PHYSICAL REVIEW B VOLUME 23, NUMBER 12 15 JUNE 1981

Thermoluminescent processes involving Cu^- and *F* centers in NaCl:Cu irradiated at room temperature

L. Delgado and J. L. Alvarez Rivas

Junta de Energía Nuclear, Madrid-3, Spain

(Received 12 March 1980; revised manuscript received 5 November 1980)

The thermoluminescence of NaCl:Cu (115 ppm) samples irradiated at room temperature has been studied in some detail. It has been found that the emission spectrum shows two bands peaked about 365 and 445 nm which have been respectively ascribed to the annealing of *F* centers and Cu^- ions induced by irradiation. The results indicate that the Cu^- ions formed during irradiation can be compensated by anion vacancies. This allows us to propose that the glow peaks which are simultaneous with annealing steps in the *F* and Cu^- optical-absorption bands are caused by the recombination of interstitial halogen atoms thermally released from traps both with *F* centers and with anion vacancies. In the latter case, short-lived V_K centers are formed, which in turn recombine with Cu^- ions. Thus, the crystal lattice is brought back to its preirradiation state.

I. INTRODUCTION

There is a vast amount of phenomenological information dealing with thermoluminescent processes in irradiated alkali halides.[1,2] Most of them have been attributed to radiative recombinations of electrons and holes thermally released from traps in which they are stabilized during irradiation. However, it has been recently established that many of the thermoluminescent processes observed in alkali halides are related to the thermal annealing of radiation-induced lattice defects. The recombination of mobile interstitial halogen atoms thermally released from traps with *F* centers is a rather common thermoluminescent process either below or above room temperature.[2-9] It has also been found that in the light-emitting stage of the $F+H$ recombinations below room temperature, self-trapped excitons are formed.[3,4,7] This has received theoretical support.[10] However, intrinsic luminescence above room temperature has not been observed either in nominally pure or alkaline-earth-doped alkali halides.[8,9,11] Nevertheless, it is believed that in this case the predominant emission band observed is the II band of a self-trapped exciton perturbed by a nearby divalent impurity-cation vacancy dipole.[12]

An interesting case in the thermoluminescence of irradiated alkali halides is found in samples doped with impurities such as Mn^{2+}, Pb^{2+}, Tl^+, Ag^+, and Cu^+ whose valence states vary by irradiation.[1] These impurities can act as electron or hole traps, and below room temperature they are, respectively, compensated by V_K centers or trapped electrons. In this case, thermoluminescence in which the mobile entities are either electrons or holes has been observed.[1] This view has also been invoked to explain the thermoluminescence of NaCl:Cu samples irradiated at room temperature.[13-16] Recent work on the thermoluminescence of NaCl:Mn samples irradiated at room temperature has shown that the glow peaks are simultaneous with the recovery of Mn^{2+} ions and annealing stages of *F* centers. This result has been ascribed to the simultaneous release of holes and interstitials trapped together somewhere in the lattice.[17]

The purpose of this paper is to present a study of thermoluminescent processes of NaCl:Cu irradiated at room temperature in a large dose range to elucidate the role that thermally activated processes involving either electronic or atomic rearrangements may have in the thermoluminescence of alkali halides doped with impurities whose valence states are altered by irradiation. From the results found in this work it is proposed that the recovery of the impurity valence state and the annealing of *F* centers are two branches of the same process, i.e., the thermally released interstitials recombine either with *F* centers or with α centers nearby impurities, the latter causing the formation of short-lived V_K centers[18] which in turn recombine with Cu^- ions. It is shown that Cu^- ions can be electrically compensated by anion vacancies instead of by trapped holes as is usually assumed.

II. EXPERIMENTAL

Square platelets about $1\times1\times0.1$ cm^3 were cleaved from a NaCl:Cu single-crystal block (kindly supplied by Professor Jaque). Atomic spectrographic analysis has shown that in these samples there are 115 and 26 ppm of copper and calcium, respectively. They were irradiated at room temperature either in a ^{60}Co source at 1100 rads^{-1} or with x rays through an aluminium plate 1 mm thick with a Siemens tungsten anode tube operated at 50 kV and between 5 and 20 mA. Some samples were quenched in air from 500 °C to room temperature by removing the sample from a furnace and putting it on a metal plate within a few seconds.

The thermoluminescence measurements have been made in an apparatus previously described[19] at a heating rate of 5 °C min^{-1}, and with a Philips 153AVP photomultiplier. The spectrum of the emitted light was scanned with a Bausch and Lomb monochromator (high-intensity model) mounted between the photomultiplier and the chamber quartz window, while the temperature of the sample was kept at a constant value. No effect on the wavelength values of the emission band peaks due to the light-intensity decrease during the scanning time was revealed by forward and backward scans. Some spectra were also obtained with a Jarrell-Ash monochromator (0.25 m) driven by an automatic wavelength scanner provided by Dr. A. Delgado which allowed us to obtain emission spectra while the sample temperature is increased at a constant rate. The scanning speed was about 6 nm s^{-1}. This system is equipped with an EMI 9659B photomultiplier. No differences in the peak wavelengths of the emission bands have been observed by using both experimental rigs. Depending on the monochromator slits, the resolution varies between 5 and 19 nm.

The optical-absorption measurements were made at room temperature with a Cary 17 spectrophotometer. The thermal stability of the optical-absorption bands was obtained with a Perkin Elmer 350 spectrophotometer operated in the $1T$ transmission mode for the most-colored samples. The expanded scale $10T$ was used for less-colored samples. The variation in transmission at the wavelength of the maximum of each absorption band at room temperature is recorded while the sample temperature is increased at the same rate as in the thermoluminescence runs. It is assumed that no large variations with temperature occur in the Cu-related bands and in the M band.[20-22] The F-center annealing curves have been corrected because of the temperature-induced variation in the F band shape.[23] This correction of the raw data may alter the position of the F-band step in about 5 °C at most.

Glow curves and optical transmission variation have been continuously recorded. The spectrum of the emitted light has been obtained either continuously while the sample is heated or at several selected wavelengths, the sample being kept at a fixed temperature. The points presented in the figures are taken from these continuous graphs. Lines have also been drawn to help the reader. All glow curves are plotted in the same arbitrary units.

The sample bleaching was made with a Bausch and Lomb monochromator equipped either with a deuterium lamp or a tungsten lamp with some additional Corning filters to obtain an adequate spectral purity of the bleaching light.

III. RESULTS

A. Glow curves

Figure 1 shows the evolution of the thermoluminescence spectrum with dose. The glow curve of a sample x irradiated at a dose estimated around 4000 rads exhibits two peaks at about 54 and 116 °C, respectively. These glow peaks are also

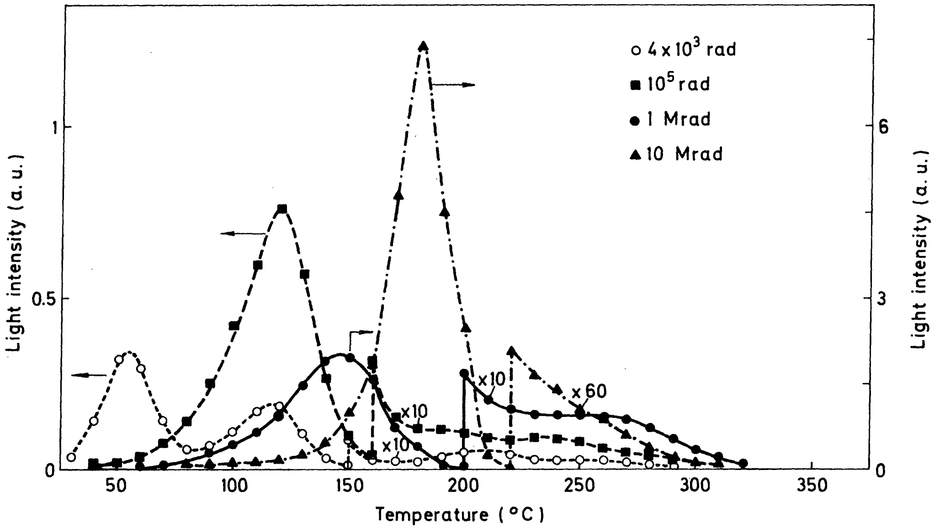

FIG. 1. Variation of the glow curve with dose.

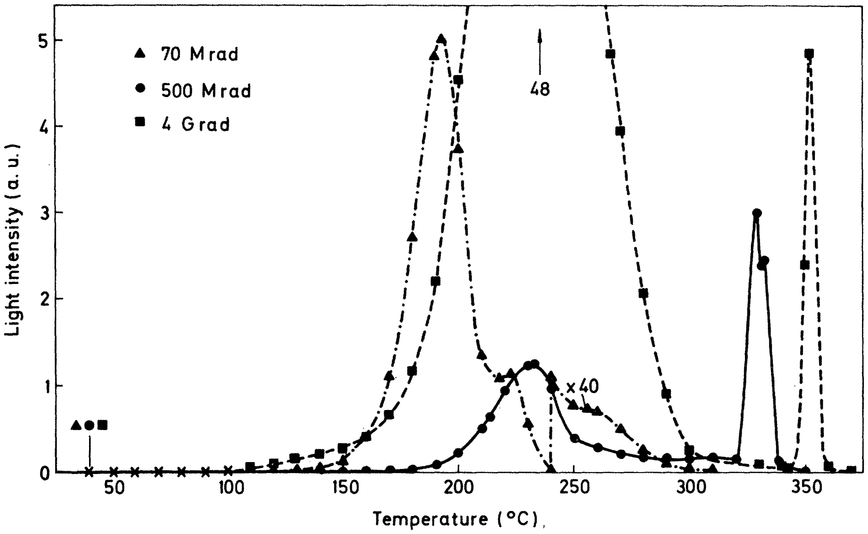

FIG. 2. As in Fig. 1 for higher doses.

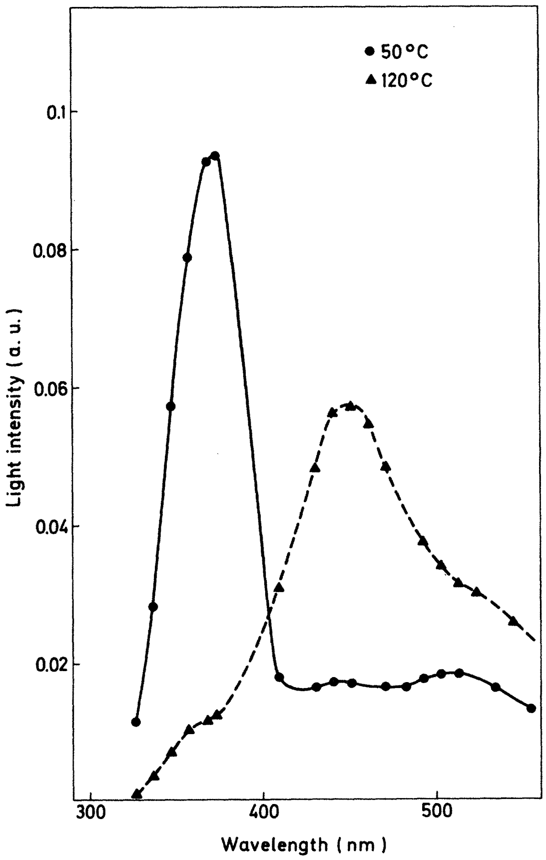

FIG. 3. Emission spectra of a sample irradiated at 4000 rad.

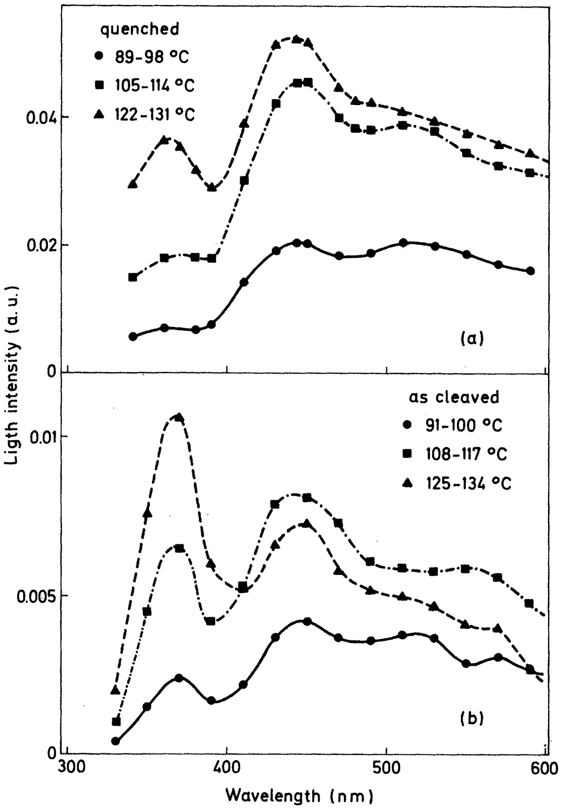

FIG. 4. Effect of quenching on the emission spectrum of samples irradiated at 10^5 rad. The temperature intervals indicate the initial and final temperatures of the sample while the emitted light is scanned from 300 to 600 nm.

observed at lower doses (~200 rad). It should be noted that in our x-ray irradiation system it is difficult to determine the irradiation dose at such low levels.

In gamma-irradiated samples at doses up to about 10^5 rad at which F-center concentrations around $8\times10^{16} F\,\mathrm{cm}^{-3}$ are obtained, the thermoluminescence spectrum exhibits a dominant glow peak at 120 °C as well as two poorly defined peaks centered at about 194 and 236 °C, respectively. In the glow curve corresponding to the sample irradiated at 1 Mrad, the main glow peak is around 147 °C. At this dose the F-center concentration ranges about $2\times10^{17} F\,\mathrm{cm}^{-3}$. In samples irradiated about 10 Mrad ($5\times10^{17} F\,\mathrm{cm}^{-3}$), the predominant glow peak occurs around 180 °C as it is also shown in this figure. The evolution of the thermoluminescence spectrum for further increasing doses appears in Fig. 2. At about 70 Mrad a glow peak at 197 °C is dominant and the glow peaks occurring at lower temperatures in less-irradiated samples have been practically erased. This effect is already noted for lower doses in Fig. 1. Two glow peaks at about 223 and 260 °C, respectively, appear also at this dose. For doses around 500 Mrad ($\sim 2\times10^{18} F\,\mathrm{cm}^{-3}$), no glow peaks below 200 °C are observed and a peak at about 232 °C with a shoulder around 260 °C is present. However, the more interesting feature of this glow curve is the narrow peak occurring around 330 °C which seems to be overlapped with another narrow peak at 333 °C. The total width of these peaks at half maximum is about 9 °C for a heating rate of 5 °C min^{-1}. Samples irradiated at about 4 Grad in which the F-center concentration is about $4\times10^{18} F\,\mathrm{cm}^{-3}$ also exhibit a narrow glow peak around 350 °C with a half-width of about 6 °C. This peak is more intense than the peak at 330 °C in the sample irradiated at 500 Mrad which is not present in these more irradiated samples. These narrow glow peaks are rather unusual in the thermoluminescence of irradiated alkali halides and to our knowledge they have not been reported before, even for very high doses.[24] It should be noted that in samples irradiated at 4 Grad there is also a huge glow peak centered around 236 °C whose existence seems to break the general rule that for increasing doses the high-temperature glow peaks dominate the spectrum while the low-temperature peaks progressively fade out. This peak shall be commented on later.

Figure 3 shows the emission spectrum at 50 and 120 °C of a quenched sample x irradiated at 4000 rad. At 50 °C the spectrum exhibits a dominant emission band peaked around 365–370 nm (3.40–3.35 eV) and two low-intensity bands at about 445 (2.78 eV) and 510 (2.43 eV) nm, respectively. At 120 °C the emission band around 445 nm dominates the spectrum but the emission bands at 365 and 510 nm are still clearly observed. Efforts have been made to detect the emission band at 350 nm (3.54 eV) observed by other authors[14,16,21] in NaCl:Cu samples x irradiated at low doses but they were unsuccessful. It seems that the 350-nm emission band is severely decreased for Cu^+ ion concentrations as high as the concentration used in this work.[15] Moreover, Tsuboi has reported that in electrolytically colored NaCl:Cu samples, no emission band at 350 nm is observed by photostimulation in the Cu^+ absorption band once Cu ions are formed which seems to be the dominant process in our samples.[20]

The effect of sample quenching on the thermoluminescence of this material has also been studied in samples irradiated at about 10^5 rad. It is shown in Fig. 4 that in quenched samples the ratio of the 445-nm band intensity to the 365-nm band intensity is larger than in as-cleaved samples.

The emission spectrum of as-cleaved samples irradiated at 1 Mrad in which the 147 °C glow peak is dominant appears in Fig. 5(a). As it can be

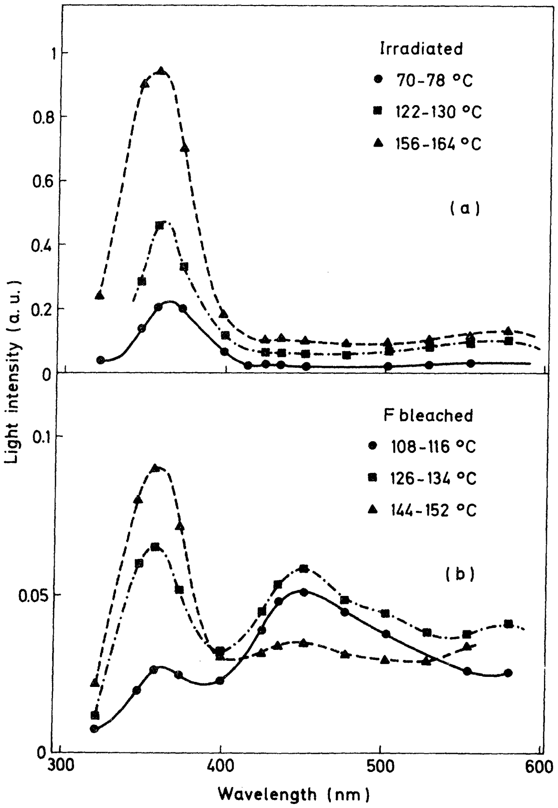

FIG. 5. Effect of F bleaching (4 hours) on the emission spectrum of samples irradiated at 1 Mrad. Temperature intervals same as in Fig. 4.

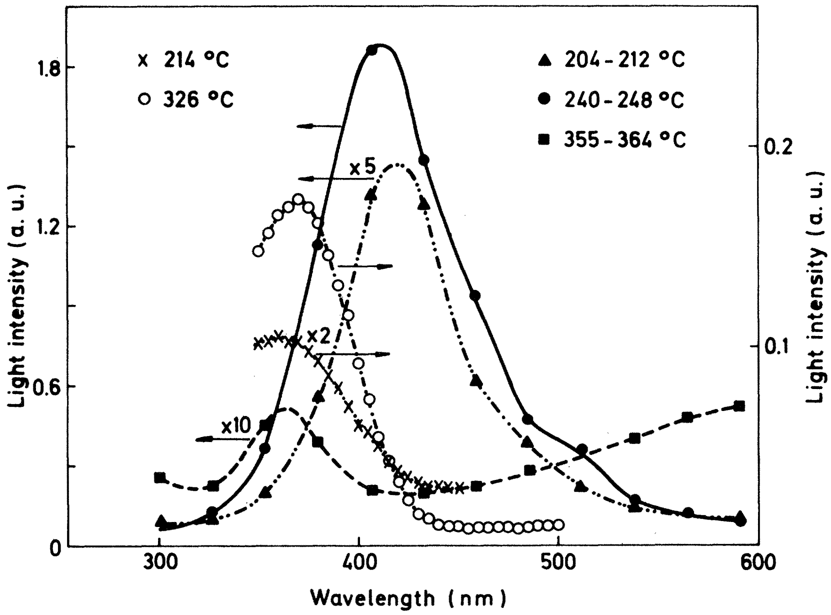

FIG. 6. Emission spectra of samples irradiated at 500 Mrad (×,○) and of samples irradiated at 4 Grad (▲,●,■). The temperature intervals in the samples irradiated at 4 Grad, as in Fig. 4.

seen in this figure the 365-nm emission band is dominant in this glow peak. A small emission band around 445 nm is also observed. This dominance of the 365-nm emission band on the 445-nm emission band has also been observed in the 180, 193, and 223 °C glow peaks which are progressively dominant for increasing doses. It can be seen in Fig. 5 that the light intensity emitted by a sample which has been irradiated at 1 Mrad and then bleached with F light is much less than in an as-irradiated sample. The main effect of F bleaching is to largely reduce the intensity of the 365-nm emission band. It has also been observed that this variation in the emission spectrum shape induces a slight shift towards lower temperatures in the 147 °C glow peak of F-bleached samples.

The small width of the glow peaks observed around 330 and 353 °C occurring in samples, respectively, irradiated at 500 Mrad and 4 Grad makes it difficult to obtain a reliable emission spectrum. Nevertheless, it has been measured either at fixed temperatures or while the sample was being heated at 5 °C min^{-1}. The results are shown in Fig. 6 and they indicate that also in these narrow peaks the main emission band occurs at 365 nm. No clear sign of an emission band peaked around 445 nm has been found in these peaks.

As it was pointed out before, the existence of the huge glow peak at about 236 °C in samples irradiated at 4 Grad does not fit into the general evolution pattern of the thermoluminescence spectrum with increasing dose. The particular character of this glow peak is also reflected in its

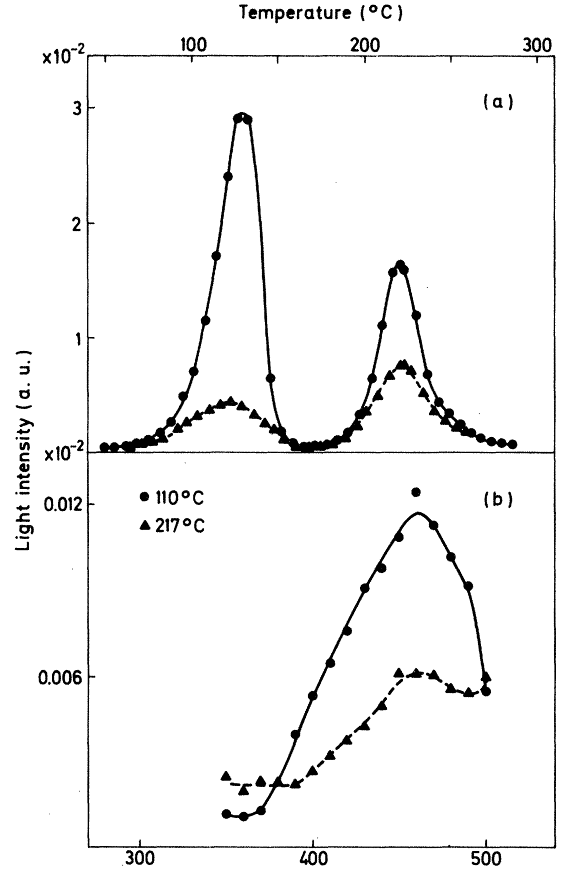

FIG. 7. (a) Glow curve induced by illumination with 254-nm light of as-cleaved samples during 16 (▲) and 63 (●) hours. (b) Emission spectrum of these samples.

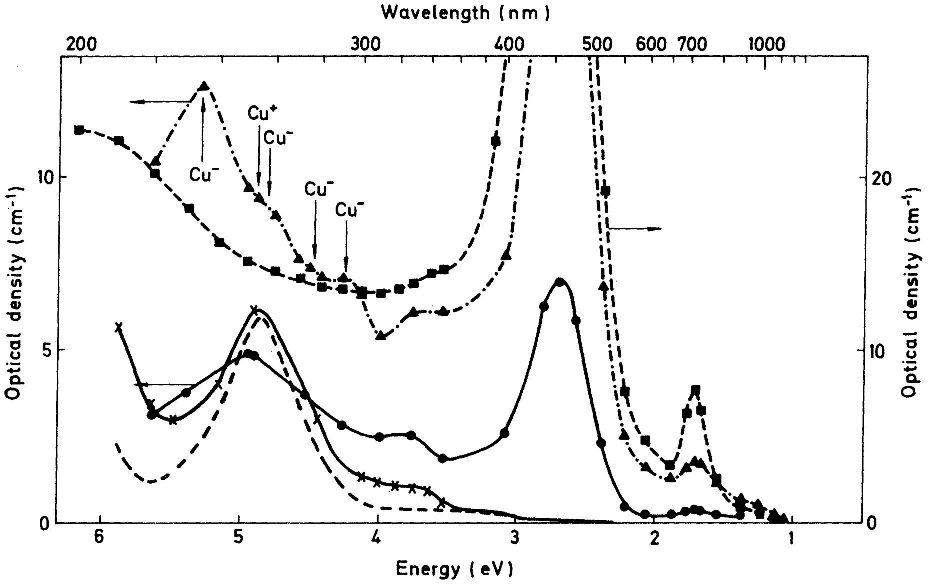

FIG. 8. Optical-absorption spectra corresponding to samples irradiated at: 10^5 rad (●), 1 Mrad (▲), 70 Mrad (■); and to unirradiated samples: as-cleaved (×), quenched (–).

emission spectrum which shows a main band peaked around 410 nm which coincides with the emission band observed in the thermoluminescence of calcium-doped NaCl samples.[25] No indication of the 365-nm band has been found in this glow peak.

As-cleaved samples were illuminated with 254-nm light to excite Cu$^+$ ions. The thermoluminescence of samples illuminated in this way during 16 and 64 hours are shown in Fig. 7(a). Two glow peaks at 125 and 220 ℃, respectively, are observed in these spectra. Their intensity increases with illumination time, and no shift in temperature is observed. The emission spectrum [Fig. 7(b)] of these samples shows a band peaked around 460 nm which is obviously related to copper ions. It seems sensible to assume that the emission band at 445 nm found in x- and gamma-irradiated samples, might actually be this 460-nm band perturbed by the absorption of the *F* band induced in the irradiated samples. Tsuboi[20] has reported that in electrolytically colored NaCl:Cu samples, an

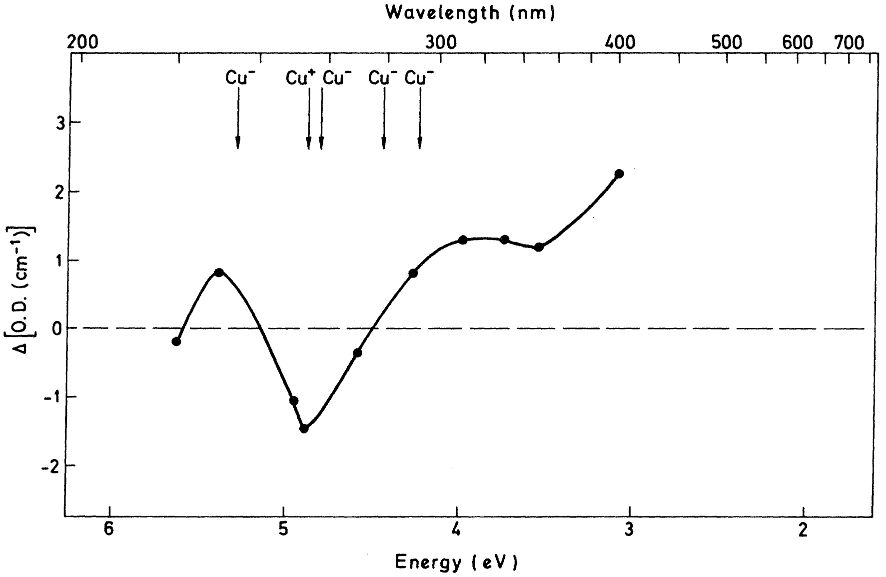

FIG. 9. Difference optical-absorption spectrum between a sample irradiated at 10^5 rad and an as-cleaved sample.

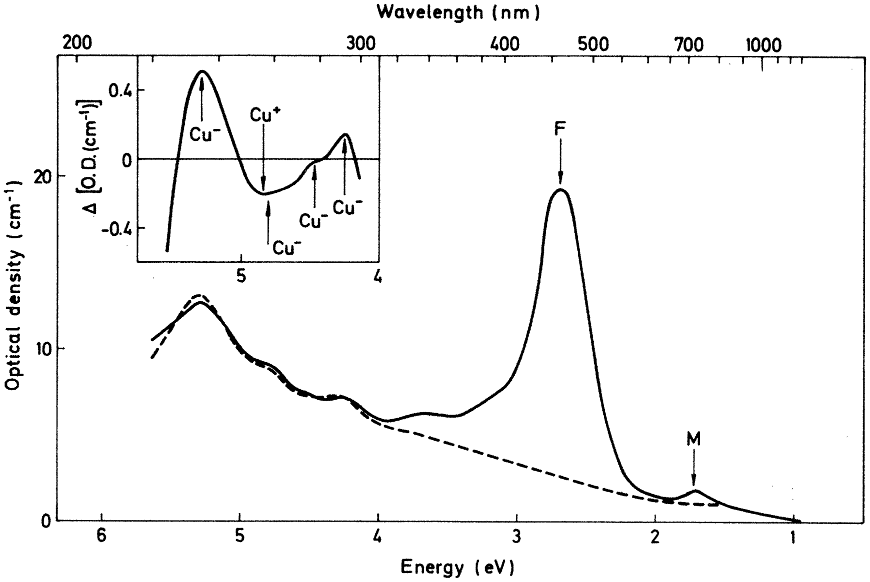

FIG. 10. Effect of F bleaching (4 hours) on the optical-absorption spectrum of a sample irradiated at 1 Mrad.

emission band peaked around 430 nm is induced by illumination in the Cu^- absorption band.

B. Optical-absorption measurements

Figure 8 shows optical-absorption spectra of unirradiated samples as well as of samples irradiated at several doses. Unirradiated samples present an absorption band at 254 nm (4.88 eV) which is due to Cu^+ substitutional ions; there is also a small absorption band peaked at 330 nm (3.75 eV) which vanishes in quenched samples. It might indicate that this band is related to some copper aggregates which are dispersed by quenching.[21] Nevertheless, this band is regenerated by irradiation in quenched samples.

Besides the F and M bands, some other bands related to copper ions are also observed in irradiated samples. Thus, in samples irradiated at 1 Mrad, four bands at 292 (4.24 eV), 278 (4.46 eV), 258 (4.80 eV), and 234 nm (5.3 eV), respectively, are clearly seen. These have been ascribed to transitions of the Cu^- ion.[20] It should be noted that in samples irradiated at and above 70 Mrad, all

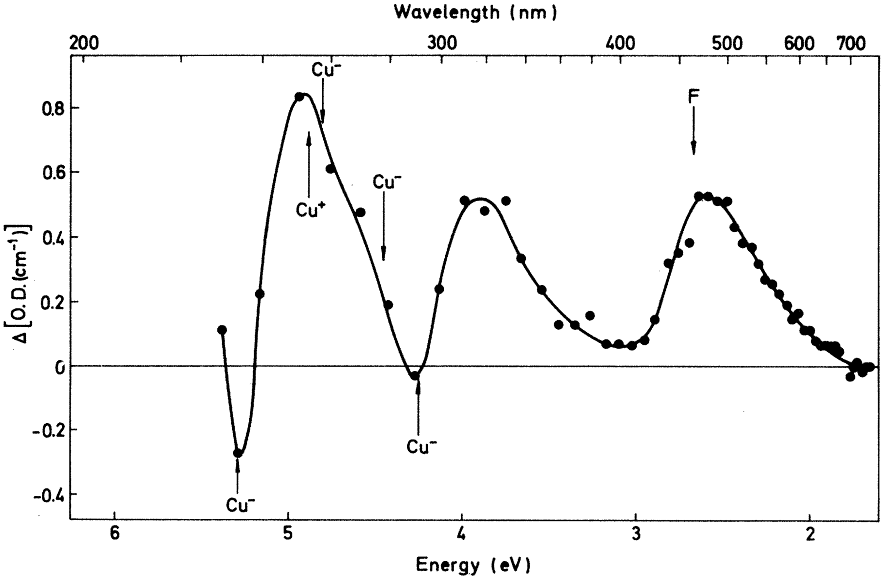

FIG. 11. Variation induced by illumination (4 hours) with 258-nm light in the optical-absorption spectrum of a sample previously irradiated at 1 Mrad and then bleached with F light (4 hours).

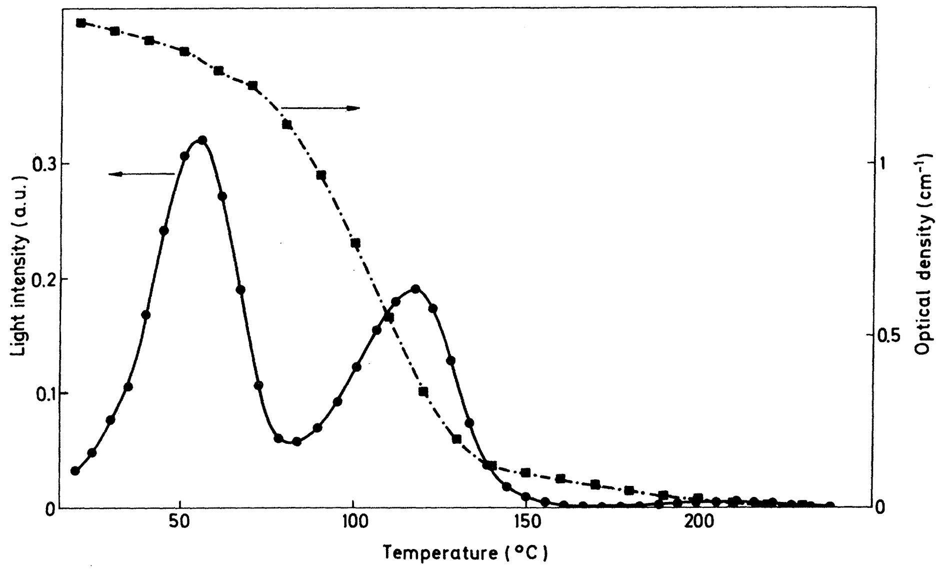

FIG. 12. Glow curve (●) and F-band annealing curve (■) of a sample irradiated at 4000 rad.

the copper associated bands seem to be covered by a broad band peaked somewhere below 200 nm. The occurrence of the Cu$^-$ bands in samples irradiated at doses below 1 Mrad is less apparent in Fig. 8 because they overlap with the Cu$^+$ absorption band. Nevertheless, Fig. 9 shows the difference spectrum between a sample irradiated at 10^5 rad and an unirradiated sample. It can be seen that while the Cu$^+$ band decreases, the Cu$^-$ bands are actually formed. The variation in the absorption spectrum induced by F bleaching of these samples is shown in Fig. 10. It is clearly seen in the inset of this figure that the Cu$^-$ absorption bands increase while the Cu$^+$ absorption band decreases. This indicates that some of the electrons released from F centers are captured by copper ions. It is noteworthy that the F centers and even the M centers seem to be more easily bleached in these samples doped with impurities whose valence states are altered by irradiation, than in nominally pure samples with similar F-center concentrations.

Figure 11 shows the difference between the optical-absorption spectra after and prior to illumination with light in the 258-nm absorption band (Cu$^-$ band) of a sample which has been previously irradiated and F bleached. As expected the Cu$^-$ absorption bands decrease and the Cu$^+$ ab-

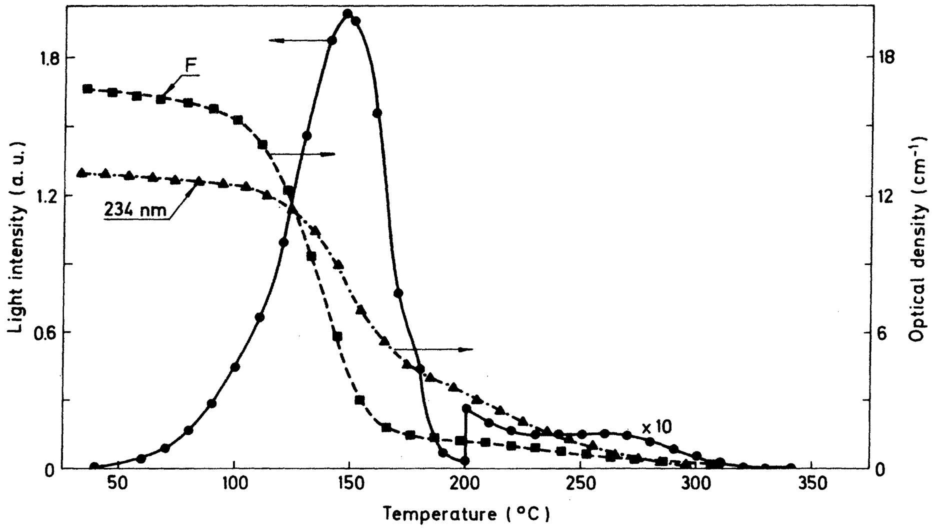

FIG. 13. Glow curve and annealing curves of the F and 234-nm bands of a sample irradiated at 1 Mrad.

sorption band increases, but the more important result is that a small *F* band grows again. It is also observed in this figure that the 330-nm absorption band which decreases by bleaching with *F* light (Fig. 10), it is also regenerated by illumination with 258-nm light.

The possible correspondence in temperature among the glow peaks and the thermal annealing steps in the optical-absorption bands has also been investigated. Figure 12 shows the correspondence of the *F*-band annealing steps around 54 and 120 °C and the main glow peaks occurring in samples irradiated at 4000 rad. The small *F* annealing occurring at around 54 °C is clearly observed in the recorder chart. This step has also been observed in samples irradiated at doses as low as about 200 rad.

Figure 13 shows that the main annealing steps in the *F* band and the Cu^- related band peaked at 234 nm occur close to 147 °C at which the dominant glow peak in samples irradiated at about 1 Mrad also occurs. It should be noted that the annealing curve of the 234-nm band is not corrected by the growth of the nearby Cu^+ absorption band (254 nm). Nevertheless, this result supports the idea that both the *F* centers and the Cu^- ions are involved in the thermoluminescent process. It was not possible to obtain the thermal annealing curve of the Cu^- band in samples irradiated at doses at which other glow peaks are dominant, because at both low and high doses these bands are, respectively, masked either by the Cu^+ absorption band or by the broad band peaked below 200 nm which was shown in Fig. 8.

Figure 14 shows the correlation among the glow curve and the thermal annealing curves of the *F* and *M* bands as well as the variation of the optical density at 565 nm, since the formation of colloids by heating these heavily irradiated samples ($\sim 4\times 10^{18} F\,cm^{-3}$) was expected. The *F* annealing curve shows a small step around 175 °C. Some *F*-center aggregation occurs in this temperature range in which a small increase in the optical density of the *M* band is also observed, but a clear corresponding glow peak is not found. Both the *F* and *M* annealing curves exhibit a step close to 236 °C at which the maximum of the main glow peak occurs. Around this temperature there is no increase in the optical density at 565 nm which indicates that neither *R* centers whose absorption bands are at wavelengths close to this, nor are colloids formed. Therefore, the correlation between this glow peak and the annealing steps of both the *F* and *M* centers implies that these centers are involved in the thermoluminescent process.

It seems remarkable to us that about 65% of the *F* centers initially present in the sample are thermally stable up to about 300 °C. They are annealed between 320 and 350 °C. In heavily irradiated NaCl samples either pure or doped with calcium, the *F* centers are completely annihilated below 250 °C.[24,26] It is known that no colloids are formed in NaCl samples irradiated at room temperature.[27] Hence, the initial optical absorption at 565 nm is mainly due to the low-energy tail of the *F* band and to the *R* bands (545 and 596 nm) before the thermally assisted colloid formation occurs. Thus the annealing step observed around

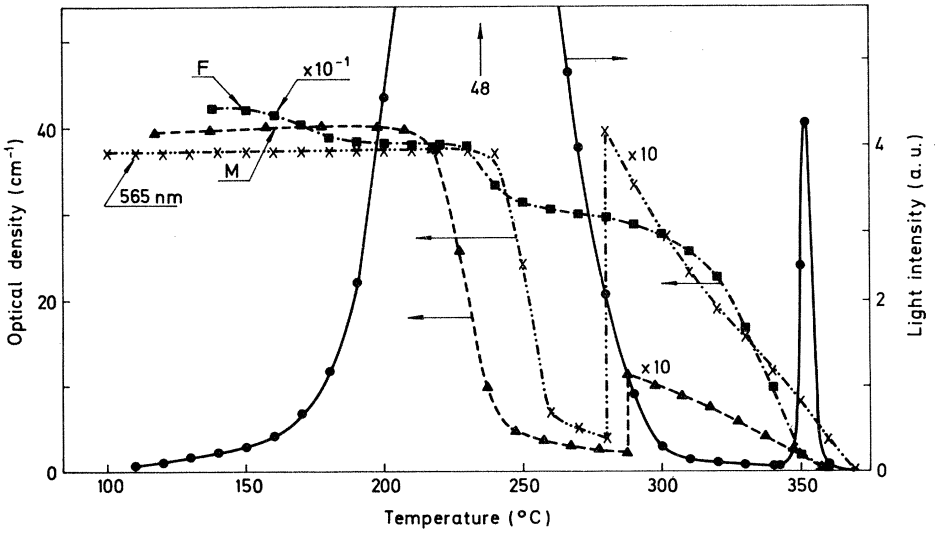

FIG. 14. Glow curve, annealing curves of the *F* and *M* bands, and variation of the optical density at 565 nm of samples irradiated at 4 Grad. The *F*-center concentration at room temperature was estimated from the shape of the *F* band.

250 °C is likely due to the combined decrease of these bands. At variance with the results obtained in pure NaCl samples,[24,26] no clear growth of the colloidal band is observed when these samples are heated. Nevertheless, between 320 and 350 °C where the main F-center annealing step occurs without any correlated glow peak and where there is also a small inflection in the M-band annealing curve, the decreasing rate of the optical density at 565 nm slows down which seems to indicate that some colloids are formed. This colloidal band shows a wide annealing step around 350 °C where the narrow glow peak appears.

IV. DISCUSSION

The results obtained in this work indicate that except for the narrow glow peaks occurring at and above 330 °C which will be discussed later, there is a one-to-one correspondence between glow peaks and F-center thermal annealing steps, i.e., at the temperature at which a glow peak takes place there is also a partial annihilation of F centers. Therefore, it has to be concluded that the F centers are involved in these thermoluminescent processes. It has been shown in Fig. 13 that in samples irradiated at doses at which the thermal annealing of the Cu^- bands can be properly studied, both the F centers and the Cu^- ions are annealed at the temperature at which the main glow peak occurs. Since that, except for the 236 °C glow peak and the narrow peaks occurring at a high temperature in heavily irradiated samples, the emission spectrum exhibits both the 365- and 445-nm bands in all the glow peaks, it seems sensible to assume that these peaks are related to simultaneous annealing steps in the F and Cu^- bands. On the other hand, it has also been shown that the relative intensity of the 365- and 445-nm emission bands can be varied by sample treatments such as quenching prior to irradiation and by F bleaching after irradiation. This indicates that these two bands result from two recombination processes (different in some way) which are triggered by the same initial thermally activated process. These two recombination processes should be, respectively, related to the annealing of F centers and to the annealing of Cu^- ions.

The effect of F bleaching on the emission spectrum is to reduce the relative intensity of the 365-nm emission band as well as to increase the Cu^- absorption bands. On the other hand, the 460-nm emission band observed in unirradiated samples which have been excited by illumination in the Cu^+ absorption band, should be obviously ascribed to the thermal recovery of Cu^+ ions. These results lend support to relate the 365-nm emission band to the annealing of F centers while the annealing of Cu^- bands could be related to the 445-nm emission band which might be the 460-nm band perturbed by the F-band absorption in irradiated samples.

The evolution of the glow curve for increasing doses is the same as that found in other either nominally pure or alkaline-earth-doped alkali halides irradiated at room temperature, i.e., the low-temperature glow peaks progressively vanish for increasing doses.[8,9,11,24] It has been proposed that the thermoluminescence of alkali halides irradiated at room temperature is due to recombination of F centers with mobile interstitial halogen atoms thermally released from traps.[8] In this model the indicated dependence on dose of the glow curve has been related to the formation of large interstitial clusters. If this model is also to be applied to these copper-doped samples, one has to provide a mechanism by which the Cu^- ions are transformed into Cu^+ ions at the time the F centers are also annihilated, both processes being triggered by interstitial release.

It has been shown that the Cu^- absorption bands increase when irradiated samples are F bleached as well as that if these samples are then excited by light in the Cu^- absorption bands, the F band is partly regenerated. This important result indicates that the Cu^- ion formation can be electrically compensated by anion vacancies instead of by trapped holes, i.e., during irradiation at room temperature the Cu^+ ions are able to trap the electrons of some nearby F centers. It is worthwhile to note that this way of compensating the charge-state variation of impurities is not at variance with the well-known V_K center formation at low temperatures. This result allows a simple explanation of the thermoluminescence of these samples: When an irradiated NaCl:Cu sample is heated, interstitial chlorine atoms are released from traps and they recombine with F centers inducing the 365-nm emission band but some of these interstitials recombine with the compensating anion vacancies forming short-lived V_K centers[18] which then recombine with Cu^- ions provoking the 445-nm emission band.

As it was pointed out in the Introduction the $F+H$ recombination above room temperature induces an emission band peaked at 425 nm in nominally pure NaCl samples and at 410 nm in NaCl:Ca and NaCl:Mn samples.[9,25] It is believed that this band is the II intrinsic emission band, which in this material is around 360 nm at low temperature, perturbed by a divalent impurity-cation vacancy dipole nearby to the $F+H$ recombination site. It seems plausible that the 365-nm band observed in these samples might be the Π emission band perturbed by a nearby Cu$^+$ ion. Nevertheless, this point as in the case of doping with divalent impurities needs further work to be ascertained.

It has been already noted that samples irradiated at 4 Grad show a huge glow peak whose emission spectrum exhibits a single band peaked around 410 nm as in NaCl:Ca samples. Since in our samples there are about 26 ppm of calcium, it seems sensible to assume that this glow peak is caused by the recombination of F and M centers with interstitial chlorine atoms which are stabilized during irradiation near calcium ions. These ions would become relevant as interstitial traps once the interstitial stabilization around copper ions (115 ppm) is practically saturated at high enough irradiation doses.

The rather unusual width of the narrow glow peaks seems to indicate that they are not due to the thermal release of a mobile entity (interstitial) from a well defined energy trap but to a somehow more complex process.[24] For example, it should be noted that at this temperature, F centers are also mobile and they can recombine with interstitials at clusters. A few eV are released in an $F+H$ recombination.[28] This energy might provoke some instability in the interstitial cluster and induce a fast release of interstitials. Vice versa, the thermal release of interstitials from clusters might also induce an enhanced evaporation of F centers from colloids. Both processes are possible but at this stage their relative importance can not be ascertained.

An important result obtained in this work is the large thermal stability of the F centers against thermal annealing or F aggregation processes as compared with nominally pure samples[24,26] (Fig. 14). This indicates that somehow the thermal migration of the F center is inhibited by the copper impurity ions. This is consistent with a recent result which shows that F centers are formed near impurities where the interstitials are stabilized.[29] The closeness of F centers to copper ions is also consistent with the transfer of electrons between F centers and copper ions shown in this work.

The close localization of F centers and impurities which seems to be in copper-doped samples larger than in nominally pure samples whose relevant background impurities are mainly alkaline earths, might also explain that while in nominally pure samples heavily irradiated, the emission band is peaked at about 460 nm (Ref. 24); in these copper-doped samples the corresponding emission band has its maximum at 365 nm.

Finally, we would like to remark that from the results presented in this work, the phenomenology found in these rather heavily doped samples, such as the dose dependence of the glow curve, is different from that one reported in previous work on NaCl:Cu systems irradiated at low doses in which the formation of Cu$^-$ centers has not been considered.[14-16,21] Cu$^-$ ions might become substitutional in the anion sublattice.

V. CONCLUSIONS

From the results obtained in this work, it is proposed that the thermoluminescence above room temperature of NaCl:Cu is due to the recombination of interstitial halogen atoms thermally released from traps, either with F centers or with anion vacancies near radiation-induced Cu$^-$ ions. A tentative assignation of the emission bands associated to both processes has been made. Key results supporting this model are the dose dependence of the glow curve, the correlation among glow peaks and annealing steps in the optical-absorption bands as well as the F-band regeneration by illumination in the Cu$^-$ bands.

This model might allow unified view of the thermoluminescence above room temperature of alkali halides either nominally pure or doped with many of the usual impurities.

ACKNOWLEDGMENTS

We are indebted to Dr. A. Delgado for providing the continuous scanning monochromator. We are also grateful to the Chemistry Division members who carried out the sample analysis.

---

[1] E. Sonder and W. A. Sibley, in *Point Defects in Solids*, edited by J. H. Crawford, Jr. and L. Slifkin (Plenum, New York, 1972), Vol. I, Chap. 4.

[2] J. L. Alvarez Rivas, J. Phys. (Paris) C6, 353 (1980).

[3] A. E. Purdy and R. B. Murray, Solid State Commun. 16, 1293 (1975).

[4] K. Tanimura, M. Fujiwara, T. Okada, and T. Suita, Phys. Lett. A50, 301 (1974).

[5] K. Tanimura, T. Okada, and T. Suita, Solid State Commun. 14, 107 (1974).

[6] K. Tanimura and T. Okada, Phys. Rev. B 13, 1811 (1976).

[7] M. Jiménez de Castro and J. L. Alvarez Rivas, Phys. Rev. B 19, 6484 (1979).

[8] V. Ausin and J. L. Alvarez Rivas, J. Phys. C 5, 82 (1972).

[9] D. F. Mariani and J. L. Alvarez Rivas, J. Phys. C 11, 3499 (1978).

[10] N. Itoh, A. M. Stoneham, and A. H. Harker, J. Phys. C 10, 4197 (1977).

[11] A. Rascon and J. L. Alvarez Rivas, J. Phys. C 11, 1239 (1978).

[12] M. Ikeya, Phys. Status Solidi B 69, 275 (1975).

[13] Y. V. G. S. Murti and K. R. N. Murthy, J. Phys. C 5, 2827 (1972).

[14] M. Herreros and F. Jaque, J. Lumin. 9, 380 (1974).

[15] K. Inabe and N. Takeuchi, Jpn. J. Appl. Phys. 17, 831 (1978).

[16] N. Takeuchi, M. Adachi, and K. Inabe, J. Lumin. 18/19, 897 (1979).

[17] F. J. López, F. Jaque, A. J. Fort, and F. Agulló-López, J. Phys. Chem. Solids 38, 1101 (1977).

[18] D. Schoemaker, Phys. Rev. B 3, 3516 (1971).

[19] V. Ausín, J. Herrero, A. J. Goñi, and J. L. Alvarez Rivas, J. Phys. E 4, 289 (1971).

[20] T. Tsuboi, Can. J. Phys. 55, 1316 (1977).

[21] M. Herreros, thesis, Universidad Autónoma de Madrid, 1977 (unpublished).

[22] W. D. Compton and H. Rabin, Solid State Phys. 16, 121 (1964).

[23] R. K. Dawson and D. Pooley, Atomic Energy Research Establishment (United Kingdom) Report No. R-5946 (1968) (unpublished).

[24] V. Ausin and J. L. Alvarez Rivas, J. Phys. C 7, 2252 (1974).

[25] M. Aguilar, F. J. López, and F. Jaque, Solid State Commun. 28, 699 (1978).

[26] J. M. Bunch and E. Pearlstein, Phys. Rev. 181, 129 (1969).

[27] A. B. Lidiard, Comments, Solid State Phys. BVIII, 73 (1978).

[28] A. E. Hughes, Comments Solid State Phys. BVIII, 83 (1978).

[29] E. R. Hodgson, A. Delgado, and J. L. Alvarez Rivas, J. Phys. C 12, 4393 (1979).