

## Photostimulated Emission of Some Activated Alkali Halide Phosphors\*

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The intensity of the photostimulated ultraviolet emission of x-ray excited phosphors of NaCl-Tl, KCl-Tl, NaCl-Ag, and KCl-Ag has been measured as a function of the wavelength of the incident light. The results indicate that, in the first thirty days following excitation at least,  $F$  centers are primarily responsible for the storage of energy. Thus, the storage properties depend upon the nature of the host material, rather than upon the intentionally added activator. Evidence is also presented which seems to indicate the presence of a deep trap associated with the silver ions of KCl-Ag which has a period of decay comparable to that of the  $F$  centers. Excitation, storage, and all measurements were carried out at 22°C. Polycrystalline materials, prepared by the writers, were used throughout the investigation.

### INTRODUCTION

THE photostimulated emission of activated phosphors gives a measure of the "light storage" which is in turn proportional to the number of electrons stored in traps of the solid. In order to ascertain the amount of storage, a procedure is followed in which excited phosphors are irradiated by light, and the resulting photostimulated emission of "stored light" observed. Temperature is a parameter in these measurements, because both electron trapping and the efficiency of the luminescence centers for conversion of potential energy into light may vary as the temperature is changed. Consequently, to obtain a true measure of storage, excitation, storage of the excited materials in darkness, and subsequent photostimulation—all operations—were carried out at room temperature (22°C). In the studies to be described in this paper, the photostimulating light had a wavelength,  $\lambda$ , of more than 3000Å, and the stimulated emission a wavelength of  $\lambda' \sim 2500$ Å. Photosensitive G-M tubes were employed as detectors, having a maximum of spectral response at 2500Å and no detectable response for values of  $\lambda$  of 3000Å or more. Since the detectors did not respond to the photostimulating light, it was possible to observe the stimulated emission while the photostimulating light was acting. Investigations employing this technique have been previously described by the writers.<sup>1,2</sup> The measurements of the present paper differ from the earlier observation<sup>1,2</sup> in that the intensity of the photostimulated emission has been measured as a function of the wavelength of the photostimulating light. From the earlier measurements it was evident that since the stored energy had a very long period of storage, relatively large trap depths must be involved. Furst and Kallmann<sup>3</sup> have studied in particular NaCl-Ag and have given some qualitative estimates of the depths of the traps con-

cerned with storage. They have also speculated<sup>4</sup> as to whether the traps responsible for the long period storage might be negative ion vacancies in the crystal lattice, forming  $F$  centers when trapping electrons. They also noticed that the extent of coloration of crystals of NaCl-Ag appeared to be directly related to their response to photostimulation.

The various measurements of energy storage which have been carried out by Kallmann *et al.*<sup>3,4</sup> have consisted for the most part in observation of a post-stimulation phosphorescence; that is, a phosphorescent afterglow was observed after the photostimulating light was extinguished. Their detector was a photomultiplier tube (RCA-1P28) which responded not

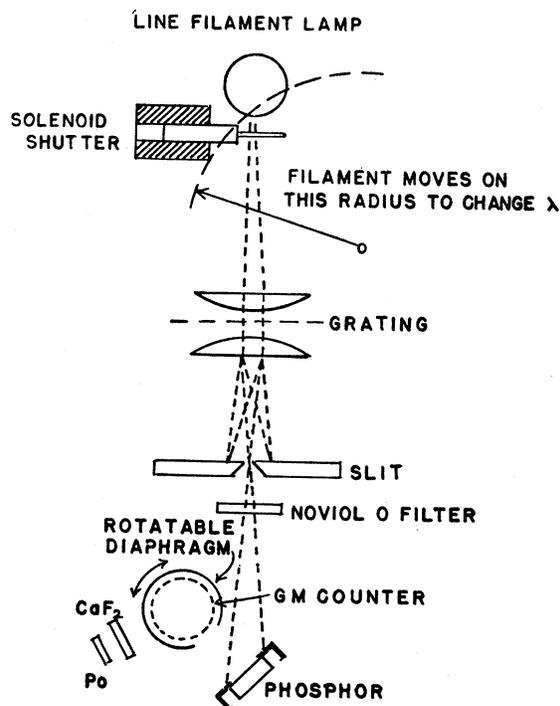


FIG. 1. Schematic diagram of the apparatus.

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<sup>1</sup> C. E. Mandeville and H. O. Albrecht, *Phys. Rev.* **91**, 566 (1953).

<sup>2</sup> H. O. Albrecht and C. E. Mandeville, *J. Franklin Inst.* **257**, 353 (1954).

<sup>3</sup> M. Furst and H. Kallmann, *Phys. Rev.* **91**, 1356 (1953).

<sup>4</sup> H. Kallmann and M. Furst, *Phys. Rev.* **83**, 674 (1951).

only to the photostimulated emission but to the stimulating light as well; therefore, it was possible to observe only the phosphorescent emission which persisted after the photostimulating light was turned off.

In the present investigations, light from a tungsten lamp was passed through a Coleman monochromator and allowed to fall upon an excited phosphor adjacent to which was placed a photosensitive G-M tube in which was recorded, as a function of the wave length of the incident light, the photostimulated ultraviolet emission. The monochromator supplied photons ranging in wavelengths from 3000Å to 7000Å in a channel of constant width 100Å. The number of photons lying in the channel was determined at each setting of the wavelength by a thermopile calibration. A schematic diagram of the apparatus used for the photostimulation studies is shown in Fig. 1. The constancy of the sensitivity of the counter was frequently checked by counting ultraviolet from Po- $\alpha$ phas on fluorite.

The purpose of the investigation was to determine the nature of the traps responsible for the relatively long-period energy storage. Consequently, measurements were commenced only after sufficient time had elapsed that any phosphorescence arising from thermal agitation at room temperature was no longer detectable. Thus, the relatively shallow traps had emptied so that the results cannot be compared with other available data.<sup>5,6</sup>

#### THE MEASUREMENTS

The photostimulated ultraviolet emission of two phosphors is plotted in Fig. 2 as a function of the wavelength of the incident light. Figure 2(A) applies to NaCl-Tl (thallium chloride concentration 0.1 mole percent) and Fig. 2B to KCl-Tl of the same mole percent concentration of activator. Both samples had received the same x-ray dosage, 65r. This dose was applied in a time of 10 seconds and the excited phosphors were immediately stored in darkness. At various times after excitation, as indicated on the curves, the photostimulated emission was observed. The practice was usually followed of commencing in the red and proceeding in steps of 100Å to 250Å through the peak of the curve to shorter wavelengths.

In the case of both curves of Fig. 2, the maximum of photostimulated emission occurs at the peak of the *F* band of the host material. Many investigations of *F* bands by earlier workers using the more conventional absorption methods have located the maximum of absorption in the *F* band at 4750Å for NaCl and 5750Å for KCl. The half-widths of the observed curves of Fig. 2 are in agreement with those of the *F* bands found by the absorption method. Thus, the curves of Fig. 2 may be interpreted as showing that *F* centers are destroyed by the photostimulating light, the released electrons entering the conduction band whence they proceed to the filled band by way of a luminescence center; that is, recombination with a positive hole occurs at the luminescence center where the ultraviolet light is also emitted. The ultraviolet emission

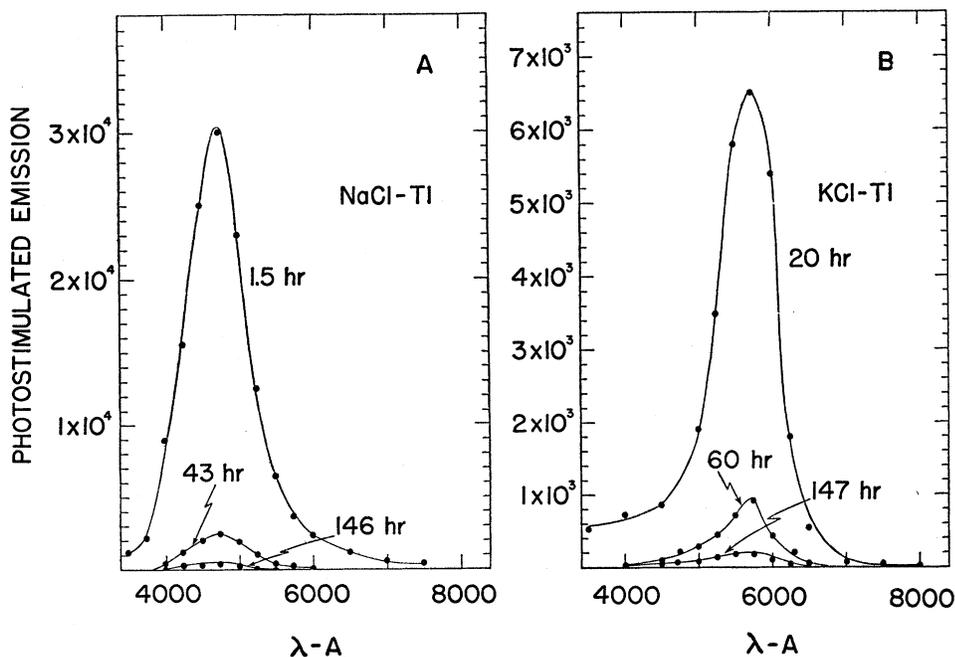


FIG. 2. Photostimulated emission of thallium-activated NaCl and KCl (TlCl concentration 0.1 mole percent) as a function of wavelength. The location in  $\lambda$  and widths of the peaks are identical with the *F* band observed in conventional absorption studies. Excitation, storage, of samples in darkness, and all measurements at 22°C.

<sup>5</sup> W. Buenger and W. Flechsig, *Z. Physik* **69**, 637 (1931).

<sup>6</sup> P. D. Johnson and F. E. Williams, *J. Chem. Phys.* **21**, 125 (1953).

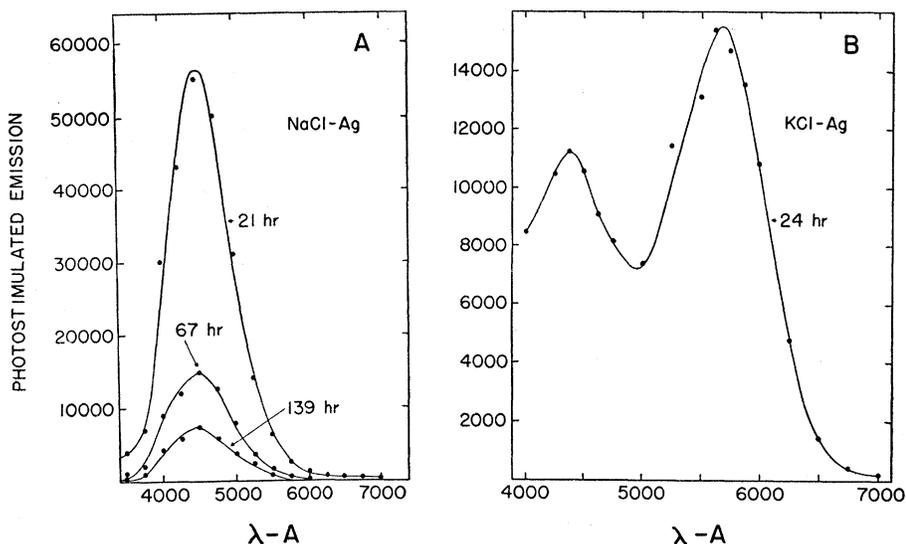


Fig. 3. Photostimulated emission of silver-activated NaCl and KCl (AgCl concentration 0.1 mole percent) as a function of wavelength. In addition to peaks corresponding to the  $F$  band of either host crystal, a strong maximum at 4500Å is detected in KCl-Ag. Excitation, storage, and all measurements at 22°C.

was observed at each point of the curves of Fig. 2 simultaneously with application of the photostimulating light. The time of photostimulation at each point was usually a period of a few seconds. The time of completing an entire curve was about one hour.

It is clear from the curves of Fig. 2 that the long-period storage of energy in the thallium-activated alkali halides arises from the trapping of electrons to form  $F$  centers.<sup>7</sup>

The photostimulated emission of NaCl-Ag and KCl-Ag (AgCl concentration 0.1 mole percent) is shown in Figs. 3(A) and 3(B). In this case, NaCl-Ag was x-rayed for five seconds (33r), and KCl-Ag for five minutes (2000r). The time after initial excitation at which each curve was obtained is specified in the figure. Here again the  $F$  bands of the host crystals are clearly in evidence.<sup>8</sup> However, in the case of KCl-Ag, an additional band peaked at 4500Å is present with a considerable intensity. As indicated by Fig. 2(B), this intense band is not present in thallium activated KCl. It is reasonable to assume, therefore, that this short-wave band is in some way related to the presence of the silver ion.

To obtain information as to any possible relationship between the two peaks of intensity of photostimulated emission of KCl-Ag, the excited phosphor of Fig. 3(B) was bleached at 6500Å, and the relative intensities of the two bands were determined at their respective peaks as the bleaching proceeded. The total number of

photostimulated counts recorded during bleaching was taken as a measure of the extent of bleaching. Short bursts of photostimulated ultraviolet emission were drawn from the phosphor first at the peak at 5750Å, then at the peak at 4500 Å, to measure the heights of those peaks as bleaching at 6500Å continued. The bleaching was halted, of course, for a time sufficiently long to permit these intensity measurements. During a bleaching time of 62 minutes, a total of  $1.28 \times 10^6$  counts of photostimulated ultraviolet emission was recorded in the photosensitive G-M tube. The rate of decrease of the peak value of the  $F$  band and of the band centered at 4500Å is shown in Fig. 4(A), the bleaching being carried out at 6500Å. The intensity of the short wave peak was clearly relatively unaffected, but the  $F$  band peak diminished rapidly. A similar curve is given in Fig. 4(B) where the respective heights of the two peaks are plotted as exhaustion proceeds by photostimulation at 4000Å. In this case, both peaks were bleached as might be expected, since the photostimulating light was sufficiently energetic to reduce either peak. Since, as indicated by the curve of Fig. 4(A), bleaching in the  $F$  band does not reduce the intensity of the peak at 4500Å, it must be concluded that the photostimulated emission at 4500Å must correspond to some type of trap other than  $F$  centers; that is, the 4500Å peak in KCl-Ag appears to be unrelated to the  $K$  band of pure KCl.<sup>7</sup> Further confirmation of this point lies in the obvious fact that no peak at 4500Å of an intensity comparable to that of KCl-Ag is found in KCl-Tl [Fig. 2(B)].

To examine further the nature of the maximum of photostimulated emission at 4500Å in KCl-Ag, additional samples were prepared having AgCl concentrations of 0.006 mole percent and 0.2 mole percent respectively. Curves of the photostimulated emission from these materials are shown in Fig. 5(A) and Fig.

<sup>7</sup> Examination of the curves to the blue of the  $F$  band in each case shows that there is a greater amount of photostimulated emission resulting from irradiation of KCl-Tl in that spectral region than from NaCl-Tl. This increased emission may be related to the  $K$  band reported in absorption studies of x-rayed KCl [see F. G. Kleinschrod, Ann. Physik 27, 86 (1936)].

<sup>8</sup> The curves of Figs. 2(A), 2(B), and 3(A) show a reduction of peak intensity with time which is partly fictitious. The photostimulating light was sufficiently intense that the measurements themselves appreciably decreased the number of stored electrons.

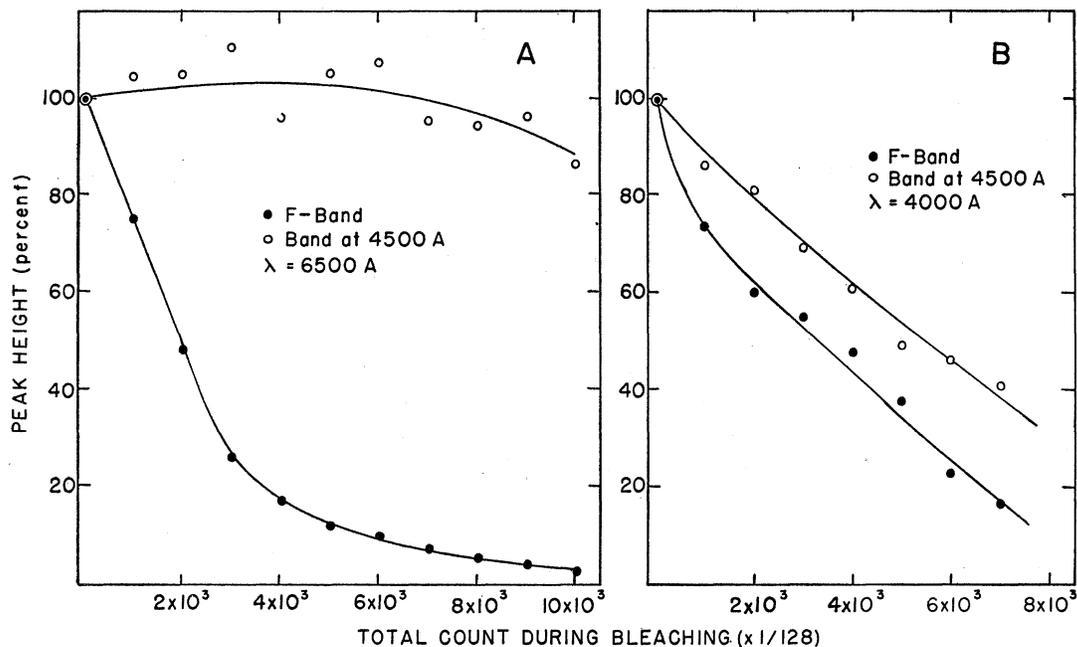


FIG. 4. Heights of the peaks of photostimulated emission of KCl-Ag as a function of bleaching time; curves A, at 6500Å, curves B at 4000Å. All measurements at 22°C.

5(B) where it is clear that the peak of emission at 4500Å decreases relative to the *F* band peak with decreasing silver concentration, further substantiating the view that the short-wave peak of KCl-Ag derives from the presence of Ag ions in the crystal lattice. A

possible explanation is that quanta of wavelength 4500Å are sufficiently energetic to remove trapped electrons from a long-lived metastable state to a higher state from which a return of the electron to the light-emitting levels of the luminescence center is allowed.

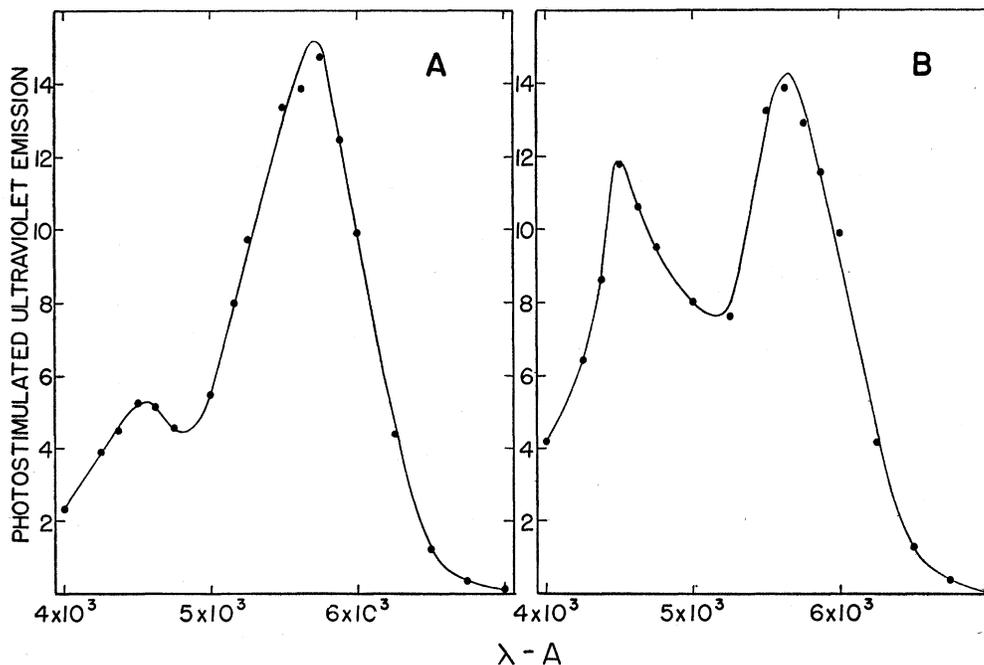


FIG. 5. Photostimulated emission of KCl-Ag. Curve A, mole concentration of AgCl 0.006 percent; Curve B, 0.20 percent. These curves were obtained 24 hours after initial excitation.

In Fig. 6 are plotted decay curves of the stored energy in KCl-Ag, KCl-Tl, NaCl-Ag, and NaCl-Tl. It is evident from the curves that the decay is essentially the same for a given host crystal, irrespective of the nature of the activator ion. Thus, the differences in storage times relate purely to the variations in host material. In Fig. 6, all samples of KCl, thallium-activated or silver-activated, decay with approximately the same slope as do those of NaCl. However, it is also clear that storage is more long-lasting in NaCl than in KCl. Not shown in the figure, a single point taken for each curve at a time of forty days left unchanged the conclusions above, which are based upon behavior during the first twenty days as plotted in Fig. 6. To obtain the decay curves of Fig. 6, a short burst of photostimulated emission of duration six seconds was drawn from the phosphor at the indicated intervals of time. The intensity of the photostimulated emission was taken to be proportional to the number of electrons remaining stored in traps in the solid. It has often been suggested that long-period storage may depend upon the nature of the activator ion. For example, in a previous publication,<sup>2</sup> some results of the writers seemed to indicate that the stored energy in KCl-Tl decayed more rapidly than that in KCl-Ag and similarly for thallium- and silver-activated NaCl. The results were in error, because too intense a photostimulating light was employed; that is, the observation of the number of stored electrons destroyed too many  $F$  centers, giving the impression of a rapid decay of the stored energy in the thallium-activated materials. In the present measurements, a very faint photostimulating light was employed and tests were performed which showed a negligible loss to arise from the measurements themselves. In observing the decay of energy storage in KCl-Ag, the reduction with time of both peaks was followed as indicated. The supposed metastable state appears to decay with about the same period as do the  $F$  centers. There is always the possibility that the metastable level is "fed" by electrons which have been removed from the  $F$  centers.

The luminescent materials were produced at Bartol by fusion in a platinum crucible and subsequent rapid cooling on an aluminum plate. A polycrystalline structure resulted. No single crystals were employed.

#### CONCLUSION

From the data presented in the foregoing sections, it is clear that the long-period storage of energy in the activated alkali halides results from the trapping of electrons to form  $F$  centers in the host material. The

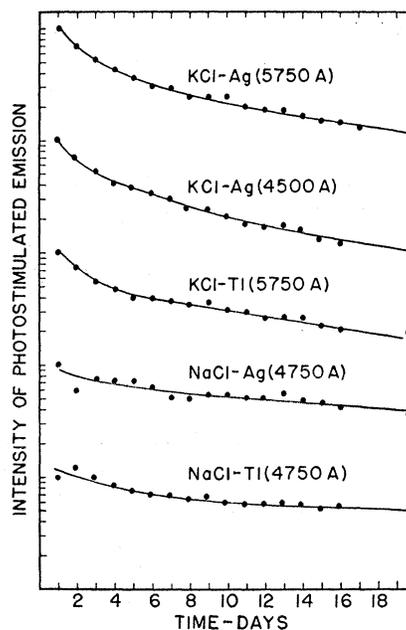


FIG. 6. Decay of stored energy in thallium- and silver-activated alkali halides. These curves show that the rate of decay depends primarily upon the nature of the host crystal, not upon the type of activator. Excitation, storage, and all measurements at 22°C.

decay curves of Fig. 6 can be related to the expression<sup>9</sup>

$$n = n_0 \exp(-ste^{-E/kT}),$$

where  $n$  is the number of trapped electrons,  $s$  a constant characteristic of the host crystal, and  $E$  the thermal dissociation energy of the  $F$  centers. The mean life of the  $F$  centers of NaCl has been calculated to be much greater than 86 days,<sup>9</sup> whereas the curves of Fig. 6 indicate a much shorter lifetime.<sup>9</sup>

It is to be remembered that the measurements under discussion pertain to those traps which are dominant in storage over the first thirty days following initial excitation.<sup>10</sup> The possibility of existence of still deeper traps of lesser population remains. Study of any such traps must await an extended aging of the x-rayed materials.

*Note added in proof.*—The peak of photostimulated emission of KCl-Ag centered at 4500A may correspond to the  $E$  band of recent absorption measurements. See H. W. Etzel and J. H. Schulman, *J. Chem. Phys.* **22**, 1549 (1954).

<sup>9</sup> F. Seitz, *Revs. Modern Phys.* **26**, 7 (1954). See Sec. 29, "Bleaching," which also includes a discussion of reasons for the observed unduly rapid early decay of  $F$  centers.

<sup>10</sup> For remarks concerning the effects of retrapping upon the observed lifetime of  $F$  centers, see R. S. Alger, *J. Appl. Phys.* **21** 30 (1950).