Recent measurements[22] show, however, that H^- ions which are formed from OH^- ions during thermochemical reduction greatly extend the lifetime of *F* emission in other oxides, but we have not yet been able to confirm the presence of H^- ions in reduced α-Al_2O_3.

Another possibility which we have considered is that the trap responsible for the 260-K thermoluminescence peak is structural in nature rather than chemical. The thermoluminescence measurements described in Sec. III C were performed partly to investigate this possibility. The 260-K peak was most intense in type-I and electron-irradiated samples. The neutron-irradiated samples showed a relatively weaker luminescence but previous measurements have shown that the luminescence intensity per *F* center is about 20 times weaker in these samples than thermochemically-colored samples because of concentration quenching.[16] Although the 260-K peak is also introduced by γ irradiation, it cannot be introduced as intensely as in electron-irradiated or type-I samples. The key question is whether the irradiation (or the growth conditions) simply introduce more luminescent centers or also more traps. The fact that the intensity of the 260-K peak decreases at the same rate as the *F*-center concentration does not resolve this question. However, the data are not inconsistent with the trap bring small clusters of interstitials possibly associated with dislocations. Another suggestive piece of evidence for this conclusion is given in Figs. 2 and 3. The shoulder in the photoresponse near 5 eV in type-I samples appears to be the excitation spectrum of the trap responsible for the F^+-F interconversion process. An optical-absorption band similar to this is formed when type-I samples are heated to 1500°C, Fig. 2. This suggests that possibly some kind of aggregation of previously isolated defects has occured during the heating process and that there are some of these aggregates present in smaller concentrations initally. It is clear that this suggestion is only speculative but the experimental results are consistent with the conclusion. It is possible that light scattering experiments might be useful in resolving this question.

There are several other electron traps present, in particular deeper ones, whose thermoluminescence spectra are excited only above room temperature.[23] In some samples, Fig. 1, the intensity of the F band can be increased by heating the crystal to 400 °C. During this process a strong blue luminescence characteristic of F centers is produced. The magnitude of the decrease in F^+ centers produced during the annealing process does not seem sufficient to explain the increase in F center produced, Fig. 1, which suggests that bare oxygen vacancies might be present in the crystal. X irradiation, however, is apparently not effective in producing more F centers by filling these vacancies.

In summary, we have shown that the interconversion of F and F^+ centers in α-Al_2O_3 is possible mainly because of an electron trap which is also responsible for the 260-K thermoluminescence peak and the long-lived photoconductivity observed in some samples. The activation energy for thermal release of the electron from this trap is 0.73 ± 0.02 eV. An absorption band associated with the optical release of the electron from this trap is observed in the photoresponse and has a peak at 5 eV and a half-width of about 0.6 eV. Some evidence is given that the trap may be a structural defect rather than a chemical impurity.

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