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Effect of Plastic Deformation on the Thermoluminescence of γ-Irradiated KCl Crystals

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The effect of plastic deformation on the thermoluminescence of nominally pure Harshaw KCl samples γ irradiated at room temperature has been studied up to 450 °C. In samples plastically strained prior to irradiation a new glow peak appears. It has been found that this glow peak does not follow either first- or second-order kinetics. It is shown that the phosphorescence decay curves of the glow peak are the superposition of five exponential processes. The activation energies and the preexponential factors of these decays are given. Besides this glow peak, in samples strained after irradiation a glow peak at higher temperatures has been observed. It follows second-order kinetics. The study of thermal annealing of the *F* centers while the temperature of the sample is linearly increased shows that there is an annealing step corresponding to each strain-induced glow peak. These results are discussed in terms of a recently proposed model to explain the thermoluminescence of as-cleaved γ-irradiated samples. In this model the *F* center behaves as a recombination center for the interstitial atoms thermally released from traps. At some stage in this process an electron-hole recombination takes place and light is emitted. The relation of these results to the well-known enhancement of the *F* colorability by ionizing radiation and also to the enhanced thermal stability of the *F* centers in plastically deformed samples is discussed.

I. INTRODUCTION

It has been recently shown[1] that there is a close relation between *F* centers and the thermoluminescence of KCl γ irradiated at room temperature. In Harshaw KCl samples, six glow peaks were found from room temperature up to 450 °C. It has been observed that there is an annealing step of *F* centers at each temperature at which a glow peak becomes operative. There is a one-to-one correspondence between the glow peaks and the annealing step of *F* centers. After the highest-temperature glow peak fades out, there are no *F* centers left in the sample. From this result, and from the measured values of the activation energies and the preexponential factors of the six thermoluminescence peaks, it was concluded that these thermoluminescence processes arise from a recombination of mobile interstitial atoms with the *F* centers. The last ones play the role of recombination centers. At some stage in this process an electron-hole recombination takes place and light is emitted. Additively colored samples do not show either thermoluminescence or *F*-center annealing in this temperature interval. Thus, the measurements of thermoluminescence in irradiated alkali halides can be very useful to study the processes in which the interstitials play a major role.

The purpose of this work is to study in detail the effect of plastic deformation on the thermoluminescence of irradiated KCl.[2,3] Besides this, a better insight into the effect of plastic deformation on the thermal bleaching of the *F* centers[4,5] and on the *F* colorability by ionizing radiation in alkali halides[6] is expected.

II. EXPERIMENTAL

Samples of 1.5×1.5 cm^2 and 1 mm thick were cleaved from nominally pure Harshaw single-crystal blocks of KCL. They were annealed at 350 °C for 3 h in a vacuum, then allowed to cool down to room temperature in 4 h. The samples were strained along their short dimension in a hand vise. They were γ irradiated at room temperature in a ^{60}Co source at dose rates between 10^4 and 6×10^4 R/min.

The thermoluminescence measurements were made with a heating system described elsewhere.[7] A heating rate of 0.225 K sec^{-1} was commonly used. The light was measured with the 153 AVP and 153 UVP Philips photomultipliers. The spectrum of the emitted light was analyzed with a Bausch and Lomb (high-intensity) monochromator. However, the total light was usually measured.

The optical-density measurements were made with a Perkin Elmer 350 spectrophotometer either in the absorbance mode or in the expanded transmission modes in the case of low optical densities. A small furnace was made to heat the sample, within the cell of the spectrophotometer, at the same rate as that in the thermoluminescence experiments.

III. RESULTS

A. Thermoluminescence Measurements

It has been shown[1] that the thermoluminescence spectrum in as-cleaved and annealed samples of Harshaw KCl single crystals displays six glow peaks (I, II, ..., VI). In the first or fast stage of the *F*-coloring curve, the six glow peaks can be

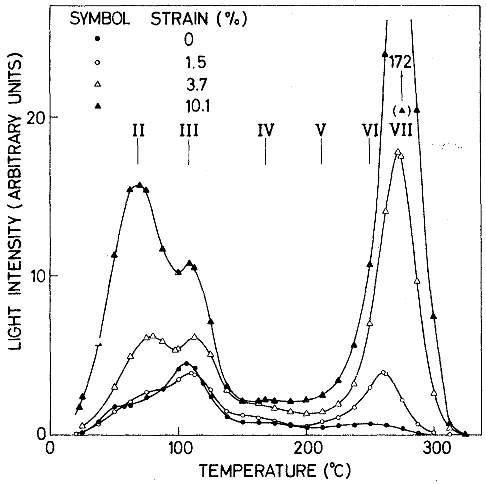

FIG. 1. Dependence on the strain of the thermoluminescence spectrum of samples plastically deformed prior to irradiation at the same low dose (0.5 min at 1.8 MR/h).

observed, but glow peak III is dominant. As the dose or irradiation time is increased (second and third stage of the F-coloring curve) glow peak IV becomes predominant. The roman ordinal numbers used to label the glow peaks increase as the temperature of the maximum of the corresponding glow peak increases.

Figure 1 shows the thermoluminescence spectra of samples plastically deformed prior to irradiation at the same dose. Besides some effects on glow peaks II–VI that will be considered later, a new glow peak labeled VII that is induced by plastic deformation is clearly observed.[2] This glow peak increases as the strain increases. All these samples were irradiated for $\frac{1}{2}$ min at 1.8 MR/h and their F-center concentrations are well into the first stage of their corresponding coloring curves. Similarly, Fig. 2 displays the thermoluminescence spectra of samples with different plastic strain that have been deformed prior to irradiation at the same high dose (2 h at 3.6 MR/h). Their F-center concentration is in the third stage of their F-coloring curves. Finally, to complete this information, the dependence on the irradiation time of the thermoluminescence spectrum of samples with the same plastic strain (2%) is shown in Fig. 3.

It is interesting to point out some features of the thermoluminescence spectra shown in these three figures. First, glow peak VII is typical of the strained samples and increases as the strain and/or the irradiation dose are increased. Some plastically strained samples were irradiated at very high dose in order to see if this glow peak becomes saturated; in samples with 5×10^{17} F center/cm^{-3}, there was no clear sign of saturation. Second, glow peaks I–VI characteristic of these KCl samples in the as-cleaved condition are also affected by the plastic deformation. They become wider than in the as-cleaved samples. The broadening of these peaks is compatible with the presence of an additional nonluminescent trapping of interstitials competive with the F-center interstitial recombination. Moreover, it is clearly observed in Fig. 2 that glow peak IV decreases with increasing plastic strain in contrast to peak VII. This behavior might well indicate that glow peaks I–VI are interacting with glow peak VII; i.e., the interstitial atoms released from traps I–VI are partly trapped in trap VII, where they are stabilized up

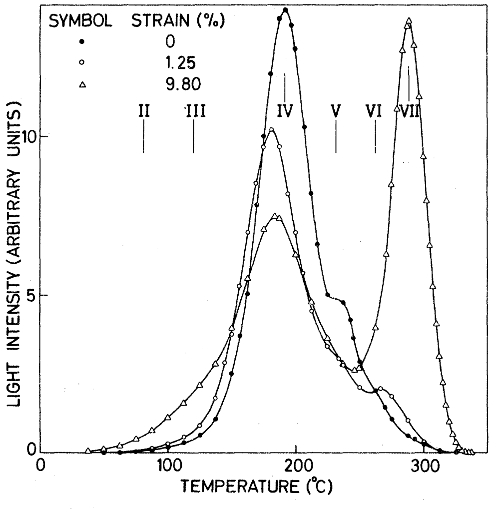

FIG. 2. Dependence on the strain of the thermoluminescence spectrum of samples plastically deformed prior to irradiation at the same high dose (2 h at 3.6 MR/h).

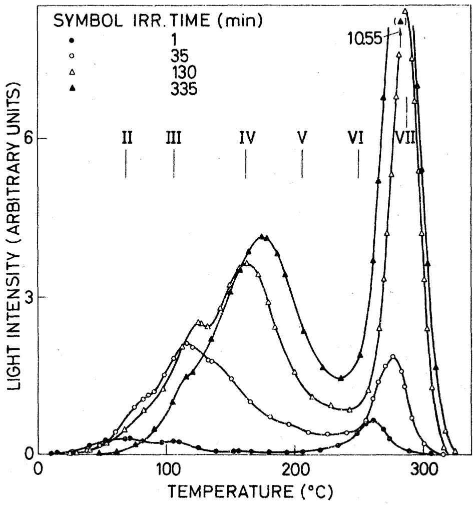

FIG. 3. Dependence on the irradiation time of the thermoluminescence spectrum of samples plastically deformed prior to irradiation. All the samples are strained at 2%.

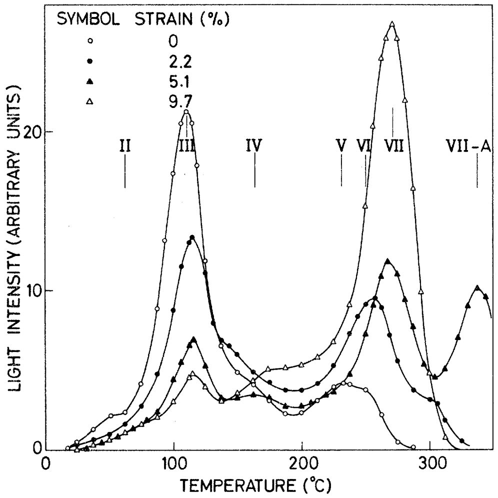

FIG. 4. Dependence on the strain of the thermoluminescence spectrum of samples plastically deformed after irradiation at the same dose (5 min at 0.6 MR/h).

to higher temperatures. This gets further experimental support with the results presented in Fig 4. In this figure the thermoluminescence spectra of samples plastically deformed *after* being irradiated at the same dose are shown. It can be seen how regions I–VI of the thermoluminescence spectrum decrease and glow peak VII increases with increasing plastic strain. Moreover, the area under the thermoluminescence spectrum is roughly the same for all these samples. That is, the total light emitted by the samples is independent of their plastic strain after irradiation.

There is an interesting difference that will be studied in detail later between the thermoluminescence spectra of a sample deformed prior to or after irradiation. In the last case, at low strains a glow peak at higher temperatures than peak VII is observed in Fig. 4. This new peak, labeled VII-A, vanishes with increasing strains.

The activation energy and the preexponential factor of glow peaks I–VI have been reported recently. To repeat, those measurements in plastically deformed samples were considered quite useless due to the interaction already indicated among the glow peaks in these samples. Thus, efforts were concentrated to make a careful study of glow peaks VII and VII-A which are characteristic of the plastically deformed samples.

It was observed that glow peak VII does not follow either first- or second-order kinetics. The temperature of its maximum intensity varies between 520 and 590 K and the width at half-maximum varies between 20 and 40 K. These changes appear in a quite uncontrolled way. Some thermoluminescence runs were made at a low heating rate (5 K/min) in order to see if this glow peak was composite, but the thermoluminescence spectrum did not show any structure.

To determine the kinetics of the annealing process of glow peak VII, the phosphorescence of this peak induced by plastic deformation prior to irradiation was studied at several temperatures. Figure 5 shows the decay of the light intensity at temperatures at which only glow peak VII is operative. All these samples have the same plastic strain and irradiation time or dose. Again, the analysis of these decay curves shows that they do not follow either first- or second-order kinetics. The same negative result was obtained by considering a uniform or exponential distribution in energy of traps.[8] The more interesting characteristic of these decay curves is that they show a maximum of intensity which is more clearly noted in the curves obtained at lower temperatures. It is worthwhile to point out that at this temperature traps I–VI are already empty. Moreover, the presence of some remainder of a low-temperature glow peak would produce an upward concavity but not a maximum in the decay curve. Since the temperature of the sample during the whole run of phosphorescence is kept constant within at least 0.3 K, the maximum cannot be attributed to changes in the temperature either.

The existence of this maximum indicates that the trap that produces glow peak VII is being simultaneously filled from one or more nonthermoluminescent traps; that is, the interstitial atoms are trapped in a variety of traps and are thermally released and then trapped again in trap VII before the luminescent recombination can take place. In some way these processes are analogous to those ocurring in a radioactive series.[9] With this analogy in mind these decay curves at different temperatures of more than 50 samples with a variety of plastic strains and irradiation dose were studied by an exponential analysis. It was found that in all cases the decay curve can be written in the form

$$I=\sum_{n=1}^{5} (-1)^{n+1} A_n e^{-t/\tau_n}, \tag{1}$$

where I is the light intensity, t the time, A_n constants, and τ_n the corresponding lifetimes. Thus, the decay curves of all the studied samples can be represented by the algebraic sum of five exponential terms.

It is clear that the exponential terms in Eq. (1) might be mathematical artifacts without any physical meaning. However, if they represent physical processes it should be proved that, as usual, $1/\tau_n = s e^{-E_n/kT}$, where s is a preexponential factor, k Boltzmann's constant, T the temperature, and E_n the activation energy of the corresponding process. That this is the case is shown

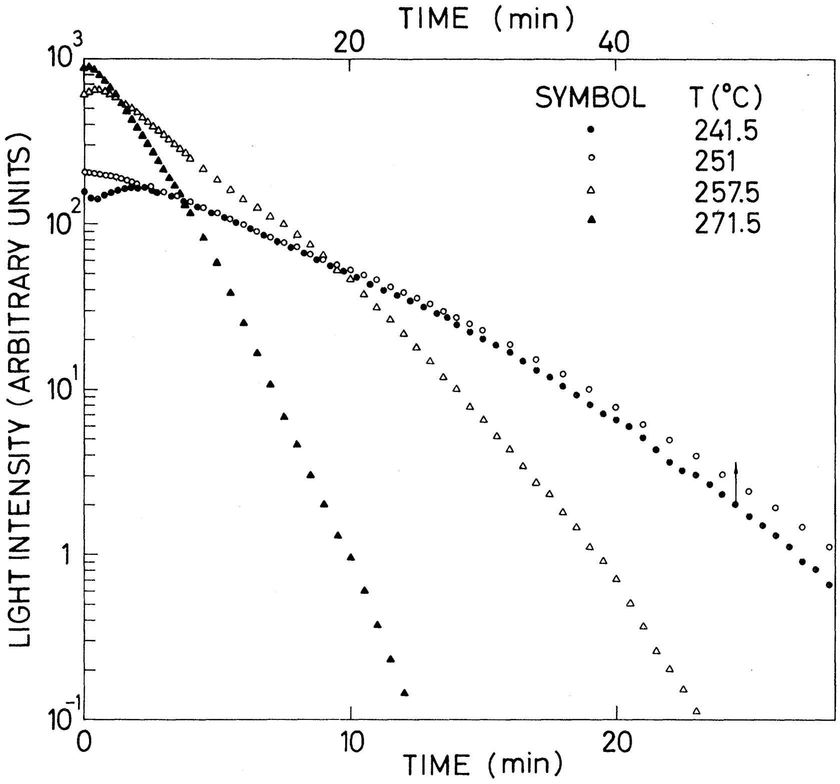

FIG. 5. Variety of phosphorescence decay curves at different temperatures corresponding to strain-induced glow peak VII in samples plastically deformed prior to irradiation.

in Fig. 6, where $\ln 1/\tau_n$ is plotted against $1/T$. The straight lines are fitted by the least-squares method to the experimental points. As can be seen in the study of the radioactive series,[9] the A_n's are functions of the initial concentrations and of the lifetimes of the whole set of traps. Probably, the jitter observed in glow peak VII is due to uncontrolled changes in the values of the initial concentration in every trap which are dependent on the method used to strain the samples. Indeed, the best method to check the physical meaning of the exponential analysis is to produce experimental conditions in such a way that each exponential term can be isolated from the others. It was attempted to produce those conditions by using small strains, but without success. However, it was found that the exponential terms $n = 1, 2, 3$ successively fade out as the irradiation dose decreases. The inset in Fig. 6 shows the activation energies E_n and the preexponential factors of the five processes. They are obtained from the adjusted straight lines.

It has been pointed out already that when the samples are plastically deformed after irradiation, a glow peak (VII-A), besides glow peak VII, appears at higher temperature and then disappears at high levels of plastic strain. A typical phosphorescence decay in a sample strained after irradiation is shown in Fig. 7. It can be observed that for long times the concavity of the decay curve continues upwards, as it should due to the presence of glow peak VII-A. The tail of the decay curve follows second-order kinetics, as is shown in the inset of this figure. After subtracting this second-order component from the decay curve, the remainder is analyzed by the above-indicated exponential analysis. It is found that there are five exponential terms with lifetimes corresponding to the case of a sample plastically strained prior to irradiation. The activation energy and the preexponential factor of glow peak VII-A are $E = 3.2 \pm 0.2$ eV and $s' = 6\times 10^{13}$ .cm^3 sec^{-1} from measurement of phosphorescence. The thermoluminescence measurements yield $E = 3.1 \pm 0.3$ eV and $s' = 4. \times 10^{13}$ cm^3 sec^{-1} for this glow peak.

Finally, the spectrum of the emitted light was also analyzed with a monochromator with the same result obtained in the undeformed samples. There is a unique emission band with its maximum at about 440 nm.

B. Optical-Absorption Measurements

It is known[1,10] that the concentration of F centers in the sample before the run of thermoluminescence is always proportional to the area under the thermoluminescence spectrum in as-cleaved samples. For low strains, the same ratio has been approximately found in strained samples, i.e., 5.6×10^{-6} photons/(F center). However, for

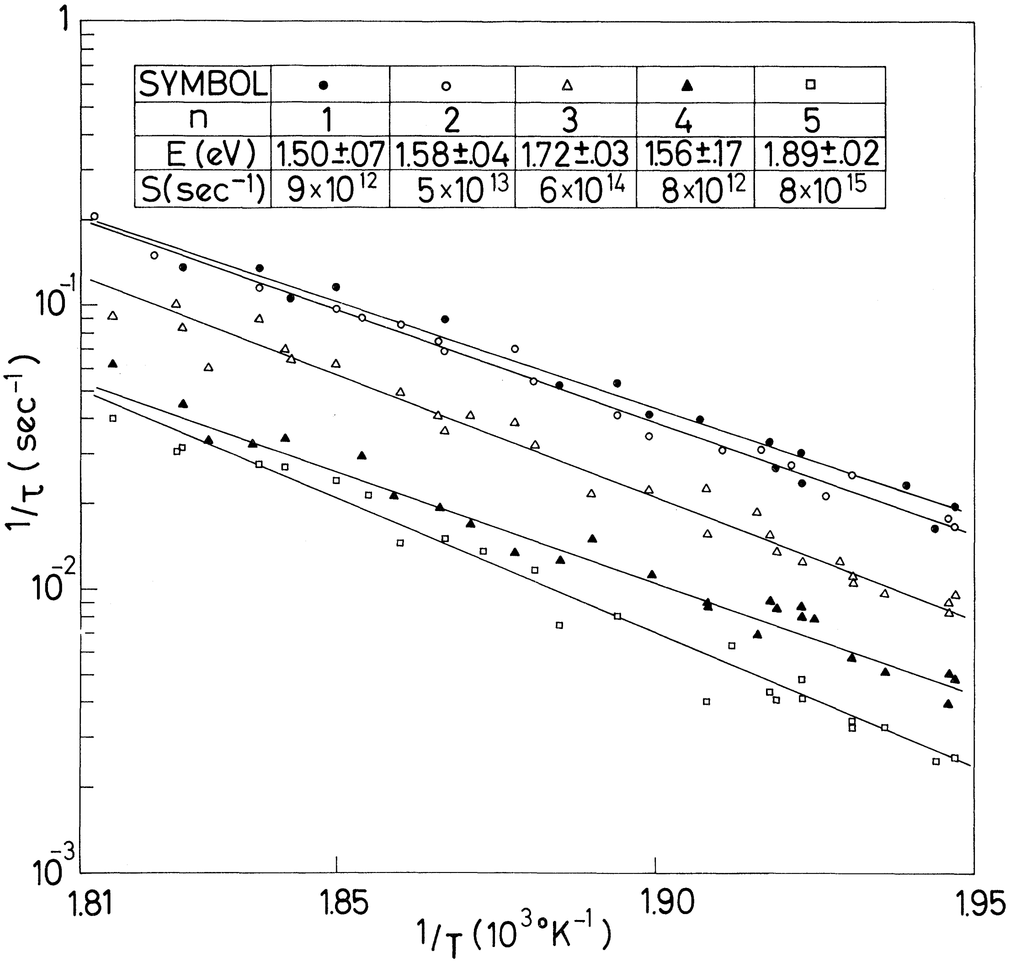

FIG. 6. Dependence on $1/T$ of the inverse lifetime of the five exponential components of glow peak VII.

strains of 4 and 8% the light yield decreases down to 4×10^{-6} and 3×10^{-6} photons/(F center), respectively. Nevertheless, this ratio is independent of the F-center concentration in samples with the same percentage of strain. These values of the light yield have been obtained from the overall gain supplied by the photomultiplier manufacturer.

In samples in which only glow peak VII remains after thermal erasing of the glow peaks at lower temperatures, the optical-absorption spectrum only shows the F band. These samples show an annealing step of F centers during a linear temperature rise at the rate used in the thermoluminescence experiments. This new annealing step[1] characteristic of the deformed samples is shown in Fig. 8, and it appears at temperatures at which glow peak VII occurs. In samples in which glow peak VII-A is produced, a corresponding step of F centers has also been observed.

It has been found that the effect of the plastic deformation on the thermoluminescence spectrum is removed if the sample is heated after straining for 7 h at 450 °C.

IV. DISCUSSION

We shall attempt to discuss the results presented in this paper according to the model[1] outlined in Sec. I. The specific calculational methods of thermoluminescence applicable to holes and/or electrons can also be used[1] to obtain glow-peak parameters in this type of thermoluminescence, since the equations employed in those methods involve the same chemical rate equations[11] applicable to annealing of point defects.

It has been shown that the ratio between the number of photons emitted per unit of volume of sample and the F-center concentration before a thermoluminescence run is constant for samples with the same percentage of strain. Consistent with this relation is the existence of an annealing step of F-center densities which occur at the temperature of glow peak VII as well as the step connected with glow peak VII-A. These results show that the F

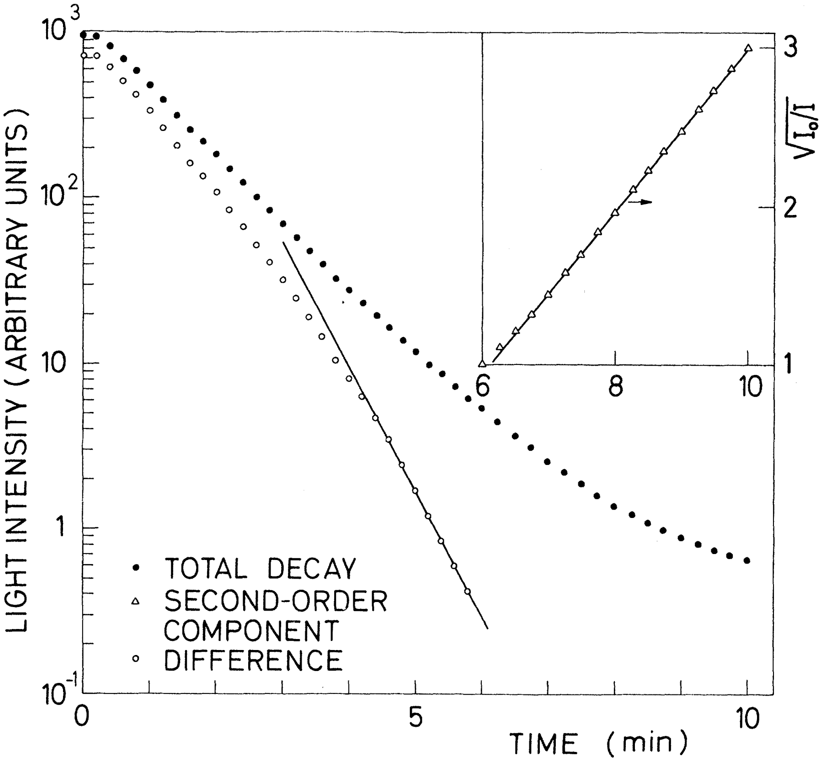

FIG. 7. Typical phosphorescence decay curve in a sample plastically deformed after irradiation, at a temperature of 267 °C. The inset shows that the tail of the decay curve follows second-order kinetics corresponding to glow peak VII-A. By subtracting this from the total decay curve the decay corresponding to glow peak VII is obtained (empty circles).

center plays the same role in strain-induced peaks VII and VII-A as in the glow peaks found in as-cleaved samples.[1] The result obtained in samples plastically deformed after irradiation shows that these traps are generated by the plastic deformation itself and not by the irradiation process. Figures 1–3 show that trap VII contains interstitials even at the low irradiation dose that corresponds to the first stage of the F-coloring curve; this result agrees with the well-known fact that the plastic deformation enhances the first stage of the F-coloring curve.[5,12] The increase of the thermal stability of F centers in plastically deformed samples[4,5] is also in agreement with the existence of interstitial traps created by plastic deformation.

More experimental support for the proposed model has been found by studying the role of the F aggregate centers in the thermoluminescence process. Some as-cleaved or strained samples were irradiated at room temperature. Then they were bleached with F light in order to obtain as high an M-center concentration as possible. It was found that the thermoluminescence spectrum is the same for these bleached samples as for the unbleached ones. However, the ratio between the area under the thermoluminescence spectrum and the F-center concentration is higher for the F-bleached samples than for the as-irradiated ones. But if in this ratio the sum $F + 2M + 3R$ is substituted for the F-center concentration F, the ratio is again the same for the bleached samples as for the as-irradiated ones. This means that F aggregate centers play the same role that F centers play in the thermoluminescence process; i.e., they are recombination centers for the intersti-

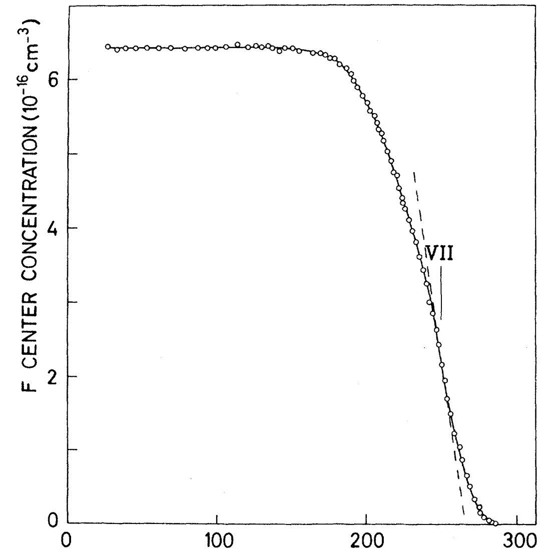

FIG. 8. Annealing of the F centers with linear heating in a sample in which all the glow peaks but glow peak VII have been thermally erased.

tial atoms.

In the model proposed[1] to explain the thermoluminescence of γ-irradiated KCl, the kinetics of each glow peak will be first order if the interstitial trap is correlated with nearby F centers. On the other hand, if the recombination is at random (not correlated) the glow peak should obey second-order kinetics[11] since the radiation creates equal numbers of interstitials and F centers. Glow peaks I–III follow first-order kinetics and glow peaks IV–VI obey second-order kinetics.[1] It has been shown that glow peak VII induced by plastic deformation either after or prior to irradiation does not follow any of these simple kinetics. The existence of a maximum in the phosphorescence decay curves corresponding to glow peak VII and the fact that this is not composite give to the processes involved in this peak some similarity to the well-known phenomenon of a radioactive series. The analysis of the decay curve with the radioactive-series scheme yields that they are formed by a finite number of exponential decays in a wide variety of experimental conditions, that the lifetime of these five exponentials terms shows the usual dependence on temperature, and that at low irradiation dose some of the fast exponential decays vanish. These results give support to the belief that the exponential decays represent physical processes. Thus, the interstitials move from one trap of the series to another and only the slowest exponential decay represents a recombination with F centers. Since they are first-order kinetics, they mean that the annealing is correlated. Actually, it is sensible to assume that the whole annealing process occurs in very localized regions of the samples.

It has also been shown that, in samples deformed after irradiation, the glow peak VII-A that follows second-order kinetics appears. It has been observed that this peak fades out on increasing the plastic strain, and in this case only glow peak VII remains. This means that at low strains the interstitials that are released from the traps induced by the plastic deformation recombine at random with F centers that are not in the highly damaged regions where the interstitial traps are. By increasing the plastic strain all the F centers become close to a highly damaged region and only glow peak VII appears in the thermoluminescence spectrum.

It is believed[13,14] that the enhancement of the F colorability by ionizing radiation in plastically strained samples is caused by the debris left by the moving dislocations. The results presented here are in agreement with the idea that the debris produces interstitial trapping. It has also been shown[15] that the F absorption band shifts towards higher energy in plastically deformed samples. In this work, no change was found in the F absorption band measured at room temperature. However, a clear shift towards the blue is observed at liquid-nitrogen temperature (LNT) in plastically strained samples as compared with the as-cleaved samples. Moreover, a sample was strained about 1% and then irradiated at room temperature; the optical absorption was recorded at LNT. The peak of the F band was found at 536 nm. Afterwards, the sample was heated in order to erase a glow peak and the optical-absorption spectrum was again recorded at LNT. This process was repeated while increasing the annealing temperature. It was found that the shift of the F band towards the blue increases as the annealing temperature is increased. Thus, the F band shows the maximum shift (534 nm) when the F centers left in the sample are only those which anneal simultaneously with glow peak VII. This result gives further support to the proposal that glow peak VII results from recombination of interstitials with F centers in very localized regions (debris).

An important point in the model[1] proposed to explain the thermoluminescence observed in KCl irradiated at room temperature is that at some stage in the process of interstitial F-center recombination an electron-hole recombination occurs and light is emitted. It might be that just before the luminescent recombination takes place a trapped hole center with a very short lifetime is produced and some increase in the optical absorption of the V region could be observed. It depends on how short the lifetime of the trapped-hole center is. This possibility was investigated in the following way. Several samples were irradiated as-cleaved up to an F-center concentration of 5×10^{17} cm^{-3}. Then they were heated at a rate of 10^3 °C min^{-1} within the cell of the spectrophotometer and the transmission at a fixed wavelength was recorded with each sample. A Corning filter was used to eliminate the luminescence of the sample. A small temporary absorption band with its maximum 360 and 370 nm has been detected. At all the measured wavelengths the highest optical density occurs when the temperature of the sample is 120 °C. It is not realistic to conclude from these measurements alone that the trapped hole center exists, but at least they may be considered as a positive indication that it is worthwhile attempting to improve the sensitivity of the measurement of this temporary absorption band and, if possible, to use some other techniques to learn the nature of this band which could prove to be a crucial point of evidence in understanding the thermoluminescence processes in irradiated alkali halides.

V. CONCLUSIONS

In samples deformed prior to irradiation, it has been found that plastic strain induces a glow peak (VII). The phosphorescence decay curves corresponding to this glow peak show that it does not follow either first- or second-order kinetics. Nevertheless, the annealing kinetics of this glow peak have been studied with a scheme analogous to that of a radioactive series in nuclear physics. It has been found that these decay curves are formed by five exponential decays. The activation energies and the preexponential factors of these exponential terms are given. The physical meaning of these exponential terms has been examined.

In samples plastically deformed after irradiation a glow peak (VII-A) that follows second-order kinetics is also observed; this appears at higher temperatures than glow peak VII. Its activation energy and preexponential factor have been obtained. Glow peak VII-A fades out in highly strained samples.

The complex annealing kinetics of glow peak VII appear to be the superposition of several first-order kinetics which are due to correlated processes. This indicates that the processes occur in localized and highly damaged regions (debris). This is in agreement with the widely accepted role of the debris in the enhancement of the *F* colorability by ionizing radiation in plastically deformed samples. The debris traps interstitials and operates to stabilize *F* centers. The results obtained in samples strained after deformation confirm that the debris acts as a trap of interstitials. The presence in this case of an additional glow peak with second-order kinetics merely indicates that some interstitial atoms have to migrate from the region of high debris density to recombine randomly with the *F* centers already present in the sample before deformation.

Samples plastically strained after or prior to irradiation annealing of the *F* centers during a linear temperature rise show a new annealing step at temperatures at which strain-induced glow peak VII is operative. In samples exhibiting glow peak VII-A a corresponding annealing step is observed.

As in a previous work,[1] it is concluded that in this strain-induced thermoluminescence the *F* center also plays the role of a recombination center for the interstitial atoms which are simultaneously produced with the *F* centers during the irradiation. The *F* aggregate centers are also found to be recombination centers. The interstitials are stabilized in traps produced during the process of plastic deformation.

It is obvious that the enhancement of the thermal stability of the *F* centers in plastically deformed samples is produced by the interstitial trapping at the strain-induced traps.

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